Laboratory Experiences in Glasses and Traditional Ceramics

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Abstract

In the Ceramic Engineering department at the University of Missouri-Rolla, students develop strong experimental skills through a series of laboratory classes. At the sophomore level, students explore a variety of processing and characterization methods. Two specific examples of laboratory exercises are discussed in this paper: 1) the formulation and fabrication of triaxial porcelains, and 2) the processing and characterization of glasses.

As the name suggests, triaxial porcelains contain three components, clay, feldspar and flint. Each plays an important role in the processing, microstructure development, and final properties of the ceramic. Understanding the function of each component during processing and in the final fired ceramic is important so that compositions can be designed for use with specific forming methods or to meet performance specifications. The role of each component in forming and in the fired component is described and a simple design exercise is outlined.

Glasses are fascinating because of their unusual structure and properties. Within certain compositional windows, the properties of glasses such as density, thermal expansion coefficient, refractive index, and glass transition temperature are linearly dependent upon composition. An experiment is described in which students prepare and characterize a series of glasses to elucidate relationships between composition and properties.

I. Introduction

Ceramic materials are often the "enabling" technologies at the heart of practical devices.[1] This classification implies that the function of a device is dependent on the special properties of a ceramic part, which, in turn, depends on the processing history, chemical composition, and crystal structure of the ceramic. A simple example would be the piezoelectric quartz crystal that drives most of modern watches and clocks. The performance of the ceramic is vital to the accuracy of the device, but the ceramic remains hidden unless the system is disassembled. Most new functional ceramics are designed by applying knowledge of structure-property relations, but development requires extensive experimentation. Thus, it is essential that undergraduate students in ceramics/materials programs develop strong experimental skills. Properly designed laboratory exercises aid in the development of these skills, plus they can be an excellent method to reinforce topics from lecture classes with hands-on experience.

At the University of Missouri-Rolla, the curriculum in the Ceramic Engineering department is designed to provide undergraduates with a mix of fundamental understanding and practical, hands-on skills.[2] The sequence of seven required laboratory classes in the department are listed in Table 1.[3] The sophomore and junior labs are designed to help students build a portfolio of experimental skills that can be used during the senior year to complete the capstone "senior design" class. During the sophomore year, the exercises concentrate on familiarizing the students with equipment and processing that they will use throughout their time at UMR and in their careers as ceramic engineers. A listing of specific exercises in the sophomore laboratory classes is given in Table 2. During the second semester, two of the exercises have strong design elements. The purpose of this paper is to describe these exercises in more detail. The design aspects will be highlighted, and the relation of the exercises to other courses in the curriculum and the specific experimental skills needed for each experiment will be discussed.

Table 1. The Ceramic Engineering laboratory sequence at University of Missouri-Rolla.

Year	Semester	Course/Number	Focus
Sophomore	Fall	Materials Lab I/111	Equipment usage, raw materials
	Winter	Materials Lab II/122	Traditional processing methods, glasses
Junior	Fall	Processing Lab I/231	Processing methods, design of experiments
	Winter	Processing Lab II/242	Microstructure design and characterization
Senior	Fall	Charcterization/362	Mechanical, electrical, & optical properties
	Fall	Design Lab I/261	Capstone project
	Winter	Design Lab II/262	Capstone project

Table 2. Sophomore laboratory exercises in Ceramic Engineering.

Fall Semester	Winter Semester
• Density measurement	• Plaster of Paris mold making
• Raw materials collection	• Glass formulation/characterization
• Comminution and sieve analysis	• Viscosity measurement
• Furnaces, temperature measurement	• Extrusion of porcelains
• Granulation and dry pressing	• Slip casting, glazing, and firing
• Sintering and SEM analysis	

II. Triaxial Porcelains

Traditional ceramics are prepared from industrial minerals such as clays, other silicates, or quartz bearing minerals such as flint or sand.[4] Fired traditional ceramics almost always contain a significant amount of silica-rich glassy phase. For most traditional ceramics, a single composition is used in many different applications. In contrast, *modern* ceramics are phase-pure materials such as SiC and $BaTiO_3$ or composites such as Al_2O_3 toughened by adding ZrO_2

particles.[5] Modern ceramics do not contain appreciable amounts of silicate glasses. Generally, the processing and microstructure of modern ceramics are optimized for a specific application.

Porcelain is a traditional ceramic prepared from clay, feldspar, and flint and fired to a non-porous state. The term "triaxial" implies that three raw materials are used in varying proportions. The generic composition of porcelain is 50 percent (all compositions by weight) clay, 25% feldspar, and 25% flint. The mineralogy of the constituents is summarized in Table 3. The proportions of the constituents can be varied to meet process requirements or to tailor the properties of the fired ceramic to certain applications, hence the design aspect. Fired porcelain ceramics contain multiple phases including very fine needle-like mullite ($3Al_2O_3 \bullet 2SiO_2$) grains and flint particles bonded by a glassy phase. Common applications include dinnerware, electrical insulators, and decorative objects such as vases. Porcelains are distinguished from other clay-based traditional ceramics by their high mechanical strength, high electrical resistivity, low porosity, and translucency. At UMR, students learn about the science of traditional ceramics from a sophomore lecture class, Ceramics in the Modern World, in addition to the laboratory class.

Table 3. Components and typical composition of a triaxial porcelain.

Component	Amount (wt. %)	Types	Mineral Composition(s)
Clay	50%	Ball Clay China Clay	$Al_2O_3 \bullet 2SiO_2 \bullet 2H_2O$ (all types)
Feldspar	25%	Soda Feldspar Potash Feldspar Anorthite	$Na_2O \bullet Al_2O_3 \bullet 6SiO_2$ $K_2O \bullet Al_2O_3 \bullet 6SiO_2$ $CaO \bullet Al_2O_3 \bullet 2SiO_2$
Flint	25%	Quartz Flint	SiO_2 (all types)

The individual components of porcelain are mixed with water to achieve the consistency needed for the chosen forming method. Typical forming methods include dry pressing, extrusion, and slip casting, each of which has a specific range of water contents associated with it.[6] A single composition can be formed by any of the methods by simply changing the amount of water added for processing. Each of the components of porcelain has a specific role during processing/forming. Clays enhance formability of the batch because they develop *plasticity* when mixed with water. Materials that are plastic deform under applied load, and then hold that shape when the load is removed. Clays that have high plasticity also undergo large shrinkage as the water added for processing is removed by drying. Drying shrinkage can lead to development of stresses that result in warping and cracking during drying or firing. Often, two or more different types of clays are used to produce adequate plasticity for the chosen forming method without producing excessive shrinkage. A mixture of ball clay (high plasticity and shrinkage) and china clay (moderate plasticity and shrinkage) is usually employed. The feldspar and flint are referred to as non-plastics because they do not deform plastically when mixed with water.

Instead, they provide strength to the shaped body and reduce the amount of shrinkage that occurs during drying. The relative plasticity, formed or green strength, and drying shrinkage of each of the components of porcelain is summarized in Table 4.

Each of the components of porcelain also has a specific role in microstructure and property development during firing. As the formed part is heated, the first change to occur is the formation of meta-kaolin by the removal of chemically combined water from the clay below 400°C. As the temperature increases, the feldspar forms a molten siliceous phase due to the fluxing action of the alkali or alkaline earth oxides between 950°C and 1200°C. This begins the process of *vitrification*, that is the formation of a glassy phase that bonds the crystalline phases together.[7] As heating continues, the meta-kaolin begins to dissolve into the siliceous phase. As dissolution continues, mullite crystals begin to precipitate from the molten phase. These crystals are needle-like and small, less than 1 μm in length. They provide strength to the porcelain. When the conversion of meta-kaolin to mullite is complete, the porcelain is said to be fully developed. Typically, firing temperatures in excess of 1400°C are required to produce a translucent porcelain that is free of pores and remnants of clay particles. As the body is cooled, the siliceous phase forms a glassy phase that bonds the mullite crystals and flint particles. Flint is nearly inert during firing, but its presence in the final microstructure provides strength.

Table 4. Function of each component during forming and firing of triaxial whitewares.

	China Clay	**Ball Clay**	**Feldspar**	**Flint**
Particle Size	Medium	Fine	Large	Large
Plasticity	Medium	High	None	None
Green Strength	Low	High	Medium	Medium
Drying Shrinkage	Medium	High	Low	Low
Firing Temperature	Increase	Decrease	Decrease	Increase
Fired Strength	Low	High	Medium	Medium

A new laboratory exercise has been outlined to put a greater emphasis on the design aspects of formulating porcelain compositions. Previously, the emphasis was on learning to use the laboratory extruder. Students were assigned a specific composition and told to formulate and extrude it. The laboratory groups then measured drying shrinkage and firing shrinkage for each batch. The new laboratory exercise will emphasize understanding and applying the information in Table 4 along with use of the extruder. The laboratory handout will describe the role of each constituent of porcelain and give the generic composition (25% ball clay, 25% china clay, 25% feldspar, 25% flint). Each group will be asked to modify the overall composition of their batch by varying the ratios of the constituents. They will then batch, mix, and extrude bars to meet the assigned specifications. After extrusion, groups will measure drying shrinkage, dried/green strength, and firing shrinkage to determine if the modifications that they made were indeed appropriate. For example, a group might be asked to adjust the batch composition to lower firing temperature without affecting formability (plasticity). Several choices exist, but the simplest would be to increase the feldspar to flint ratio without changing the ratio of plastics (clays) to non-plastics (feldspar and flint). Increasing the amount of feldspar would increase the fluxing action producing more liquid phase at a given temperature. By holding the ratio of the clay to non-clay components constant, the forming should not be affected. If this modification is made correctly, the green strength and drying shrinkage should not change, but the firing shrinkage would be higher for a given firing temperature compared to the standard composition. In the laboratory report, the group would also have to suggest what property was degraded when their modification was made. In this example, increasing the amount of feldspar would increase the amount of glassy phase in the finished product, which would probably degrade the fired strength. Some other design challenges and potential batch modifications are listed in Table 5.

Table 5. Some suggested design challenges for the porcelain extrusion laboratory.

Design Challenge	Possible Solution(s)	Other Effect
Reduce drying shrinkage	Increase china clay:ball clay ratio	Reduced plasticity
Increase dried strength	Increase non-plastic:plastic ratio	Reduced plasticity
Increase plasticity	Increase ball clay:china clay ratio	Increased drying shrinkage

III. Glasses

Glasses are important commercial ceramics. They are aesthetically pleasing and technologically important. It is necessary to understand structure-property relations in glasses to design and formulate compositions to meet ever-changing industrial needs. The majority of commercial glasses are silicate-based due to good strength, excellent durability, and low cost. Borates and phosphates are the other two major glass forming systems. For borate formulations, B_2O_3 is the main glass network former. Alkali and alkaline earth oxides are modifiers that tend to lower the melting temperature and alter properties by *de-polymerizing* the glass network, i.e., modifier additions reduce the number of network-forming B-O bonds. Intermediates such as Al_2O_3 strengthen the network, but do not form glasses on their own. At UMR, students learn about glasses in a sophomore lecture class, Atomic Structure of the Glassy State, and the lab class.

In the sophomore laboratory sequence, students investigate composition-structure-property relations in borate glasses. Borates are used for two main reasons: melting temperature and compositional flexibility. First, borates melt at lower temperatures than silicates, making them easier and safer to process. Borate glasses can be formed by heating to around 1000°C, compared to above 1500°C for many silicates. Figure 1 shows two UMR students pouring a borate melt. Second, borates have a wide compositional forming range, allowing for the investigation of several different additive effects. The laboratory assignment described in this paper requires groups to investigate and to report on the effect of compositional changes on the properties of borate glasses. The broad categories of changes are summarized in Table 6.

Figure 1. UMR students pouring a molten borate glass.

Table 6. Glass composition variations and property trends.

Composition Change	Property Effect Investigated
Use various alkali oxides	Cation field strength
Multiple alkali additions	Mixed alkali effect
Increasing modifier content	Borate anomaly
Alumina additions	Increase in strength and melting point
Transition and rare earth metal additions	Color intensity (Beer's Law)

The nominal composition used in this experiment is 80% B_2O_3 and 20% Na_2O (compositions by weight). The effect of cation field strength (valence to bond length ratio) is studied by replacing the alkali modifier, Na^+, with Li^+ or K^+. In theory, substitution of ions with higher field strength (Li^+ for Na^+) will lower the glass density and refractive index. The mixed alkali effect is investigated by adding multiple alkali modifiers (Na^+ and K^+) to the glass. The glasses are characterized to measure the deviation from the linearly additive properties observed when only one modifier is used. The *borate anomaly* is examined by adding large amounts of modifying cations. The borate anomaly is caused by a change in boron coordination number from three to four at high modifier contents, which results in significant changes in glass properties. The effect of adding Al_2O_3 is also examined. Alumina strengthens the glass and makes it more durable, but it increases the melting temperature drastically. The final compositional effect examined is the coloring of borate glasses with transition metals and rare earths (Co^{3+}, Cr^{3+}, Fe^{3+}, Nd^{3+}, Er^{3+}, Pr^{3+}). The intensity of the color change it then related to composition using Beer's law. For the laboratory assignment, each group examines one of the compositional changes. For the report, groups share data so that each group can discuss all of the effects.

The laboratory assignment requires each group to batch, melt, and cast at least three different glass compositions to examine one of the compositional effects listed in Table 6. After the glasses are annealed, the physical properties and optical absorption are characterized. The physical property measurements include density, refractive index, glass transition temperature (T_g), crystallization temperature (T_x), and coefficient of thermal expansion (CTE). Optical absorption is measured to quantify color effects. After heating the glasses to induce crystallization, the major crystalline phases are determined by x-ray diffraction (XRD) analysis. The students perform all of the characterization after appropriate training by the instructors. The characterization techniques used and properties measured are summarized in Table 7.

Table 7. Characterization techniques and properties measured for glasses.

Property(ies)	Characterization Technique
T_g, T_x	Differential thermal analysis
Density	Achimedes' technique
Refractive Index	Becke line test
CTE	Dilatometry
Predominant crystalline phases	X-ray diffraction
Optical absorption	UV-VIS spectroscopy

In the laboratory report for the glass experiment, students are asked to apply the data that was gathered. In a typical year, more than twenty glasses are prepared and analyzed, more than enough to create a useful composition-property map. This map can be used as a design tool to suggest potential compositions for "real world" applications. For example, students may be asked to suggest a glass composition that could be used to join two metals with dissimilar coefficients of thermal expansion. The design challenge would be to find a glass (or the crystalline phase produced from a glass) that has a CTE that lies between those of the two metals. Another example would be to predict the rare earth additives needed to form a glass that approximates the optical absorption of gemstones. Many possible design problems exist.

IV. Summary

Quality, hands-on laboratory experiences are a powerful learning tool. Ideally, a laboratory assignment should enhance the experimental skills of the student and reinforce material discussed in lecture classes. It is also possible to incorporate elements of design into laboratory exercises. Two examples from a sophomore level laboratory class in the Ceramic Engineering department at University of Missouri-Rolla were described in this paper. In the first, students were given a standard porcelain composition and asked to modify it to meet specific design requirements. Their ability to meet these requirements was measured by characterizing the drying shrinkage, dried strength, and firing shrinkage of extruded porcelain bars and comparing them to a reference composition. The exercise also familiarized students with a common ceramic forming technique, namely extrusion. In the second exercise, the effect of composition on properties of borate glasses was examined. Each laboratory group batched, melted, and cast several compositions. The density, T_g, T_x, refractive index, thermal expansion coefficient, and optical absorption of their glasses were characterized by the students. The results were shared among groups so that a larger map of composition-structure-property relations could be created, and, potentially, applied to design compositions to meet specific performance requirements. Finally, each student prepared a laboratory report that described the effect of changes in composition on the properties in this glass forming system and that addressed the idea of designing glasses to meet certain performance requirements.

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