Research Article

Silicate Glasses and Glass Forming Systems of the Clays: A Perspective for the Future

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Abstract The new century ushered in development of colloidal processing approaches to develop complex microstructures, particularly cellular materials. Many different types of near net shaping processes have now been applied to a wide variety of different ceramic materials. The clays used in ancient pottery are the earliest examples of colloidal materials that exhibit forming ability and consistency that allows for the production of complex ceramic shapes. Despite these very early examples, the colloidal phenomena underlying such remarkable plasticity and shaping ability were only elucidated much later. The gaps in knowledge in these fields are discussed to provide our perspective on where the field may support advances in glass in the future. The challenges in glass science and engineering identified here build on these and other recent advances and emerging opportunities. This study is about silicate glasses and glass forming systems of the clays in a perspective for the future.

Introduction

A motivational history to inspire increased exploration of the materiality of glass in the history of scientific instruments. Historians of science point to the scientific revolution of the 17th century as a period marking the onset of modern science. The pace of technological change increased dramatically when the scientific discoveries of the 17th century abruptly broke the rhythm of (a long evolutionary) process and etc. created the conditions necessary for an expansion no longer based on evolution, but on invention [1]. The major scientific instruments invented in the 17th century, five involved glass in a fundamental way; telescope, microscope, thermometer, barometer, and air pump (the pendulum clock is the other). For both barometer and thermometer, the glass tube held the liquid whose movement signified changes in air pressure and temperature and provided a window through which those changes could be seen and measured. The microscope appears in the historical record without fanfare, without a clear date, without an immediate name, and without immediate impact or purpose [2]. The glass receiver of the air pump was required not just for providing a strong vessel that could resist the power of the vacuum.

The telescope, the earliest of these vitreocentric devices, stirred up matters from the start. For both telescope and microscope, moving from the two eyes of nature to the one glass eye of scientific instruments took considerable adjustment. For 450 years, telescopes and microscopes have provided us with access to distant and tiny worlds. A detailed history of the telescope or microscope written today would look quite different from its predecessors of centuries past, and not just for reasons one might expect. The microscope appears in the historical record without fanfare, without a clear date, without an immediate name, and without immediate impact or purpose. It is known that Galileo (1564-1642) used one by 1610, and that by 1620, the innovator Cornelius Drebbel (1572-1633) had been using one for about a decade. As magnifiers of various kinds had for some time already provided enlarged views of

small objects, a microscope did not provide the novelty of a telescope. It was not obvious that this device would yield anything valuable; it did not immediately reveal anything as earthshaking as Galileo's telescopic observations. The field of glasses-ceramics began to display notable interest in colloid science when it was reported that the plasticity, and hence the wet strength of green body clays, was a function of the amount of colloidal matter present in the clay mixture. Ashley [3] presented a detailed study in 1909 where the author applied the knowledge of colloid theory at the time to describing and measuring the properties of clays. The author also detailed methods of measuring the plasticity of the clays by the amount of dye absorbed by the colloidal matter. The increasing use of ceramics and ceramic-based materials around the beginning of the 20th century in both building and engineering applications led to further studies on understanding certain material processing-property relationships of clay bodies. Increasing the wet strength of clays was of particular interest since it would allow for better formability and hence final dimensional control of ceramic components.

However, as encountered in many technological breakthroughs both in the past and in the present day, the empirical knowledge was still not understood from a fundamental scientific point of view. The traditional approach for glass research is largely empirical. A rational design approach to develop new glasses with desired properties and functionalities is usually hampered by the lack of understanding of the impact of composition and processing conditions (thermal or pressure history) on the resulting glass structures and macroscopic properties. For multicomponent glasses consisting of atoms of similar sizes, accurate structure identification remains a challenging task. Furthermore, structure factors and pair distribution functions obtained from diffraction measurements are one-dimensional functions that are inherently unable to fully capture the three-dimensional glass structure. Advanced atomic scale imaging based on electron microscopy complements diffraction techniques by providing direct visualization of glass structures in real space. For instance, electron tomography is now applied to the reconstruction of three-dimensional amorphous structures with nanometer spatial resolution. Overall, construction of realistic glass structural models for first principles predictive modeling of mechanical, electronic, electrochemical, and optical properties in glasses remains a standing challenge.

Furthermore, designing new and novel glasses that function under such extreme conditions is likewise important for a variety of applications, including electrochemical, aerospace, and biomedical. Among the extremes, pressure and temperature are important basic thermodynamic variables that determine the structure, dynamics, and macroscopic properties of glasses and glass forming liquids. On the other hand, hot compression of glass in the nonrigid state in the glass transition range may also provide a means to study the structure and properties of glass forming liquids under pressure, which is of critical importance to understand geological processes in the earth's interior. Overall, construction of realistic glass structural models for first principles predictive modeling of mechanical, electronic, electrochemical, and optical properties in glasses remains a standing challenge. Resolving this challenge will entail the development of new efficient modeling techniques as well as reliable, large-scale structure characterization methods.

Exploring modes of communication between different communities, say between glass artisans and natural philosophers at this time, is essential for understanding the extent of the overlaps of, and gaps between, their vitreous knowledge and practice, and remains to be carried out. Nonetheless, by the end of the 17th century, there were two kinds of glasses available for optics, with quality a random and chance parameter identified by luck, as well as by trial and error [4]. The current status and future outlook of glass science and engineering were recently discussed in two splendid reviews. The challenges in glass science and engineering identified here build on these and other recent advances and emerging opportunities. This study is about silicate glasses and glass forming systems of the clays in a perspective for the future.

Materials and Methods

Glass played two broad roles in the investigation of nature prior to the emergence of modern science: The first was in the service of optics. Johannes Kepler (1571-1630) provided a theoretical framework for positive (double convex)

and negative (double concave) lenses, explained the principles of the Galilean telescope, and described a telescope with two positive lenses, the astronomical or Keplerian telescope (shown below, Fig. 1).
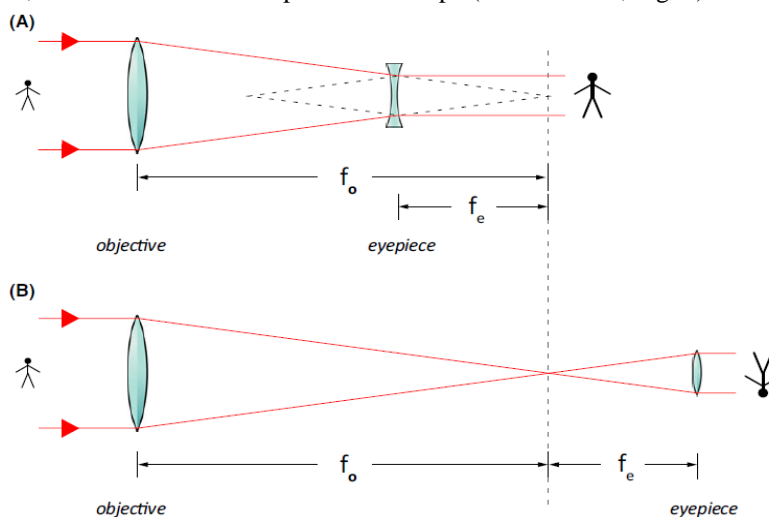

Figure 1: (A) Galilean telescope and (B) Keplerian telescope "the figures illustrate the orientation of the image, not the magnification-magnification occurs because the rays entering the system are spread out by the lens combination"

The second prescientific context for glass was alchemy. Long derided, alchemy appears in recent scholarship with significant roles in both glass history and in the emergence of science, stemming from the close connections between alchemy and glassmaking; glass serving as an indispensable vessel for chemical experimentation, the transmutation of ordinary sand and ash into glass, and glass as a product that imitates natural gems and minerals. In here for both instruments; the most important task is not magnification but improved resolution, enabling an observer to distinguish details indistinguishable with an unaided eye. Consider two coins at a distance (or two tiny dots very slightly separated) so that an observer cannot distinguish them. If a magnified image of such a pair is too blurry, it is still impossible to distinguish them; little is gained from this empty magnification.

Increasing resolution is not the only task of a telescope (or microscope). Consider viewing these coins at night (or dots in a darkened room), so that the incoming amount of light yields an image too dim to see. With a sufficiently large telescope (or microscope), that is, with an opening or aperture that gathers or collects enough light, the magnified image becomes bright enough so that the coins (or dots) are detectable to the retina of the human eye. Thus, a (traditional optical) telescope or microscope gathers an incoming beam of light photons, and spreads that beam of light to create an expanded and enlarged image that increases the resolution of the object(s) under consideration. In optical telescopes and microscopes, glass lenses (as well as metal or glass-based mirrors) perform the central task of gathering and spreading light, as described by geometrical optics. Although a simple microscope uses just one lens to produce an image, compound microscopes and telescopes use multiple lenses and sometimes mirrors to manipulate light to create an image. Telescopes and microscopes combine diverse combinations of positive and negative lenses. For example, in a microscope, a positive object lens can be placed at a distance from the sample equal to the lens's focal length, creating a parallel beam of light that can be manipulated by a suitably chosen eyepiece or pass directly to the eye, as in a simple microscope.

Until the 20th century, most lenses were produced using techniques employing randomized orientations of grinding strokes, producing surfaces of revolution and thus spherical curvatures; nonspherical curvatures were exceedingly difficult to make, and rarely produced. The most famous maker of simple microscopes, made over 500 tiny lenses using three different methods: 1) by heating a glass rod and creating a very small sphere formed by surface tension, 2) by grinding both sides of a tiny piece of glass to spherical curvatures and polishing their surfaces, and 3) by blowing into a thin glass rod to create a tiny glass bubble [5]. All but two of his dozen surviving microscopes include a lens of the second type, the other two a lens of the third.

Almost without exception, telescope and microscope lenses were made by grinding and polishing glass (included clay). Grinding removes material from a glass blank in order to produce a lens with the correct shape; polishing removes the surface's tiny mountains and valleys to create a smoother surface with limited unwanted reflection. In most instances, the exact methods remained proprietary secrets. The invention of lasers in 1960, coupled with computer-driven technologies and analytic software, enabled the development of mathematic descriptions of optical parameters, increasingly sophisticated interferometry techniques, and nonspherical lenses accurately ground to within fractions of the wavelength of light. In simple telescopes, and basic compound microscopes, the lens nearest the object is called the objective, whereas the lens nearest the eye is known as the ocular or eyepiece. The ocular is placed at its focal length distance from the focal point of the objective lens, creating an afocal system. Galilean and Keplerian microscopes work by placing the sample beyond the focal point of the objective lens, creating a converging beam that the negative or positive eye lens, respectively, collimates. In telescopes and microscopes, by combining lenses of different shapes (and, as we shall see, of different glass compositions), one can determine the light path of various colors, control magnification and image orientation, minimize aberrations, and improve image quality [4, 6].

A soda lime or crown glass-positive lens and a flint (lead-containing) glass-negative lens combined to make an achromatic doublet lens, one that would focus red light and blue light at the same point (Fig. 2). The achromatic solution, although in principle well known, did not transfer to microscopes so quickly, as it proved far more difficult to produce the precise complementary curvatures needed for tiny lens pairs. As was the case with the achromatic telescope, the story of the achromatic microscope is quite complex. In fact, the latter case is much more complex.
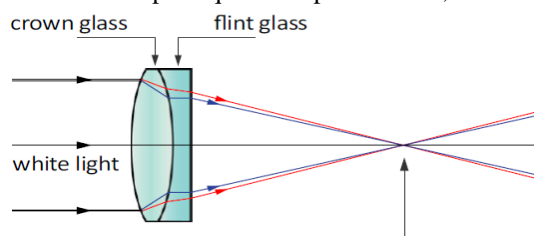

Figure 2: Crown and flint glasses with different dispersion and refractive indexes combine to create an achromatic lens [4]

In addition to augmenting the lens of the human eye, glass has also served as a retina. Early photography used glass plates to record camera images, motivating astrophotography. The era's great refractors and lesser instruments cataloged the stars by recording them on glass plates, whose dimensional stability still makes them valuable resources for noting stellar changes over the past century. Those plates have since given way to other sensors serving as retinas onto which modern telescopes direct incoming light.

The mirror substrates of contemporary instruments typically consist of extremely low thermal expansion fused silica glass or ultra-low thermal expansion glass ceramics. From the most famous of all such telescopes, the Hubble Space Telescope, to the Subaru telescope on Mauna Kea and to the Great Canary Telescope [2, 4], all of the great optical telescopes made since Yerkes coated with a suitably reflective surface and feature a prime mirror made of vitreous materials (Fig. 3). Glass has also played various supporting roles in microscopes. Early examples using reflected light needed only an opaque support for the sample, but light passing through a sample required transparency. Early mounts, made of bone, ivory, or hardwood, held mica disks to support the sample, covered with another layer of mica or paper to protect the sample. From the 1820s, glass became increasingly common as the transparent support substrate, but it took several decades for thin glass to fully replace mica's role as slide cover. Adaptive optics systems, operating on periods of hundredths of seconds, use a feedback loop to monitor atmospheric changes and to signal actuators that alter the shape of deformable mirrors to compensate for atmospheric distortion; a variation in this technique is also used in microscopy to overcome variations in refractive index within a specimen, as well as various aberrations.
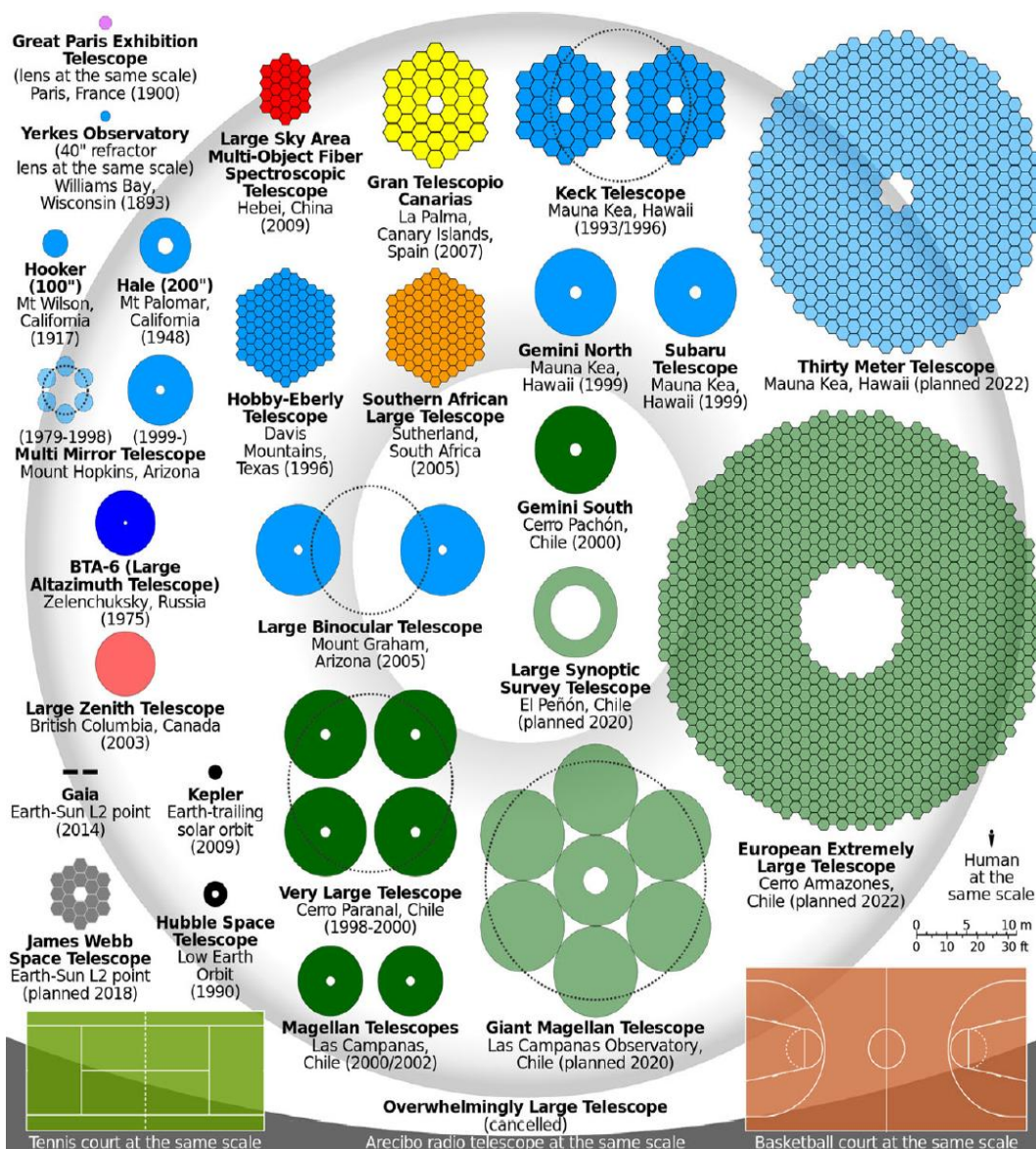
Figure 3: Relative sizes of telescope mirrors in from the late 19th to early 21st centuries [4]

Microscopes are different, as mounts are more obvious and integral elements that typically remain with optical components. The evolution of microscopes until the 19th century is intimately connected with focusing improvements in particular. Increased stability also marks the improvement of telescopes from the 19th century on, as their lenses increased in size, requiring far larger mechanical supports filling rooms and buildings, and as the need for precise and accurate movements dramatically increased. Today's innovative telescopes and microscopes are increasingly active, incorporating and taking advantage of the experience and context laden aspects of seeing.

Viscosity of glass forming systems

As one of the most important properties of glass forming liquids, viscosity has drawn significant attention in both glass manufacturing and fundamental research. This review the recent scientific progress in viscosity of glass forming systems, including both the liquid and glassy states. The viscosity of glass forming systems depends on temperature, composition, and thermal history. However, the nonequilibrium viscosity of glass is also critically important for understanding and predicting the low-temperature dynamics and relaxation behavior of glass. Shear viscosity is perhaps the single most important property of glass forming liquids. Adequate control of flow behavior

of the melt is required during all stages of industrial glass production. Moreover, viscosity is also critical for understanding the glass transition and the relaxation characteristics of liquids and their corresponding glasses.

In modeling the temperature dependence of viscosity, great acknowledgment should be given to introducing the Vogel-Fulcher-Tammann (VFT) equation. This equation works well for strong glass forming liquids, for example, oxide glasses, but performs more poorly for fragile systems. Many subsequent interesting and important studies have been carried out building upon Fulcher's pioneering work. The VFT equation is of great historical importance for describing the temperature dependence of viscosity over much of the past century [7, 8]. Although the VFT equation has met with remarkable success, it over predicts viscosity values at low temperatures due to its divergence of viscosity at finite temperature. To predict viscosity accurately in both high and low temperature ranges, several other viscosity equations have been developed following the VFT equation. The recently proposed VFT viscosity equation shows an improved description of temperature dependence of viscosity in the both high and low temperature ranges, since it is physically derived based on the energy landscape analysis and the temperature dependent constraint model.

The viscosity of an isobaric glass forming system is a function of temperature, composition, and thermal history. The temperature dependence of viscosity has been investigated intensively; however, the composition dependence of viscosity is still a challenging topic. The direct application of conventional atomistic modeling techniques is prohibited due to the long time scales involved with glass transition and relaxation phenomena. Temperature dependent constraint theory plays an important role in describing the composition dependence of glass viscosity. This approach works well in predicting glass transition temperature and fragility, and it is also useful in understanding the structural and topological origins of various other glass properties. The thermal history dependence of viscosity has also drawn limited attention since the nonequilibrium viscosity is difficult to study from both experiment and theory. However, it is very important for understanding and predicting the low-temperature dynamics and relaxation behavior of glass. In describing the nonequilibrium viscosity of glass, several phenomenological models have been developed. Unfortunately, none of the historical models can yield a satisfactory prediction of nonequilibrium viscosity [9].
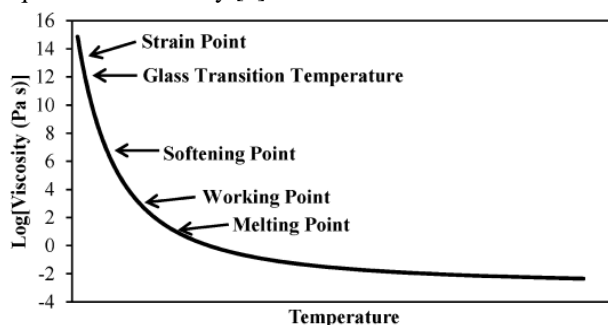

Figure 4: Typical curve for viscosity as a function of temperature for a soda lime silicate melt

Viscosity is of great importance for every step of industrial glass production, including melting, fining, forming, and annealing. Several specific viscosities have been designated as reference points for common practical use. These reference points are shown on a typical viscosity temperature curve for a soda lime silicate melt (Fig. 4). A homogeneous melt can be obtained at the melting point, where viscosity equals 10 Pa·s. The working point is the viscosity at which a melt is delivered to a forming device, typically around 10^3 Pa·s. The softening point is the minimum viscosity that can prevent the glass from deforming under its own weight on a typical glass working time scale, which corresponds to $10^{6.6}$ Pa·s. The temperature range between the working point and the softening point is defined as the working range. After the glass is formed, the internal stresses which result from the glass forming process need to be released by annealing. The annealing point (typically 10^{12} or $10^{12.2}$ Pa·s) is defined as the temperature where stress is substantially relieved within a few minutes, whereas at the strain point ($10^{13.5}$ Pa·s) the stress release is achieved within several hours [10].

Rotation viscometers are commonly used to measure the high temperature viscosity of glass melts. In the viscometer, a platinum cylinder is rotated inside the glass melt with a constant velocity. The viscosity is calculated based on the ratio of torque required to maintain a fixed speed of rotation to the rotational velocity. Fiber elongation is another one of the most important techniques for measuring viscosity. The glass fiber is suspended in a furnace, and the viscosity is determined by measuring the rate of fiber elongation with a known dimension under a known load. According to their original topological constraint theory, the atomic structure of a glass or glass forming liquid may be regarded as a network of bond constraints. Each atom in the network has three translational degrees of freedom in the three-dimensional space, and the degrees of freedom of the glass network are removed by the presence of two-body (radial bond) and three-body (angular bond) constraints. Fig. 5 (A: Each pairwise bond constitutes a single two-body constraint. B: There are five independent bond angle constraints "i.e. three-body constraints" for a rigid tetrahedron. C: A two-coordinated atom such as selenium has one rigid bond angle.) shows the typical linear and angular constraints associated with different structure units in covalent Ge-Se glasses. When the number of constraints exactly equals the number of degrees of freedom, the network is optimally constrained. The network can also be floppy (underconstrained), or stressed rigid (overconstrained), when the average number of constraints is fewer than or greater than the degrees of freedom, respectively.
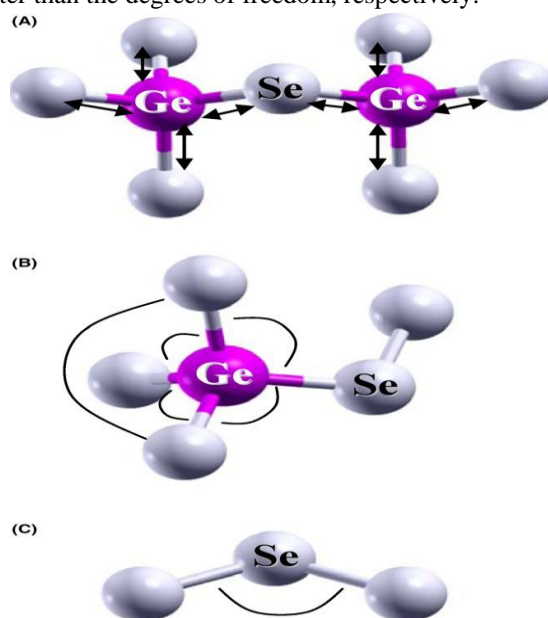

Figure 5: Basic structural building blocks in covalent Ge-Se glasses and their associated constraints, adapted from [8]

The relaxation time of molecular and polymer glass systems could be determined directly by dielectric constant measurements. However, the relaxation time of inorganic glasses requires an alternative method due to the high temperatures involved [11]. Viscometry has been the general approach to study the relaxation behavior of inorganic glasses. Viscosity plays an important role in understanding the glass transition and the relaxation characteristics of liquids and their corresponding glasses. Similar to viscosity, the relaxation time of the glass forming system is a function of composition, temperature, and thermal history.

2.2. Ceramic-based processing with clays

With clays being the catalyst of how colloids and colloidal processing can aid in the formability and properties of ceramic materials, investigation into how to make nonclay ceramics plastic began. In addition, the strength imparted by the addition of sodium hydroxide was translated to the fired clay that was also reported as having the greatest strength of all the modified clays. Colloidal bentonite to traditionally nonplastic clays was able to alter their formability and produce crack free hollow forms, enabling the use of a wider range of clays on brick and tile machines. Furthermore, the addition of aluminum silicate fibers to clay colloids was also used as a mechanism to

greatly increase the strength of ceramic bodies while decreasing shrinkage during firing [12-14]. The colloidal nature of the clay allowed for an even dispersion of the aluminum silicate fibers so that during the firing process, as organics were oxidized, the fibers were able to grow longitudinally and fill the voids occupied by the organic matter [15]. It showed that the same held for other alkali-aluminosilicate glasses prepared in the same way, many subsequent infrared (IR) studies of silicate glasses have confirmed that molecular water and hydroxyl groups coexist in silicate glasses with greater than ~1.5 weight percent total water [14].
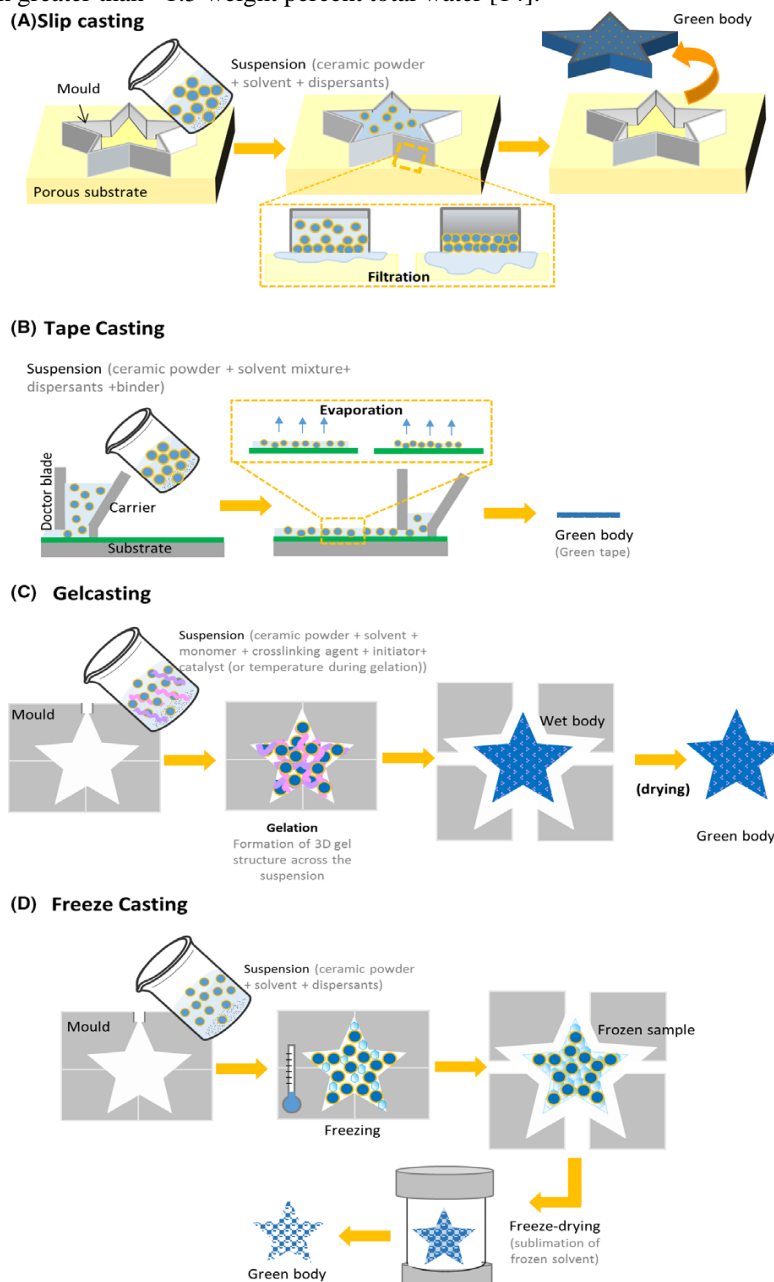

Figure 6: Colloidal shape forming processes

Although the use of ceramics in various industries was increasing, glass-ceramic colloidal processing received little attention in terms of technological applications onwards of the 1940s, with techniques such as hot pressing being the preferred method for shaping and processing oxide and non-oxide ceramic materials and colloidal processing being primarily applied to clays. Simultaneously but independent of the ceramic processing work on clay and other

ceramic-based products was the development of understanding of surface forces and their role in colloidal stability. Ceramists began to incorporate knowledge of colloidal particle interactions into their thinking about processing advanced ceramics in the 1960s and 1970s with focus on oxides (including dielectrics) and silicon carbide (SiC). By the end of the 1970s ceramists began to realize that to produce higher quality ceramics with fine grains and minimal porosity, they needed to use finer powders and pack them to higher and more uniform density which could be accomplished using colloidal processing but generally not with dry pressing [8].

During the 1980s and 1990s a range of near net shape forming techniques such as injection molding, gel casting, direct coagulation casting (DCC) and freeze casting began to be developed in addition to the traditional colloidal shaping processes of ram pressing, jiggering, extrusion, slip casting, and tape casting [16]. The details of the most significant of these processes are illustrated in Fig. 6.

The resulting suspension in general must comply with the following requirements: (i) stability, to avoid segregation and sedimentation of the ceramic particles during the consolidation stage; (ii) low viscosity, to allow ease of flow and filling of the mold; (iii) homogeneity, to ensure a uniform green body with high particle packing, that will lead to dense sintered material; (iv) dispersed state, where the particles are present as individual particles, free of agglomerates and aggregates to minimize flaws in the green body. There are numerous shaping techniques based on the colloidal processing approach. Some of the most common routes are shown in Fig. 6. The consolidation mechanisms are the following: (A) Filtration-slip casting; (B) Evaporation-tape casting; (C) Gelation gelcasting; (D) Freezing-freeze casting. Other techniques such as electrophoretic deposition, spin coating, pressure casting, direct coagulation casting, and additive manufacturing are also based on the principles of colloidal processing. Most of these techniques allow the near-net shaping of both dense and porous ceramic components [12, 17].

This group of processing techniques allows for the shaping of dense and porous ceramic components. Suspensions of ceramic powders with additives (dispersants, monomers, crosslinkers, binders, surfactants, and cryoprotectants) are prepared in the appropriate solvent to control the interparticle forces. The van der Waals interaction produces an attractive force between particles of the same material. In dry systems, there is no effective means to counteract the van der Waals attraction. For instance, while static charge produced by friction may initially lead to electrostatic repulsion in air, this dissipates with time and is significantly reduced by humidity. In wet systems there are a variety of mechanisms that can be used to produce repulsion, which overwhelms the van der Waals attraction. The interaction forces between particles are important because they control the suspension behavior such as viscosity and yield stress, particle packing (green density) under applied pressure, and interaction of particles with interfaces such as air-water and oil-water interfaces. Most of these materials have a van der Waals gap between the separable layers [18, 19]. In some cases, the materials can be exfoliated in solution simply by sonication. In other cases, ions may be intercalated into the gap, increasing the separation of layers, and thereby reducing the strength of the bonding between layers, making exfoliation possible in appropriate solutions. When the bonding between the layers is stronger, it has also been shown that the layers can be separated by etching or protonation in strong acid. The free standing layers described above are produced at low temperature and are kinetically stable in this form. In addition, there are also spontaneously forming two-dimensional ceramic interfacial phases, which are called "complexions" to differentiate them from the three-dimensional bulk phases rigorously defined by Gibbs. These two-dimensional materials can be thought of as thermodynamically stable nanoscale coatings or atomic level surface modifications that can be controlled by changing the temperature or chemical potential of the constituents to alter the transport and catalytic properties [20].

Here are eight challenges reached by consensus, each describing the fundamental science required to forward basic understanding of ceramics and glasses and enable advances in, among others, energy, environment, manufacturing, security, and health care [21]:

- Ceramic processing; programmable design and assembly
- The defect genome; understanding, characterizing, and predicting defects across time and length scales
- Functionalizing defects for unprecedented properties [22]
- Ceramic flatlands; defining structure-property relations in free standing, supported, and confined two-dimensional ceramics

- Ceramics in the extreme; discovery and design strategies [23]
- Ceramics in the extreme; behavior of multimaterial systems
- Understanding and exploiting glasses and melts under extreme conditions [24]
- Rational design of functional glasses guided by predictive modeling

Results and Discussion

By studying the responses of glasses and melts to extremes in temperature, pressure, deep super cooling, or steep chemical, electrochemical, and magnetic gradients using in situ or operando characterization tools and methods, knowledge of the glassy state can be substantially extended. Furthermore, designing new and novel glasses that function under such extreme conditions is likewise important for a variety of applications, including electrochemical, aerospace, and biomedical. Among the extremes, pressure and temperature are important basic thermodynamic variables that determine the structure, dynamics, and macroscopic properties of glasses and glass forming liquids. Furthermore, hot compression of glass in the nonrigid state in the glass transition range may also provide a means to study the structure and properties of glass forming liquids under pressure, which is of critical importance to understand geological processes in the earth's interior.

Fast intercalation of not only lithium, but also sodium, potassium, and multivalent ions (aluminum or magnesium) into electrodes built of free standing two-dimensional glass-ceramic nanosheets may lead to improved batteries. Additionally, two-dimensional glasses-ceramics may dramatically expand the range of solutions for automotive power systems and the large-scale stationary storage of renewable energy, once they can be produced in large quantities. In addition, emerging energy storage devices entirely based on solid state (glass-ceramic) technology are currently limited by the structure and properties of the two-dimensional heterointerfaces through which they are spatially coupled. Thus, a fundamental understanding of interface stability and transport properties is the first step to remove existing performance bottlenecks [25].

The next obvious step in advancing the science of two-dimensional ceramics is understanding structure property relations. To date, it is not possible to predict how the properties of oxides only known to exist in the bulk state change when those oxides are made into nanometer thin sheets. Similarly, predicting the properties of (both free standing and confined) two-dimensional materials that have stoichiometries and structures that do not appear in the bulk is not feasible. Two-dimensional ceramics possess characteristics that make them scientifically interesting and potentially useful. For example, enhanced transport properties in two-dimensional ceramics can enable energy storage devices and may play a role in cold sintering. The rich catalytic properties of two-dimensional ceramics enable reactions that are important for the production and utilization of solar fuels. Interface complexions, which have been shown to be thermodynamically stable, undergo transformations that control the evolution and properties of the microstructure [26]. The properties are tunable by temperature, pressure, and chemistry, and may even be switchable by external fields. Two-dimensional structures create opportunities and challenges that are distinct from one-dimensional or three-dimensional materials. In particular, their high anisotropy in mechanical, electrical, and transport properties lead to both novel scientific phenomena and unique functional and structural capabilities. It has been known for decades that it is possible to delaminate or exfoliate layered crystals into two-dimensional sheets a few atoms thick.

However, there has been a recent growth of research in this area and the range of materials available has grown enormously. Among the glasses-ceramics that can be produced in single layer form are clays, hydroxides, oxides, and transition metal carbides. Models of water solubility in silicate melts, although differing in their details, are typically based on the proposition that H_2O enters the melt by reaction with oxygen ions in the melt to produce two hydroxyl groups. Several lines of evidence have been offered to support this proposition: The proportionality between the fugacity of water and the square of the mole fraction of dissolved water at very low total water contents is consistent with solution models involving essentially complete reaction of water molecules to hydroxyl groups on interaction with the melt. The dramatic increases in the fluidity, electrical conductivity and cationic diffusion coefficients of acidic silicate melts that accompany increases in dissolved water content are consistent with solution

of water in highly polymerized melts by interaction of H_2O molecules with bridging oxygens in the melt framework. Despite the apparent success of models based on the assumption of essentially complete reaction of water dissolved in silicate melts to hydroxyl groups, considerable evidence is available that silicate "glasses" quenched from melts contain both molecular water and hydroxyl groups.

Conclusion

Eight grand challenges for fundamental ceramic and glass science research form the basis for progress in creating knowledge with transformational technological impact potential. These challenges focus on strategies for the design of new materials and understanding of their structure and properties. The challenges demand innovation in both experiments and models; in the former, for example, at extreme conditions of temperature, pressure, or radiation flux, while in the latter, for instance, models for defect-defect interaction, particularly for cases with large defect concentrations, are particularly vexing. It is anticipated that these challenges will provide inspiration for research in the ceramic and glass communities with societal and industrial import. Embracing these considerations for assembled structures, including defect engineering as an additional design parameter, processing tunable defect structures will open access to a new range of materials and phenomena. So far, these approaches remain relatively underdeveloped; however, there is potential for considerable progress, if defects can be harnessed in this manner.

In summary, the recent discovery of many two-dimensional structures has outpaced the understanding of their properties. Establishing an understanding of structure property processing relations for two-dimensional structures is expected to lead to easily tunable properties through small changes in chemistry, processing, or external fields. These two-dimensional structures may have impact on energy applications (batteries, supercapacitors, and catalytic materials), miniaturization of switching devices, low energy computing, and novel functional and mechanical properties.

The study of two-dimensional systems also presents challenges and opportunities for modeling. Specifically, the analysis of the atomistic stability of two-dimensional glass-ceramic structures, including the calculation of the structure, while incorporating intrinsic and extrinsic defects into the formulation remains a challenge. For example, the calculation of energies of formation for charged point defects (while conserving the charge neutrality condition), energy barriers for ionic diffusion, the impact of phonon-defect, defect-defect, and photon-defect interactions, surface-atmosphere or solution interactions, and their impact on the stability of two-dimensional ceramic structures is still done on a case by case basis. From that perspective, challenges are identified in ceramics for extreme environments, one related to discovery and design strategies for new materials and the other to improved understanding of complex systems (including interactions across interfaces) under extreme thermal, chemical, and mechanical environments.

Acknowledgment

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