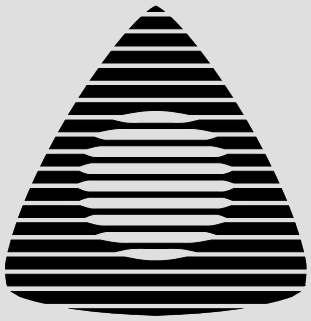


Experiments/ Demonstrations

Ceramics

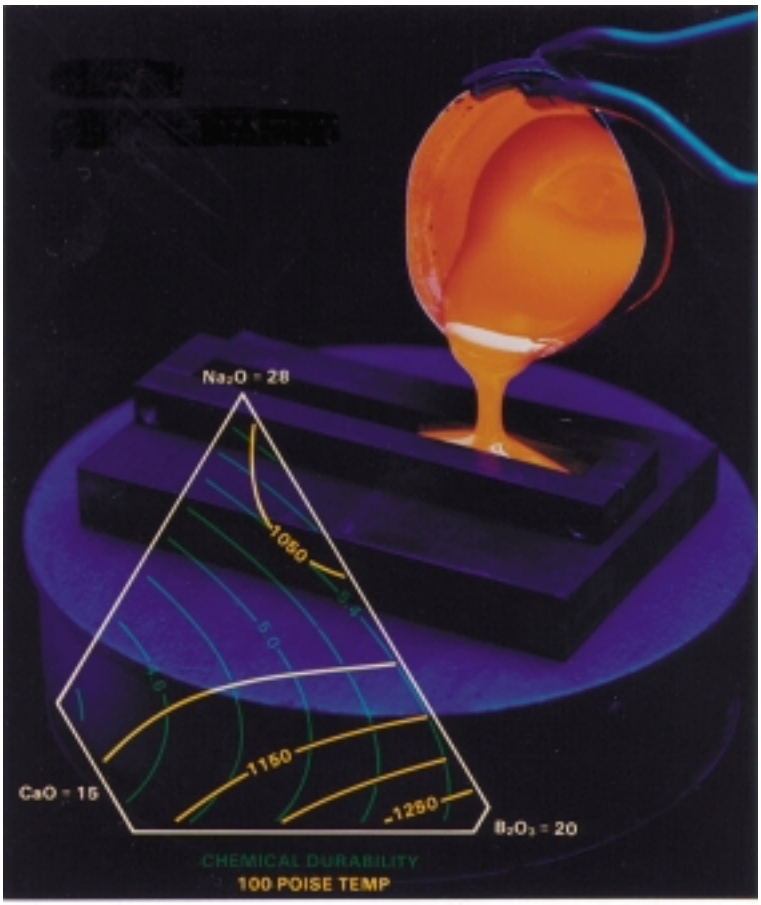
Ceramics

Introduction

Ceramics are non-metallic and inorganic and are made from raw materials that are either mined from the earth or chemically synthesized. They are hard, generally resistant to heat and most chemicals, and lighter than most metals.

Traditional ceramic materials include glass windows, insulating bricks, pottery, and china. However, the fiber-optic phone lines that provide today's clear voice communication are also ceramic, products of high-technology glassmaking. Likewise, the space shuttle is insulated against the searing heat generated as it returns from near space through the earth's atmosphere. Its aluminum hull is shielded by incredibly light bricks made from tiny glass fibers.

Ceramics are compounds that are generally formed by reacting a metal with other elements such as oxygen, nitrogen, carbon, or silicon.



The bonding is usually ionic and is very strong, making ceramics comparatively stable chemically. (Ionic means the joining of a positively charged atom to a negatively charged atom, usually metal atoms to non-metallic atoms.) This ionic bonding occupies the outer electrons of the metal, making the electrons incapable of moving in an electric field; thus, most ceramics are poor conductors of electricity. Ceramics also include glasses, which are composed of metals, oxygen, and silicon. By their nature, glasses do not crystallize as other ceramics do. As they cool from the liquid state, they become progressively stiffer until they are solid, which gives them different properties from other materials, such as not having a definite melting point.

Where resistance to extreme temperatures or molten metals is desired, ceramic materials emerge as extremely important. Without ceramics, it would probably be impossible to melt or cast metals; other materials will not resist the heat or chemical environment, and other materials allow heat to leak away, because they are not effective insulators like ceramics.

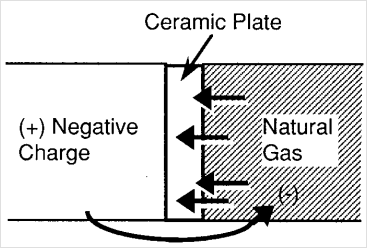
The powerful bonding forces in ceramics have some negative features, one of them being brittleness. Ceramics cannot be bent like metals or most other common materials, and they tend to break without warning. Tiny surface defects, too small to cause much of a problem with a metal, can greatly reduce the strength of a ceramic material. In a metal, flow at the defect location would reduce the effect of that defect; this flow is not possible in a ceramic. So cracks stay sharp and ceramics break instead of bend. (Metallic flow is the movement of one plane of atoms over another.)

Humankind first made ceramics in ancient times. Fire, probably at that time a relatively new discovery, was used to make clay vessels less likely to revert to a gooey mess when contacted by water. During this firing process, materials in the clays reacted, forming small amounts of glass that cemented the rest of the materials together. Glass was born in similar fireside experiments, and in Roman times, was more precious than gemstones and used similarly for decoration.

The future of ceramic materials is even more interesting. Scientists have created ceramics that, while not as tough as metals, are many times tougher than those made just a few years ago. These tough materials are being used increasingly as parts in automobile engines because of their lightness and resistance to wear.

Other ceramics have been made electrically conductive or able to allow oxygen ions to penetrate them. Both of these characteristics are needed for high-temperature fuel cells that can convert fuels such as natural gas directly to electricity more efficiently then any other method (see Figure 6.1).

Ceramics are being formed by methods similar to those used for mass production of plastic parts, so that increasingly intricate parts can be made cheaply. All these developments combined ensure that ceramics will continue to play important roles in modern life.



Oxygen atoms (-) negative charge flow through ceramic to combine with (+) positively charged particles. An electric potential is created and electricity is “birthed.”

Figure 6.1. Electrically Conductive High-Temperature Fuel Cell

Thermal Shock
Instructor Notes

Reliability

This experiment works well if the materials are the same as what is described herein.

Estimated Time for Activity

One class period.*

Teacher Tips

1. Thermal shock is a mechanism often leading to the failure of ceramic materials. Many uses for ceramics involve high temperature. If the temperature of a ceramic is rapidly changed, failure may occur. Thermal shock failures may occur during rapid cooling or during rapid heating. As an example, consider rapid cooling, which is easier to visualize. If a ceramic material is cooled suddenly, the surface material will approach the temperature of the cooler environment. In doing so, it will experience thermal contraction. Because the underlying material is still hot, the skin material stretches and so experiences tensile stress. If the resulting strain is high enough (0.01% to 0.1% for most ceramics), the ceramic will fail from the surface, and cracks will propagate inward. Even if these cracks do not cause immediate failure, the ceramic will be severely weakened and may fail from mechanical overload of forces it would normally withstand.
2. When comparing different ceramics for thermal shock applications, it is common to use a figure of merit or index of thermal shock performance. This is a number (ratio) that is useful for both choosing materials and for visualizing the thermal shock process. Because the index should be high for a thermal shock resistant ceramic, its numerator should contain properties that are numerically large when good thermal shock performance is exhibited by a material. Tensile strength (S) and thermal conductivity (K) are therefore placed in the numerator, the former for obvious reasons and the latter because a high value of thermal conductivity tends to decrease thermal gradients, other factors being equal. The denominator of the thermal shock index is composed of the thermal expansion coefficient (A) and Young's Modulus (E), which is a measure of

*One class period is approximately 1 hour.

the stress resulting from a given strain. These numbers should be a low value for good thermal shock performance. Combining these factors,

$$\text{Thermal Shock Index (TSI)} = \frac{SK}{AE}$$

Where the units of measurement should be consistent within a given comparison.

In the case of common glasses, all the properties except thermal expansion fall into a relatively narrow range. By choosing a glass with low thermal expansion, thermal shock failure can be avoided in most cases. See, for example, the index values for soda-lime glass, borosilicate glass, and fused silica in Table 6.1. Note the large difference between the thermal shock indices of aluminum oxide and graphite. This difference is backed by experience; it is extremely difficult to cause graphite to fail by thermal shock, principally because its Young's modulus is so low and its thermal conductivity is high.

Table 6.1. Thermal Shock Index (TSI) for Some Common Ceramic Materials

Material	K,[1] W/cm-°C	S, MPa	A, $°C^{-1}$, x 10^{-6}	E, GPa	TSI
Soda-lime-silica glass	2E-2	68[2]	9.2	69	2.1
Borosilicate glass	2E-2	68	3.3	63	6.5
Fused SiO_2	6E-2	68	0.6	72	94
Aluminum Oxide	3E-1	204	5.4	344	33
Graphite[3]	1.4	8.7	3.8	7.7	416

(1) Thermal conductivity and expansion coefficients from *Thermophysical Properties of Matter*, Y. S. Touloukian, ed., Plenum Press, New York, 1970.
(2) Because glass tensile strength is so dependent on surface condition, a single "reasonable" value was chosen for all glass strengths.
(3) Values are typical of nuclear-grade graphite, from *Industrial Graphite Engineering*, Union Carbide Corp., 1959

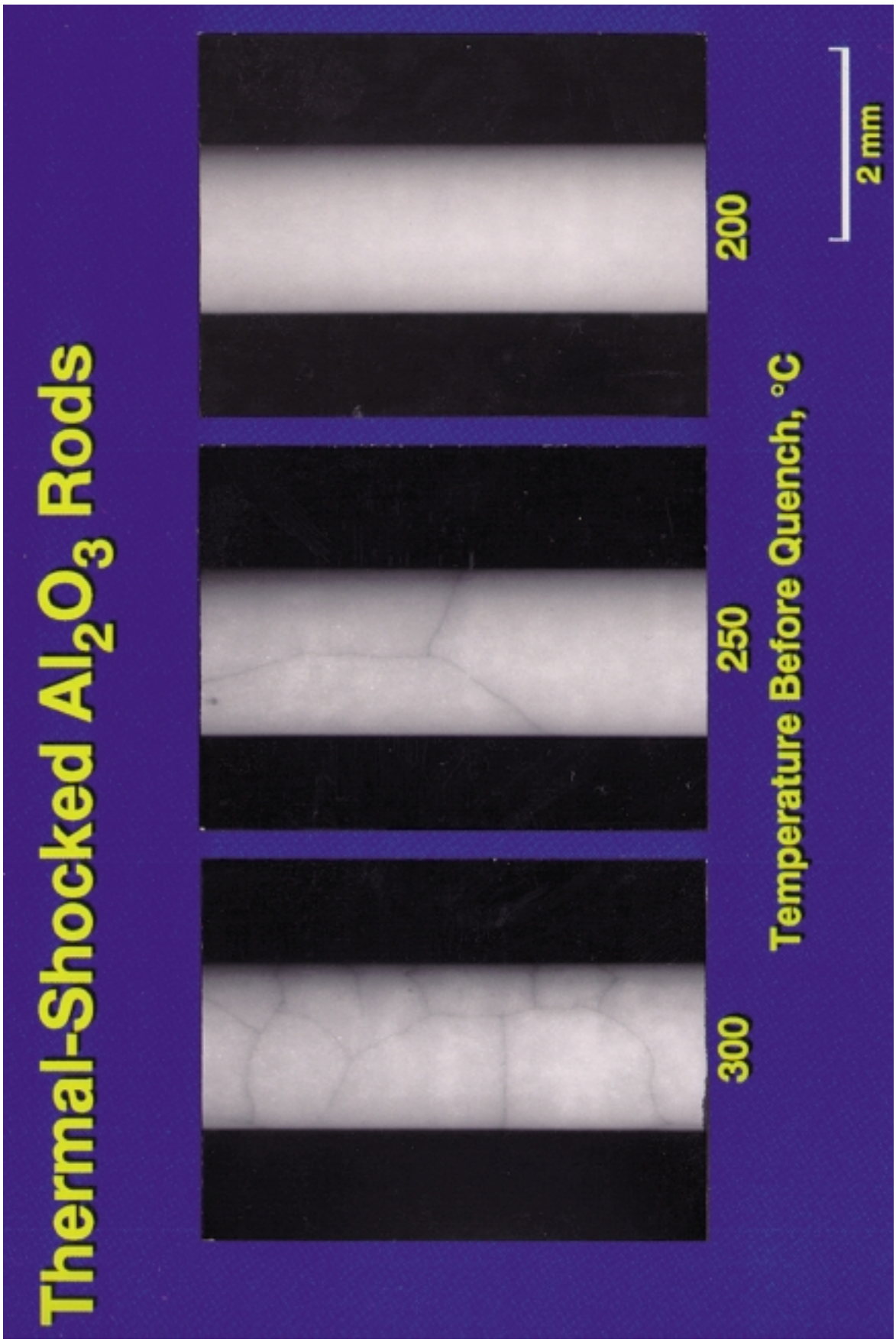
Teacher Tips for Demonstration

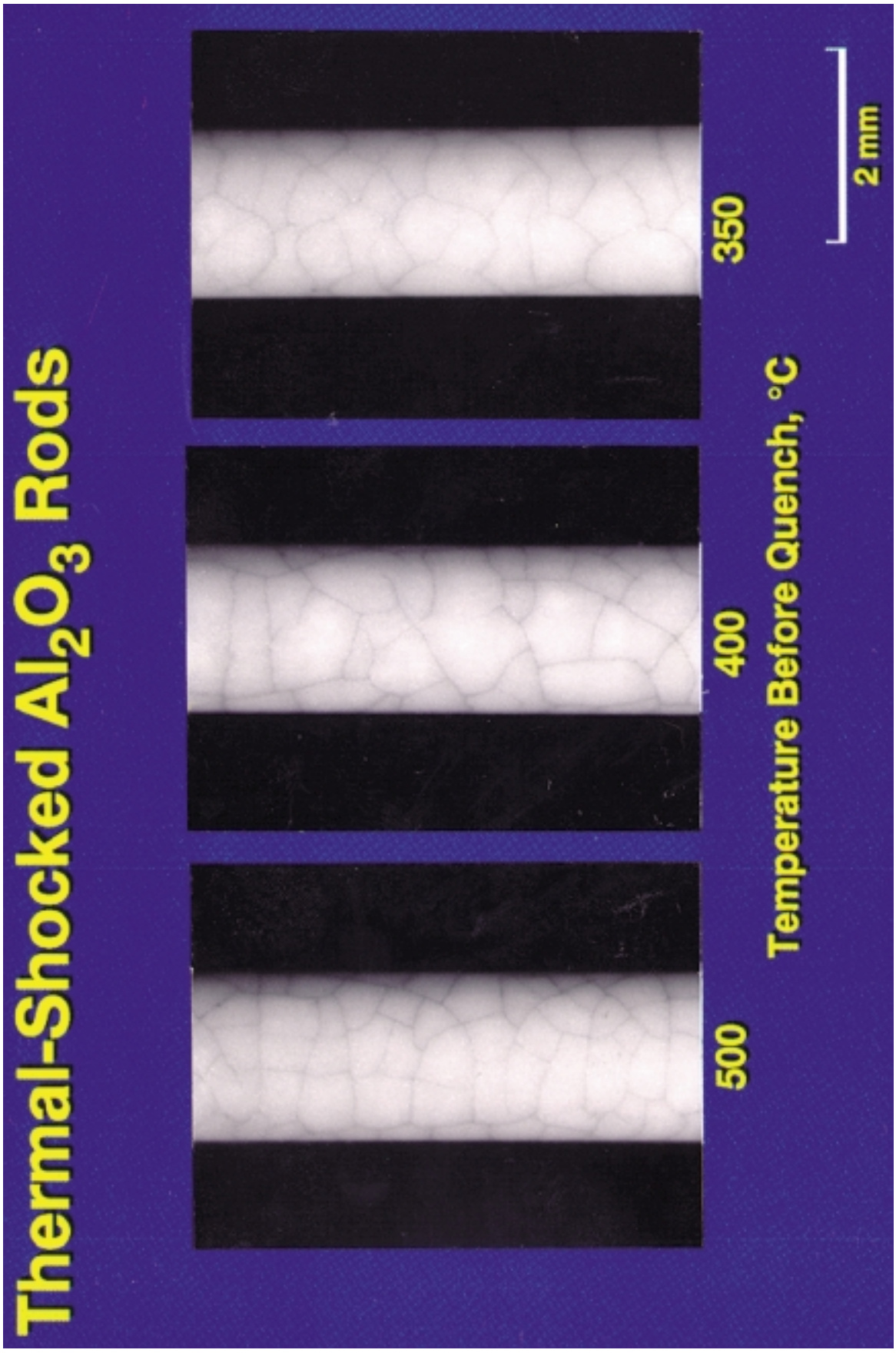
1. Thrown into water (quench), the water changes to steam.
2. Steam forms at the surface of the specimen, absorbing energy (539 calories per gram).
3. This causes the surface to cool to 100°C, almost instantly.
4. The result is a shrinking surface encasing a large, hot specimen, causing thermal shock and cracking.
5. The temperature difference and coefficient of thermal expansion of the material determines the amount that the material will crack.
6. The larger the TSI value, the more likely the material will withstand thermal shock.

Extension Activity

A similar thermal shock experiment to demonstrate follows:

Place about 10 aluminum oxide rods, 3 mm x 10 cm in length, into a stainless-steel beaker or a small metal pan and heat to 500°C in a suitable furnace. Remove the container from the furnace, and quickly quench the rods in a bucket of water. Dry them overnight at about 100°C. The following day, dip the rods in ink, which acts as a crude dye penetrant to make any cracking visible. Wipe excess ink from the rods, handling care-fully to avoid breaking. Note, if broken, the partial penetration of the ink shows that the cracks do not extend into the centers of the rods. This is because the cracks start at the surface in a tensile stress area, but propagate into regions of lower stress until they stop. When a quench is performed on rods heated at lower temperatures (down to about 300°C) crack density is lower and crack depth is shorter (see attached Figures of Al_2O_3 rods). A quench temperature that is lower still will not result in any detectable damage. This temperature is not a constant, but is a function of both configuration and material heated at designated temperatures and quenched). The alumina should be >95% dense, but can be of any purity greater than 95%.


Thermal-Shocked Al_2O_3 Rods
300
250
200
Temperature Before Quench, °C
2 mm


Thermal-Shocked Al_2O_3 Rods
500
400
350
Temperature Before Quench, °C
2 mm

Demonstration: Thermal Shock

Student Learning Objectives

At the end of the activity students will be able to:

- use in writing and discussion the following terms related to the thermal shock index (TSI)

  Strength
  Thermal conductivity
  Coefficient of expansion
  Young's modulus

- explain in writing and discussion the effect of varying rates of expansion and TSI on different kinds of materials.

Materials

- Pyrex glass
- Window glass
- Corning ware
- Fused silica glass (optional)
- Water

Equipment

- Lindberg furnace
- Tongs, long-handled
- Bucket
- Safety glasses

Procedure

1. Cut equal sized pieces of each of three or four materials.
2. Preheat Lindberg furnace to 800°C. Place pieces of materials into the oven.
3. About 5 min after the pieces become luminous, quickly remove them with tongs, and plunge them into a bucket of water.
4. Observe each material's reaction to the quench. Record your observations in your journal.
5. On the blackboard or overhead, diagram the formula for TSI:

$$TSI = \frac{KS}{aE}$$

Definition of symbols.

K = thermal conductivity
S = strength
α = coefficient of expansion
E = Young's modulus

6. On the blackboard or overhead define:

   a. *Thermal conductivity*—How well a material transmits heat. *High number*—better thermal conductivity.

   b. *Strength*—How well a material resists being broken. Expressed in load bearing capacity as pounds per square inch (PSI) or pascals (Pa), using international units for measurement.

   c. *Coefficient of expansion*—The ratio of the change of length per unit length, or change of volume per unit volume, to the change of temperature.

   d. *Young's modulus*—Stress divided by strain. How hard was the material and how far did it stretch?

Glass Bead on a Wire
Instructor Notes

Reliability

Several problems occur with this experiment: 1) the molten beads fall off the wire, 2) the wire gets too hot, and it melts, and 3) students do not melt the crystals completely and, therefore, don't get the colorful effects that they desire. All these problems can be overcome by following the directions carefully and trying the process several times.

Estimated Time for Activity

One class period.

Teacher Tips

1. The glass bead on a wire test was used by early miners to determine types of ore found in mineral deposits.
2. The wire used in the "Drawing a Wire" activity can be used to make a glass bead on a wire. If you do not want to draw copper wire out, purchase 16-18 gage wire.
3. To get different colors, use dilute solutions of nitrate salts of Ni, Co, Cu, Fe, or Mn. Make the solutions by adding 5 g of the salt to 100 g of water Dip the nichrome wire with a glass bead into a solution and reheat.

Safety

1. Wear safety glasses at all times.
2. Warn students of hot glass beads. They fall off the wire, splatter, and can cause burns.

Activity: Glass Bead on a Wire

Student Learning Objectives

At the end of the activity students will be able to:

- make a glass bead with ordinary household materials and equipment
- describe through writing and discussion the effect of some metal oxides on glass.

Materials

- Nichrome wire (0.81 mm)
- Copper wire, 12 ga
- Borax, 20 Mule Team or sodium borate ($Na_2B_4O_7$)
- Grease

Equipment

- Propane torch/bunsen burner/oxy-acetylene torch
- Draw plate
- Wire cutters
- Needle nose pliers
- Vise grip pliers

Procedure

Caution: Wear safety glasses at all times. Wear leather gloves when working with the hot, molten chemicals.

1. Cut or obtain a 12 cm to 15 cm length of nichrome wire.
2. With needle-nose pliers, form a closed, oblong loop on the end of the wire approximately 7 mm long and 3 mm wide (see Figure 6.2).
3. Heat loop end of wire with available torch until it begins to turn red in color. Note: If the wire gets too hot it can melt.
4. Dip heated end into borax, then carefully heat with torch until glass bead is formed. If bead is too small or incomplete, then dip it in borax again and heat until desired bead is formed. Continue melting the bead until it forms a droplet that is glassy and transparent. To keep the bead from dripping, gently rock or rotate the wire. Note: Overheating will evaporate the borax, do the melting in the cool, outer portion of the flame as demonstrated in Figure 6.2.

5. Obtain a length of copper wire from the instructor, and draw it through the draw plate using a pair of vise grips until it is approximately 0.81 mm. (for details, see Metals section, *Drawing a Wire Lab*). If you have a piece of copper wire approximately 0.81 mm in diameter, you may skip the drawing process.
6. Repeat steps 2-5.
7. Record your observations in your journal. Compare the beads, and describe any other observations you made while making the glass bead, i.e., what differences did you notice in color and why? What differences did you notice in the wires?

Extension Activity

Using nichrome wire, from a molten glass bead following steps 2-5 above, then dip the hot glass in solutions of metallic salts of nickel (Ni), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), etc.

Your instructor will assist you with preparing the solutions or let you know where they are located in the laboratory.

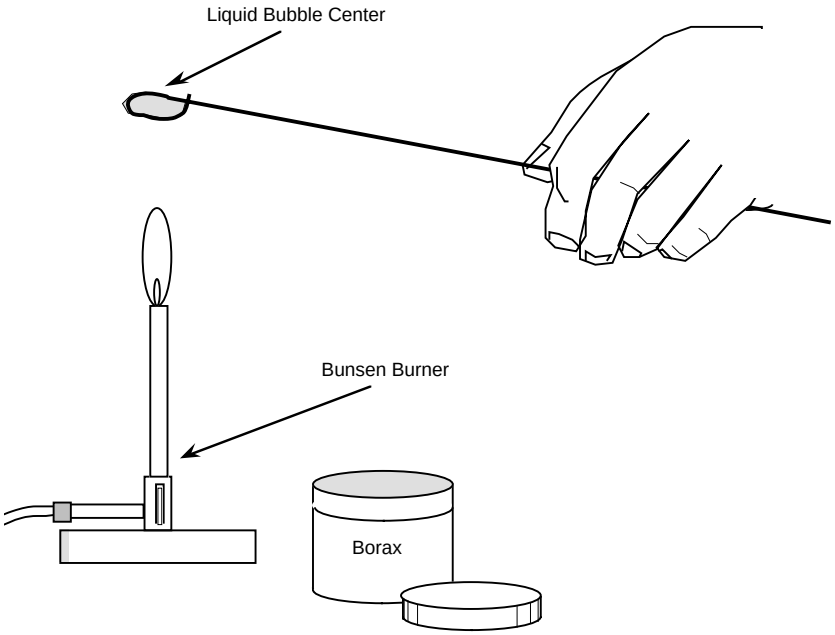


Figure 6.2. Glass Bead on a Wire

Glass Bending and Blowing
Instructor Notes

Reliability

Students really enjoy this experiment, and it works well. The only part that sometimes causes disappointment is blowing the glass, it is difficult to do.

Teacher Tips

1. Buy an inexpensive variety of glass rod or tubing such as flint glass, which has a low melting point. The 6-mm glass tubing works well. Other types of glass such as borosilicate glass (laboratory glassware) and soda-lime-silica glasses (glass containers that food products come in and window glass) have melting points above 500°C and are difficult for most people, except skilled glassblowers, to work with.
2. Bunsen burners usually do not get hot enough to be successful in blowing glass. Propane burners are hot enough to do some glass blowing. If students blow too hard, two things frequently happen, either they blow a bubble too large and thin that it collapses, or they blow a hole in the glass.
3. Encourage students to discover that you really don't "blow" glass. Professional glassblowers know that hot air expands. They "puff" air into the tube that has been sealed on the other end and use their tongues or fingers as plugs. With the volume of the tube sealed, they reheat a portion of the glass to soften it. The expanding hot air inside pushes out a bubble. They repeat this cooling, sealing, and reheating process until they get the shape they want.
4. Optical fibers are thin fibers, usually glass or plastic, used to transmit light. Have the students try making a glass fiber as they are working.
5. Glass may be remelted and/or recycled.
6. Glassblowers use wooden tools soaked in water. Why?

Safety

See Activity.

Disposal

See Activity.

Activity: Glass Bending and Blowing

Student Learning Objectives

At the end of the activity students will be able to:

- heat glass to make it soft enough to manipulate
- make a smooth right-angle bend and fire polish the ends
- cut glass tubing using a file
- draw tubing to make a pipette
- blow a small bubble with at least twice the diameter of the original tubing
- melt a piece of glass rod to make an optical fiber
- describe and demonstrate how polarized film may be used to detect stresses in glass
- use the expansion of heated air to work the glass.

Materials

- Glass tubing, 5 mm
- Glass rod

Equipment

- Safety glasses
- Burner
- File
- Polarized film
- Light table (or overhead projector)
- Laser or other bright light
- Container for finished glass pieces

Procedure

Observe the demonstrations given by your instructor.

Caution: Wear safety glasses and leather gloves at all times during this activity. Potential for serious burns exists when working with hot glass. It cools slowly and cannot be quenched in water like metal. Keep all hot surfaces on a heat-resistant, ceramic pad until cool.

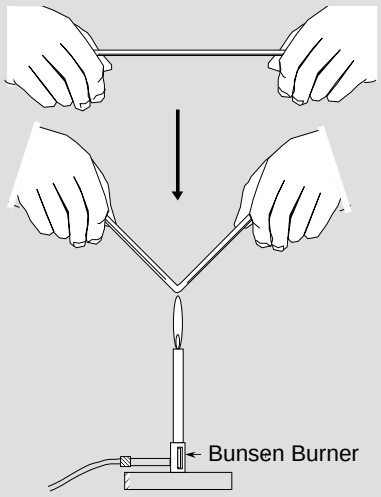


Figure 6.3. Glass Bending

Glass Bending: Use a file to cut a 15- to 20-cm piece of glass tubing. Use the burner to heat the glass near the center (see Figure 6.3). Rotate the glass as it is heated. When the heated portion is soft, remove the glass from the heat. Bend the ends of the glass upward. Cool, then fire polish the ends.

Caution: Heated portions retain heat and require several minutes to cool before handling.

Making a Pipette: Cut a second piece of tubing 10- to 30-cm long. Heat as you did above; when hot, remove the tubing from the heat, and pull the ends apart (as demonstrated). You must pull vertically. Cut the pipette. Carefully fire polish it after the glass has cooled.

Blowing a Glass Bubble: Obtain a third piece of tubing at least 20 cm long that is fire polished and has cooled on the end. You may need to fire polish this yourself. Heat the end of the tube you will blow until molten, then seal the end with pliers. Reheat the sealed end, then blow into the cool end. Continue to rotate the tubing as you blow. This process may need to be repeated several times until you have a bubble with at least twice the diameter of the tubing. Try "blowing" glass and the "puff, seal, and reheat" technique described by your teacher and used by professionals to "blow" glass.

***Note**: Propane burners get hotter than bunsen burners and may enhance this step.*

Making an Optical Fiber: Obtain a piece of glass rod. Heat it as demonstrated and form an optical fiber. You may want to try both the gravity and pulling techniques demonstrated to form an optical fiber. Let the glass cool, then use the laser (or bright light) to see if your fiber acts as an optical fiber (transmits the light).

Glass Disposal: Throw all glass into a special collection container labeled clearly: BROKEN GLASS—CAUTION

- Use polarized material to check your glass pieces for stress (as demonstrated). First hold the polarizers against each other, and rotate them until no light is transmitted through them. Then insert the glass between the polarizers in this orientation.
- As you clean up, place your bend, pipette, blown glass, and optical fiber in a plastic bag or container that has your name on it.
- Write a summary of this lab in your journal. Include not only what you did, and how, but your thoughts and responses to the activity.

Caution: Hot glass can cause incredibly thorough burns on skin, lab benches, books, and back packs! Place all hot glass on a heat-resistant, ceramic surface to cool.

Standard Glass Batching
Instructor Notes

Reliability

This experiment works well. Students always get some kind of glass. The quality depends on student accuracy. Encourage students to be patient when calculating. It takes time to feel comfortable with the numbers.

Estimated Time for Activity

One class period.

Teacher Tips

1. Ziplock bags can be used.
2. Washing soda is a cheap source of Na_2CO_3. Borax can be used for a boron and sodium source. Both are inexpensive at local grocery stores in the laundry section. Boric acid is available in drug stores.
3. If you use borax ($Na_2B_4O_7$ x 10 H_2O), you get $Na_2O + 2B_2O_3$. Be sure and account for the ten water molecules in each Borax compound that will be driven off when heated. You can heat the borax in an oven at 80°C overnight to remove most of the water.
4. The silica (SiO_2) from Fisher (240 mesh) works very well. Coarser materials take longer to melt and can cause other problems.

Suggested Questions

Have students show their work where math is required.

5. If each candy bar weighs 2 lb and we have 30 lb of candy bars, how many candy bars do we have?
6. If a certain size of nail weighs 0.04 lb, and we need 500 nails, what weight of nails would we buy?
7. How many nails would we have if we had a mole of nails?
8. Your girlfriend calls you “mole breath.” How many breaths would you have to take to have a mole of breaths?
9. Tell how much a mole of each of the following weighs: uranium (U), table salt (NaCl), copper (Cu), and carbon dioxide (CO_2)
10. Why are chemicals measured by weight?
11. You want 3 moles of silica (SiO_2). How much would that weigh?
12. Your friend asks you how many pennies are in a huge pile. How could you easily determine this fairly accurately?

Safety

1. Be careful when mixing to avoid creating dust. Breathing fine dust particles of any kind is a health hazard. Ventilation of batching area is recommended.

Background Information: Mole Percent

When batching glasses, you need to perform calculations to figure out the weights of various chemicals needed. The concept of the "mole" needs to be developed before these calculations are done. The following background information will help you understand the mole.

Three ways of buying things commonly exist: volume (gallons of gasoline), number (dozen eggs), and weight (pounds of oranges). Volume is fairly good for liquids, and it is convenient, but it isn't very reliable for solids because of such things as air gaps and irregularities. Also, volume changes with heat and pressure. Number is fine for regular things, but it is unfair to sell apples by the number since some are large and some are small. (Some of us have the same feelings about shoes and shirts too!) Most things are sold by weight, although these are usually pre-packaged, so we really buy them by the number of packages. Most of the things we buy by weight are "bulk" items. A few examples are bananas, grapes, candy at a candy store, coal, and nails.

One of the reasons nails are sold by weight is because small ones would be too boring and time consuming to count each time they are sold. If this were done, the price would also rise. In general, things are measured by weight to determine their number if things are too small to be conveniently handled. Two formulas that are used are:

#1 $$\text{Number} = \frac{\text{total weight}}{\text{weight of one}}$$

#2 $$\text{Total weight} = (\text{weight of one})\,(\text{number})$$

These ideas and formulas are also used with chemicals. Atoms combine to form chemical compounds. For example, experiments enable us to know that two atoms of hydrogen combine with one atom of oxygen to form one molecule of water (H_2O). Unfortunately, atoms are far too small to be counted. Therefore, we use weight and the above formulas to determine numbers of atoms.

Because two atoms of hydrogen combine with one atom of oxygen to form one molecule of water, it follows that two dozen atoms of hydrogen combines with one dozen atoms of oxygen to form one dozen molecules of water. Also, 200 atoms of hydrogen combine with 100 atoms of oxygen to form 100 molecules of water. Atoms are far too small to see hundreds, millions, or even trillions of them; so, a new number called a "mole" is used with atoms. It is huge! A mole is 602,000,000,000,000,000,000,000. This can also be written: 6.02×10^{23}

Therefore, two moles of hydrogen atoms combine with one mole of oxygen atoms to make one mole of water molecules. Mole is a number that works just like "dozen" but is much larger. The mole seems like a weird number, but is was selected because it works with the atomic weights that are found on the periodic table. For example, carbon has an atomic weight of 12.0, and one mole of carbon atoms has a weight of 12.0 g. It so happens that one mole of any element equals its molecular weight.

To determine the weight of molecules in a material or a chemical, each element that is part of the molecule must be considered. Just as 1 dozen watermelons does not weigh the same as 1 dozen doughnuts, so 1 mole of carbon atoms does not weigh the same as 1 mole of oxygen atoms. They are equal in number, but not in weight. To determine how much a mole of atoms of a chemical weighs, we add up the atomic weights of all of the atoms in the formula for the chemical. For example, sodium hydroxide (NaOH) and ammonia (NH_3):

Chemical	Element	Atomic Wt.	Number of Atoms	Total Wt.
NaOH	Na	23.0	1	23.0
	O	16.0	1	16.0
	H	1.0	1	1.0
			Wt. of 1 mole NaOH =	40.0 g
NH_3	N	14.0	1	14.0
	H	1.0	3	3.0
			Wt. of 1 mole NH_3 =	17.0 g

Therefore, one mole of NaOH molecules weighs 40.0 g, and one mole of NH_3 molecules weighs 17.0 g, although there are equal numbers of each chemical.

Remember, a mole is just a term to represent a very large number. If we know the type of chemical, we can use the periodic table to determine how much a mole of that chemical weighs. Therefore, moles allow us to use weight to determine numbers of atoms or molecules.

In the glass batching lab, the concept of the mole will be used to determine the amount of each chemical to add to the glass. The calculations are explained in the following section.

Loss on Ignition

In this lab, almost 140 g of source chemicals are required to produce 100 g of glass. When you melt your glass, check to see how close you come to 100 g, and explain any differences. This loss of weight when melting material is called “loss on ignition” and must be accounted for when preparing the glass.

You may want to check to see how this loss on ignition works by performing a simple decomposition experiment. Gently heat a known amount of boric acid (H_3BO_3) or Twenty Mule Team Borax ($Na_2B_4O_7*10H_2O$) above its decomposition temperature, and then re-weigh the material after it cools. Compare the loss on ignition you measure to the one you calculate. If there are differences they may be caused by extra moisture in the sample, impurities in the sample, or vaporization of the sample. In most cases, the differences will be minor.

Activity: Standard Glass Batching Calculations

Student Learning Objective

At the end of the activity students will be able to:

- use two equations:
  1. Number = $\frac{\text{total weight}}{\text{weight of one}}$
  2. Total weight = (weight of one) (number) in problem solving
- state how large a mole is
- apply the mole concept in determining molar masses
- describe why the mole concept is used
- use the mole concept in problem solving
- complete a chart in their journal that includes the precise amount of source chemicals to combine in producing glass of a specific composition
- use the process of conversion from a glass formula to the actual amounts of source chemicals for a glass batch.

Materials

- Periodic chart
- Sample reagents

Procedure

Note: *This procedure takes you through the entire process for calculating a glass composition. As you become familiar with these calculations, you will be able to quickly extract parts of these calculations to use in determining a glass composition. Be patient, it may take some time to understand all the concepts presented. After batching a number of glasses you will become familiar with these calculations.*

1. The desired glass composition to be produced must be expressed as a mole fraction of each constituent. For example, a simple borosilicate glass could be expressed as $Na_2O \bullet B_2O_3 \bullet 2\ SiO_2$. This chemical formula simply states that glass formers will exist in the glass in the ratio of one mole of Na_2O (sodium oxide), to one mole of B_2O_3 (boron oxide), to two moles of SiO2 (silicon dioxide or silica).
2. Determine from the periodic table the weight of one mole of each of the oxide components of the glass expressed as grams per mole (grams/mole). This is a process for obtaining the molecular

weight of a compound or chemical. For example, in determining the molecular weight of B_2O_3, we find the molecular weight of boron to be 10.81 g, and the molec-ular weight of oxygen to be 15.99 g. The weight of one mole of B_2O_3 is equal to 2(10.81) + 3(15.99), which is 69.62 g/mole. The calculations for all three glass components are shown below.

Na_2O	Na = 22.99 g/mole, O = 15.99 g/mole Na_2O = 2(22.99) + 15.99 = 61.98 g/mole
B_2O_3	B = 10.81 g/mole, O = 15.99 g/mole B_2O_3 = 2(10.81) + 3(15.99) = 69.62 g/mole
SiO_2	Si = 28.09 g/mole, O + 15.99 g/mole SiO_2 = 28.09 + 2(15.99) = 60.08 g/mole

3. Determine the total molecular weight of the $Na_2O \cdot B_2O_3 \cdot 2SiO_2$ glass by summing the weights contributed by each glass component.

Na_2O	61.98 g
B_2O_3	69.62 g
2 SiO_2	2(60.08) = 120.16 g
Total	251.76 g

4. Normalize each molecular weight fraction to 100 to determine weight percent. See below.

Na_2O	$\frac{(61.98)}{(251.76)}$ x (100) = 24.62 weight percent
B_2O_3	$\frac{(69.62)}{(251.76)}$ x (100) = 27.65 weight percent
2 SiO_2	$\frac{(120.16)}{(251.76)}$ x (100) = 47.73 weight percent

5. The sum of the weight percentages for all glass constituents must equal 100%. This is a good double check of the calculations.
6. Many raw materials are available as compounds that decompose to the desired oxide upon heating. Compounds such as Na_2O and B_2O_3 are unstable in air and so are almost impossible to obtain as pure compounds. Na_2O, is purchased as Na2CO3 (sodium carbonate. In the glass-making process, the Na_2CO_3 decomposes to form the desired Na_2O. Because we will start with Na_2CO_3, this

is called a "source chemical." Listed below are our glass components, their sources, and changes that occur:

Source Chemical	Source Chemical Formula	Glass Component + Off Gas
Sodium carbonate	Na_2CO_3	Na_2O + CO_2
Boric acid	$2\ H_3BO_3$	B_2O_3 + $3\ H_2O$
Silica	SiO_2	SiO_2

We need to determine what mass of the source chemical is needed to produce one gram of component. This is our "conversion factor." Formula masses are used to determine this for each component.

a)

Na_2O Compound	Element	Mass	Atoms	Total Mass
Na_2O	Na	22.99	2	45.98
	O	16.00	1	16.00
		Mass of 1 mole	=	61.98 g
Na_2CO_3	Na	22.99	2	45.98
	C	12.00	1	12.00
	O	16.00	3	48.00
		Mass of 1 mole	=	105.98 g

Because 1 mole of Na_2CO_3 produces 1 mole of Na_2O, the ratio is:

$$\frac{\text{Source}}{\text{Component}} = \frac{1\ Na_2CO_3}{1\ Na_2O} \qquad \frac{105.98}{61.98} = 1.710$$

Therefore, 1.710 g of Na_2CO_3 will produce 1.00 g of Na_2O. This is our conversion factor.

b)

B_2O_3 Compound	Element	Mass	Atoms	Total Mass
B_2O_3	B	10.81	2	21.62
	O	16.00	3	48.00
		Mass of 1 mole	=	69.62 g
H_3BO_3	H	1.01	3	3.03
	B	10.81	1	10.81
	O	16.00	3	48.00
		Mass of 1 mole	=	61.84 g

The B_2O_3 component contains two boron (B) atoms, and the source contains only one B atom. Therefore, we need twice as much source. The ratio is:

$$\frac{\text{Source}}{\text{Component}} = \frac{2\ H_3BO_3}{1\ B_2O_3} = \frac{2\ (61.84)}{69.62} = \frac{123.68}{69.62} = 1.776$$

Therefore 1.776 g of H_3BO_3 is needed to produce 1 g of B_2O_3. This is our conversion factor for this chemical.

c) $\underline{SiO_2}$ Because we are using SiO_2 as our source, the ratio:

$$\frac{\text{Source}}{\text{Component}} = \frac{1}{1} = 1.000 \text{ g}$$

Therefore, 1.00 is the conversion factor in this case. Note: no decomposition takes place with SiO_2.

7. We will now go through a procedure to summarize our previous steps.

   a) Divide a sheet of paper into 5 vertical columns with the following headings:

Glass Component	Weight %	Source Chemical	Conversion Factor	Amount Needed (for 100 g)

   b) Fill in the component column with the compounds from step 1.

   c) Fill in the weight percent column with the values calculated in step 3.

   d) In the "source" column, place the formula of the actual chemical to be used in batching as noted in step 6.

   e) For each source chemical, place the conversion factor that was calculated in step 6.

   f) Multiply the number in the weight percent column by the corresponding conversion factor to calculate the amount of source chemical needed to make 100 g of glass. Place this number in the "Amount Needed" column. A completed work-up sheet is provided below for batching 100 g of $Na_2O \cdot B_2O_3 \cdot 2\ SiO_2$ glass:

Glass Component	Weight %	Source Chemical	Conversion Factor	Amount Needed (for 100 g)
Na_2O	24.62	Na_2CO_3	1.710	42.10 g
B_2O_3	27.65	H_3BO_3	1.776	49.11 g
SiO_2	47.73	SiO_2	1.000	47.73 g
			Total	138.94 g

Activity: Standard Glass Batching

Student Learning Objectives

At the end of the activity the student will be able to:

- measure, combine, and homogeneously mix dry chemicals (generally in the form of oxides and carbonates) to be melted to form a glass.

Materials

- Ice cream carton
- Plastic bags
- Permanent markers
- Spatula/spoon
- Crucible (DFC)
- Silica (SiO_2)
- Boric acid (H_3BO_3)
- Sodium carbonate (Na_2CO_3)

Equipment

- Top-loading electronic balance with accuracy of $\pm$ 0.1 g

Procedure

1. Prepare a glass recipe workup sheet listing your source chemicals and relative amounts (generally expressed in grams) of each component to be used in the glass.
2. Collect all source chemicals into a common area (usually somewhere near the balance); clean area to avoid contamination of source chemicals.
3. Using a permanent marker, record glass oxide composition, weight percent, and **your** initials on the plastic bag.
4. Inflate the plastic bag to check for defects or leaks. Place the plastic bag inside the ice cream container. Replace lid.
5. Tare* the balance, weigh the empty ice cream container, and record the weight on the container.
6. Place weigh boat onto balance. Tare balance.

**Tare* means return balance to zero.

7. Carefully clean spatula or spoon with water or ethanol, then dry it. Be very careful not to contaminate chemical sources with other chemicals or laboratory grit.
8. Weigh out each of the source chemicals, one at a time. Transfer from weigh boat to the ice cream container, and check off the weighed chemical on the workup sheet. **Note**: Accuracy and cleanliness are important.

> **Caution**: Avoid creating dust as the chemicals are being emptied into the collection container. Fine particles of any material are a health hazard.

9. When all constituents have been weighed out, a gross weight is then taken to ensure that no major constituent was omitted.
   a. Obtain gross weight by 1) removing weigh boat from balance, 2) tare balance, and 3) weigh ice cream container with added chemicals.
   b. Subtract tare weight of original empty ice cream container (step 3) from gross weight (step 6.) This weight should equal the total batch weight from the batch workup sheet. A deviation of $\pm$ 0.5 percent is acceptable.
10. The powder is now ready to be blended to obtain a homogenous mixture. Gently stir, avoiding making dust, to develop a fine uniform mixture free of lumps. The best method for mixing is to seal the open end of the plastic bag with air trapped inside the bag. Shake the chemicals for several minutes. With your fingers crush any lumps of chemicals, and reshake the batch. This process is known as “shake and bake.”

Extension Activities

1. Discuss why a mixture of carbonates and oxides is used. Look up the melting points and decomposition temperatures for the various chemicals used (i.e., *CRC Handbook;* the chemistry teacher will have reference books like this). To get high melting point compounds [i.e., silica (SiO_2) or alumina (Al_2O_3)] into solution at much lower temperatures, glass modifiers such as sodium oxide (Na_2O), lithium oxide (Li_2O), and calcium oxide (CaO) are used. These chemicals have a relatively low melting point and are very corrosive in solution—especially a molten solution. Boron oxide (B_2O_3) is a glass network former as are silica and alumina. These chemicals form the network in the glass and keep the modifiers “locked up” or chemically stable in the glass.
2. Note that mixtures melt at lower temperatures than the pure compounds. Compare your glasses to more common mixtures like adding salt to ice water to lower its freezing point (i.e., making ice cream and clearing icy sidewalks).

Glass Melting
Instructor Notes

Reliability

This experiment works well. The quality of glass produced, though, depends on the formula, furnace temperature, and time at melt temperature.

Estimated Time for Activity

Two class periods.

Teacher Tips

1. Preheat furnace to 1050°C. Do not exceed limit on furnace temperature.
2. Hot plate should be set on "high" and the annealing oven at 500°C. If the glass sticks to the hot plate or stainless steel, lower the hot plate temperature to "medium." This usually alleviates the sticking problem.
3. A good source for crucibles is DFC Ceramics (see Vendor List in Appendix). When ordering, ask that the crucibles be shipped UPS; this is less expensive than freight.
4. If you do not have a ceramic crayon, you can mark the crucible using a small brush and an iron salt or an iron oxide solution. Write on the crucible with the solution, and allow it to dry.
5. Stress to students that overfilling the crucible (more than 1/2 full) is a problem. As the chemicals heat and release gases, foaming will occur. It is often wise to check the melt about 5 min after it is placed in the furnace to see if foaming is a problem. This is especially true if the students are trying different ratios or formulas of glass that they are not familiar with and do not know how much foaming to expect. Remove the crucible from the furnace if foaming is excessive. Start the melting over with a new crucible and even less of a chemical batch so the foam will be contained in the crucible. If foaming continues to be a problem, check the chemical formulation; one of the chemicals may have too much water in it and need to be pre-treated to dehydrate it before further use.
6. First pour powder into a glass beaker. If students pour powder directly from a plastic bag, heat from the crucible melts the bag.
7. Glass may soak at 1050°C overnight to get good mixing but **be sure** your furnace maintains a stable temperature.

8. Students pouring glass for the first time are nervous. They often lift the pouring glass stream upwards, and as a result, the viscous glass puddle is pulled off the pour plate.
9. Usually, glass will have some bubbles in it. These bubbles are usually small and are remains from the foaming stage (decomposition of chemicals). The glass industry uses many techniques to remove bubbles from the molten glass. The students' best technique will be time—lots of melting time if bubbles are not wanted.
10. Watch students as they cut the glass streamer. Sometimes they get burned, especially if scissors are too small. Cut the glass streamer close to the crucible to prevent hot "strings" from developing.
11. If spatula for transferring glass bars is not preheated on the hot plate, the bars will often crack. Keep the spatula hot until the moment the glass is to be transferred to the annealing furnace, then move the glass quickly, but safely.

Safety

1. Hot and cold glass are the same color, beware! Move hand slowly over glass to determine if it is hot.
2. Students must wear safety glasses.
3. Have students wear gloves when handling hot material.
4. Have students remove metal articles from their persons, especially rings. These materials transfer heat quickly.
5. Have students practice before they do the actual glass pour, using tongs and moving crucibles while they are cool.
6. Watch out for cracked crucibles, they may break if excessive force is used while moving or pouring.

Disposal

1. Follow school regulations for normal broken glass disposal.

Activity: Glass Melting

Student Learning Objectives

At the end of the activity the student will be able to:

- melt, pour, air quench, and/or anneal a glass
- practice safe procedures for glass making.

Equipment

- Safety glasses (to be worn at all times)
- Heat-resistant gloves
- Ceramic crayon
- Tongs and spatula
- Ceramic brick to place hot crucible on after pouring glass
- Furnace
- Hot plate and stainless-steel pour surface
- Annealing oven
- Beaker, 250 mL
- Stainless steel bar
- Stainless steel stirring rod
- Stainless steel beaker
- Polarizing film

Procedure

Warning: Wear safety glasses.

1. Pre-heat furnace to appropriate temperature (usually 1050°C).

***Note**: Schedule time to accommodate pre-heat. It takes approximately 1 hour to heat the furnace from room temperature to 1050°C.*

If annealing, pre-heat hot plate, stainless-steel pour surface, spatula and annealing oven approximately 1 hour before pouring. Set up bar molds.

2. Use a ceramic crayon to label a crucible with your initials, class period, and common name of glass.

3. In the fume hood, fill the melting crucible 1/2 full with the blended glass powder. Place the remaining powder, if any, into a Pyrex beaker, and set it aside.
4. Carefully open furnace door. Using gloves and tongs, transfer the crucible plus powder to the melting furnace. If oven is too hot, have your partner shield door with a ceramic heat shield. Close the furnace door. Allow glass powder to soak heat at temperature for approximately 20 min.
5. Remove the crucible and observe the melt. Powder should be molten with a viscosity of approximately 100 poise (consistency of honey). If it is not molten, increase set point temperature by 50°C and repeat step 4. This step should be repeated as many times as necessary until the powder melts and resulting glass has viscosity near 100 poise or the furnace temperature capacity is reached.

Caution: Do not exceed furnace temperature limit.

6. Remove the crucible from the furnace and carefully pour the blended powder from the Pyrex beaker onto the top of the molten glass until the crucible is 2/3 full. Replace crucible in furnace. Several powder additions may be required before all glass is in the crucible.
7. Soak for 1/2 hour at 1050°C. The melt soak time begins after the **last** addition of dry chemicals to the melt.
8. At 30-min intervals, stir the melt to ensure homogeneity by removing the crucible containing the glass and, while holding the crucible with metal tongs, mechanically stir the melt using a clean, 1/4-in. stainless-steel rod. This step can be skipped if care was taken in diligently mixing the chemicals. **Note**: Bubbling and foaming during the initial part of the melt also aid the mixing of the batch.

Pour Procedure

10. Using gloves, safety glasses, and tongs, remove the crucible from the furnace and either 1) air quench or 2) pour glass bars for annealing, according to the following steps:
    a. **Air quench** - pour the molten material quickly onto a stainless steel pour plate. You may need to cut the glass from the crucible using scissors. Allow the material to cool until the glass surface is no longer dented by a slight tap of a metal spatula. Slide glass off pour plate into a stainless-steel beaker to contain flying particles produced when glass fractures upon cooling.

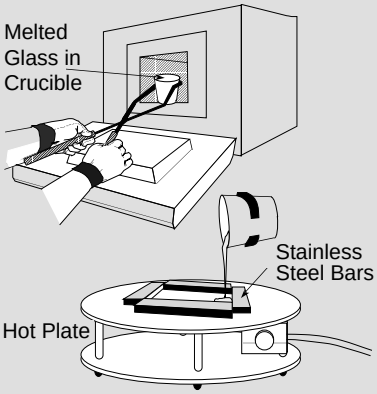


Figure 6.4. Glass Making

Caution: The stainless-steel beaker may become quite hot.

***Note**: Set hot plate on high (~300°C) and annealing oven at 500°C.*

Safety Precaution: Heat-resistant gloves, reflective face shield, and safety glasses must be used when handling the molten glass!

b. **Glass bars** - Remove molten glass from furnace, and pour into heated bar molds as quickly as possible (see Figure 6.4). Allow this material to cool until top surface of bar is no longer dented by a slight tap from metal spatula. Dismantle bar mold rapidly, and transfer the bar to the annealing oven using a heated spatula. Soak at annealing temperature for 2 hours, then turn the oven off and oven-cool to room temperature. Do not open furnace until it has completely cooled; otherwise, the annealing process is disrupted and the 2-hour annealing must begin again. Sometimes the glass will crack or shatter if the annealing process is disrupted.

***Note**: This experiment may be interrupted or stopped at many places, which allows students to do the work over several days. Use caution, however, when allowing the glass to soak for extended periods (i.e., 4 hours) in the furnace. This will cause the crucible to erode. Moreover, certain chemicals such as calcium oxide or large amounts of sodium oxide can cause the crucible to erode in less than 30 min.*

Checking Annealed Glass

11. If the glass is clear and has been annealed, the glass can be checked for stresses by using two pieces of polaroid film. Sandwich the piece of glass between the two layers of polarized film, and hold the assembly so that direct light from an overhead projector or a fluorescent lamp passes through the materials. Rotate one of the polarized films 90° so the light waves passing through the assembly are altered. Stresses in the glass will appear as reddish bands. In an unannealed or poorly annealed glass, the stress lines will be thin and numerous. In a glass partially annealed, and stress almost totally relieved, the bands will be broad and have almost no color. In a glass fully annealed, no lines or red bands will be observed.
12. For glass that did not anneal well, place the glass back into a cool furnace, turn it on, and allow it to heat 25°C higher than previously annealed. Let it anneal for 3 more hours, then let it cool down in the furnace over night. Check for stress lines using polarized film the following day.

Dragon Tears/Dragon Dribble
Instructor Notes

Reliability

Not every tear falling into the water will be whole. Many break upon cooling. Make many dragon tears, and a few will hold together.

Estimated Time for Activity

One class period.

Teacher Tips

1. Heat glass before class period begins.
2. When molten glass is poured into water, the rapid cooling of the glass exposed to the water and the slower cooling of the glass in the interior causes severe stress. This result is the glass surface is placed under compression. This compression may be demonstrated by taking a piece of the dragon dribble and breaking it. The stress is released by breaking the glass, which shatters into very small pieces. Use extreme caution, the flying glass can be dangerous. It's safest when done in a plastic bag.
3. The outside surface of the tear (drop) freezes as it hits the water.
4. The outside surface of the tear freezes in a low-density condition. The inside cools more slowly, resulting in a higher density.
5. The inside material is contracted relative to the outer skin. This results in a surface in compression (25,000 - 50,000 p.s.i. or much higher). Ceramics are strong in compression.
6. Cutting the "tail" off the dragon tear upsets the forces of equilibrium, which causes the dragon tear to break up into **dust**!
7. Examine a dragon tear, tempered glass, using polarized film. Follow step 11 on page 6.36.
8. Industrially tempered glass is air cooled by jets of air.
9. Students may also remove a tear from the water and anneal the tear to observe the change in the way the face fractures. Follow Step 12 on page 6.36.

10. With your students in a classroom setting, discuss tempered glass and why highly stressed glasses are made. (All automobile glass is tempered except for the windshield). Note the rainbow spots of the “temper shift” in the glass. Car windows and plate glass will often get oily looking “rainbow” spots on them. This is the “temper shift.” Tempered glass is very strong glass, designed to break into small pieces so people do not get severely cut in an accident. In the discussion of glass tempering be sure to include the terms compressive and tensile forces and their role in tempering.
11. Corelle dishes are a good example of a highly stressed material.

Safety

1. Students must wear safety glasses.
2. Cut tail in a plastic bag.

Disposal

1. Put crucible in normal trash.
2. Put glass in a science department glass disposal container.

Activity: Dragon Tears

Student Learning Objectives

At the end of the activity students will be able to:

- produce a “dragon tear”
- successfully cut the dragon tear in order to observe the effect of tempering and internal stresses.

Materials

- Plastic bag
- Glass from previous experiment
- Crucible

Equipment

- Melting furnace
- Metal tongs
- Stainless steel beaker
- Safety glasses
- Heat-resistant gloves
- Scissors or diagonal (dike) pliers
- Polarizing material
- Light source

Procedure

Warning: Wear safety glasses at all times.

1. Use the standard Na_2O, B_2O_3, $2SiO_2$ glass composition. Melt a small amount of glass (approximately 50 g) in the furnace at 1050°C for 1/2 to 1 hour. Fill stainless-steel beaker with cold water, and place it near oven.
2. Remove the molten glass from the furnace, and slowly pour the glass, drop by drop into the beaker containing water. Allow long fibers to trail from each droplet of glass. It will take some experimentation to produce whole droplets. Be patient.

3. When glass becomes too viscous to pour, return crucible to furnace for approximately 10-15 min. Step 2 can then be repeated. Set hot crucible on appropriate heat-resistant surface.

Caution: Step 4 is a dangerous step. Make sure all people in the laboratory are wearing their safety glasses.

4. After cooling, remove droplets with their long trailing fibers from the beaker. Place droplet in plastic bag with end of fiber exposed. Hold the droplet with one hand and begin cutting fiber, using diagonal-cut pliers, at the farthest point from the droplet. Continue cutting fiber, moving progressively closer and closer to droplet. At some distance (usually less than 3-4 cm) the dragon tear will explode into sand-sized particles in the bag.

Activity: Dragon Dribble

Student Learning Objectives

At the end of the activity students will be able to

- demonstrate the forces placed on glass when it is cooled rapidly.

Materials

- Batch of pre-melted glass [a ratio of 1:1:2 (Na_2O, B_2O_3, $2SiO_2$) works well] in crucible

Equipment

- Lindberg furnace
- Tongs
- Leather gloves
- Scissors
- Plastic bag
- Large Can (No. 10), bucket, or stainless steel-beaker
- Burner
- Safety glasses and/or face protection
- Polarized film

Procedure

Warning: Wear safety glasses and leather gloves for this experiment.

1. Use the gloves, tongs, and eye protection to remove the melted glass from the furnace.
2. Pour the glass in a small continuous stream into the can, bucket, or stainless-steel beaker containing water (see Figure 6.5). (The glass should form a continuous ribbon about the thickness of a dime or slightly thicker.)
3. After the glass has cooled, remove it from the water. (Any long pieces may be cut by melting with a Bunsen burner.)

Caution: Make sure everyone in the laboratory is wearing safety glasses. The tempered glass is dangerous if it shatters.

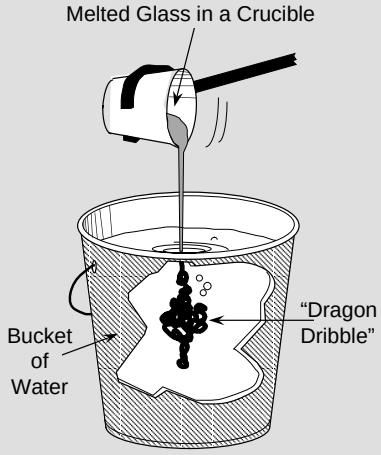


Figure 6.5. Draggon Dribble

4. Examine the glass with two pieces of polarized film. Orient the polarized film so little or no light is transmitted through it. Then place the glass between the polarized film and describe what you observe. Compare this to glass that was allowed to cool slowly. Check step 11 on page 6.36 for further details.
5. Place a piece of dragon dribble glass in a transparent plastic bag.
6. Break the glass in the bag. It should shatter into tiny pieces.
7. Record all observations in your journal.

Glass Coloring
Instructor Notes

Reliability

Students love this one! The biggest problem is using too much metal oxide; it makes the glass opaque.

Estimated Time for Activity

Two class periods.

Teacher Tips

1. This activity generates a lot of enthusiasm. It is a good example of the multicomponent conceptual learning process students encounter as they do the stained glass project (see Figure 6.6).
2. Varying the amount of the metal oxide varies the color intensity and sometimes the color. Color can also be affected by melting temperature.
3. Having ovens and furnace at operating temperature before class saves much time.

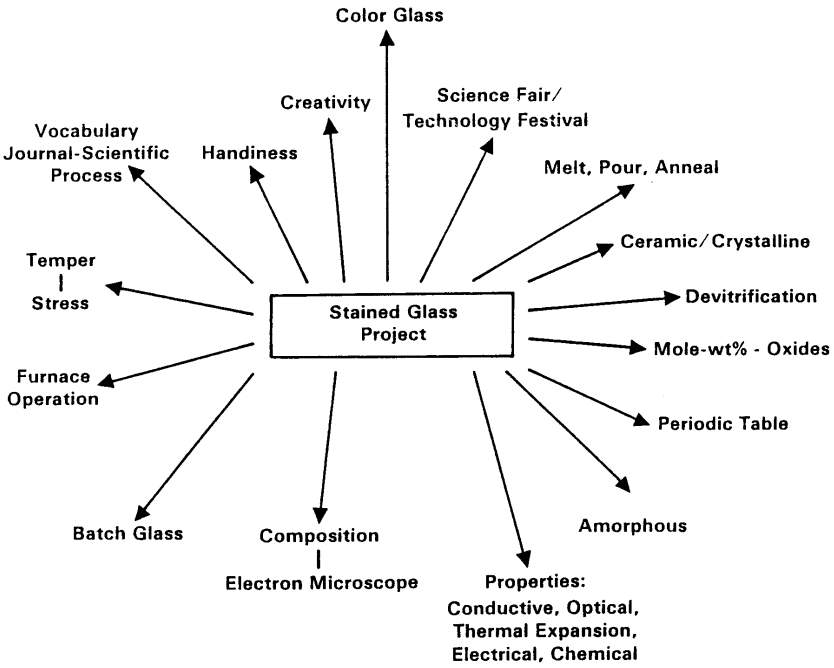


Figure 6.6. Diagram of the Multicomponent Conceptual Learning Students Encounter as they do a Stained Glass Project

4. Glass can be batched and colored one day—melted, poured, and annealed a second day.
5. You do not need to use oxides; carbonates work very well. They decompose to oxides during heating.
6. Art supply stores can give very good prices on carbonates as they are used in glazes.
7. Color is an excellent way to introduce students to spectroscopy and the electronic structure of atoms. Discuss what color is. Use a prism to generate simple spectra of your glasses.
8. Discuss color *control*. Can students make the same color twice?
9. Reference: Nassau, K. 1983. *The Physics and Chemistry of Color—The Fifteen Causes of Color,* Wiley, New York.

Safety

1. If crushing glass from previous lab, be careful. Students must wear goggles.
2. Use caution when pouring and annealing hot glass.

Disposal

1. Normal science department procedures.

Activity: Glass Coloring

Student Learning Objectives

At the end of the activity the student will be able to:

- describe the effect of adding a metal or metal oxide to a glass batch
- identify which metal oxides are responsible for which color changes.

Materials

- Glass from *Glass Melting* experiment or materials for melting glass from *Glass Melting* experiment
- Chromium (III) oxide, Cr_2O_3 (green)
- Neodymium oxide, Nd_2O_3 (light blue)
- Cobalt (II) oxide, CoO (dark blue)
- Copper (II) oxide, CuO (royal blue)
- Iron (III) oxide, Fe_2O_3 (brown)
- Crucible
- Plastic bag

Equipment

- Safety glasses
- Face shields
- Gloves
- Annealing oven
- Furnace
- Hot plate and stainless-steel pour surface
- Tongs
- Spatula
- Stirring rod
- Balance
- Weigh boat
- Stainless steel beaker
- Thick metal rod for breaking glass

Procedure

Safety Precaution: Safety glasses, face shield, and gloves should be worn when crushing glass or handling molten glass.

1. Prepare a batch workup sheet for a Na_2O, B_2O_3 $2SiO_2$ glass, or use previously melted borosilicate glass.
2. Batch the chemicals if you are going to prepare a new glass for this experiment. If you use glass prepared during a previous lab, crush the glass in the stainless steel beaker using a thick metal rod. Transfer your chemical batch or crushed glass to a crucible.
3. Weigh out 0.20 g of the desired metal or metal oxide in a small weigh boat.
4. Pour this into the crucible and stir.
5. Follow the melt and pour procedure in the Glass Melting lab. (Steps 5-10 using 10b for glass bars).

Extension Activities

1. Observe how color varies with thickness and concentration.
2. Try to identify the elements that color common glass (like 7-Up bottles, Coke bottles, beer bottles, etc.)
3. Not all the raw materials used to introduce color may be colored. How can this be possible?
4. Oxidation state will also affect color. (Note: Iron can be green or brown, depending on its oxidation state.)
5. Anneal the glasses until they crystallize, and examine them for changes in color and intensity.

Glass Fusing*
Instructor Notes

Reliability

This lab may take some experimentation. The actual temperature of your furnace, the type of glass used, and where the glass is placed in the furnace may affect how well the glass fuses. You may have to try it a few times to determine what gives the best results. Students appreciate this activity.

Estimated Time for Activity

One class period, but then the furnace should be monitored.

Teacher Tips

1. Fusing is the process of placing compatible glasses on a kiln shelf in a kiln. The temperature of the glass is slowly raised to around 800°C, and the glass is then cooled slowly through the annealing region.
2. Glasses from different manufacturers frequently have different ingredients, and this results in different coefficients of expansion. When this occurs, the glasses are said to be incompatible. Sometimes different glasses from the same manufacturer have different coefficients of expansion. When glasses have different expansion rates, they will fuse but then shrink at different rates. This will result in a high amount of stress, which usually leads to cracks eventually forming in the project. Some manufacturers sell a type of glass specifically designed for fusing. (Although it is fairly expensive, dichroic glass gives a nice effect when fused.)
3. Devitrification (forming of crystalline material) may occur as the fused glass is allowed to cool slowly in the annealing process. An unattractive change in the appearance of the glass may result from this. To prevent the formation of crystalline material, an overglaze is used. You may purchase “Spray A,” or you may make your own from 20 Mule Team Borax. Mix 5 parts water with 1 part Borax by volume. Heat this mixture until the Borax dissolves. The Borax overglaze should be applied when it is hot, and it is most easily applied by spraying.

*This activity was developed by Spectrum Glass, Woodinville, Washington.

4. A kilnwash or shelf primer is recommended to be used on the surface upon which the glass is placed in the fusing process. If not used, the fused glass may stick to the surface. A mixture of 40% kaolin and 60% alumina hydrate by weight is a kilnwash recommended by Spectrum Glass.
5. Polarizing film may be used to check the fused glass project for stress that could exist due to the incompatibility of the glass.
6. Several good books are available on glass fusing, including: *The Fused Glass Handbook* (revised edition) by Gil Reynolds, (distributed by Fusion Headquarters, P.O. Box 69312, Portland, OR 97201 and *Glass Fusing, Book One* by Boyce Lundstrom and Daniel Schwoerer, published by Vitreous Group/Camp Colton, Colton, OR 97017.
7. Terms used in the lab:
   Set point - The temperature the kiln is set for in this step.
   Soak time - Length of time the temperature remains at the set point.
   Flash vent - Turn off furnace. Open furnace door for 8 seconds. Close.
   Drift - Allow the furnace temperature to decrease with power off and door closed.
8. Students may want to attach pins or clips to these to use as jewelry.

Safety

1. Students need to be careful of cutting themselves on the scrap glass, which is usually used for this activity. Students must wear goggles.
2. Use caution when heating glass in a furnace or opening furnace door when hot.

Disposal

1. Place waste glass in a glass disposal container.

Activity: Glass Fusing

Student Learning Objectives

At the end of the activity students will be able to:

- show a finished product that demonstrates creativity
- tell why an overglaze spray is used
- tell about the compatibility of different glasses
- explain the purpose of kilnwash
- explain the fusing process.

Materials

- Stained glass pieces
- Overglaze spray
- Kilnwash
- Ethyl alcohol (optional for cleaning)

Equipment

- Steel wheel glass cutter/tapper
- Self lubricating carbide wheel cutter
- Combination breaker grozier pliers
- Furnace
- Kiln shelf or other high temperature, flat, smooth surface
- Gloves
- Metal tongs
- Safety glasses

Procedure

Warning: Wear safety glasses at all times when working with glass.

*1. Make a sketch of your planned fused glass project. (Your first trial should be with pieces no larger than about 10 cm [4 inches] square.)

*If your item is much larger than 10 cm on a side, check with your instructor for a good estimate on programming your furnace.

2. Either find pieces of scrap glass or cut out pieces using a glass cutter and some pliers. Use the glass suggested by your teacher.
3. Either place kilnwash on the surface you will be using or use a surface that already has been prepared.
4. Thoroughly clean all glass pieces you will be using with warm water. If they have oil on them, you may need to use ethyl alcohol.
5. Use overglaze spray to coat all exposed surfaces and edges.
6. Arrange the pieces of glass on the surface which has been kiln-washed and is ready for the oven. You may stack them 2 or 3 pieces deep, or you may want to place some crushed glass on other glass pieces.
7. Place the surface holding your project into the cool furnace; set the furnace for 788°C (1450°F) with a ramp time of 90 minutes, and turn on the furnace. Your instructor may need to okay this procedure.
8. When the temperature reaches the set point (788°C), let soak for about 10 minutes (or until it appears well fused). Then turn off the furnace, open the furnace door for 8 seconds, and then close the door and let the furnace cool. The opening and closing of the door is called flash venting.

Extension Activities

Recommended Firing and Annealing Charts for Fusing Glass

(These are suggested by Spectrum Glass for their glass. They are a good guide, but you may find through experimentation that other possibilities exist depending on the type and size of glass and the appearance of the product you are seeking.)

Fusing project	Ramp time	Set pt.	Soak time
Projects approximately 10 cm across and 2 layers deep	1. 90 min	788°C	10 min
	2. Flash vent		
	3. Drift	Room temp.	
Projects approximately 30 cm across and 2 layers deep	1. 2.5 hr	788°C	10 min
	2. Flash vent		
	3. Drift	510°	3 min
	4. 3 hr	371°C	
	5. Drift	Room temp.	
Projects approximately 50 cm across and 2 layers deep	1. 2.5 hr	788°C	10 min
	2. Flash vent		
	3. Drift	510°C	90 min
	4. 6 hr	465°C	30 min
	5. 3 hr	316°C	
	6. Drift	Room temp.	

Note: Drift means to allow the furnace to cool with power off and door closed until the next set temperature is achieved.

Project: Stained Glass - Sun Catcher or Window Panel

Student Learning Objectives

At the end of the activity students will be able to:

- show a finished product.

Materials

- Solder 50-50 lead tin alloy
- Flux
- Felt pen (non water soluble)
- Copper foil - copper wire
- Patina
- Finishing compound
- Stained glass
- Glass cleaner

Equipment

- Steel wheel cutter/tapper
- Self lubricating carbide wheel cutter
- 80-100 watt soldering iron - stand
- Sponge
- Combination breaker grozier pliers
- Breaking pliers
- Running pliers
- Glass grinder

Notes

1. Pattern shears reduce 1/32 in. of paper to allow for copper foil and solder.
2. Select colors and grain/pattern of glass, numbering each piece.
3. Keep iron **off** of foil to prevent cracking (thermal) and damage to adhesive backed foil.
4. Refer to text for difficult cuts.
5. Visit your local experts.
6. Reference: Wardell, Randy and Judy. 1983. *Introduction to Stained Glass*: *A Teaching Manual*. Wardell Publications, Belleville, Ontario.

Procedure

Warning: Wear safety glasses

1. Select a pattern (see Figure 6.7).
2. Trace pattern pieces onto glass with felt pen.
3. Score glass with self-lubricating wheel cutter
4. Tap bottom of score to promote crack growth. (Tap within 6 sec before molecules relax and dull the crack.)
5. Use grozier pliers or running pliers to snap pieces loose along score lines.

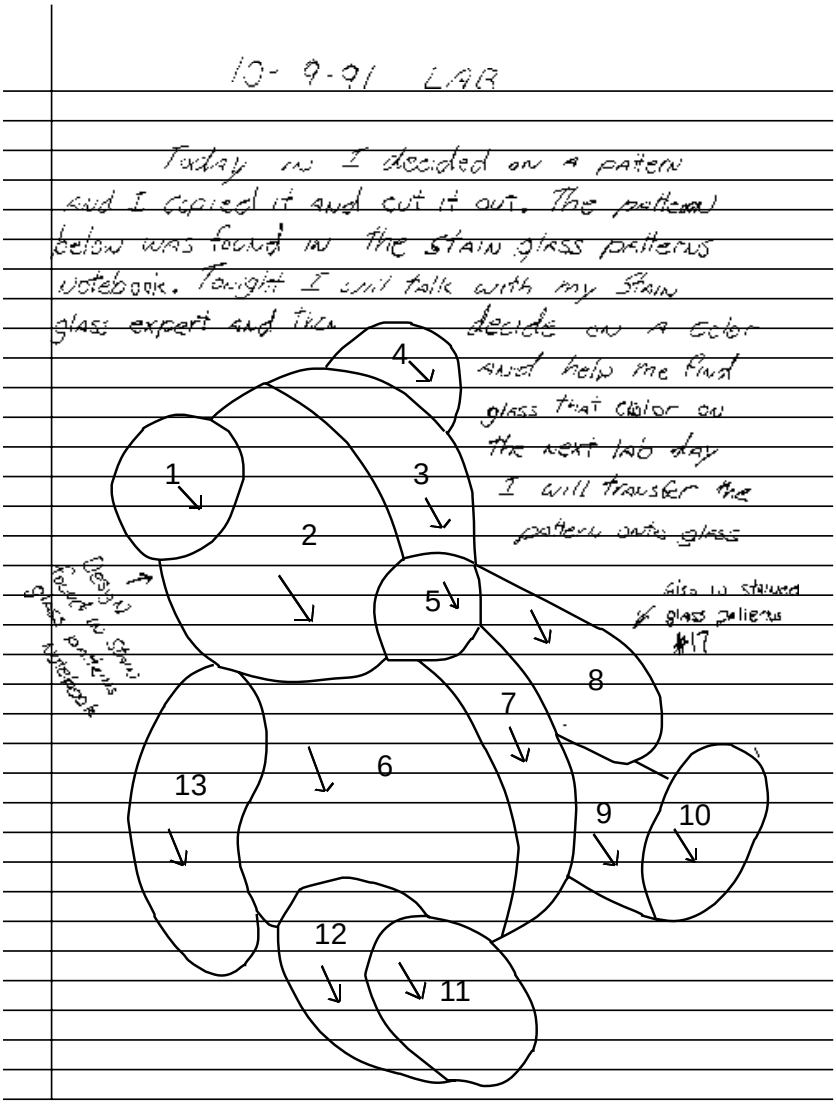


Figure 6.7. Pattern for a Project from Richland High School MST Student

6. Using the bench grinder, grind the edges of each piece to fit pattern.
7. Clean glass with glass cleaner.
8. Apply copper foil to each piece of glass with 1/4 in. overlap.
9. Fit pieces to form pattern shape.
10. Apply flux with small brush.
11. Tack with solder.
12. Solder both sides.
13. Clean glass.
14. Attach copper wire ring.
15. Apply patina to the solder to darken it.
16. Apply polishing compound.

Making Raku
Instructor Notes

Reliability

This experiment is very reliable. Students get excited about it. The only problem occurs when transferring project from charcoal to water. A piece may break.

Teacher Tips

1. This lab can be done over several days or weeks.
2. If you load the kiln with the pots to be raku fired and turn on the kiln about 3 hours before class starts, the pots will be ready for the students to do the exciting part. Once the pots have the characteristic red color and shiny appearance, they will stay at that state for quite some time in the hot kiln. Opening the kiln to remove a pot drops the temperature temporarily and should be done as quickly as possible to avoid damage to the ware and kiln.
3. An alternate to two separate firings is to use the raku firing to do both jobs. This is actually the way it was done originally. The problem is students tend to handle the green pots too roughly and they get broken before the firing.
4. The clay and glaze are readily available from pottery suppliers. Often the catalog will state that the clay or glaze is suitable for raku.
5. Have students try using clay from the banks of a river or stream.
6. Some students are very leery of reaching into the hot kiln to remove their pot because of the extreme heat they experience. It is best to quickly remove the pot as the lost heat cools the other pots, and they must reheat. Small kilns recover in about 5 min.
7. An art teacher can be an excellent resource person for this lab. Have the art teacher do the pinch pot technique teaching for your students. If that is not possible, try asking if one of your students knows the technique. Often, this is the case, and it gives that student a chance to be “special.”
8. Give students a copy of the paper, using the Raku Glazing Process to show oxidation-reduction in chemistry. They enjoy the story of the potter. The recipes for other glazes is included for those that would like to go further. Other effects than copper and cobalt are very interesting. Try using those two metals as they are readily available and give good results.
9. Pottery is significant in many ancient cultures, and this lab can easily be tied into history and social studies.

10. When the pots come out of the water, they often are crazed. Because the glaze and ceramic pot cool at different rates the glaze gets a cracked appearance. This is normal and is considered part of the aesthetics of the pot. If the pot is not quenched, the reduction is reversed as oxygen recombines with the exposed metal. It is nor-mal for the appearance of the pot to change over the first few days.

Safety

1. Take care when dropping the red hot pot in the sawdust to cover immediately; it will flare up. Be careful when removing the lid as the sawdust may burst into flame as oxygen re-enters the pail.
2. Use long tongs to handle all ware.
3. Work in teams where everyone has a job, i.e., 1) open kiln and close; 2) grab pot and move to sawdust; 3) bury pot.
4. Keep spectators far away.
5. When near an open kiln, remove **all** metal from your body. Coins, belts, eyeglasses, and earrings they can get hot enough to burn you.
6. You may want goggles that filter ultraviolet radiation and visible light for looking into the hot kiln.

Project: Making Raku

Student Learning Objectives

At the end of the activity students will be able to:

- make a clay pot using the pinch pot method
- describe the change in the pot after vitrification
- coat the pot with a raku-type glaze
- perform the raku technique upon the pot to observe the reduction and/or oxidation resulting from this technique.

Materials

- Clay, low-fire type
- Glaze, low-fire type
- Copper carbonate or other glaze metals as interest and budgets allow (see attachment)
- Paper cup or other container for glaze, 6 oz.
- Sawdust
- Nail for scratching initials
- Paint brush for applying glaze

Equipment

- Oven or kiln
- 5-gal metal bucket with lid
- Large pail for water
- Nylon string or wire
- Heat-resistant leather gloves
- Goggles
- Long-handled, 80 cm, tongs

Figure 6.8. Pinch Pot (Raku)

Procedure

1. Cut a softball-sized piece of clay from the brick, and work it into a ball shape.
2. Work the clay into a cup (pot) shape as demonstrated by the instructor. Try to make it a uniform thickness (see Figure 6.8.).
3. Set the pot aside to dry over night (or longer).

4. Turn the dry pot over, and scratch your initials into the bottom.
5. Turn the pot in to the instructor to be bisque fired, or bisque fire the pot at cone 4.
6. Observe and record the differences in the pot after it has been bisque fired.
7. Fill a 6-oz. paper cup 1/2 full of raku glaze. This is equal to about 100 g of dry glaze. To the glaze, add between 1 and 5 g of either of the two metal carbonates. Mix thoroughly. If the glaze becomes too thick, a little water may be added to maintain original consistency. It should be about as thick as heavy cream or cake batter.
8. Coat your pot with the glaze using a brush. Do not coat the bottom 0.5 cm of the pot. Use several thin coats. The glaze should be between 2 and 3 mm thick. Allow the glaze to dry completely.
9. Place the glazed pot into the kiln. Turn on the kiln, and allow it to heat until the pot is glowing cherry red and the outer surface is bright and shiny. The time will depend on the number of pots in the kiln. It will take about 3 hours. Once the pot is ready, you must have the pails with the sawdust and water close by and ready to use.
10. Put on the heat-protective leather gloves. Have a partner quickly open the kiln. Using the long-handled tongs, quickly grasp your pot, and immediately drop it into the pail of sawdust. You may push the pot into the sawdust if you wish. Place the lid on the pail, and leave it on for about 3 min. As soon as your pot has been removed, your partner should close the kiln.
11. After 3 min take the lid off of the pail. Watch out for a flare up! Using the long-handled tongs, remove your pot, and drop it immediately into the pail of water. Once the pot has stopped steaming, carefully remove it using a pair of tongs. Be careful, the water may be quite warm. Take the pot to a sink and clean it up. Be careful. Gentle scrubbing will remove black carbon deposits. On the cobalt pots the cobalt appears as a dark metallic coating. Don't scrub it off.
12. Observe and record the differences in the pot in your journal after the raku process.

Extension Activities

1. Compare raku pots to conventionally fired pots with the same glaze.
2. Discuss the terms "oxidized" and "reduced."
3. Measure pots for firing shrinkage, i.e., measure the diameter of the pot before firing and after firing. Record the results in your laboratory notebook. Theorize what is occurring. Discuss these results in your class or with your teachers.

Using the Raku Glazing Process to Show Oxidation-Reduction in Chemistry

(Whitaker, G. 1983. Prepared as a master's thesis, Western Washington University, Bellingham, Washington)

Introduction

The art of raku was conceived and developed in Japan during the last quarter of the sixteenth century, specifically for the production of ceramic wares for use by the Zen Buddhists in the Tea Ceremony. The name "raku" meaning "pleasure or enjoyment," was given to the descendants of the famous sculpture-potters. Raku applies solely to the art and products of the raku family masters but it has also come to mean a ceramic technique that has been traditionally used by them. Raku is committed to the basic premise that the pot is the product of a process of mutual interaction and refinement between man and nature and that through this involvement man discovers his own significance. Raku places great reliance on maintaining a close and intimate relationship between the pot and its maker at all stages of production, and particularly so during the moments of truth when the pot is subjected to severe and sudden changes (Cooper).

The Making of Raku Ware

Raku wares are made by carving and refining forms down from larger leather-hard ones, which have been raised by a pinching technique. The Raku forms made by the joining techniques must have particular attention paid to welding the parts into a totally unified structure. Otherwise the wares will later split apart under the stresses of thermal shock. After drying the wares should be bisque fired, (bisque firing is the initial firing to vitrify (harden) the form) to a temperature of 850° to 900° Centigrade. It is important that raku bodies never approach their maturation temperature during firing. After the forms are removed from the kiln (see Figure 6.9), they are placed in a safe place to cool.

Oxidation and Reduction

Simply, oxidation is the addition of oxygen. Thus, when iron and steel are allowed to become wet and are exposed to the air, the subsequent process of rusting, in which the metallic iron acquires oxygen from the air, is known as oxidation. An example of this process is:

$$4\ Fe + 3\ 0_2 \longrightarrow 2\ Fe_20_3$$

The metallic iron becomes an oxide and is said to have been oxidized. In ceramic firing, processes of oxidation are commonplace. Most ceramics and most metal enamels are fired in an oxidizing atmosphere with a copious air supply, so that all materials actively seeking oxygen can acquire it during the process (Shaw).

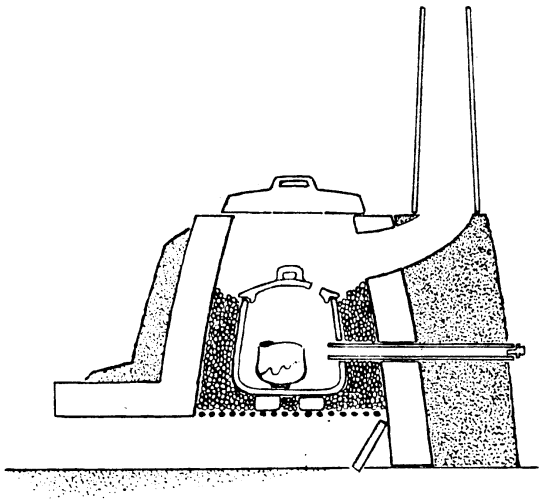


Figure 6.9. Small circular raku kiln burning coke or smokeless fuel. The saggar is the heart of the kiln and the main wall follows its profile. The walls may be made of common brick for a temporary kiln or of firebrick for a more permanent structure. The belly of the kiln is transversed by a number of fire-bars that both support the saggar and contain the fuel. The rectangular air intake tunnel may be used to direct fire from a flame gun to the center of the kiln if fast firing is desired. The kiln may be lit either with wood and the coke gradually added from above or by means of the flame gun. The chimney is a commercial chimney pot, and the whole kiln has an insulation of banked earth. The development of the glazes within the saggar may be observed at intervals through the viewing tube that may be made of metal or clay. The kiln will reach glazing temperature in 2 to 3 hours.

Reduction

There is an old Chinese legend that tells of a potter who lived many centuries ago. One day he was firing his kiln and was having a lot of trouble. It was one of those days when everything goes wrong. The fire wouldn't burn properly, the chimney wouldn't draw, the place was full of smoke, and the air was filled with a horrible odor. The potter was afraid that most of the ware, which he had glazed with a lovely green copper glaze, would be ruined.

When he opened the kiln he found his fears were justified, for piece after piece came out blistered, blackened, and dull. But in the very center of the kiln, there was one vase that was a beautiful blood red. Such a color had never been seen before on any piece of pottery. The potter's neighbors and co-workers marvelled at it. It was so beautiful that it was sent to the emperor as a gift. The emperor in turn admired the color so much that he had the vase broken and the fragments set in rings as though they were precious stones. Then he sent the potter an order for a dozen more red vases.

The potter's troubles began. He tried again and again but he could not reproduce that red color. He checked his glaze formulas carefully and used exactly the same ingredients that he used that day, but all the pots came out green. The emperor grew impatient. Messengers arrived from

the palace, saying *produce or else!* Finally our potter was in despair. He decided to fire one last kiln and loaded it with vases covered with glazes as before. But during the height of the fire, his courage failed him. He opened the door of his kiln and jumped in.

His assistant ran up quickly. The kiln fire was smokey and there was a bad smell in the air. They shut down the flames and allowed the kiln to cool, and when they opened it, what did they find? No trace of our poor potter, but yes, you've guessed it—the kiln was full of beautiful red pots.

And there, according to the legend, was discovered the secret of reduction. The potter's assistants reasoned that if a human body produced such results, maybe a dead pig would work and they tossed a pig into the next fire. Again they got beautiful red pieces. Then they tried substituting such things as wood and straw, and still the trick worked.

Reduction results when the fire is overloaded with carbon. When this happens, the green oxide of copper loses some of its oxygen and becomes a red oxide.

$$2\ C + 4\ CuO \text{ —> } 2\ Cu_2O + 2\ CO_2$$

Likewise, a red oxide of iron loses some of its oxygen and becomes a black oxide. This reduction process is shown by the chemical equation:

$$Fe_2O_3 + CO \text{ —> } 2\ FeO + CO_2$$

Iron oxide exists in several different combinations, and each proportion of iron to oxygen has a characteristic color as follows:

Fe_2O_3	Ferric iron	red
Fe_3O_4	Ferrous-ferric	yellow
FeO	Ferrous iron	black
Fe	Metallic iron	no color

Red oxide of copper produces the *sang-de-boeuf* or ox blood color, while the black oxide of iron produces the gray-green color known as celadon (see Table 6.2).

Reduction is obtained in the down draft type of kiln by closing the damper and adjusting the burners so that the flame does not get enough air and burns yellow (see Figure 6.9). This sends free carbon into the kiln. There is loss of heat during this process, so in high fire work the potter has to alternate periods of oxidation and reduction. With the muffle type of kiln, it is not so easy to produce controlled reduction, for the flames do not touch the ware, and, if the muffle is tight, even though the flame releases free carbon it will not get a chance to act on the pieces. Reduction can be produced, however, by putting some organic material such as sawdust, straw, or dry leaves, which will ignite instantaneously inside the muffle. In the case of low fire luster glazes, organic material is actually mixed with the glaze itself (Kenney).

An American version of the classic Japanese raku technique also involves a reduction process. A specially prepared glazed pot is fired to a deep red color, then while still glowing red hot, it is quickly plunged into a container filled with organic matter such as straw, sawdust, or oil. The pot will acquire a smoked appearance, and I a copper glaze will give a red color due to the now present copper or a luster glaze due to metallic copper forming.

Table 6.2. Coloring Action of Oxides In Glazes*

Oxide	Percent	Color in Lead Glaze	Color in Alkaline Glaze	Color When Reduced
Chromium oxide	2%	Vermilion at cone 012 Brown at cone 06 Green at cone 06		
Cobalt carbonate	0.5%	Medium blue	Medium blue	Medium blue
	1%	Strong blue	Strong blue	Strong blue
Copper carbonite	0.5%			Copper red
	1%	Green	Turquoise	Deep red
	2-3	Deep green	Turquoise	Red and black
	8%	Green with metallic areas	Blue-green with metallic areas	
Ilmenite	3%	Tan specks	Gray-black specks	Spotty brown
Iron chromate	2%	Gray-brown	Gray	
Iron oxide	1%			Celadon
	2%	Pale amber	Pale tan	Olive green celadon
	4%	Red-brown	Brown	Mottled green
	10%	Dark red	Black-brown	Saturated iron red
Manganese carbonate	4%	Purple-brown	Purple-violet	Brown
Nickel oxide	2%	Gray-brown	Gray	Gray-blue
Rutile	5%	Tan	Gray-brown	
Vanadium stain	6%	Yellow	Yellow	
Cobalt carbonate Iron oxide	0.5% 2%	Gray-bIue	Gray-blue	
Cobalt carbonate Manganese carbonate	0.5% 4%	Blue-purple	Aubergine	
Cobalt carbonate Rutile	0. 5% 3%	Gray-blue	Gray-blue	Textured blue
Copper carbonate Rutile	3% 3%	Textured green blue-green	Textured	
Ilmenite Rutile	27% 2%	Textured brown	Textured gray-brown	Spotty brown
lron oxide Cobalt carbonate Manganese carbonate	8% 1% 3%			Black
Cobalt carbonate Iron oxide Manganese carbonate	3% 2% 2%	Mirror black		
Manganese carbonate Iron oxide	6% 3%	Luster brown		

*Source: Nelson, G.C. 1957. *Ceramics Reference Manual*, Burgess Publishing Co.

Raku Glazes

Raku glazes are usually better applied thickly, and the relationship to glazed and unglazed areas carefully considered as the blackened reduced body can be very attractive. The pots are put into the kiln when it is estimated to have reached a sufficiently high temperature that can be judged by color—a rich red orange—or measured by a pyrometer. During the firing, the glazes will begin to bubble as they melt and when they have settled evenly and have a shiny reflective surface, the glazes have matured. Depending on the efficiency of the kiln, this will take about 20-40 min. When the pots are taken from the kiln, they will oxidize as they are brought into the air, and, if reduction is required, it should take place now. Burying the pot inside a metal dustbin full of sawdust or other material and then covering the bin with a reasonably well fitted lid will ensure a well-reduced glaze. Dark gray acrid smoke will be given off indicating a good reducing atmosphere. If copper is present in a glaze or in painted decoration, a rich lustrous surface will result from this heavy reduction. The body will be turned black by carbon.

After about 15 to 20 min, remove the pot and quench it immediately by placing it quickly into water to prevent reoxidation in the atmosphere. If the glaze is still molten when placed into water it will froth to give an unpleasant surface.

(A frit is a glaze that has been fired in a crucible and once cooled has been ground into a powder form for use. This process is used to seal in toxic glazes such as lead because of the high toxicity of this substance.) Alkali frit, lead frit, and borate frit, can be combined with about 10% whiting and 10% ball clay to give glazes that will work well. Additions of 5-10% tin oxide will give a rich white glaze that will usually crackle to give a large network of black lines. This contrasts well with the black matte body. Additions of coloring oxides will give the following results:

Copper	2-3%	turquoise
Cobalt	0.5%	blue
Manganese	1-2%	purple-brown
Iron	2-6%	creams-ambers

(Also see Table 6.3 for other coloring metals.)

After the pots have cooled, the glaze surface needs to be cleaned to remove soot and dirt with a stiff brush, wire wool, or an abrasive cleaning powder. Care should be taken not to remove the reduce metal if you have strived to get that appearance.

Now we come to an area where almost anything goes and daring experimentation is half of the fun! Because of the low temperature of raku firing, potters can use such things as lead all alone to make a glaze, but because of the hazards of raw lead, it seems wiser to use colemanite, (a natural mineral containing both calcium and borate) and various frits as fluxes (a substance that promotes melting).

Borax mixed into a paste with water and brushed thickly on a piece will form a glaze; so will Boraxo.

Interesting lusters often develop during reduction in glazes containing copper. Metallic lusters can be achieved by adding 1-3% silver nitrate or 2-5% tin chloride (see Table 6.3).

Table 6.3. Suggested Additions of Coloring Oxides to Reduction Glazes*

Cobalt carbonate	1/2%	medium blue
Cobalt carbonate	1/2%	light blue
Cobalt carbonate	1/2%	turquoise
Chrome oxide	1%	
Cobalt carbonate	1/2%	warm textured blue
Rutile	3%	
Cobalt carbonate	1/2%	grey-blue
Nickel oxide	1%	
Nickel oxide	1%	grey or grey-brown
Manganese carbonate	4%	brown
Manganese carbonate	4%	Textured brown
Rutile	2%	
Ilmenite	3%	spotty brown
Ilmenite	2%	textured yellow-brown
Rutile	2%	
Iron	1%	celedon
Iron	2%	dark olive celedon
Iron	4%	mottled green or brown
Iron	10%	saturated iron red
Copper	1/2%	copper red
Copper	1%	deep copper red
Copper	3%	red to black
Cobalt	1%	black
Iron	8%	
Manganese	3%	

*Source: Nelson, G.C. 1957. *Ceramics Reference Manual*, Burgess Publishing Co.

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Ceramic Slip Casting
Instructor Notes

Reliability

This lab takes some experimentation. You may have to try it a few times for experience and best results, but it is worth it.

Teacher Tips

1. The chemical composition of plaster of paris (which the slip casting molds are made from) is calcium sulfate ($CaSO_4 \cdot 0.5 H_2O$). When the plaster of paris is mixed with water, it hydrates and cures into a solid, hard structure with the chemical composition $CaSO_4 \cdot 2H_2O$. If slip casting molds are heated above 56°C (135°F), the waters of hydration can be driven off, and the mold will begin to crumble. Be cautious when drying the mold; 38-47°C (100-120°F) is hot enough to dry them.
2. Clay used for slip casting is a mixture of components that helps reduce the firing temperature (see Table 6.5). Compositions vary slightly, so it's a good idea to check and see if you have the proper pyrometric cones for the clay slip you have acquired. More than likely you will, because most clay slip sold at local ceramic shops is nearly the same composition.

Table 6.5. Typical Casting Slip Composition*

Whiteware Slip			Refractory Slurry	
Material	Concentration (Vol%)		Material	Concentration (Vol%)
Nonplastics	25-30		Alumina (<45 μm)	40-50
Clay	15-25		Ball clay	0-10
Water	45-60		Water	50-60
		Additives** (wt%)		
Na_2SiO_3, Na polyacrylate, Na lignosulfonate	<0.5	Deflocculant	NH_4 polyacrylate	0.5-2
$CaCO_3$	<0.1	Coagulant	$MgSO_1$	0-0.1
$BaCO_3$	<0.1			
Clay < 1 μm	Variable amount	Binder	NH_4 alginate, carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose	0-0.5

*Source: Reed, J. S. 1988. *Introduction to the Principles of Ceramic Processing*, Wiley

**Percentage by weight of solids in slurry.

3. Most slips (slip casting slurry) are sold by local ceramic supply outlets as a slurry ready for casting. If you need to buy the ceramic slip as a powder, then follow the manufacturer-recommended mixing instructions by measuring the appropriate amount of water into a bucket or pitcher then adding the powder while stirring the water. Continue to stir the slurry until all lumps are gone.
4. Instead of using rubber bands to hold the slip casting mold together, old inner tubes from automobiles can be cut into bands and used to tightly secure the mold.

Safety

1. The kiln or furnace, and its contents, can be hot. Place a sign (Caution - Hot) to warn students the furnace is being used. Wear leather gloves and safety glasses when working with a hot furnace or kiln.

Activity: Ceramic Slip Casting

Student Learning Objectives

At the end of the activity students will be able to:

- handle molds and materials while making a useful article with clay slip
- use pyrometric cones to measure temperature
- make and fire an object following the slip casting procedure.

Materials

- X-acto knife
- Clay slip [clay, water, and sodium silicate or sodium polyphosphate (calgon)]
- Cone stand
- Rubber bands
- Small bucket or pitcher
- Small sponge

Equipment

- Furnace or kiln
- Kiln furniture (shelves and setters)
- Plaster of paris mold

Procedure

1. Separate slip cast mold and clean any dirt; the mold should be dry. (Your tongue will stick to a dry mold). Molds may be stored at ~38°C (100°F) to keep them dry. Put the mold together by matching holes. Carefully secure mold with rubber bands.
2. Pour ceramic slip into mold slowly and evenly. Fill mold slightly above the pouring hole to form a sprue.
3. Let the ceramic slip sit for approximately 15 min or until desired thickness is reached (about 1/8 in.) If you are doing several castings, monitor the thickness as a function of time.
4. Pour the excess slip out of the mold back into the pouring container. Leave the mold inverted to drain.
5. Turn the mold over, and let it sit for at least 1 hour or until firm.

6. Carefully remove the casting from the mold by removing the rubber bands and lifting it out. Try not to twist or deform the casting as this may cause it to warp as it dries. (Make note of any pieces that get deformed, so you can observe if they dry or fire differently.) Put the mold away where it can dry out and stay clean. [Do not dry or store plaster molds at temperatures above 57°C (135°F.)]
7. Using an X-acto knife, remove the sprue. Be careful not to damage the ware.
8. Let the casting set for 24 hours before continuing.
9. After the casting is hard and dry to the touch it is still very fragile, but can be handled.
10. Using an X-acto knife and a damp (NOT WET) sponge, fettle the casting. Fettling is trimming off any excess clay and removing the "seam" marks made by the mold. Pay special attention to the rim and bottom. Rub any chips down with the sponge. Generally, "patching" does not work, so be careful. (Put your initials and date on the bottom of the casting.) On test pieces, score registration lines 1 in. apart in various locations on the ware. Measure the distance between the lines as accurately as you can.

    If the piece is complex it may need some assembly. Attach handles etc. by making a paste of clay and water (thickened slip works well), scoring both surfaces to be joined, and covering it with the paste. Firmly press the pieces together, and wipe away any excess clay with a damp sponge. Allow the piece to dry overnight before firing.

Caution: Furnace may be hot. Use leather gloves and safety glasses when working with hot materials or equipment.

11. Set the casting on a clay stilt or other suitable piece of kiln furniture. Place it in the furnace.
12. Place the cone appropriate for the clay composition (#5) on the cone stand, and place it in the furnace so you can see it without opening the door. If the furnace is large and there are a lot of castings, you will want to place several sets of cones throughout the furnace even if you can't see them all. This way you can get an idea of how uniform the temperature is throughout the furnace and note its effect on the ware.
13. When filled, close the furnace and set the temperature to 750°C. (This is called the "set point." It is the temperature you want; it is not necessarily the temperature the furnace is currently at.) This is not the firing temperature of the clay. You want to heat the clay slowly to the firing temperature to allow the water and any organic material plenty of time to get out of the clay. If you don't, the castings will break from the pressure of steam and other gases trying to escape.

14. Let the furnace sit undisturbed for 45 min. Then check to see if it has reached 750°C. Wait for the furnace to reach the set point before continuing. If the furnace is not allowed to reach the set point it can draw too much power and overshoot the set point by a large amount, and then you will never really know what temperature the furnace is.
15. Turn the temperature up to 915°C.
16. Wait another 45 minutes to check to see if the furnace has reached 915°C. Wait for the furnace to reach 915°C before continuing.
17. Increase the set point to 1075°C and leave for 1-1/2 hours.
18. Once the furnace has reached the set point, check the cones every 15 min or so by looking through the peep hole. If the furnace does not have a peep hole, you will have to estimate the firing time from the set points used. When the cones have slumped to the proper position turn the furnace off. DO NOT OPEN THE FURNACE. Let the furnace cool down for 24 hours before opening. If you open the furnace when it is hot, it and the ware inside will cool so fast it can break (thermal shock).
19. After the cool down period, “crack” the furnace by opening it slightly. Use a wedge if necessary to keep the door open only an inch or so.
20. When the ware is cool enough to touch, remove it. Make note of the location and condition of the cones in the furnace.

Suggested Questions

21. How does the slip flow and handle? Does it respond to stirring, standing?
22. How long did you leave the slip in the mold, and how thick did the casting become? Compare you results with other groups. Plot thickness as a function of time in minutes.
23. Describe the appearance of the casting during the stages of drying. Did the color change? Hardness? Did any cracks appear? How much did it shrink? Remeasure the distance between the registration lines you made on the unfired ware.
24. Did the castings fired in different parts of the furnace look different after firing? What about the cones? Did any of the castings deform during firing?
25. Why do you think we used plaster molds? What do you think the plaster does to the slip? (Hint: Stick your tongue on a clean plaster mold.)
26. What is the relationship between the set point and the actual temperature of the furnace?

27. Why do we use pyrometric cones in addition to the set point and firing schedule?
28. When does the casting shrink? Why does the casting shrink?
29. Explain why any castings deformed during firing.
30. What are the limitations on the shapes of slip cast pieces?
31. Why doesn't the clay settle out of the slip?

Extension Activities

1. Glazing (see the glazing section in "Making Raku").
2. Make your own plaster molds and discuss some of the unique properties of plaster.
3. You may want to heat the cones in the furnace to record the effects of various time and temperature schedules. Can you find different schedules that result in the cones having the same appearance?
4. Identify as many slip cast objects as you can at home. (Don't forget the toilet!)

Making Glass from Soil
Instructor Notes

Reliability

This activity is an experimental study to develop glass from the soil in your geographic area. Most soils can be melted into glass.

Estimated Time for Activity

Two class periods.

Teacher Tips

1. Most soils are high in silica (SiO_2), the main ingredient in the network of most common glasses. It would be a good experience to try to make glass from soil.
2. This experiment is designed to let students use a scientific method to make the best material from given conditions. For example, the melt temperature will not exceed 1050°C, and the chemical ingredients will be soil and anhydrous borax ($Na_2B_4O_7$).
3. Students initially will need to try a number of samples. A suggested range would be 30 weight percent (wt%) soil/70 wt% borax, a 50/50 wt% ratio, and a 30 wt% borax/70 wt% soil ratio. Depending on how these samples melt, you can narrow the compositional range. First you can eliminate samples that do not fully melt . Likewise, if the glass is very fluid, you can observe some of the soil settled at the bottom that did not dissolve. You can also eliminate these samples because they have too much borax and the crucible may be attacked by the glass and leak before the settled soil is dissolved. Additional glass compositions (i.e., 45 wt% borax/55 wt% soil) can be made.
4. When the compositional range of acceptable glass samples (i.e., 50/50 wt% and a 45/55 wt% of soil to borax ratio) is determined, test these samples for durability. Break or cut these samples, and place an approximately 5-g sample in a clean plastic container with 40 to 50 mL of water. Measure the pH of the solution 24 hours later. If the pH has changed significantly (i.e., <8.5), students may want to narrow the compositional range even further to make a better glass. These glasses will need to be tested for durability to check if they have improved.
5. You can make soil glass by following the procedures for glass batching and melting found in the Ceramics Section of your MST handbook, or by experimentally trying it as if it were a new material never researched before. In all cases, use caution, knowledge, and safe practices to perform experimentation.

Safety

***Note**: Because students are working under experimental conditions, they need to use extreme caution when initially melting the glass. Excessive foaming can occur in some chemical reactions.*

1. When loading the melting crucible, students should fill it only about 1/4 full, and then melt it. Watch the initial reaction by checking the melt after 7 to 10 min. If excessive foaming occurs or has occurred, proceed with extreme caution while melting the remaining glass batch. If foaming is "normal," follow usual melting procedure.
2. Use borax anhydrous ($Na_2B_4O_7$) as a borax chemical additive. Anhydrous means "without water." Twenty Mule Team Borax, which is available at most grocery stores, contains the maximum amount of water allowed to chemically bond with borax ($Na_2B_4O_7 \cdot 10\ H_2O$). If the borax has water, this increases melt foaming and can lead to crucible spillover. If you use borax with water, drive off most of the water by pretreating the borax to about 200°C. Borax has a melting point of 741°C.
3. Follow notes found in the glass batching and melting section of the MST handbook.

Extension Activities

Students can learn a lot about phase behavior, melting, and phase dia-grams by doing a series of melts that includes the entire composition range for borax and soil. This activity is very similar to the Alloying Tin and Lead experiment in the Metals section of this handbook except some of the borax/soil compositions will not melt. Table 6.6 provides 11 compositions with a suggested amount of batch size for this experiment.

Table 6.6. Display of Borax/Soil Compositions

	$Na_2B_4O_7$ (Borax)		SiO_2 (Soil)	
	g	wt%	g	wt%
1.	50	100	0	0
2.	45	90	5	10
3.	40	80	10	20
4.	35	70	15	30
5.	30	60	20	40
6.	25	50	25	50
7.	20	40	30	60
8.	15	30	35	70
9.	10	20	40	80
10.	5	10	45	90
11.	0	0	50	100

Students will batch each composition (see Standard Glass Batching for proper batch instructions). They will begin melting the compositions at 725°C. Wait until the furnace temperature has reached equilibrium, then check the crucibles. Follow safety procedures found in the Glass Melting instructions. If one of the compositions is melting or has melted, record the temperature, and remove that crucible. Raise the temperature of the furnace 25°C, and wait until temperature equilibrium has been reached (10-15 minutes should do). Check the crucibles. If any of these compositions has melted, remove them. Continue rasing the temperatures and checking the crucibles until all the compositions are melted or a maximum of 1150°C is reached.

Note: *Temperatures above 1150°C are very difficult to work at because of the intensity of the heat. Do not try melting activities above this temperature.*

This activity may take a week or more depending on how carefully the students melt the glass and how long they wait for the furnace temperature to increase. When students are finished, they can do several activities with the results:

1. Plot the data to determine the effects of composition on melt behavior (see Figure 6.10). Does your composition have a eutectic? Which composition looks like it makes the best glass?
2. Make a display using the crucibles. Label each crucible clearly with glass composition and melt temperature. The display will visually show changes in melt characteristics and glass behavior. It can be a great learning tool.

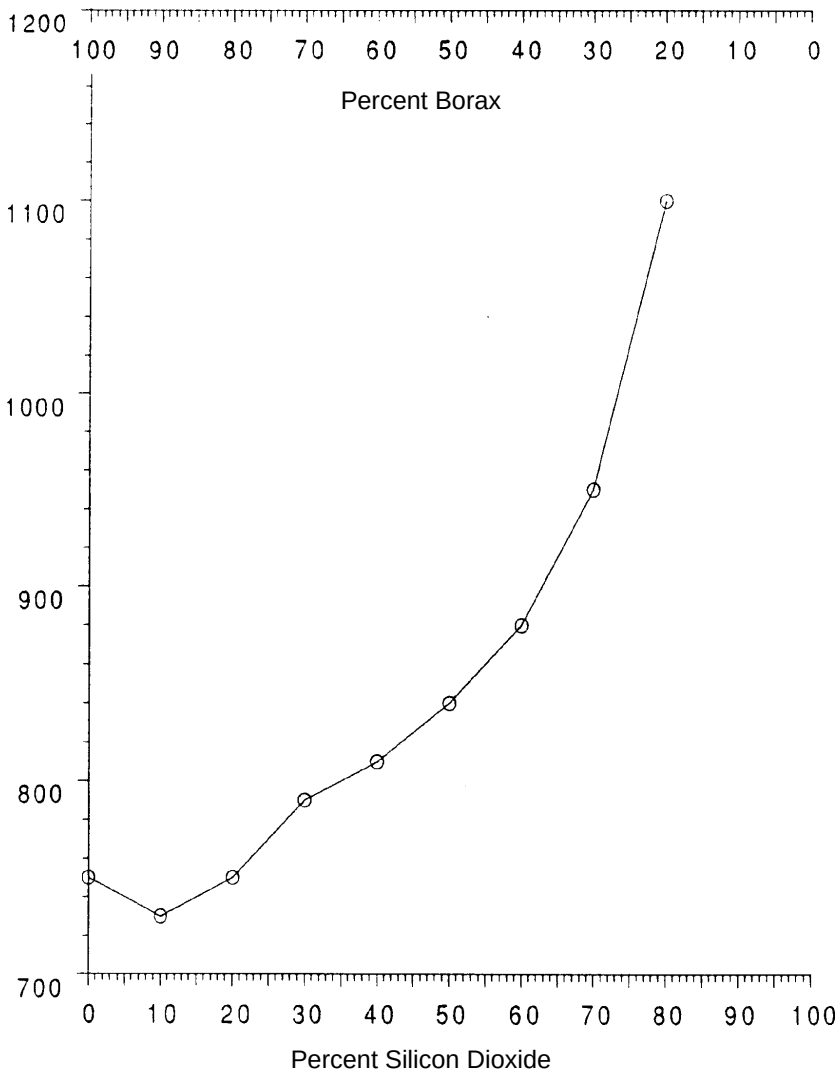

Figure 6.10. Melt Behavior of Borax/Soil Compositions

Making and Testing Superconductors
Instructor Notes

Teacher Tips

1. Superconductors are conductive materials that have an extremely low resistance to the flow of an electric current. That is, they have a theoretical resistance (R) equal to zero ohms. Most materials that exhibit superconductivity possess this property only at very low temperatures. Until 1986, these temperatures were close to absolute zero (0°)K). Superconductivity has been achieved at temperatures above that of liquid nitrogen (77°K). The race is on in the scientific community to create a superconductor that can conduct electricity without resistance at increasingly higher temperatures. Although the new "high temperature" superconductors are in the developmental stage, some day they may be used in superfast computers, magnetically levitated trains, high-powered electric cars, and energy transmission lines that transmit electricity with virtually no power loss.

2. Follow the procedure described in this section to make a ceramic superconductor from three metal oxides: yttrium oxide (Y_2O_3), barium peroxide (BaO_2), and copper (II) oxide (CuO). $BaCO_3$ can be used in place of BaO_2. The molar ratio of the three metals in the complex is 1:2:3, yttrium to barium to copper. The following is one way of expressing a molecular formula for this particular superconductor:

   $YBa_2Cu_3O_{7-x}$ (ideally $YBa_2Cu_3O_7$)

Caution: Some chemicals used in making superconductors are toxic. Please check the content of these materials in a chemical safety book. When students process chemicals when weighing or open-container grinding, the work should be done in a ventilating (fume) hood. Disposable plastic gloves should be worn, and it is advisable to wear a good-quality particulate mask for added safety.

3. Superconductivity, was first discovered in 1911 by Heike Kamerlingh Onnes while observing mercury at liquid helium temperatures (4°K, -452°F). The critical temperature (T_c) at which a material is superconductive has remained very low since that first discovery, rising only about 4°K per decade with research. By 1973, the best of the superconductors possessed a T_c of 23°K (-418°F). The discovery in 1986 of a superconductor with a T_c greater than the temperature of liquid nitrogen (77°K, -321°F) was a giant step toward making the process more practical. Cooling with liquid helium is expensive, whereas the cost of a gallon of liquid nitrogen is comparable to the cost of a gallon of milk!

4. The greenish material mentioned in step 8 of the experiment has been seen in several experiments with this superconductor. The greenish material is a non-superconductive phase, which has the composition of Y_2BaCuO_5. The black phase is the desirable superconducting material, approaching the ideal composition of $YBa_2Cu_3O_7$.
5. The Meissner effect is a phenomenon that all true superconductors exhibit while in their superconductive state. When cooled to its proper temperature (the critical temperature, T_c), the superconductor repels all magnetism regardless of polarity. The classic picture of a magnet suspended in mid-air above a superconductor is a result of the Meissner effect.
4. The mixing and grinding of these chemicals is very important. The smaller the particle size, the better the chance superconductivity will occur. Any number of grinding methods can be used, preferably automated. If hand grinding is necessary, be certain to grind as long as possible. One way to do this would be for a group of students to share the work, each taking a 10-minute turn at grinding. If a rock tumbler is used, operate overnight, and check the consistency of the material the next day to see if it is finely powdered.

   The grinding/mixing process allows for the dispersion of atoms to form the $YBa_2Cu_3O_7$ crystalline structure. The compounds used to make this type of superconductor are hard, refractory, but brittle, materials. They do not diffuse readily during the heating process, which allows the crystal structure to form. So the material must be ground again and again to allow these hard—and on the molecular level—large compounds to be broken and moved around so they can be close to the $YBa_2Cu_3O_7$ crystals that are forming. The finer the powder of the original material and the finer the powder from grinding, the easier it will be to form the superconducting crystalline matrix.
5. Samarium cobalt magnets have an extremely strong magnetic field for their size. This is important because common magnets are generally bulky and have weak magnetic fields. The weight of the magnet can overcome the force of the electric field and the levitating (Meissner) effect will not be seen. Samarium Cobalt magnets can be purchased commercially; these same magnets are commonly used in light-weight head phones, in case you have an old pair to take apart.

Activity: Making and Testing Superconductors

Student Learning Objectives

At the end of the activity students will be able to:

- make a superconductor using chemical batching, mixing and grinding (pulverizing), heating, pressing, and tempering
- test for superconductivity using the principal of the Meissner effect or testing for resistance using a micro-ohmeter
- describe what mechanism makes a material superconductive.

Materials

- Yttrium oxide, Y_2O_3
- Barium peroxide, BaO_2, (or barium carbonate)
- Copper (II) oxide, CuO
- Solvent: toluene or trifluorotrichloroethane
- Disposable protective gloves (such as PVC gloves)
- Safety glasses
- Zinc stearate
- Alcohol, (C_2H_5OH)
- Liquid nitrogen, $N_2(l)$
- Samarium cobalt magnet

* Tweezers (non magnetic)

- Oxygen gas (optional)
- Particulate mask
- Polystyrene cup

Equipment

- Balance
- Furnace capable of achieving 950°C
- Furnace controller to ramp temperature at controlled rates
- Hydraulic press
- Grinding chamber (disc mill), rock tumbler, or automated mortar and pestle (standard, hand-operated mortar and pestle may be used)
- Die to form superconductor
- Micro-ohmeter (four-point type) (optional)
- Annealing oven capable of achieving 475°C
- Fume hood

Procedure

Making Superconductors

1. Make calculations for the batch using the 1:2:3 ratio. Table 6.7 shows an example for a 0.1 mole batch, which is enough to make several superconductors. To achieve a ratio of 1:2:3 (Y, Ba, Cu), use a molar ratio of 1:4:6 for (Y_2, Ba, Cu).

Table 6.7.

Ratio	Compound	Molecular Weight (g/m)	Multiplier (for 0.1 mole)	Mass (g)
1	Y_2O_3	225.81	0.1	22.58
4	BaO_2	169.33	0.4	67.73
6	CuO	79.54	0.6	47.72

2. Weigh the chemicals, and place them in a container to go into a grinding chamber or mortar and pestle. If a grinding chamber is not available, use a rock tumbler with a very hard object such as a chunk of stainless steel or a piece of quartz added to help the grinding process.
3. Add 30 g of toluene to aid in mixing.

Caution: Vapors from toluene are not healthy. Work in a fume hood.

4. Grind for 1 hour. The smaller the resulting particles, the better. Grinding the material to the smallest possible size is ***very*** important in producing this type of superconductor material.
5. Let the toluene evaporate in a fume hood.
6. Place the powdered mixture in the furnace at 900-925°C for 18 hours.
7. Remove from furnace, cool, and repeat steps 3 – 7.
8. After you remove the mixture from the furnace for the second time, examine the mixture to see if any greenish-colored material is evident. If so, repeat steps 3 – 7. More than 25% greenish material indicates an incorrect mixture of chemicals, poor chemical quality, or improper oxidation. If this occurs, mix a new chemical batch.
9. Grind again to a fine powder—once again, the smaller the particles, the better.
10. Weigh out quantities of the material to make pellets. The quantities are determined by the size of the mold to be used. (12-g and 15-g quantities have been used to form pellets about 9 x 17 x 42 mm).
11. Clean the die with alcohol. Lubricate with a very light dusting of zinc stearate used as a mold release agent.
12. Place the superconducting material in the die, and distribute evenly.
13. Press with a hydraulic press.
    a. Gradually increase the pressure to 5000 lb (pressure of 5000 to 6000 lb for a 1.0 in^2 surface area).
    b. Hold the pressure for a couple of minutes.
    c. Let the press gradually release the pressure itself.
14. Remove the top part of the die, and extract the pellet.
15. Place the pellets in the oven for sintering.
    a. Heat the oven at 300°C/hour.
    b. Heat pellets at least 8 hours at 950°C.
    c. Cool at 50°C/hour to bring furnace back to room temperature.
16. Place the pellets in the annealing oven at 450°C for 18 hours. If oxygen gas is available, bubble 0_2 over the pellets while they are being annealed. After the allotted time, let the oven cool to room temperature with the pellets inside.
17. Remove the pellets from the annealing oven. They are now ready to be tested for superconductivity.

Testing the Superconductors

1. Attach the micro-ohmmeter (four-point type) to a pellet and take a resistance reading at room temperature. Now submerge the pellet in liquid nitrogen, and take a second reading. In its cooled state, the resistance measurement should read zero ohms. (Readings from this measurement can be erratic due to poor contact or high-contact resistance).
2. Test for the Meissner effect using a Samarium cobalt magnet and liquid nitrogen.
   a. Place the superconductor in a pool of liquid nitrogen. A polystyrene cup cut down to 1 in. high works well in containing the liquid N_2 when testing the superconductor. The pellet can be placed on a small metal block (brass or aluminum works well) acting as a pedestal while in the liquid N_2.
   b. Allow the superconductor to cool for a few minutes. Continue replenishing the liquid nitrogen supply around the pellet as the N_2 dissipates.
   c. With the tweezers, carefully place the magnet so that it is just above the superconductor. The height at which the magnet will remain suspended in air varies depending on the strength and size of the magnet—the smaller and stronger the magnet, the better. Once the magnet is balanced above the pellet, it can be set into a spinning motion with the flick of a finger or tweezers.

Vocabulary—Ceramics*

Alumina
Amorphous
Annealing
Blowing
Brittle
Casting
Crystal
Crystalline
Drawing
Fiber optics
Fire
Glassy
Inorganic
Meissner effect
Optical
Phase change
Pores
Pressing
Refractory
Resistance
Silica
Sinter
Superconductor
Tempering
Thermal shock
Viscosity

*Instructor may vary vocabulary to suit particular content presented.