# Metals vs. Ceramics

| Metals | Property | Ceramics |
|---|---|---|
| yes | crystalline | yes |
| "free roaming" | valence electrons | tied up in bonds |
| metallic | type of bonding | ionic & covalent |
| good | electrical conductivity | poor (insulator) |
| good | thermal conductivity | poor |
| opaque | optical properties | transparent |
| high | tensile strength | low |
| low | shear strength | high |
| malleable and ductile | workability | brittle |
| yes | plasticity | no |
| yes | elasticity | yes |
| more | density | less |
| nonporous | porosity | initial high porosity |
| medium | hardness | very high |
| good | impact strength | poor |
| varies (less than ceramics) | melting point | high to very high |
| easily corroded | corrosion | corrosion resistant |

T-C

# Introductory Ceramic Demos

## Aluminum vs. Alumina

(Al vs. $Al_2O_3$)

### Heat Transfer Demo – metal vs. ceramic

**Purpose**: contrast metals and ceramics in terms of these properties:

- thermal conductivity
- electrical conductivity
- density

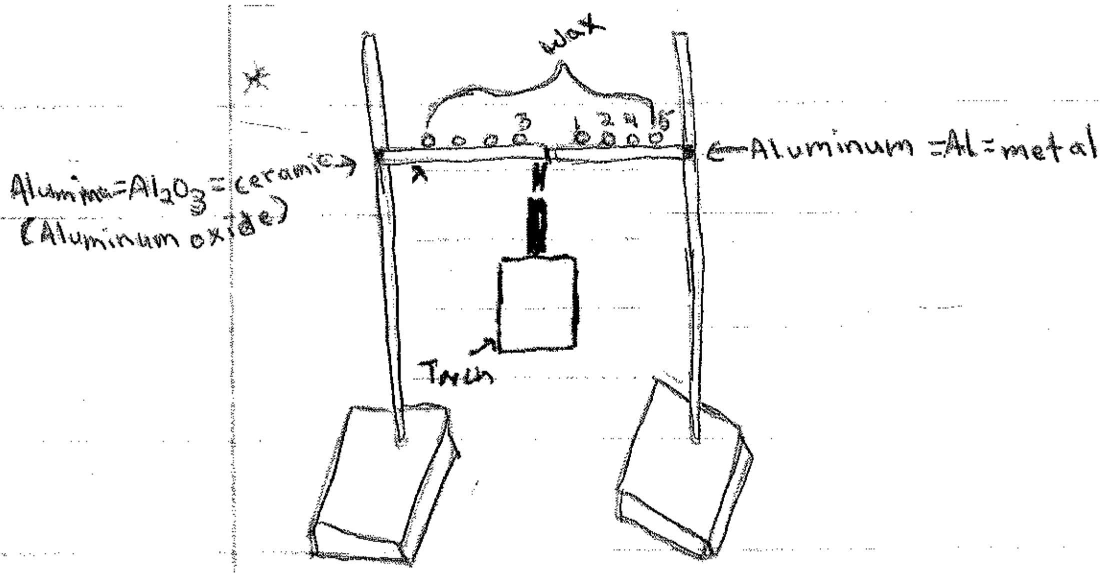
**Materials:**

Alumina rod – ceramic knife sharpening rod
- 3/8" diameter – 8 ½" length
- http://www.knifecenter.com/kc_new/store_keywords.html
- Part number – AC71

Aluminum rod
- 3/8" diameter – cut to 8 ½" length
- Lowe's or Home Depot

2 ring stands with clamps
propane torch or Bunsen burner
wax (candle or sprue)
digital meter
balance

**Set-up:**



**Procedure:**

- Place 4 drops of wax evenly spaced about 1 inch apart on each rod. (Touching molten drops to the rod works well.)
- Students make and record observations as the rods are heated by a propane torch - **thermal conductivity**.
- Check the electrical conductivity of each rod using a digital meter - **electrical conductivity**.
- Students predict which rod has the greatest density. Since the two rods have the same volume, relative density can be compared by massing each rod.
- Mass each rod - relative **density**.

**Comments:**

Alumina is aluminum oxide.

Typically about half the students predict that the metal will have the greatest density while the other half vote for the ceramic. Many of the students rely on their previous experiences with ceramics which involve larger, heavy objects or working with wet clay which leads them to believe that ceramic is a dense material. They know that aluminum is a lightweight metal. This can cause students to come to the conclusion that the alumina is denser than the aluminum. After the masses are measured, give the students an opportunity to hypothesize why the aluminum is in fact more dense than the alumina. In the alumina rod, some of the aluminum atoms are replaced by lighter weight oxygen atoms. The way in which the atoms or ions are packed will also have an effect.

## Melting Aluminum Wire

**Purpose:**

- contrast metals and ceramics in terms of melting points
- expose students to a discrepant event

**Materials:**

- thick gauge aluminum wire
- propane torch
- pliers

**Procedure:**

- ask students if the propane torch will be hot enough to melt aluminum - aluminum melts at 660° C and the propane torch burns at 1360°C so the answer is "yes"
- ask students how they will know when the aluminum has melted - as a pure substance (element) aluminum has a specific melting temperature and it will drip
- heat end of thick gauge Al wire with a propane torch
- when it glows red-orange hot ask the students if the aluminum should be melted by now - yes it should be
- the wire will have "sagged" by this point and the end will be "flexible" and will "jiggle"
- ask students why the metal isn't dripping if it has melted - give them time to think and discuss

- the outside of the wire oxidizes from the heat making $Al_2O_3$ - a ceramic
- inside will be molten aluminum which is encased by a thin solid ceramic layer
- ceramics (metal oxides) have higher melting points than the pure metal
- let molten Al drop onto a metal sheet or ceramic tile
- observe any differences between Al and $Al_2O_3$
- the alumina (aluminum oxide) will be darker in color and usually radiates outward from the center in thin strips like the spokes on a bicycle wheel
- the aluminum metal will be shinier and make up the bulk of the solid disk

# Lantern Mantle

This demonstration is found in the Battelle Handbook starting on page 4.34.

Show students mantle - ask if they know what it is, how it works.

Pass around unburned mantle

Heat mantle using propane torch. Burn off rayon sack. Turn off lights and let students see how brightly it glows. This is incandescent light. Pass around heated/burned mantle.

Mass the "before" and "after" mantles. Sample data: before = 1.25 g, after = .27 g

Have stereoscope set up to look at "before" and "after" mantles.

Ceramic embedded in a polymer fiber. Polymer burns away leaving a brittle, fragile ceramic mesh.

Ask students why the polymer is needed since all we do is burn it away when we use it. What trade-offs are involved in the material selection? How do we accommodate for these trade-offs?

Very few high temperature materials can be used as mantle material. Most materials do not produce visible light at these temperatures. Instead, they emit in a very narrow wavelength of light in the infrared or ultraviolet range.

OLD - silk w/ thorium oxide - heats to 3200° C
NEW - rayon w/ yttrium oxide - heats to 2400° C

Thoria (thorium oxide) is relatively inexpensive, can w/stand high temps, and produces the best quality light. But it is mildly radioactive so it is no longer used for mantles by manufacturers in the US. Yttrium oxide is now used. You can purchase a thoria mantle from Flinn Scientific.

Use a Geiger counter to compare a thorium mantle and an yttrium mantle.

Have students read the "Why Coleman Mantles Make Your Geiger Count" and answer the 4 questions. The article is in the Battelle Handbook on page 4.36.

- Build a timeline of the history of light sources used by man.
- Give 3 reasons the mantle originally had an advantage over the light bulb.
- Name a driving force that caused the light bulb to overtake the mantle in common usage.
- Name a substance or material that blocks or stops alpha radiation emitted by thorium.

# Lantern Mantle and Light Bulb Filament

The light bulb filament lab is found in the Battelle Handbook beginning on page 4.39.

## Notes:

The ceramic mantle demo and the light bulb filament lab are great for helping students draw conclusions about the differences between metals and ceramics. It involves a discussion of metallic and ionic bonding and the properties produced by each.

The light bulb filament is tungsten metal. It has metallic bonding which has "free" valence electrons. This causes tungsten to be a conductor of electricity. The electricity is changed to heat which in turn causes the filament to produce light - incandescence.

The ceramic mantle contains yttrium oxide which is ionically bonded. Ionic bonds "tie-up" free valence electrons thus the ceramic mantle does not conduct electricity. However, it does produce light because of heat (incandescence). The source of heat is a burning fuel.

Do the mantle demonstration first. You don't have to use a lantern; just hold the mantle with a pair of tongs and use a propane torch to ignite the rayon. Most students will be familiar with a Coleman lantern but for those that aren't, pass the package around that has a picture of one. Discussion questions include:

Why bother with the rayon bag?
How long will the mantle last?
How will it fail?
What is the purpose of the glass globe?
Why is yttrium used?

Following the mantle demonstration, the students do the light bulb filament lab. There are some modifications. Have different teams of students use different wattages: 40, 60, 75, and 100. Compare the thicknesses of the filaments (using a stereoscope and digital caliper). Also use a digital meter to test their resistance. The lower the wattage the higher the resistance and the thinner the filament. Then proceed with the rest of the lab.

Ask students "what is the purpose of the glass envelope?" They have figured out that it is to keep the oxygen away from the filament. The "bare" filament without the glass envelope oxidizes very quickly and breaks when turned on.

Then ask the students "what causes a regular light bulb to 'burn out'?" They want to transfer what they just saw and say that the wire oxidizes and breaks - somehow. To disprove that oxidation is the cause of failure, do the following demo. Take a burned-out bulb and remove the glass envelope. Take out the filament and compare it to an unoxidized (new) filament and an oxidized filament from the lab. It will still be flexible and have the color and conductivity of a new (unoxidized) filament. Oxidation is not the answer.

This leads to the question: "What is inside the glass envelope?". Students most often guess a vacuum or some sort of gas. We do a demo to find out. Take a burned-out bulb and gradually heat a portion of the envelope with a propane torch. As the glass softens and the gases inside increase pressure due to the heat, a "bubble" appears on the glass protruding OUTWARD. (We call this giving the bulb the mumps). This proves it is not a vacuum. It contains an inert gas. If you allow the "bubble" to pop it will often blow out the torch - again, showing evidence of an inert gas. If you quickly heat an area a cool bulb and hold the tip of the torch flame to the glass, it is possible to make a "dimple" in the bulb that sags inward. This happens when the glass heats quickly enough to soften before the gas inside has time to heat, increase pressure, and expand. It is fun to put a "dimple" on one side of the bulb and then put a "bump" on the opposite of the bulb and have the students explain how it happened.

Next question: "Why bother with the gas; why not leave it a vacuum?" A bulb does not "burn-out" because of oxidation - there is nothing inside the envelope to cause the tungsten to oxidize. Sublimation occurs when the bulb is hot. Over time the filament gets thinner and eventually breaks or melts. Bulbs almost always burn out when they are first turned on - that is when the filament breaks or melting occurs. This is also the source of the dark ring that sometimes forms around the base of the glass envelope. The purpose of the inert gas is to increase pressure on the tungsten filament making it more difficult for sublimation to occur. This lengthens the life span of the filament.

Light bulbs have a built-in fuse. After burning the filament in a dismantled light bulb, twist the two lead-in wires together and plug it in. There is a small blue flash of light and a popping sound. The fuse "sputters" and breaks the circuit.

One more extension that I do is to use a 3-way bulb. They often do not know if it requires a "special" bulb, a "special" lamp, both, or neither. The students usually will guess that there are 3 filaments inside. This leads to a discussion of series and parallel circuits when they discover that there are only two filaments.

After completing both the lantern mantle demo and the light bulb lab, I have the students answer questions comparing and contrasting the two.

Compare and contrast a lantern mantle and light bulb filament by addressing the following topics:

1. Source of energy for light.

2. Purpose of glass covering (light bulb envelope and lantern globe). Include a discussion of the type of material and type of bonding that the mantle and filament possess.

3. State a way in which the filament and mantle are similar.

# Light Bulb Lab

## Observations

1. Describe the method you used to remove the glass envelope from the light bulb.

2. Observations and thoughts while removing the glass envelope.

3. Characteristics of the envelope:

   A.

   B.

   C.

   D.

4. Describe the filament:

   A. flexibility -

   B. color -

   C. shape -

   D. other -

5. Build a table and record data on the wattage, thickness, and resistance of the different light bulbs.

6. Observations when the bulb (without the envelope) was plugged into the electricity:

7. Compare and contrast the burn characteristics of the different wattage light bulbs.

8. Describe the filament after exposing the light bulb to electricity:

   A. flexibility -

   B. color -

   C. ability to conduct electricity -

   D. other -

9. Any additional observations and impressions or thoughts:

## Conclusions and Reflections

1. Describe the property changes that occurred in the tungsten filament when it was heated while exposed to oxygen in the air.

2. What type of material did the tungsten metal change into when it was plugged into electricity while exposed to air?

3. What is the purpose of the light bulb's glass envelope?

4. Why does the tungsten filament give off light?

5. Why is tungsten used as the filament in a light bulb?

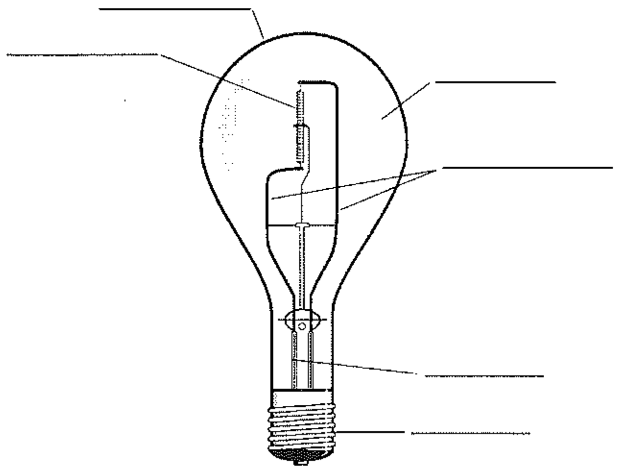
6. Do light bulbs actually "burn out" when they quit working? Explain.

7. What causes a light bulb to fail?

8. Why is there a gas inside of a light bulb instead of a vacuum?

9. What gas or gasses are used inside of a light bulb? Why were those particular ones chosen?

10. Label the parts on the sketch of a light bulb.



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11. What was the most surprising or interesting thing you learned during this lab?

12. What still confuses you?

12-C

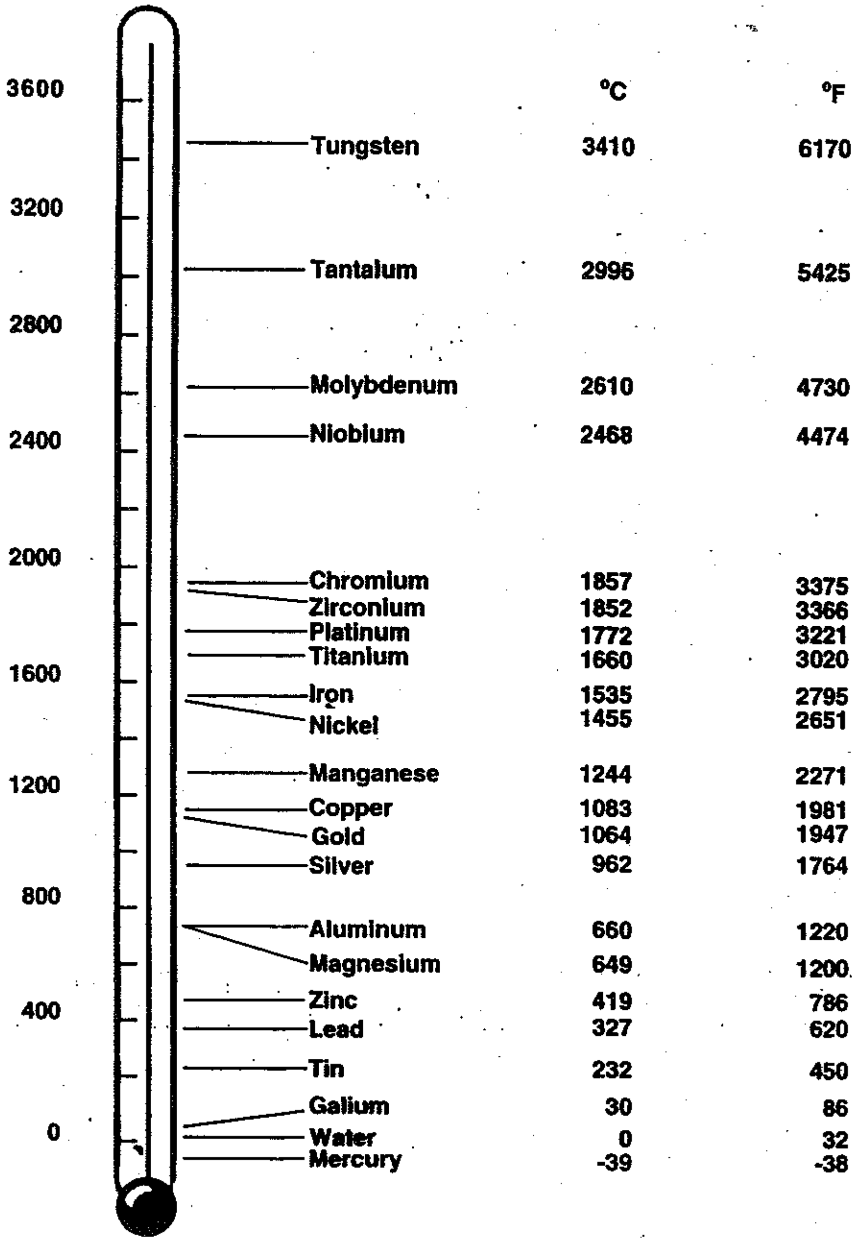
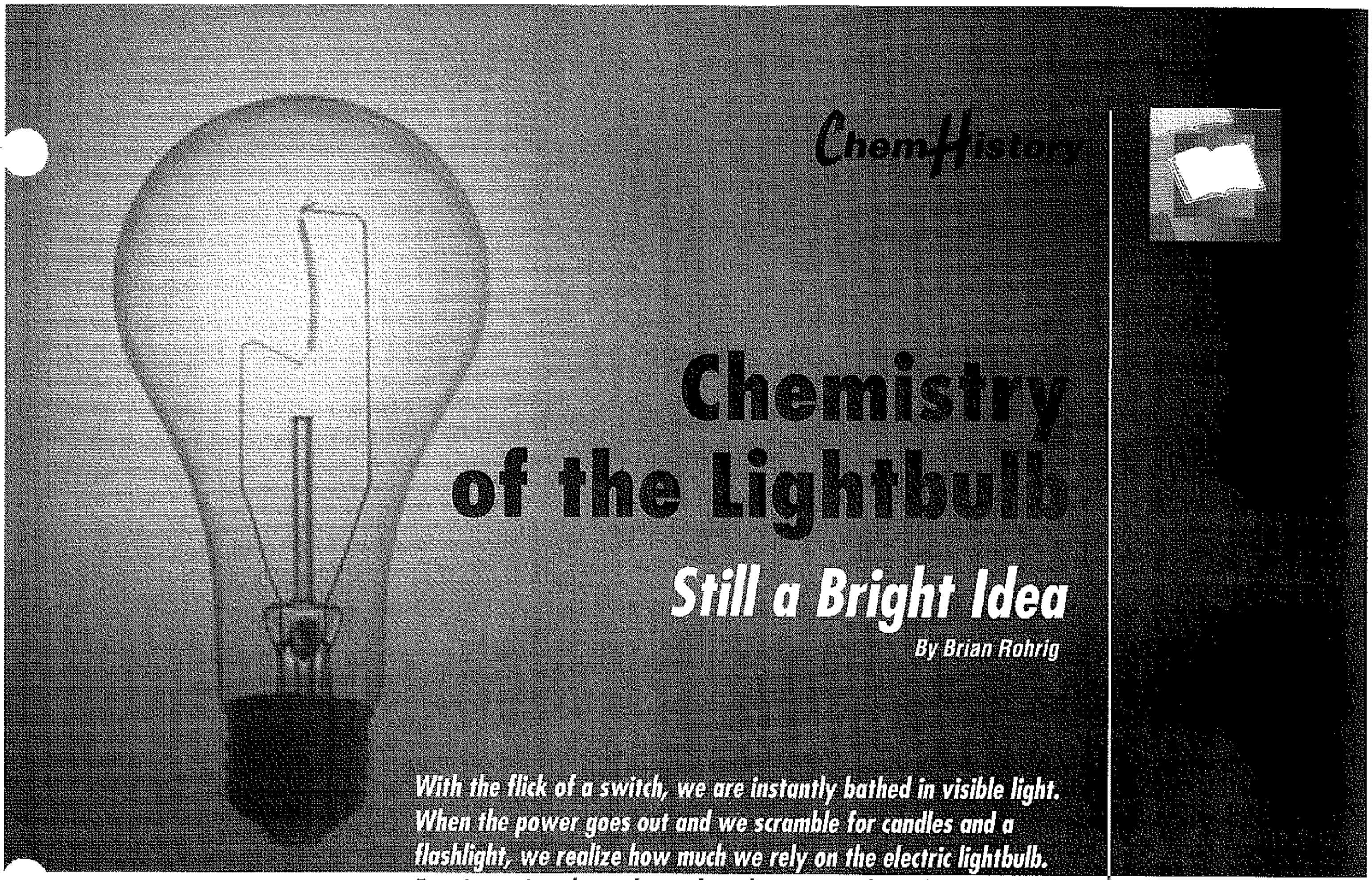


**Figure 2**
The melting points of many metals

Approximate Colors Radiated by Hot Materials

| Temperature (°C) | Color |
|---|---|
| >1400 | white |
| 1200 | yellow |
| 1000 | orange |
| 800 | dull red |
| 600 | |
| 400 | faint red |
| 200 | |



# Chemistry of the Lightbulb

## Still a Bright Idea

By Brian Rohrig

***With the flick of a switch, we are instantly bathed in visible light. When the power goes out and we scramble for candles and a flashlight, we realize how much we rely on the electric lightbulb. Few inventions have changed our lives as much as this remarkably simple, yet ingenious device.***

The fact is, we rely on the electric lightbulb. Few inventions have changed our lives as much as this deceptively simple, yet ingenious device.

With the flick of a switch, we are instantly bathed in visible light. When the power goes out, we scramble for candles and matches. But the charm of glowing firelight soon wears off, especially when sports events or homework are in the plans.

## Edison's invention

Although Thomas Edison was not the first person to patent an electric lightbulb, he made so many improvements on its design that history generally gives him the credit. Without Edison's improvements, lightbulbs would last about as long as candles. In 1879, he constructed a lightbulb that glowed continuously for 40 hours, but he was determined to do better than that. By the end of 1880, his 1500-hour lightbulb was ready for public sale. A mere 25 years later, his electric bulb had forever transformed human life by illuminating homes and cities all over the world.

PHOTO ABOVE: PHOTODISC

© NATIONAL PARK SERVICE

Thomas Edison

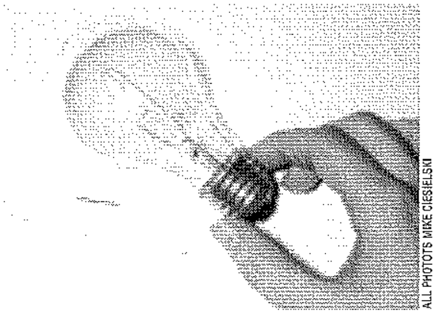
© NEW YORK PUBLIC LIBRARY

Lewis Howard Latimer

These first lightbulbs were *incandescent*, as are most of the lightbulbs in your home today. Incandescence is the property of giving off visible light when heated. The hotter the object, the more energetic the light that is given off.

As you have probably observed, a piece of metal glows if its temperature gets high enough. As the temperature increases, the color of the emitted light changes from dull red, to orange, and at about 5800 °C, to white. A typical incandescent lightbulb operates at a temperature of about 2500 °C, where it glows with a yellow-white light.

Finding just the right filament was not an easy task. Using a simple trial-and-error approach, Edison experimented with thousands of different types of filaments. He was looking for one that would be both long-lasting and affordable.



ALL PHOTOTS MIKE CIESIELSKI

**Although we talk about glowing lightbulbs, the actual glow comes from only one bulb component—a very thin wire called the filament. A typical 60-watt bulb contains about 2 meters of very thin tungsten wire only about 25 micrometers (1/1000 inch) thick. Look very closely at a clear unlit bulb, and you'll see that the filament is tightly wound into a double coil.**

The first breakthrough came when Lewis Howard Latimer, the only African-American member of the Edison research team, developed an improved carbon-based filament that yielded an extended glow. He went on to design efficient production methods for manufacturing them in commercial quantities at reasonable cost.

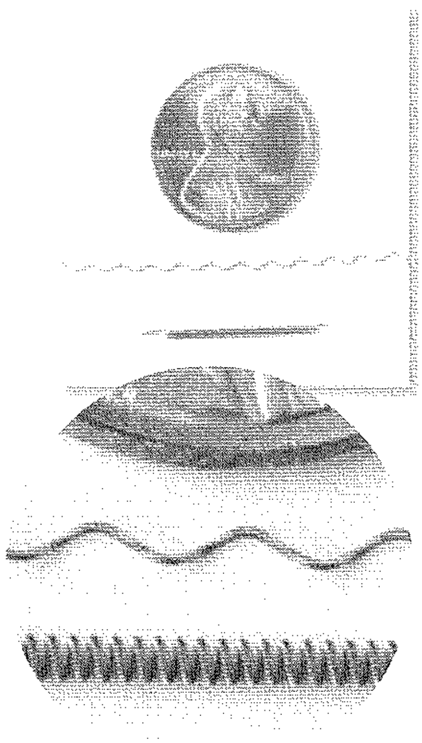
Cost was a significant consideration for the lightbulb to catch on with the public. For example, Edison's team experimented with long-lasting platinum but rejected it for its price tag.

In 1910, William Coolidge of the General Electric Company developed a tungsten filament that is still in use today. Tungsten metal, with a melting point of about 3680 °C, proved to be both affordable and long-lasting.

## How does a lightbulb light?

When electric current follows the metal pathway through an incandescent lightbulb, a tremendous amount of resistance is encountered as the electrons make their way through the very thin wire filament. Similar to students in a crowded lunch line, closely packed electrons generate friction—and that, in turn, produces heat. The thinner the wire, the more resistance the electrons encounter as they attempt to pass through. More resistance generates more heat until the wire reaches a high enough temperature to produce visible light.

Lightbulbs "burn out" when the filament breaks. At high temperatures, the tungsten metal, like other metals, *sublimes*. Sublimation is a process by which a solid is converted directly into a gas without first passing through a liquid phase—like old trays of ice cubes shrinking in your freezer.



In lightbulbs, the sublimated tungsten atoms are still sealed inside with nowhere else to go. Examine a burned-out lightbulb and you'll see a tungsten deposit on the interior surface of the glass—clearly visible as a black spot on top of the bulb. Even with its low sublimation rate at high temperatures, the tungsten filament finally wears thin and breaks. As a result, the circuit is broken. When the metal pathway breaks, electrons stop flowing, and the lightbulb ceases to glow.

Finding the right filament was only one hurdle for the early inventors. The second big problem came from the surrounding air—specifically oxygen.

We talk about "burning" lightbulbs, but the fact is that the filaments inside successful bulbs glow *without* burning. Edison found that for many filaments, the presence of oxygen caused the hot material to rapidly combust and break. Since glowing doesn't require any oxygen, Edison's early lightbulbs consisted of filaments mounted in a vacuum.

Although the vacuum solved one problem, it created another. Without any gas exerting pressure on the filament, the rate of sublimation increased. The tungsten atoms of the solid filament readily entered the gas phase at the high temperatures within the glowing bulb.

## Argon to the rescue

With the discovery of the noble gas argon in 1894, it became possible to lengthen the life of a lightbulb by filling it with this very unreactive gas. Not only did argon offer an oxygen-free filler, it also controlled the sublimation rate of the filament by transferring some of the excess heat away from the glowing metal.

The transfer process is called convection. As atoms of argon bump into the hot filament, some of the kinetic energy of the tungsten atoms is transferred to the argon atoms. This transfer cools the filament and heats the argon. The argon atoms then speed off to collide with the inner wall of the glass bulb. Upon impact, the argon atoms transfer some of their kinetic energy to the glass, raising its temperature.

In the process, glowing incandescent light bulbs become blistering hot. In fact, about 90% of the electrical energy consumed by an incandescent lightbulb is dissipated as heat.

Krypton would be a better noble gas to use in a lightbulb than argon, since it is a poorer conductor of heat. But krypton is very expensive. The only place to get krypton is from the atmosphere, where its concentration is only about 1 part per million (ppm). By contrast, argon comprises nearly 1% of the atmosphere, making it 10,000 times more abundant than krypton.

**Krypton is usually used to fill small flashlight bulbs. Because argon-filled bulbs readily transfer energy away from the glowing filament to the glass, batteries drain rapidly in the process. But when poorer-heat-conducting krypton fills the space, the bulb feels cool to the touch even after extended use, and batteries last longer.**

## Extended-life bulb

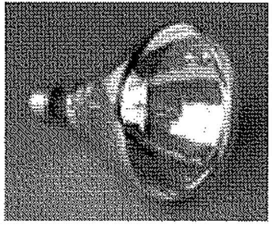
An extended-life lightbulb contains a much longer filament. As a result, there is more surface area to dissipate the heat. The filament does not get as hot and does not sublimate as quickly.

The drawback is that the light produced by the extended-life bulb is dimmer and redder. It takes a higher wattage to produce the same amount of light as a typical incandescent bulb. Wattage refers to how much energy is used per second. So, even though they last longer, extended-life bulbs may not really be a bargain. They actually cost more money due to the greater wattage required to operate them.

## Heat lamp bulb

A heat lamp is essentially an incandescent bulb with a very long filament. The filament has a long life and glows a dull red color. The cooler filament emits most of its energy as longer-wavelength infrared light, which cannot be seen but will still heat up objects on which it falls. The globe of the bulb is very large; this increased surface area allows it to radiate more heat. This design makes the heat lamp very practical, since its intended purpose is to give off heat, not light.

MIKE CIESIELSKI



## Fluorescent lamps

Since all incandescent bulbs give off a great deal of heat, cool fluorescent lamps offer a much more efficient alternative. Introduced in the 1950s, they soon became widely accepted for nearly all schools, offices, and commercial buildings.

Fluorescent lamps consist of a sealed glass tube containing a mixture of noble gases and a few drops of mercury that vaporize within the tube. When an electric current passes through the gas in the tube, some of the electrons of mercury become excited. Excitation occurs when electrons absorb energy and temporarily achieve a higher energy level. As they return to ground state, the energy previously absorbed by the electrons is primarily released as ultraviolet (UV) light, a light with shorter wavelength and greater energy per photon than visible light.

Because UV light is invisible to humans, the fluorescent lamp must convert it into visible light. This is accomplished by the white phosphor coating on the inside of the bulb. When UV light strikes this phosphor coating, it is converted into visible light. Thus, unlike incandescent bulbs, fluorescent lamps do not give off light by heating any of their components. That makes them much more energy-efficient.

If you have a UV-sanitizing cabinet for goggles in your classroom, examine the bulb inside. It will resemble a typical fluorescent bulb, but with one big difference. It's transparent. The lack of a phosphor coating means that the bulb emits UV light, with very little visible light. It is this UV light that kills microorganisms and sterilizes your goggles.

## Halogen bulb

Halogen bulbs, another type of incandescent bulb, produce intense white light. They are commonly used in car headlights, floodlights, and other applications where very bright light is needed. Halogen bulbs, as their name implies, contain the vapor of a halogen (group 17 on the periodic table), usually bromine or iodine. The halogen molecules act as chemical scavengers, picking up stray tungsten atoms that have sublimed and depositing them back on the filament. The unique ability of the halogen atoms to combine with tungsten atoms means you're not likely to find black spots on the inside of the bulb. However, the filament of the bulb eventually breaks due to uneven deposition of tungsten atoms on the filament.

Since the filament lasts much longer, halogen bulbs are designed to glow several hundred degrees hotter than a typical incandescent lightbulb. Generating intense heat, halogen lamps have been known to cause fires. Homeowners must take care to keep the lamps away from draperies and other combustibles. Furthermore, since halogen bulbs give off so much heat, their energy efficiency gets low marks.

## Neon lights

PHOTODISC

Neon signs are similar to fluorescent lamps, except that they contain no mercury or phosphor coatings. A mixture of neon and other gases within the tube gives off colored light when the electrons are excited by an electric current.

## Light-emitting diodes

Eventually, both incandescent and fluorescent bulbs may give way to light-emitting diodes (LEDs). The indicator lights on computers and the numbers on digital alarm clocks utilize LEDs—light sources based on the properties of semiconductors such as silicon. For an explanation of how these durable devices operate, see "Light-Emitting Diodes—Tune in to the Blues" in the April 2001 issue of *ChemMatters*. ▲

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***Brian Rohrig*** teaches chemistry at the Eastmoor Academy in Columbus, OH. His most recent article for *ChemMatters*, "Matches—Striking Chemistry at Your Fingertips", appeared in the December 2002 issue.

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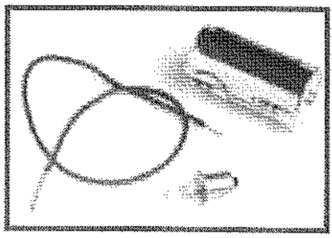
Sacks, Oliver. *Uncle Tungsten: Memories of a Chemical Boyhood;* Alfred A. Knopf: New York, 2001.

## TRY THIS!

Can you assemble these three familiar items correctly so that the light bulb lights? You'll need a 12-inch piece of insulated wire with exposed metal at each end, a C or D-cell power source, and a flashlight bulb.

If you succeed on the first try, you are a shining example to us all! A well-known video distributed to educators by the Private Universe Project in 1989 shows recent Harvard and Massachusetts Institute of Technology (MIT) grads struggling with the challenge. In the video, one frustrated individual exclaims, "I'm a mechanical engineer, not an electrical engineer!" (Private Universe Project, *A Private Universe* [Videotape], Harvard-Smithsonian Center for Astrophysics: Cambridge, MA, 1989)

The answer appears on page 20.



MIKE CIESIELSKI

# Thermal Shock Demo

Soda-lime glass rod (flint glass)
Borosilicate glass rod (Pyrex glass)
Fused silica glass rod (list source here)
Propane torch and lighter or Bunsen burner
Beaker of ice water

Have students journal observations during the demonstration.

Show the students the difference in color (looking at the ends) of the 3 glass rods. The soda-lime glass will have a definite green color (think Coke bottle green). The fused silica will be white if unpolished. Borosilicate will be in-between. The higher the percentage of silica content, the less color the glass will have. The greenish tint is due to iron oxide impurities in the silica.

Heat one end of the soda-lime glass rod in the flame.
Point out the "sodium flare" that occurs as the glass heats up.
Allow the glass to sag or slump to show softening.
Remove from flame and quench in ice water.
Thermal shock will occur and pieces of glass will break off onto the bottom of the beaker.

Heat one end of the borosilicate glass rod in the flame.
There should be less sodium flare.
Sagging or slumping should be harder to achieve but the end should fire polish.
Remove from the flame and quench.
Some thermal shock will occur. There should be fewer overall cracks than with the soda-lime glass.

Heat one end of the fused silica glass rod in the flame.
There should not be a sodium flare
No sagging, slumping, or fire-polishing will occur.
Remove from the flame and quench.
The rod will not thermal shock. No cracks should occur.

Glass is a poor conductor of heat. The outside will cool and contract much more rapidly when quenched. A lot of stress is put on the glass and it causes failure. The greater the coefficient of thermal expansion, the more likely the glass will break.

*The two most important properties that determine resistance to thermal shock in glass are **thermal conductivity** and **coefficient of thermal expansion**.*

**Thermal conductivity** – how well heat is conducted.
-hard to measure
-doesn't vary much in glass
-the better the conductivity – the more rapidly and evenly heat is distributed
*-better conductivity = less chance of thermal shock (inversely proportional)*

**Coefficient of Thermal Expansion** – amount of expansion per unit of length per °C.
-easy to measure
-varies greatly in glass
-the lower the coefficient – the less stress caused by sudden temperature changes
*-lower coefficient = less chance of thermal shock (directly proportional)*

*General guideline for determining thermal shock probability in glass:*

$$\frac{\text{Coefficient of thermal expansion}}{\text{Thermal conductivity}}$$

*Larger the value of the ratio, more likely damage will occur due to thermal shock.*

The value for thermal conductivity stays pretty much the same for all glass. Thus the coefficient of thermal expansion has the most effect.

Show the overhead of "materials and coefficient of thermal expansion".
Show overhead of "properties of silica in glass".
-soft glass = higher modifier rate
-hard glass = lower modifier rate

| **Material** | **Coefficient of Thermal Expansion (cm/cm x °C)** |
|---|---|
| Fused Silica Glass | $6 \times 10^{-7}$ |
| Borosilicate Glass | $33 \times 10^{-7}$ |
| Aluminosilicate Glass | $44 \times 10^{-7}$ |
| Porcelain | $60 \times 10^{-7}$ |
| Soda-Lime Glass | $85 \times 10^{-7}$ |
| Mild Steel | $110 \times 10^{-7}$ |
| Aluminum | $250 \times 10^{-7}$ |

## Properties of Silica in Glass

| | | |
|---|---|---|
| Lower | % of **Silica** in Glass | Higher |
| Soft | Type of Glass | Hard |
| Lower | Melting Temperature | Higher |
| Higher | Coefficient of Expansion | Lower |

Soda-lime glass has a high percentage of modifier. Fused silica glass has no modifier, it is pure silica. Borosilicate glass has an intermediate amount of modifier. A modifier is used to lower the melt temperature of the glass and increases the workability of the glass.

Another demonstration using the three different glass rods involves the index of refraction. Borosilicate glass has about the same index of refraction as vegetable oil. Immerse the three rods in a beaker or clear plastic cup containing an inch or two of vegetable oil. Only two rods should be visible in the oil. The third one, the borosilicate rod "disappears".

Sources of glass rods:
Soda-lime and borosilicate: Frey Scientific and Flinn Scientific
Fused silica glass rod: National Scientific Company - www.quartz.com

# GLASS

## An Amorphous Solid

*By Roberta Baxter*

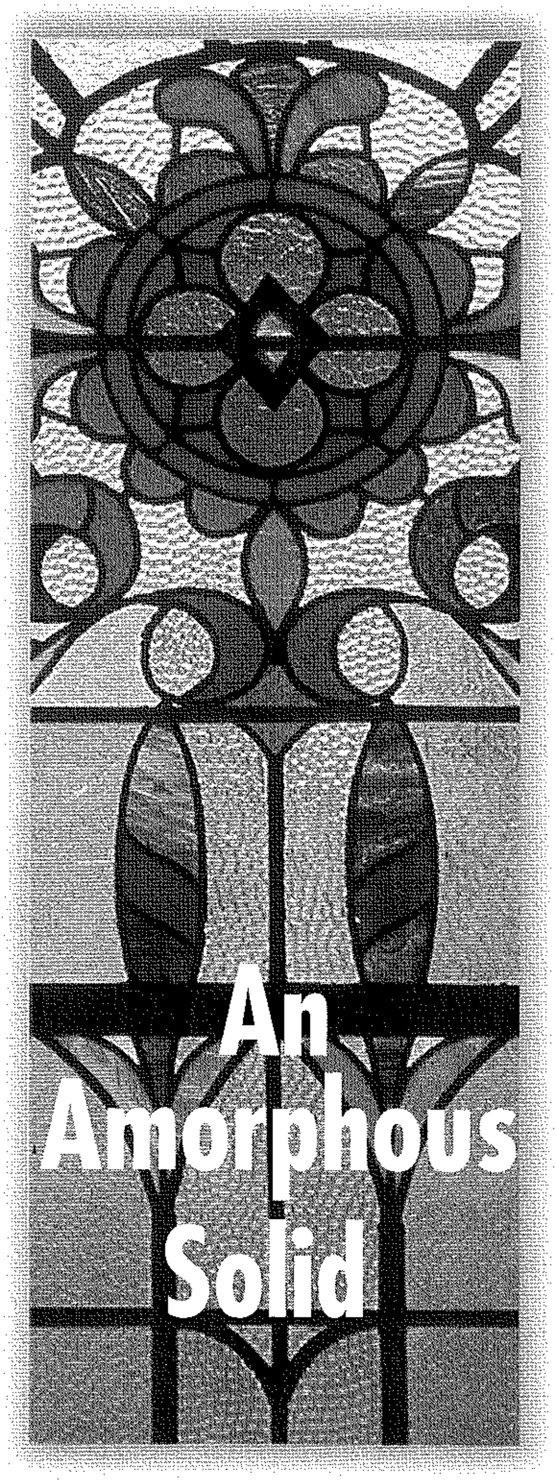
You use this material every day. It passes light into your house, allows you to see outside your car, carries the drink of water to your mouth, and transmits your phone conversation across the country. It is glass, and our life would be very different without it.

## Composition of glass

The main component of glass is silicon dioxide ($SiO_2$), also known as sand or silica. The chemical formula doesn't show the complete nature of silicon dioxide. Silicon dioxide is actually a network solid (each atom is joined to all its neighbors in a covalently bonded, three-dimensional network). It does not consist of simple molecules like $CO_2$. Instead, each silicon atom is bonded to four oxygen atoms, and each oxygen atom is shared between two silicon atoms, and this bonding continues almost indefinitely. Pure silicon dioxide glass can be made, but it requires a high melting temperature of 1,700 °C and quickly becomes too stiff to mold.

The addition of metal oxides such as sodium oxide ($Na_2O$) and calcium oxide (CaO), lowers both the melting temperature and the viscosity (resistance to flow) of the glass, making it easier to mold (see Figure 1).

To make glass, the materials are melted until they flow easily like water. Then the mixture is cooled. As glass cools, it becomes more viscous until it becomes rigid enough to become a solid. The particles from which glass is made are more or less "frozen" into place in a much more random, disorganized manner than in a true crystalline solid. Solid glass is distinguished from crystalline material because it has no long-range order, no simple repeating unit. Because there are no consistent distances between the bonded particles, they break up at different temperatures. This results in glass not having a specific, fixed melting point. Rather, heated glass becomes softer and softer as its temperature is raised until it finally is fluid enough to be called melted.



Distinct colors of glass are produced by adding different powdered metal oxides and other substances to the glassmaking ingredients during the glass manufacturing process. Some colors of glass include aqua from iron, dark green from chromium, amber from a mixture of iron and sulfur, light blue from copper, and dark blue from cobalt, and purple from manganese.

ACS GRAPHICS PHOTO FILE

Glass is called an amorphous solid. This makes for several differences compared with crystalline solids:

- Amorphous implies isotropy or having identical properties in all directions. Unlike crystals, which have defined fracture planes, glass can be cut in any direction.
- Typical crystalline materials scatter light and usually appear translucent or opaque. Glass is transparent.
- The broad melting range means that glass can be worked while it is highly viscous. Crystalline materials melt sharply and have a much smaller workable range. Imagine trying to "blow" an ice sculpture from water.

## Manufacture of glass

Glass is not composed of one single chemical compound; it can be made with many different compositions. Manufacturers vary the composition of the glass depending on its intended use.

To manufacture glass, the powdered ingredients, called the *frit,* are poured into a large furnace. Glassmakers also add chunks of the same type of glass to the mix. This is known as the *cullet,* and it speeds up the melting process, because it melts at a lower temperature than the raw materials. The furnace heats the mixture to about 1,300–1,600 °C, a lower temperature than the melting point of the other components. The cullet begins to melt and dissolves the other ingredients in it. After the glass is molten, it is poured out of the furnace, and the shaping process begins.

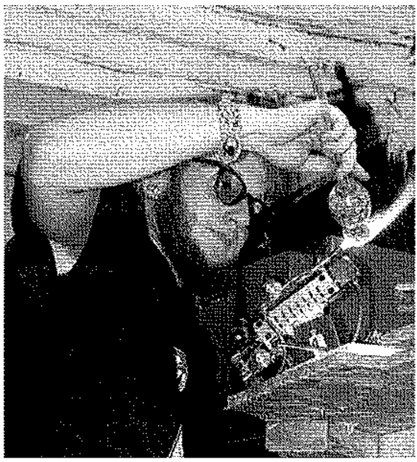


PHOTO COURTESY OF KAREN BARRICK

**Mark Nowicki of Berkeley, CA, has been glassblowing since high school. He supplements his college education by selling his glass pieces. Here, Mark uses standard glassblowing equipment.**

## Old Window Glass Legends

Many chemistry teachers are asked whether centuries-old window glass shows signs of sagging or thickening at the bottom, because some people think glass is a viscous liquid and is oozing down. The answer is no. Although the physical state of glass is an amorphous solid without any overall order, disorderly arrangements of atoms retain their structure just as orderly arrangements do.

It has been hypothesized that medieval stained glass windows that seem to have thickened glass at the bottom were in fact constructed that way. Window glass used to be made by spinning a gob of glass, producing a round disk that was not well controlled. Thus variable thicknesses would appear. The thicker parts could appear anywhere in the piece of glass after it was installed.

**Figure 1. Pure $SiO_2$ glass has no orderly arrangement of atoms in rows and columns of military precision (left). When metal ions are added (right), they fit into the glass matrix and form a nondirectional bond to oxygen atoms. This weakens the matrix and, in turn, decreases the viscosity and the melting temperature range. The new glass is now easier to work.**

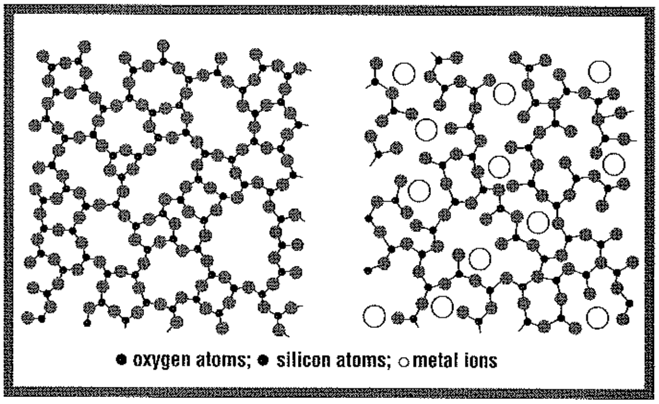


ILLUSTRATION BY ACS GRAPHICS

The final step in the process of glassmaking, the annealing process, is crucial. If hot glass is cooled too quickly, it develops stress points and easily breaks. To prevent this from occurring, glass is slowly cooled in an annealing oven, called a *lehr.*

Another interesting method of forming glass is glassblowing. A glassblower gathers a gob of glass on the end of an iron tube. The gob is rolled on an iron table to make an initial shape. Then the glassblower blows through the tube into the glass and spins the tube at the same time. He uses tools to shape the glass as he continues to blow. The glass shape is transferred to a solid iron rod, and then final shaping is done.

## Decolorizing and coloring glass

Most silica used in glass manufacturing is slightly impure because it contains tiny amounts of iron, resulting in a greenish-yellow tint. This can be neutralized by adding manganese dioxide ($MnO_2$). The purplish tint of the $MnO_2$ is complementary to the greenish-yellow of the iron impurity, allowing the glass to appear colorless.

Artisans use colored impurities to purposefully color glass. A wide range of colors was discovered by experimenting with metal oxides. During the manufacturing of glass, different powdered oxides are added to the frit and melted in the furnace with the other ingredients. The metal ions fit into the glass matrix and produce unique colors as can be seen in the stained glass on p 10.

Glass is an important material in our world. Glassmaking is an ancient art. It was used to make decorative beads in Egypt and vessels in Rome well before being used in the magnificent windows in medieval churches. It has developed into a ultramodern technology with applications in products ranging from computer screens to space shuttles. Glass also protects our eyes from ultraviolet radiation through sunglasses and keeps us informed through fiber optics. This amorphous solid provides color and beauty and allows us a glimpse into the mysteries of our molecular world. ▲

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***Roberta Baxter*** is a freelance writer who lives in Colorado Springs, CO. Her article "Sun Alert!" appeared in the ChemSumer department of the April 1998 issue of *ChemMatters.*

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# Glass Ingredients

| *Category* | *Purpose* | *Metal oxides* |
|---|---|---|
| Glass former | Gives atomic structure – makes up backbone of network solid | $SiO_2$ (silica) - primary<br>Also oxides of: B, Ge, P, As, V |
| Modifier | Lower melt temp,<br>Makes it easier to work w/ | Oxides of alkali metals *($Na_2O$ & $K_2O$) and alkaline earth metals **(CaO & MgO) |
| Intermediate | Acts as either former or modifier based on other ingredients present | Oxides of: Al, Sb, Pb, Zn, and sometimes B |

*make it chemically less stable

**restore some stability

# Most Common Types of Glass

| *Glass Type* | *Ingredients* | *Uses* | *Advantages* | *Disadvantages* |
|---|---|---|---|---|
| Soda-lime<br>(flint)<br>(most common) | Silica ($SiO_2$)<br>Soda ($Na_2O$)<br>Lime ($CaO$) | Windows, bottles, etc. | Low price,<br>Forms shapes easily | Low thermal shock resistance |
| Borosilicate | Silica ($SiO_2$)<br>Soda ($Na_2O$)<br>Alumina ($Al_2O_3$)<br>Boron oxide ($B_2O_3$) | Lab glassware<br>Cookware<br>Lamp bulbs<br>(Pyrex) | Withstands thermal shock better and higher temps | More expensive,<br>Harder to work |
| Lead-alkali<br>(lead crystal) | Silica ($SiO_2$)<br>Sodium oxide<br>Lead oxide | Art glass,<br>Expensive glassware | Sparkle,<br>High electrical resistance | Toxicity,<br>Doesn't w/stand thermal shock or high temp |

23-C

# A PHYSICAL MODEL TO HELP STUDENTS UNDERSTAND THE MELTING RANGE OF GLASSES

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**Key Words:** Glass, molecular models, amorphous, glass structure, viscosity

Prerequisite Knowledge: Little/none; this demonstration is designed for use with high school students as they begin their study of ceramic materials, including glasses.

**Objective:** After seeing this demonstration, the student should have a good concept of why glasses melt continuously, instead of having a well-defined melting point as do crystalline materials. Additionally, the student should understand how amorphous materials differ from crystalline ones.

**Equipment and Supplies:** 1-1/2 inch Styrofoam balls, available at craft stores, and common round wooden toothpicks.

**Background:** When introducing students to main concepts about glass, there are several points of difference as glass is compared to crystalline materials. There are:

1. Glass has an amorphous, disorganized network structure.
2. The primary unit of glass structure is the $SiO_4$ tetrahedron, in which each Si atom is surrounded by four oxygen atoms in a tetrahedral configuration.
3. Most oxygen atoms are shared between neighboring tetrahedra, so that the overall chemical formula of fused silica is $SiO_2$.
4. Because of the amorphous structure, the structural units are bonded with various amounts of energy; as a result of this, glass has no definite melting point. Instead, its viscosity, or resistance to flow, changes continuously as temperature increases. This behavior is the reason that glass can be formed over a relatively long temperature range.

Textbooks typically use drawings such as shown in Figure 1, from Reference 1, to communicate these ideas, but many students do not understand the concepts when communicated in this two-dimensional way. The student-involving demonstration below is an effective way to communicate all of these ideas to students in an introductory Materials Science course for high school students.

**Procedure:** Each student is given three Styrofoam balls and three standard round wooden toothpicks. I start by showing students the primary structural unit of glass, the $SiO_4$ tetrahedron, made from four Styrofoam balls representing oxygen ions, attached to each other using toothpicks. The space between the spheres in the center of the tetrahedron is large enough to accommodate a silicon ion. One of these tetrahedral is shown in Figure 2. Each student uses his three Styrofoam balls and two toothpicks to make an equilateral triangle, as shown in Figure 3. In the amorphous glass structure tetrahedral share corner oxygen ions, so I give the tetrahedron to students to pass around and attach their triangles to. Each student attaches his triangle to one of the balls of the tetrahedron, using his remaining toothpick. Figure 4 shows the first triangle added to the tetrahedron. The attachment continues, and I remind students that there is no wrong way to attach the triangles, as long as the protruding ball from a tetrahedron is placed into the center of their equilateral triangle, forming another tetrahedron. Figure 5 shows two triangles attached to the original tetrahedron, Figure 6 shows three, and Figure 7 shows four randomly-attached triangles. Note that by the Figure 7 stage, the structure shows a lot of randomness and some tetrahedra are attached at one point, some at two points, and so on. Also, the unoccupied spaces between tetrahedra are of variable size. These ideas are pointed out as the structure is built, because they are analogous to glass structure. The construction process continues until each student has joined his triangle to the network, and I collect the rather large model, which by now is composed of about 75 Styrofoam balls.

After pointing out various features of the model, it is time to simulate melting, at room temperature. Since melting of a solid occurs when enough heat energy is added so that the interatomic bonding force is overcome by lattice vibrations, a crystalline material will have a single, well-defined melting point because its atoms are all bonded with the same amount of energy. When an amorphous material is heated, its weakest-bonded structural units are freed first. As more heat is added, stronger and stronger-bonded units are shaken loose into smaller pieces until finally each structural unit is independent of the others. To "melt" the glass model structure built by the students, I simply begin shaking it, very gently at first and then gradually increasing the force level. Weaker-bonded pieces of the glass model begin to detach, and students can see that detachment of these units is breaking the network into successively smaller pieces, making the glass flow better and thus be easier to form. I continue to shake pieces of the network until individual tetrahedral units are becoming detached; at this point the glass would be completely melted and it would flow relatively easily.

I have used this model approach to understanding glass structure and melting behavior now for several years with high school students, and it appears to work well.

**References:**

1. Jacobs, James A., and Thomas Kilduff, Engineering Materials Technology: Structures, Processing, Properties, and Selection, Fourth Edition, Prentice-Hall, 2001.

**Figures:**

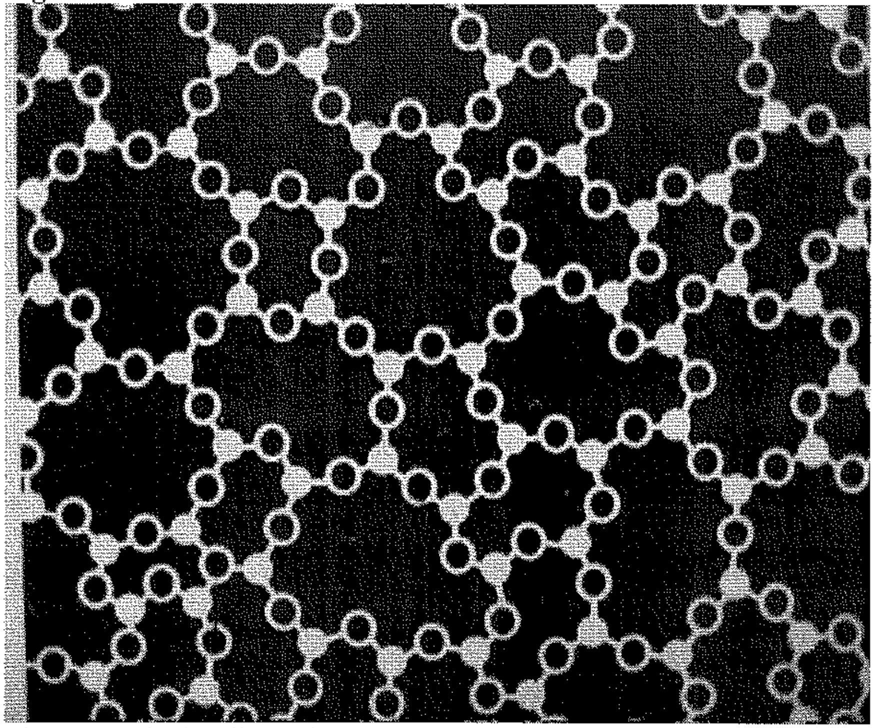

Fig. 1. Typical 2-dimensional representation of glass structure, from Ref. 1.

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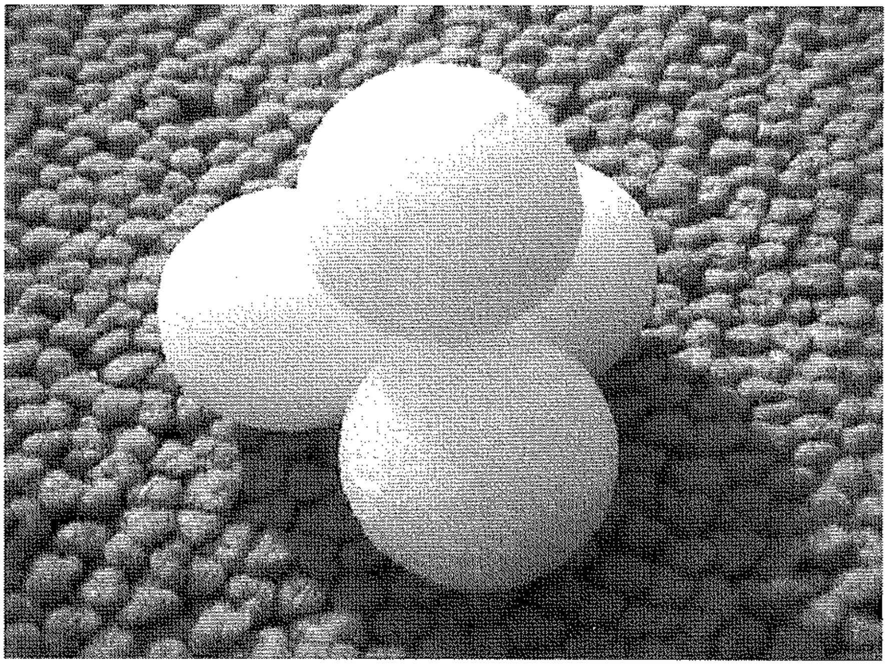

Fig. 2. The basic tetrahedral unit of glass structure; the Styrofoam balls represent oxygen atoms, and the silicon atom is in the center space at the intersection of the spheres.

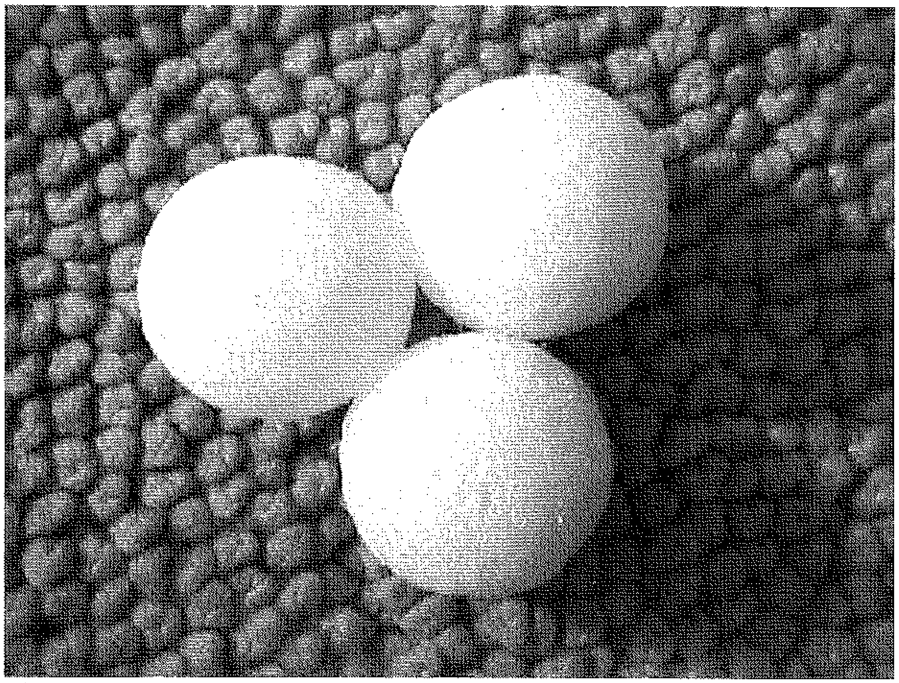

Fig. 3. The equilateral triangle unit that connects to any of the corners of the tetrahedral unit.

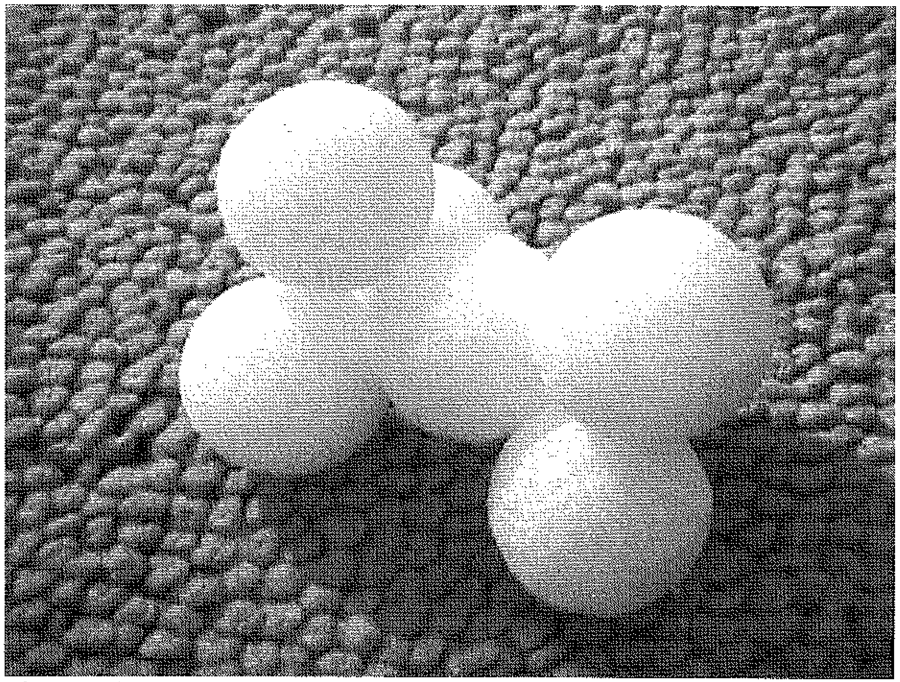

Fig. 4. The tetrahedral unit, plus the equilateral triangle, forming the beginning of a glass network structure.

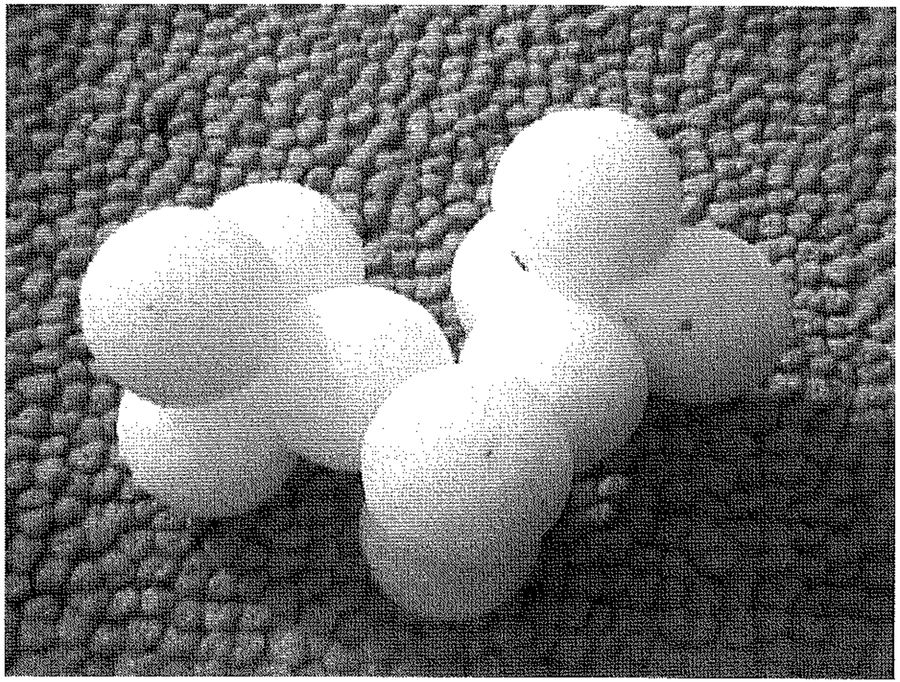

Fig. 5. Continuation of the network structure by adding a second triangle.

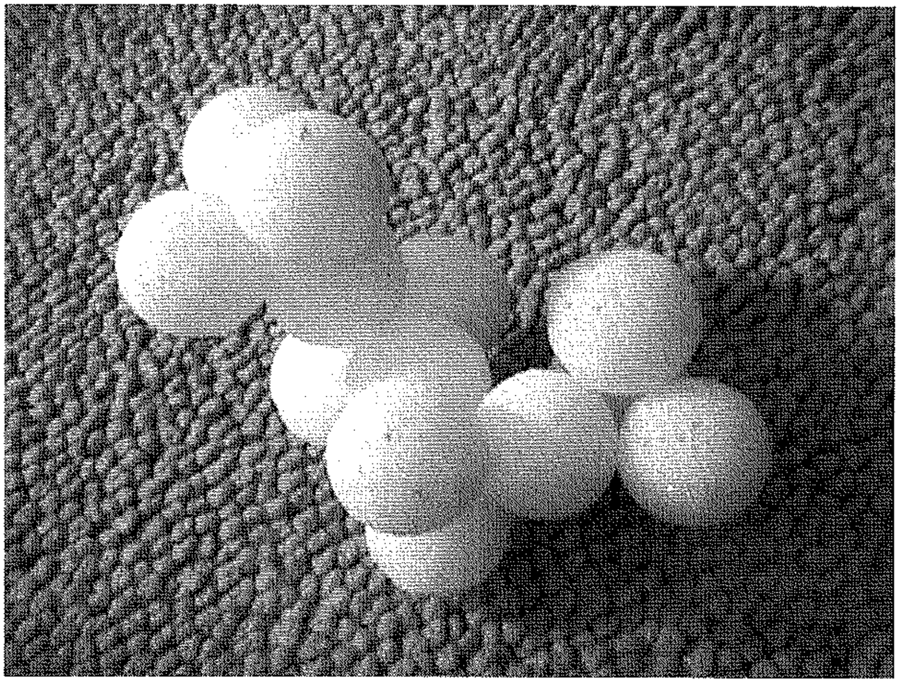

Fig. 6. Continuation of the network structure by adding a third triangle.

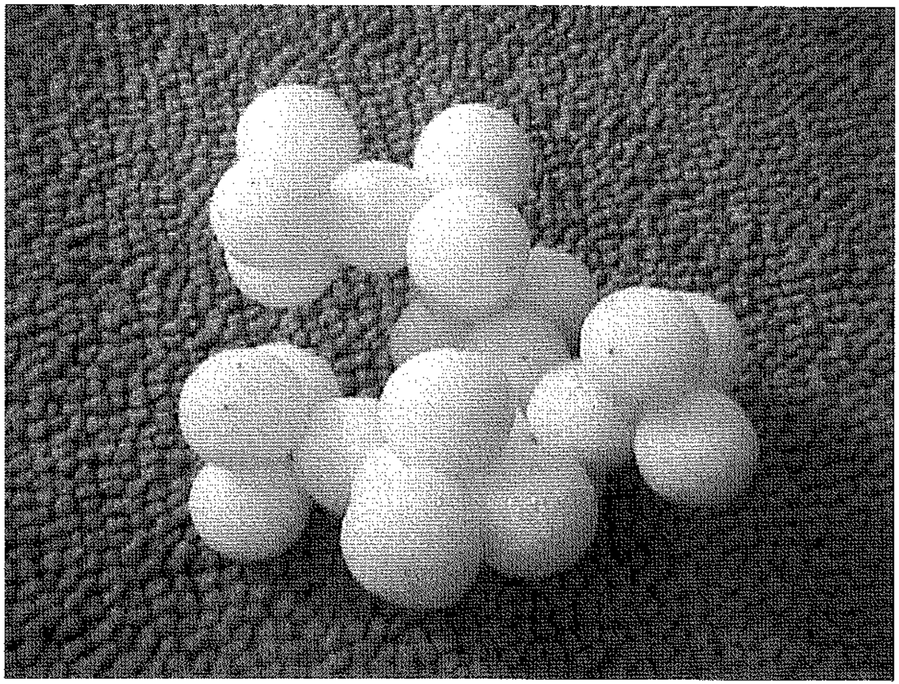

Fig. 7. Further extension of the network structure by adding a fourth triangle.
For a typical 25-student class, the network would be roughly three times this size when finished and ready for the "melting" demonstration.

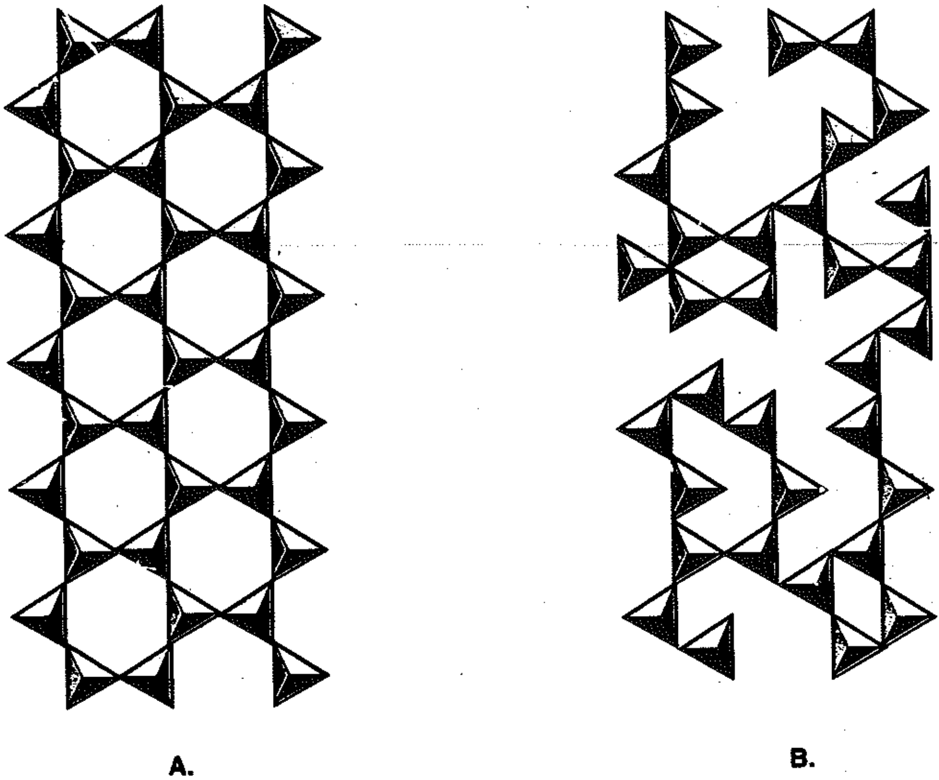

**Figure 2**
Using tetrahedra to show two dimensional representations of (A.) an ordered crystalline structure and (B.) an amorphous structure of silicon and oxygen

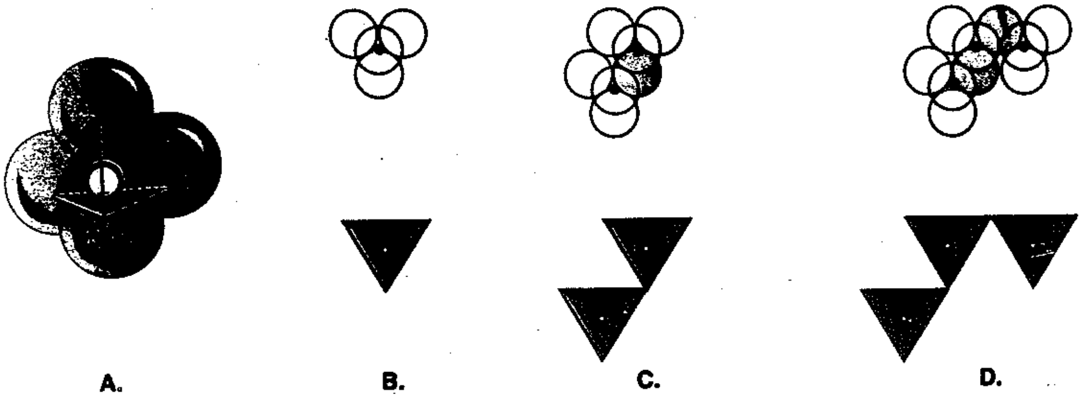

**Figure 15**
(A.) and (B.) represent tetrahedra; (C.) and (D.) are models of tetrahedra

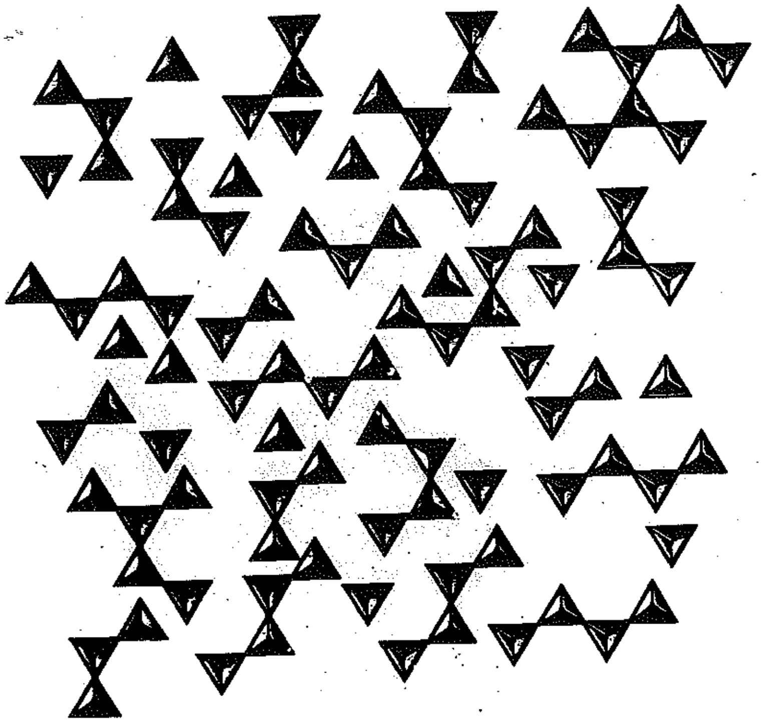

**Figure 16**
A representation of molten silica containing molecules with varying numbers of tetrahedra made of silicon and oxygen

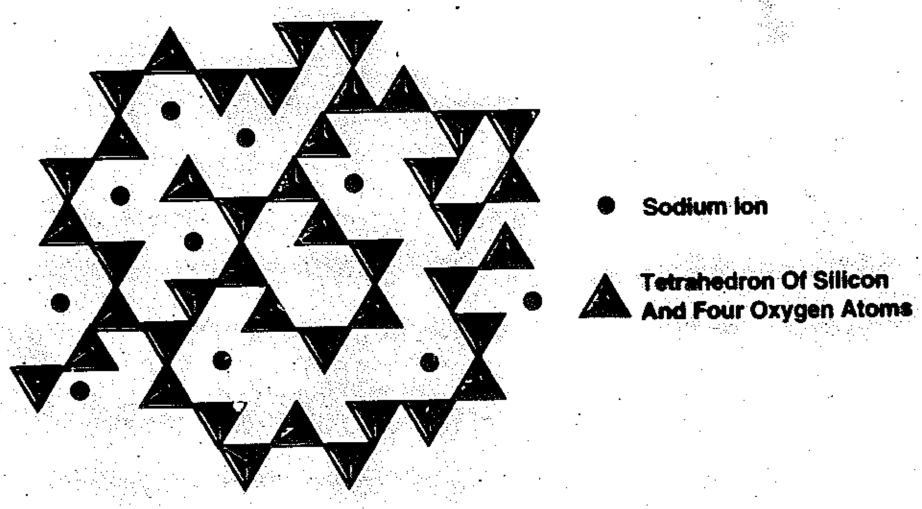

**Figure 17**
A schematic representation of a type of glass

# Glass Stations

1. **Glass Bending, Pulling and Blowing** - directions are in the notebook - page 33-C. The labs are also found in the Battelle Handbook beginning on page 6.13.
    - **Bending Glass** - Use 15 cm of 5 mm tubing - page 33-C
    - **Making an Optical Fiber** - Use 20 cm of 5 mm rod - page 33-C
    - **Blowing a Glass Bubble** - Use 30 cm of 6 mm tubing - page 34-C

2. **Glass Bead on a Wire** - directions are in the notebook (page 34-C) and also in the Battelle Handbook on page 6.10.

3. **Heat and Quench Different Types of Glass** - (Thermal Shock Demo) - Directions in the notebook - page 17-C.
    a. Compare degree of softening and workability
    b. Quench and compare degree of thermal shock
    c. Look for sodium flare

**Other stations that might be available:**

4. **Glass the Conductor** - practice using the apparatus.

5. **Glass Melting and Pouring** - this will be done as a demo - Battelle Handbook page 6.27.

6. **Dragon Tears/Dragon Dribble** - this will be done as a demo - Battelle Manual page 6.32.

# Bending Glass

WEAR SAFETY GLASSES

1. Use a triangular file to cut a piece of 5 mm tubing about 15 cm long.
2. Fire polish each end. Be sure to allow the first fired polished end to cool before attempting to fire polish the other end.
3. Grasp both ends of tubing. Hold the middle part of the tubing in the hottest part of the burner flame. Rotate the tubing to evenly heat all sides.
4. When the heated portion gets soft and wobbly, remove glass from heat. Smoothly bend the ends of the glass tubing upward to form a 90 degree bend.
5. Clean-up!

# Making an Optical Fiber

WEAR SAFETY GLASSES

1. Cut a piece of glass rod about 20 cm long.
2. Use a flame spreader on the Bunsen burner. If using a propane torch, move the rod back and forth in the flame to soften at least 4 cm of the glass.
3. Use both hands to heat the center portion of the rod. Rotate while heating.
4. When rod is fairly soft and wobbly, quickly remove the rod from the burner.
5. Rotate rod so that it is vertical. Quickly spread your arms while firmly grasping the rod.
6. Allow the fiber to cool. Measure and record the length of the thin part of the rod.
7. Check your fiber to see if it will transmit light.
8. Clean-up!

# Blowing a Glass Bubble

**WEAR SAFETY GLASSES**

1. Cut a piece of 6 mm tubing about 30 cm long.

2. Fire polish one end of the tubing and allow to cool.

3. Heat the end that has not been fire polished until it is soft. Then use a pair of pliers to seal the end or push it against a ceramic tile. It is also possible to allow the end to close on its own with enough heating.

4. Heat the tubing about one cm above the sealed end until it is soft. Quickly remove the tubing from the heat and blow into the cool end while rotating the tube. Some people prefer to leave the glass in the flame while blowing.

5. Repeat step 4 until you have a bubble with a diameter about twice that of the tubing. As the glass walls of the bubble get thinner use less air pressure to avoid bursting the bubble.

6. Clean up!

# Glass Bead on a Wire

**WEAR SAFETY GLASSES**

1. Find a partner for this lab. One person will use nichrome wire and the other partner will use copper wire.

2. Cut a piece of wire about 12 cm long.

3. Use pliers to form a small loop on the end of the wire.

4. Use pliers to hold the wire while heating. Using a Bunsen burner or propane torch heat the loop end of the wire until it gets red hot.

5. Dip the hot end of the wire into the borax.

6. Carefully heat the borax on the wire until it is melted and the loop fills in. Do not add more borax until the bead becomes clear and almost all bubbles are gone. The bead should have a color.

7. You may need to repeat steps 5 and 6 to fill in the loop and get a bead.

8. Clean-up!

# Glass Task Sheet

## Scoring and Breaking Glass

| | Date/Page # | 5 | 4 | 3 |
|---|---|---|---|---|
| Method | | | | |
| Illustration of final product | | | | |
| Observations/critique of cuts | | | | |
| Final write-up/discussion | | | | |

## Glass Bend

| | Date/Page # | 5 | 4 | 3 |
|---|---|---|---|---|
| Method | | | | |
| Illustration of final product | | | | |
| Observations | | | | |
| Final write-up/discussion | | | | |

## Glass Fiber

| | Date/Page # | 5 | 4 | 3 |
|---|---|---|---|---|
| Method | | | | |
| Length of final product | | | | |
| Observations | | | | |
| Final write-up/discussion | | | | |

## Glass Bubble

| | Date/Page # | 5 | 4 | 3 |
|---|---|---|---|---|
| Method | | | | |
| Illustration of final product | | | | |
| Observations | | | | |
| Final write-up/discussion | | | | |

## Glass Beads on a Wire

| | Date/Page # | 5 | 4 | 3 |
|---|---|---|---|---|
| Method | | | | |
| Color illustration of final product | | | | |
| Observations | | | | |
| Final write-up/discussion | | | | |

## Final Product

| | Date | Points | Bonus |
|---|---|---|---|
| Glass Scoring and Breaking | | | |
| Glass Bend | | | |
| Glass Fiber | | | |
| Glass Bubble | | | |
| Glass Beads on a Wire | | | |

## Clean-Up

| | Date | Lab | Bonus | Signature |
|---|---|---|---|---|
| Day #1 | | | | |
| Day #2 | | | | |
| Day #3 | | | | |
| Day #4 | | | | |
| Day #5 | | | | |
| Day #6 | | | | |

# Glass Task Sheet

## Final Conclusion Questions

### Final write-up/discussion points:

Write the answers in your journal and not on this page. Restate the questions in your answers.

### Scoring and Breaking Glass:

What was easy about the process?
What was difficult about the process?
Discuss strength of glass under tension and compression and how this applies to scoring and breaking glass.
State 4 rules about scoring/breaking technique

### Glass Bending/Blowing/Drawing a Fiber

Difference between tubing and rod
How to score tubing/rod
What is the purpose of fire polishing and how is it done
Advantage of fiber optics for communication
What happens to glass as it gets hotter (Hint: melting vs. softening)

### Glass Beads on a Wire

What produced the color in the glass?
Is the glass crystalline or amorphous?
What causes the bubbles in the glass?

# 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:

$$4\ Fe + 3\ O_2 \longrightarrow 2\ Fe_2O_3$$

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).

38-C

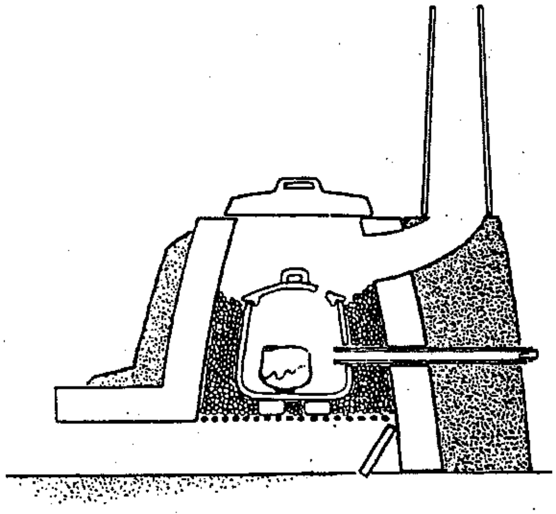

**Figure 6.9.** Small circular raku kiln burning coke or smokeless fuel. The saggar is the heart of the kiln and the main wall follows its profile. The walls may be made of common brick for a temporary kiln or of firebrick for a more permanent structure. The belly of the kiln is transversed by a number of firebars 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

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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.

$$2\,C + 4\,CuO \longrightarrow 2\,Cu_2O + 2\,CO_2$$

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:

$$Fe_2O_3 + CO \longrightarrow 2\,FeO + CO_2$$

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.

# Glossary

**Abrasive:** A hard material used to grind, cut or wear.

**Absorption:** The inclusion of the energy of a photon within a substance.

**Amorphous:** A noncrystalline substance, atoms lack long range order.

**Annealing:** Heat treatment to alter properties.

**Annealing point (glass):** Temperature at which stresses are removed.

**Atomic vibration:** Movement of an atom within a substance.

**Band gap energy:** Energy difference between the valence and conduction bands.

**Brittle fracture:** A break which occurs by rapid crack propagation.

**Capacitance (C):** Charge storing capability.

**Cement:** A material which binds particles together in a mixture.

**Ceramic:** A compound of metallic and nonmetallic elements.

**Color:** Wavelengths of light perceived by the eye.

**Component:** A part, or device.

**Conduction band:** Carries the excited conduction electrons.

**Conductivity:** The ability to carry an electric current (electricity) or thermal energy (heat).

**Covalent bond:** Bonding by sharing electrons.

**Crystalline:** A solid with a repeating three-dimensional unit cell.

**Crystal structure:** The orderly arrangement of the atoms or ions within a crystal.

**Diamagnetism:** Weakly repelled from a magnetic field.

**Dielectric:** An insulator.

**Dielectric constant:** Relative electrical permittivity of a material as compared to a perfect vacuum.

**Dielectric (breakdown) strength:** The amount of electricity needed to start an electric current flow in a dielectric material.

**Ductile fracture:** Break accompanied by large plastic deformation.

**Elastic deformation:** Change in shape which returns when a stress is removed.

**Elastic Modulus:** Ratio of stress to strain in elastic deformation, measure of elasticity.

**Electric field:** The gradient of voltage.

**Electronegativity:** The attraction of an atom for shared electrons.

**Electron volt (eV):** Unit of energy equivalent to the energy gained by an electron when it falls through an electric potential of one volt.

**Excited state:** An energy state to which an electron may move by the absorption of energy.

**Fiber Optics:** The technology of transferring information as light pulses through long thin fibers, usually made of glass.

**Firing:** High temperature processing to increase densification in a product.

**Fluorescence:** Light which is emitted a short period of time after an electron has been excited.

**Fracture toughness ($K_c$):** Measure of a material's resistance to crack propagation.

**Glass:** An amorphous solid showing characteristic specific volume behavior over a certain temperature range.

**Glass - ceramic:** Crystalline ceramic material which was formed by heat treating glass.

**Glass transition temperature ($T_g$):** Temperature at which a glass changes from a supercooled liquid into a solid.

**Grain:** Individual crystal in a polycrystalline material.

**Grain boundary:** The boundary between grains (or crystals) which are misoriented with respect to one another.

**Green ceramic body:** Ceramic object which is dried but not fired.

**Ground state:** Lowest electron energy state.

**Hardness:** Resistance to deformation.

**Heat capacity:** Heat required to produce a unit increase in temperature per quantity of material.

**Imperfection:** Flaw, any deviation from perfection, as in a crystal.

**Index of refraction:** Ratio of the speed of light in a vacuum to the speed of light in a medium.

**Insulator:** Material which does not conduct electricity (electrical) or heat (thermal).

**Ionic bond:** Electrostatic force between oppositely charged ions.

**Laser:** Source of coherent light (Light Amplification by Stimulated Emission of Radiation).

**Lattice:** The regular arrangement of points in a crystal.

**Luminescence:** Emission of visible light when an electron returns to the ground state from an excited state.

**Magnetic field strength:** Intensity of an applied magnetic field.

**Microstructure:** Structural features which can be observed with a microscope.

**Noncrystalline:** Amorphous, with no long-range atomic order.

**Opaque:** Material which does not transmit light.

**Phonon:** Quantum of vibrational energy.

**Phosphorescence:** Luminescence that lasts for more than one second.

**Photovoltaic cells:** A device capable of converting light energy to electricity.

**Photoconductivity:** Electrical conductivity induced by light.

**Photon:** Quantum of electromagnetic energy.

**Piezoelectric:** Material which produces an electrical response to a mechanical force.

**Plastic deformation:** Permanent deformation, change of shape.

**Polycrystalline:** Composed of more than one crystal or grain.

**Porcelain:** A durable ceramic composite made by firing clay, feldspar and quartz together.

**Reflection:** Deflection of light at the interface between two materials.

**Refraction:** Bending of light as it passes from one medium into another.

**Refractory:** Material which can be exposed to high temperature without deterioration.

**Resistivity:** Measure of resistance to passage of electrical current (reciprocal of conductivity).

**Semiconductor:** Nonmetallic material which has a relatively narrow energy band gap.

**Sintering:** Coalescence of individual ceramic particles into a continuous solid phase at a high temperature.

**Slip:** Mixture of clay with water which can be poured into a mold.

**Slip casting:** Method of making ceramic objects by pouring slip into a mold.

**Softening point (glass):** Maximum temperature a glass can be heated before it permanently deforms.

**Smart materials:** Materials able to detect a change in the environment and react to it.

**Specific volume:** Volume per unit mass, reciprocal of density.

**Strain:** Change in length of a sample in the direction of an applied stress.

**Stress:** Force applied to a sample divided by its cross-sectional area.

**Structural clay products:** Ceramic objects made mainly of clay and used in structural applications.

**Structure:** Arrangement of internal components.

**Superconductivity:** Disappearance of electrical resistivity at low temperatures.

**Supercooling:** Cooling below the normal temperature for a phase change, without the change occurring.

**Tensile strength:** Maximum stress without fracture.

**Thermal expansion coefficient, linear:** Fractional change in length divided by change in temperature, a measure of a material's tendency to expand when heated.

**Thermal stress:** Residual stress caused by a change in temperature.

**Thermal tempering:** The introduction of residual compressive stresses to increase the strength of glass.

**Toughness:** Energy absorbed by a material as it fractures, a measure of its resistance to fracture.

**Transgranular fracture:** Fracture by crack propagation through the grains.

**Translucent:** Transmits light diffusely.

**Transparent:** Transmits light clearly.

**Unit cell:** The basic repeating unit in a crystal.

**Whiteware:** Clay-based ceramic which turns white after firing.

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