Research Thrust: Non-traditional oxide glasses for nanocomposite hosting

Proposed Research Applicants must provide detailed information regarding the research proposed for the EFRC. This section, which may be organized in the subtasks, must:

a) Briefly sketch the background leading to the application, critically evaluate existing knowledge, and specifically identify the gaps that the project is intended to fill;

The current state of our understanding of oxide glasses has not focused on the packing of nanocomposites into the glass matrix. Previous work[2] has concentrated on the migration of ions (especially helium[3]) through the amorphous network, but not on the incorporation or fabrication of useful macrostructures within the glass. The basic research thrust at Coe College will fill the knowledge gap in the quantitative study of voids and packing, an area in which the PI's have much experience[4-6]; the control of such voids and channels through suitable chemical modifiers; and the ultimate incorporation of suitable materials in the voids. This is an area we will explore in detail, with the goal of incorporating "hydrogen sponges" into the mechanically and thermally robust oxide glass matrix.

Bismuth-containing glasses show potential for hydrogen storage because they have low packing fractions, and thus a relatively open network with larger voids and channels, and because they have also been shown[7] to form Bi metal nanoclusters under the correct processing conditions. Both of these factors (along with high He permeability for the silicates[8]) would allow for hydrogen storage, and for the incorporation of functionalized clusters that can provide adequate adsorption properties. No previous work has been carried out in this area—not in the nanocomposites nor in the direct storage.

Vanadate glasses are promising candidates for hydrogen storage as vanadium ions have a highly variable oxidation state. It is indeed the case that vanadate minerals (pascoite, huemulite, barnesite) often need water for stability. In these minerals[9], complex anions similar to those formed in highly modified glasses (e.g. $(V_2O_7)^{4-}$, $(V_3O_{10})^{5-}$), are formed and combine readily with hydrogen to form modified pyrovanadates $(HV_2O_7)^{3-}$, $(H_2V_2O_7)^{2-}$, and metavanadates $(HV_3O_{10})^{4-}$, $(H_2V_3O_{10})^{3-}$. No work has been done on their suitability as hydrogen storage materials.

b) State concisely the importance of the research described in the application

Developing a clear understanding of packing in glasses, and specifically of functional structures that will carry out adsorption and release of hydrogen on command, is critical to the development of this category of hydrogen storage materials. This will require research on the modification of the network with the goal of attaining voids and channels that are appropriate for the placement of ions and the creation of functional composites that disperse homogeneously within the network.

c) Explain the relevance of the proposed research to the needs and opportunities identified in BESAC report Directing Matter and Energy: Five Challenges for Science and the Imagination and one or more of the Basic Research Needs reports

The research on glasses by the Coe research thrust falls neatly within the fifth of the grand challenges: *How do we characterize and control matter away—especially very far away—from equilibrium?* It is also at the core of the *Basic Research Needs for the Hydrogen Economy*. Glasses are solid structures in a non-equilibrium state. Though the amorphous state is sometimes energetically close to certain crystalline analogs, a thorough understanding of their structure—and how to control it—has not yet been achieved. We propose to develop means to control a very basic property: the open volumes (voids) in the glass network by the introduction of modifiers and very rapid cooling rates then quickly moving to the control stage.

d) Describe a balanced and comprehensive program of basic research that, as needed, supports experimental, theoretical, and computational efforts and develops new approaches in these areas;

The Coe research thrust will develop glasses with significant voids and structures conducive to holding hydrogen and/or nanoclusters in bismuth-containing glasses. Promising candidates include bismuth silicates and related ternary and quarternary systems, as well as bismuth vanadates and their extended family. Both systems have relatively low packing, thermal stability, and in the case of the vanadates relatively low fabrication temperatures.

The research thrust will also carry out research on the formation of vanadate microspheres, a promising avenue to significantly increase surface area and potential hydrogen storage. The Coe groups have much expertise at forming them in lead and barium vanadate systems.

a) Open Structure Bismuth-containing Oxide Glasses

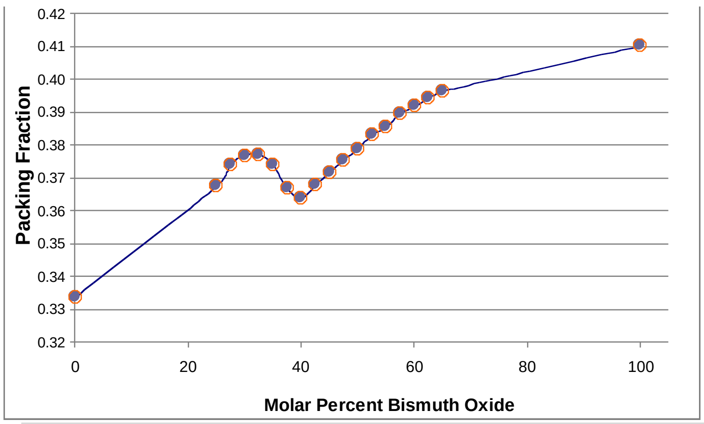

Figure 1. *Packing fractions in bismuth silicate glasses (Data from Bansal and Doremus[1]).*

The bismuth glass systems are remarkable for their relatively low packing efficiencies. Shown below in Figure 1 are the packing fractions for bismuth silicate glasses. Near 40 molar percent bismuth oxide there is a local minimum at a remarkably low packing of 36 %. Such glasses are promising as suitable "containers" for the storage of hydrogen. These glasses have considerable numbers of negatively charged non-bridging oxygens (Q_3 and Q_2 groups) and are likely to be favorable sites to hold hydrogen ions. We intend to fully characterize these glasses using nuclear magnetic resonance (NMR; on ^{1}H, deuterated ^{2}H, ^{29}Si, and ^{209}Bi nuclei), a technique with which the Coe PI's has much experience.

Recent work from our lab at Coe College employing laser desorption-time-of-flight mass spectroscopy has shown that bismuth silicates have a strong tendency to form Bi metal nanoclusters within the glasses depending on preparation conditions. This is favorable due to the inherent large surface areas present on such clusters. The Coe group will optimize the nanocluster formation through different heating and cooling regimens, and look for optimal compositions. The clusters will be characterized using TEM available at UNLV.

This research thrust will begin by attempting to minimize the packing fraction of the bismuth-containing glasses, and will also be responsible for the characterization of relevant physical properties such as thermal stability, density, packing, and glass transition temperatures. Examples of glass families that might prove better than the binary bismuth silicates are bismuth borosilicates, bismuth borovanadates, lead bismuth borosilicates, and lead bismuth borates. These more complex glasses lend themselves well to customizing compositions that may be able to hold large quantities of hydrogen, be especially stable, and have low costs of production.

The Coe group will also determine the ease of Bi nanoparticle formation. This will involve variations in thermal processing followed by detailed spectroscopic analyses by laser desorption time-of-flight mass spectroscopy, x-ray diffraction, Raman spectroscopy, and FTIR. Examples of thermal processing include varying the rates of cooling with the group's patented roller quenchers, attaining values of up to 500,000 K/s, as well as varying the processing (melting) temperatures. The Coe group has already been studying nanoparticle formation as a function of processing temperature and atmosphere with considerable initial success.

It will also be important to determine the amount of non-bridging oxygen (NBO) formation present by the use of Raman spectroscopy (calibrated against ^{29}Si MAS NMR [10]). This is especially important as the NBO sites would interact heavily with any hydrogen ions in the glass matrix. During and after all the manufacturing and characterization work we will be in touch with our EFRC collaborators, looking to optimize the properties for storage. Eventually the optimized samples will be turned over to the lab of Prof. Kristina Lipinska-Kalita to determine how much hydrogen is absorbed in such glasses under differing conditions such as composition and processing temperatures.

Bismuth vanadate glasses [11] have remarkably small packing fractions and low glass transitions temperatures (see Figure 2) while maintaining high thermal stability. Thus, they are also promising for hydrogen storage and have the added advantage of low preparation cost.

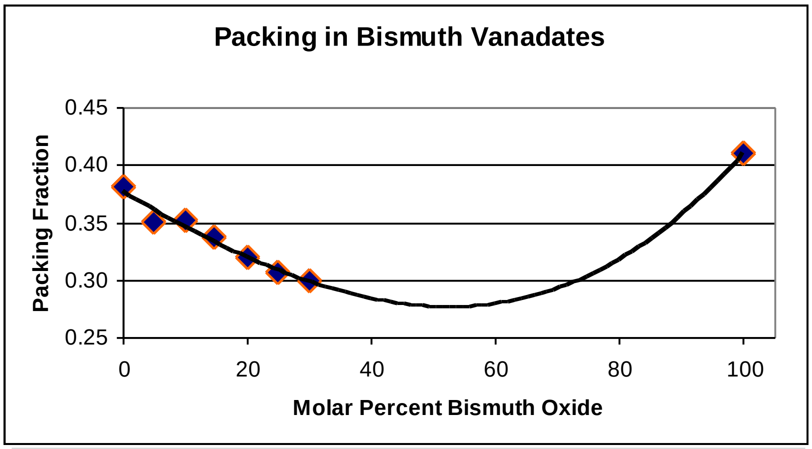

Figure 2. *Packing fractions of bismuth vanadate glasses. (measured at Coe). Note most are 35% or lower.*

These glasses have many unsolved problems. Foremost amongst these include the glass forming limits not being fully mapped out and the short-range structures are not known. Of significant interest would be the formation of non-bridging oxygen. Some of the work by the Coe group shows that alkaline-earth vanadates do produce significant fractions of vanadate groups with non-bridging oxygens as modifier is added. The physical properties need to be mapped out more thoroughly. While the packing actually decreases until at least 33 molar percent bismuth oxide and the packing of bismuth oxide is 11 % higher than that (30% versus 41%) what happens at intermediate concentrations of bismuth oxide is not known.

b) Lead and Barium Vanadate Glasses and Microspheres

As mentioned earlier, vanadate glasses are promising storage candidates for hydrogen storage. In this research thrust we will study them for a dual purpose: as direct storage materials, and as modifiable hosts. The direct storage work involves the formation of complex anions that will absorb and, upon low heating, release hydrogen. Highly modified vanadate glasses containing

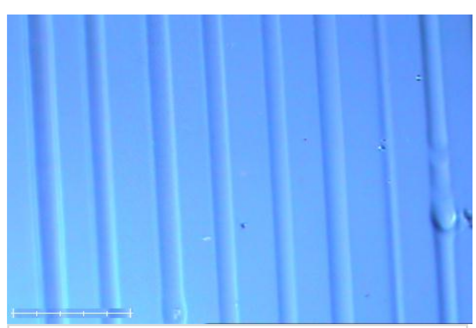

Figure 3. *Lines written in a lead vanadate glass (785 nm, 40 mW)*

lead and/or bismuth will be pursued first, as the heavy metal cations can form a parallel subnetwork that will provide mechanical stability as the vanadate component is depolymerized[12] and its anions saturated with hydrogen. The Coe groups will also carry out ^{51}V (spin 7/2) NMR measurements on the glasses, an area in which they have previous expertise. In their second application, the Coe group will look at modifying the glass by creating surface- and below surface crystals by laser irradiation. The formation of these microcrystals will open up the glass network and may well lead to other absorbing structures with large surface areas for adsorption. Figure 3 shows lines written[13] on the glass surface, which retained their amorphous character. Similar crystalline lines can also be written.

Another reason for the inclusion of vanadate glasses in this proposed work is their relatively flexible network structure. Vanadium can attain a variety of coordination states, and the structure of modified vanadates (like $50BaO \bullet 50V_2O_5$, see figure 4) is formed by flexible chains[12] that leave quite an open structure. The network is also quite able to distort (by forming octahedral units) to accommodate larger bodies within the glass.

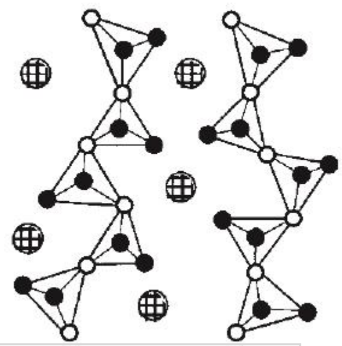

Figure 4. *Structure of alkaline-earth metavanadate glass.*

The Coe group will pursue a parallel research path, seeking to develop microspheres that will disperse inside the glass matrix and act as hydrogen sponges. Vanadium microspheres (see figure 5) were developed in the Coe labs[13] by laser irradiation and, more recently, by flame spheroidization. The latter approach allows for the manufacturing of many more spheres, albeit with less control over their size distribution. Consistency in the size distribution would then become one of the objectives of this work

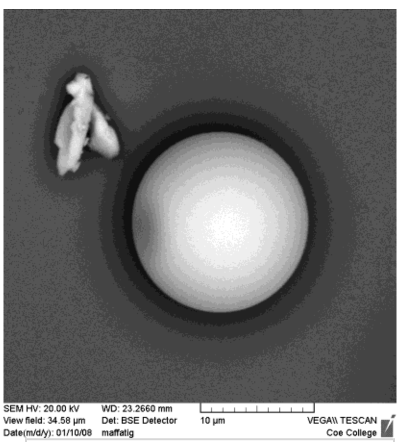

Figure 5. *Barium vanadate microsphere.*

The microspheres would provide a large surface area when in a colloidal suspension within the glass, and vanadate glass matrices with lower melting points are readily available. The Coe group is also investigating the internal structure of the spheres, and it is well known[14] that porous glass spheres can be obtained in other systems. These spheres have been shown to be permeable to gases and able to store them by the use of an appropriate absorber inside the porous sphere.

e) State the proposed approach to reconfigure research thrusts to respond to key scientific challenges and promising developments;

The Affatigato and Feller research groups will certainly pursue the most promising manufacturing avenues, those leading to glasses with the greatest storage capacities. The PI's are ready to utilize novel chemical synthesis (developed in their lab[15, 16]), roller quenching [17], laser crystallization/amorphization [13], or any process that will yield the greatest benefit.

f) Delineate plans for external collaborations and partnerships including utilization of DOE user facilities, if applicable;

The research thrust headed by Prof. Affatigato will collaborate heavily with the effort led by Prof. Kristina Lipinska-Kalita, aiming to develop nanocomposites in oxide glasses that meet the requirements of stability, mechanical strength, thermal robustness, and openness in the structure. They will also have a close working relationship with Dr. Chkrebtii, to optimize stoichiometries by modeling of the glass networks (thus saving time and effort), and provide expertise and spectroscopic capabilities to the effort headed by Prof. Easton. This will involve frequent (annually at minimum) travel to the sites at UNLV and UOIT. The Coe groups also have access to a larger variety of state of the art NMR spectrometers in collaborating laboratories, at the University of Manitoba (Canada), University of Warwick (England), and Iowa State University. Finally, we will make use of the XAFS and NEXAFS capabilities available to Dr. Carlo Segre (APS-ANL) to research short range structures in the glasses, especially the bismuth vanadates.

g) Discuss how the proposed research relates to the core research activities within the BES Materials Sciences and Engineering and Chemical Sciences, Geosciences and Biosciences Divisions

The proposed work in this research thrust fits in well with the *Synthesis and Processing Science* and *Materials Chemistry* core research activities.

h) Describe the role and intellectual contribution of the EFRC Director, each Principal Investigator, and each senior/key person in the application;

Profs. Affatigato and Feller will provide the expertise on glass science, especially on the structure of oxide glasses and novel preparation and characterization techniques.

i) Enumerate the relevant scientific and technical expertise and experience in the research disciplines needed for project success for senior/key personnel in the application;

Profs. Affatigato and Feller have a wealth of experience in the study of packing in oxide glasses. Their previous work has looked at packing across major systems; mechanical packing as a simulation of alkali glasses at compositional extremes; and amorphous-crystalline transitions induced by laser irradiation (altering the local density and increasing void space). More broadly, they have over 50 years of combined experience in the study of oxide glass structure and properties, including the development of novel glass fabrication techniques (e.g. through cooling rates of greater than 100,000 K/s and through chemical solution methods) and characterization methods like reverse-MALDI laser-ionization time of flight mass spectrometry and NMR.

j) Briefly outline the resources available to the proposed EFRC including access to existing research space, instrumentation and facilities at the host institutions and its partner;

The labs of Prof. Affatigato and Feller are well equipped for amorphous material preparation, structural characterization, and property determination. All the equipment needed for the study of packing, including pycnometers, Raman and x-ray diffraction spectrometers, as well as scanning probe microscopy and scanning electron microscopy for looking at surface features, is available at Coe for this work. For more details, see Appendices 4 & 5.

k) Describe access to research capabilities and resources, including experimental and computational capabilities, both within the EFRC and external to the EFRC;

Please see Appendices 4 & 5.

l) Address environmental, safety, and health issues associated with the proposed research;

None of the samples that we will be studying require extreme precautions. The disposal of all chemicals is handled through the College's safety officer through approved contractors, and the Coe laboratories have appropriate handling facilities (such as commercial glove boxes, hoods, etc.) for the proposed work. All personnel is trained in the handling of hazardous materials, emergency procedures, overall safety, and waste disposal.

m) (Optional) Provide an account of any preliminary studies that may be pertinent to the proposed research.

The preliminary studies we have carried out are described in the other sections above.

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