Project Description

A. Introduction

Over the next four years we propose to do basic and applied research on glass with 32 Coe College undergraduates along with up to 8 others supported through our REU site. We have shown through our program's proven success that these students are highly motivated and accomplish much, especially when given sufficient time (several years) and a real opportunity to do scientific research. The research features a diverse number of experimental and theoretical projects in glass science. Several of them are in house (laser recrystallization and SEM/AFM studies, structural packing studies, physical property characterizations of new glass forming systems, novel laser desorption TOF mass spectroscopy and Raman spectroscopy studies of glass structure, development and construction of a new generation of twin-roller quenchers, and more) while others are parts of well-established collaborations (multiple NMR projects, EXAFS, neutron scattering, and vibrational spectroscopy). Following a review of our current work the proposed new research is developed in detail. After the scientific work is discussed a significant broader impacts plan is presented. We take the subject of broader impacts very seriously and use a wide array of methods to implement them.

B. Review of work done under grant NSF-DMR 0502051: RUI: A National Model in Undergraduate Research: Glass Science at Coe College

This proposal is being written during the fourth and final year of the current grant. To date 29 undergraduates have participated in this research: 23 Coe College students and 6 REU students. The more than 25 papers from work performed under this grant are listed in reference [1]; student co-authors are numerous and are bolded. Approximately 30 conference presentations were given during this time period as well. We think this productivity is extremely cost-effective given our impact on each student in our program. Listed below is a detailed summary of work done under the current grant followed by major findings (in approximate chronological order):

Scientific Work

1. We finished a laser desorption time-of-flight mass spectroscopy, ^{29}Si MAS NMR, Raman, IR, and physical property study of lead and bismuth silicate glasses over a wide range of modifier concentrations.
2. We studied, in-house, the physical properties and structure of tellurium borates, alkali vanadates, and various silicate systems over broad compositional ranges.
3. We did a study of the differential volume changes as a function of composition of the short-range structural groups of various alkali and alkaline-earth borate systems. Also, we completed atomic packing studies of alkali and alkaline-earth borosilicates. Finally, we simulated packing using solid-body packing.
4. We completed a laser induced crystallization study of lead vanadate glasses. This led to learning how to write gratings and create micron-scale spheres. In-house AFM/SEM experiments proved crucial here. We continued with a study of laser-induced crystallization of barium vanadates and cesium borates.
5. Lead borates doped with europium were studied using LI-TOF mass spectroscopy. We saw clear evidence for europium modification in the glasses.
6. We designed and built the first of a new generation of twin-roller quenchers. These are capable of forming new glasses by cooling liquids at 500,000 K/s. They feature digital control, dry box capability, and improved operation over the previous generations of our roller-quenchers. A patent is pending.
7. We started a characterization and structure study of alkaline-earth borosilicates by examining calcium and barium borosilicates. This is part of a larger project on radioactive waste incorporation into borosilicate glasses.
8. We continued a multipronged (NMR, Raman, IR, thermal) study of mixed Li-Cs silicate glasses to understand anomalous trends in the Tg data. The Tg trends show both a minimum and maximum in Tg as lithium is substituted for cesium in these glasses.
9. We collaborated on a number of modern solid state NMR projects with Professor Diane Holland (Univ. of Warwick, Coventry, UK) and Professor Scott Kroecker (Univ. of Manitoba, Winnipeg, Canada) Projects with Diane Holland include ^{10}B pulsed NMR of borate crystals and glasses (first time observed by pulsed techniques), ^{51}V NMR study of sodium and potassium vanadates made by roller quenching, ^{29}Si MAS NMR study of extremely modified lithium and lead silicate glasses, and ^{11}B and ^{29}SI MAS NMR

studies of simulated waste glasses. We are calculating ^{10}B NMR powder patterns using third order perturbation theory and distributions of the quadrupole parameters. Some of the calculational work is being done with Professor Steve Martin of Iowa State University. Projects with Scott Kroeker include studies of borate crystals by ^{11}B MAS NMR, N_4 measurements of lithium and cesium borate glasses over very wide alkali concentrations, ^{11}B MAS NMR study of solution made borates of unusually high metal contents (up to 83 mol% alkali oxide), and ^{51}V and ^{11}B NMR studies of alkaline earth and alkali borovanadate glasses.

10. We finished an extensive study of lead aluminate glasses (with Emma Barney and Diane Holland of Univ. of Warwick, UK, and Alex Hannon of the Rutherford lab (UK). The study included glass forming using rapid cooling at 1500 ^{o}C, physical property determination, and structure by ^{27}Al MAS NMR, and neutron scattering. We continued with a study of tellurium borates by doing a neutron scattering study of these glasses and formed amorphous TeO_2 for the first time.

11. We went with Coe students to Fudan University, Shanghai, for collaborative work on non-linear optics and second harmonic generation on heavy-metal oxide borates and silicate glasses.

Conferences and Presentations (*Details of theses may be found in the papers listed in reference [1].)*

1. Seven Coe students, Mario Affatigato, and Steve Feller gave four presentations at the Fifth International Conference on Borate Glasses and Crystals (Trento, Italy, July 2005).

2. We attended (three students, Mario and Steve) and gave three presentations at the PACRIM V meeting in Maui in 2006.

3. We presented a paper, with Prof Holland, ^{10}B NMR studies of glasses. This was done at the *Society of Glass Technology* meeting at Sunderland (UK) (September 2006). A journal article was just published from this meeting.

4. We gave four presentations at the *Glass and Optical Materials Division* meeting of the *American Ceramic Society* held at Rochester, NY (May 2007).

5. In 2006 we organized the *Iowa Glass Conference* for 35 participants from Coe College, Iowa State University, Creighton Univ., Univ. of Missouri-Rolla, University of Warwick (UK), and Tsukuba University (Japan). We also hosted the 2008 *Iowa Glass Conference* that took place last August.

6. Steve Feller visited the National Hellenic Research Foundation in Athens and the University of Warwick during Jan 2008. There he gave several talks on joint research in progress and planned future research together.

7. Six Coe students, Mario Affatigato, and Steve Feller gave 6 presentations at the Sixth International Conference on Borate Glasses and Crystals (Himeji, Japan, Aug 2008).

8. Mario Affatigato, Steve Feller, and many students attended the *MS&T* meeting in Detroit (2007), the Acers *Glass and Optical Materials Division Meeting* in Tucson (2008), the *Iowa Glass Conference* in Ames (2007), and the *MS&T* meeting in Pittsburgh (2008). In total we gave over 15 presentations.

9. Steve Feller and Mario Affatigato also gave over 20 presentations on our research and how we run our research intensive research program at a liberal arts college.

10. Steve Feller visited the University of Manitoba in Winnipeg to give a colloquium on our research in October 2008.

Other broader impacts are discussed in section F on pages 13-15.

C. Major findings from NSF Grant DMR-0502051 are:

1. The first reports of ^{10}B pulsed NMR of several borate glasses and crystals [2,3]. We did both several glasses and crystals. This allows unprecedented precision in the determined quadrupole parameters. As a result of the high sensitivity, we have seen clear differences in these parameters from trigonal and tetrahedral borons in different superstructural groupings. We observed the satellite transitions in ^{10}B NMR for the first time in borate glasses and crystals. A theoretical study of integer spin powder patterns has been completed by a Coe student and, now, we are able to easily simulate the ^{10}B spectra. Simplified observations of features on the powder pattern were also characterized for close and quick approximations to the quadrupolar parameters.

2. An *in situ* Raman study of the devitrification of roller and plate quenched alkali vanadates and borates has been done [4,5]. Characterizing the surfaces of laser induced crystallization of a series of lead and barium vanadate glasses was carried out. We are able to write the crystallization into the glass in a controlled manner; for example we produced gratings with separations on the order of microns. Further, the formation of vanadate microspheres with diameters in tens of microns was achieved in several ways. There are many practical possibilities here.
3. The first clear observation from NMR of an alkali dependence on the fraction of tetrahedral borons in alkali borate glasses was found [6]. For lithium and cesium borate glasses with alkali concentrations greater than 35 mol.% alkali oxide, cesium borate have clearly lower N_4 values. Below 35 mol.% alkali oxide the N_4 is independent of alkali oxide type as determined in all alkali systems. This is an important basic result that has resolved one of the long-standing questions of borate structure.
4. Determination (quantitatively) of the relative amounts of lead oxide associated with the silicate network and the lead network in a series of lead silicate glasses with lead concentrations approaching 85 mole percent lead oxide (using our expertise in twin-roller quenching). Our students did this work at Coe and abroad. Techniques employed include NMR, laser desorption TOF mass spectroscopy, Raman, FTIR, and physical property measurements. Direct evidence for lead clustering as well as lead-oxygen bonding was found. A major paper is in preparation and nearly finished.
5. We completed a major paper on packing fractions in alkaline-earth modified glasses [7]. Universal trends have emerged that follow those reported in our earlier paper on packing in alkali modified glasses.
6. We finished a solid body simulation, using ball bearings, tetrahedra, and triangles, of packing in alkali borates and silicates. This complements the actual packing described in item 5 above. Data from random mixing of large numbers of these physical objects produced trends that matched the actual packing.
7. We completed a new sixth generation roller quencher and we are applying for a patent on it [8]. The new quencher, based on three decades of research, is the state-of-the art machine in the field. It cools liquids up to about 500,000 K/s. It is under full digital control and samples can be kept under nitrogen.

D. Collaborations

Collaborations are an important part of modern science and, planned carefully, really enhance student research and educational opportunities. A successful collaboration must be fully reciprocal. We have strong and active collaborations world-wide using the following techniques:

A. Solid State NMR

1.University of Warwick (UK)

Ten Coe College students and faculty have done much NMR work at the University of Warwick with Professors Diane Holland and Mark Smith. Projects include ^{51}V pulsed NMR of new alkali vanadate glasses, ^{10}B pulsed NMR studies of alkali borate crystals and glasses [2,3], ^{29}SI MAS NMR studies of lead and lithium silicates over extraordinary modifier concentrations [9], and ^{11}B and ^{29}Si MAS NMR and Raman studies of radioactive waste simulated glasses [10].

2. University of Manitoba (Canada)

Eight Coe students have done NMR work with Prof. Scott Kroecker. We studied the fraction, N_4, of tetrahedral borons as a function of composition at high alkali-contents [11] for glasses made by the solution method.

3. Iowa State University (Ames, IA)

We have maintained a long-standing collaboration with Steve Martin's group at Iowa State University. Last summer a Coe sophomore did simulations of ^{10}B NMR powder patterns there and at Coe. Also, in 2007, a Coe student did ^{29}Si NMR studies of bismuth silicate glasses.

B. EXAFS

University of Trento (Italy)

Recently, we have started a series of EXAFS studies of heavy metal silicate and borate glasses. Professors Dalba [12,13,14] and Affatigato are spearheading this research. Recently, Mario Affatigato spent two significant periods of time learning EXAFS in detail. We expect to start sending students there soon and they will also participate in experiments at ESRF in Grenoble, France. We are planning on their students and faculty doing research at Coe, as well.

C. Neutron Scattering
University of Reading (UK), University of Warwick, and ISIS Lab (All in UK)

We continue to study glass structure using the world's premier spallation neutron scattering facility at the Rutherford, Appleton Lab near Abingdon. We will do both inelastic and elastic scattering experiments in collaboration with Profs. Adrian Wright (Univ. of Reading), Prof. Diane Holland (Univ. of Warwick) and Dr. Alex Hannon (ISIS Lab).

D. Vibrational Spectroscopy
National Hellenic Research Foundation (Greece)

We have just completed IR and Raman studies of lead silicate glasses with this Greek group. We are also studying mixed alkali silicate glass structure. Two Coe students did FTIR work there in summer and fall of 2007. The group is led by Dr. E. I. Kamitsos.

E. Electron Spin Resonance
William Jewell College (Liberty, MO)

We are studying Coe-produced roller-quenched alkali and alkaline-earth vanadate glasses using the newly obtained William Jewell College ESR spectrometer. V^{+4} is an excellent ESR ion to look at. This is done by Jewell and Coe students and with Profs. Blane Baker and Pat Bunton of their physics department. Our first joint paper is in preparation.

E. New Work that Will Be Done Under this Proposal

In this proposal we once again expand our research topics and techniques to bring us to several new areas within glass science. It is very important to bear in mind that every aspect of the proposed research will be done with undergraduates and that we have conclusively shown that we are productive with these students at a high level. The research is briefly summarized here and then expanded in considerable detail.

We have focused on very basic research into novel glass systems using methods of sample formation that produce glasses in new compositional spaces. For example, we have prepared glasses using roller-quenching and a novel solution chemistry method. However, in addition to this fundamental work, recent work has extended to more practical aspects of glass science including laser- induced crystallization, the design of new rapid cooling machines, studying radioactive waste borosilicates, and the study of heavy metal oxide glasses. Further, we have branched out to new techniques (EXAFS, Scanning Probe Microscopy, Scanning Electron Microscopy, micro-Raman spectroscopy, and newer solid state NMR methods). For example, we have extended our considerable use of NMR to include the very first ^{10}B pulsed studies of borate glasses using a field-stepping magnet and we are using complementary surface techniques (AFM/ SEM) in our laser crystallization studies. The specific research topics follow.

1. Research on Applied Aspects of Glass Science

A). Important and novel *uses* of glasses: Topics here include:

1) Laser induced crystallization of vanadate and borate glasses for the purpose of writing micron scale features in the glasses. Samples will be studied using our in-house SEM and AFM instruments as well as by our new XRD.

2) Formation of microspheres of glass with control of the resulting diameters. This will be done by both laser irradiation and flame spheroidization. Again SEM and XRD will be important tools for this project.

3) Physical properties and atomic structure by Raman spectroscopy of multicomponent borosilicates. These are prototypes for radioactive waste glasses.

B). The construction of a new generation of digitally controlled roller quenchers with enhanced features.

2. Research on Fundamental Topics in Glass Science

A). Study of novel glass systems. Examples include calcium aluminates, highly modified alkali, alkaline-earth, and heavy metal oxide vanadates and borovanadates, highly modified alkali silicates prepared from the solution method, alkali bismuthates and more. As we have just acquired a new Bruker XRD spectrometer we plan a much heavier focus on crystal studies on those systems where we produce new glasses. Our new recirculating glove-box will be heavily used to form the very high alkali content glasses and crystals that are very hygroscopic and CO_2 sensitive. Each of these new glass systems will be studied using thermal analysis, XRD for crystals, ESR, Raman and SEM/AFM for structure and morphology. Most of our students will work on in-house projects under this rubric.

B). EXAFS spectroscopy will be performed on heavy metal oxide glasses. We are presently interested in borate and silicates but will expand this to glass and crystalline vanadates during this research period (with Prof Dalba's group at the University of Trento, Italy). The experiments take place at the ESRF Snychrotron lab in Grenoble, France. These novel glasses will be made at Coe by our students and visiting Trento students and postdocs.

C.) Intermediate range order studies of glassy and crystalline borates using ^{10}B NMR (with Prof. Diane Holland of University of Warwick, UK). Glassmaking, XRD work, and property characterization will take place at Coe.

D.) Neutron Scattering studies of borates and borosilicates (with Prof. Adrian Wright, University of Reading, UK) [15, 16, 17, 18]. It requires innovative glass formation of large quantities of ^{11}B enriched samples. We have much experience in this area and this aspect of the work is done in-house at Coe.

E.) An^{11}B study NMR study in highly ionic conducting alkali thioborate glasses ($RM_2S.B_2S_3$) glasses [19, 20, 21] (with Prof. Steve W. Martin of Iowa State University).

Each of these topics is presented in more detail.

1. a) Laser induced crystallization of vanadate and borate glasses

Vanadium pentoxide is a conditional glass-former and responds well to rapid cooling by our twin-roller quenchers. The stability of modified vanadate glasses, defined as the difference between the DSC-determined Tx and Tg is only about 10-40 ^{o}C which is quite small . This creates an opportunity of selectively crystallizing vanadate glasses for practical purposes. We have shown that we can write gratings of micron separations in these glasses, see Figure 1.

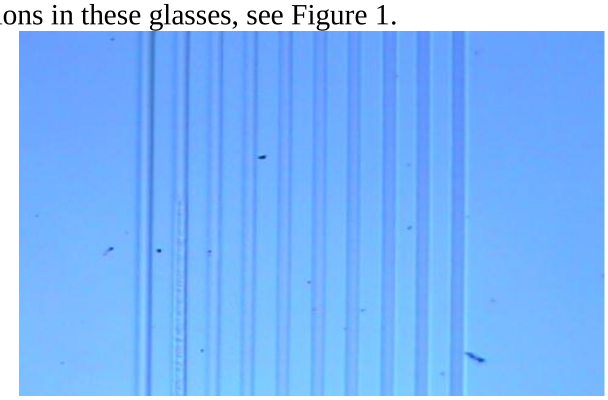


Fig. 1: An optical micrograph showing micron scale lines written into a lead metavanadate glass.

We plan to study a many modified vanadate glasses to see how to optimize this process. We will vary laser power levels, composition, and speed of writing. We expect, for example, that families with differing stability temperatures will behave differently and require different power levels to write features in glass. We have already determined that alkali vanadates have much lower stabilities (≈ 10-15 ^{o}C) versus alkaline-earth vanadates (≈ of 30-40 ^{o}C).

1. b) Formation of lead vanadate microspheres

When performing Raman spectroscopic studies of crushed and powdered vanadate glasses we have observed that the exciting laser is capable of forming micron-scale spheres. Such structures are useful in a range of applications ranging from delivery of medicine in the body to energy storage in glass. More recently, and in addition, we have formed spheres by flames spheroidization. Our goal is to produce, on demand, quantities of reproducibly uniform spheres with diameters down to a few microns. Figures 2 (a) and (b) display SEM images of some of our new amorphous vanadate spheres. We have achieved diameters down to about 5 μm.

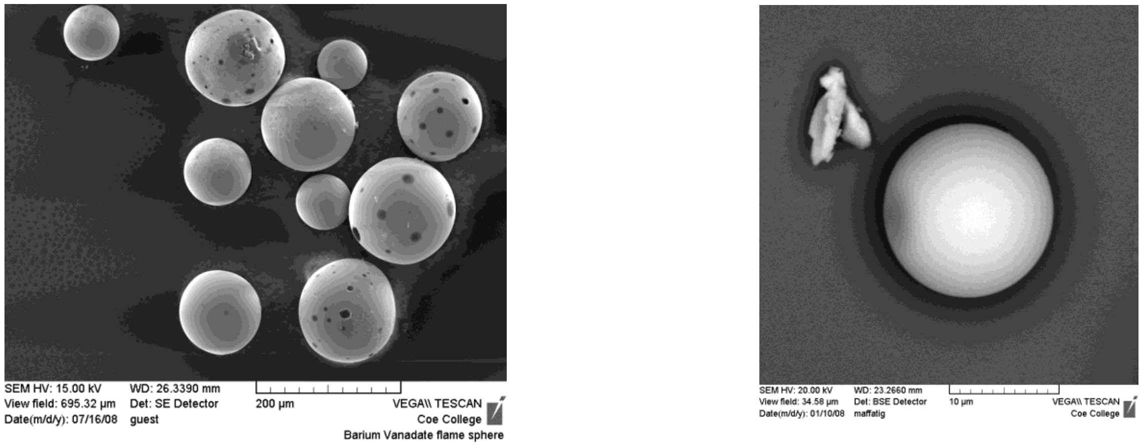


Fig. 2): Lead metavanadate microspheres seen with the Coe SEM a) flame spheroidization and b) laser irradiation.

We plan to form spheres out of a wide variety of vanadates. Besides the lead vanadates we plan to study barium and bismuth vanadates. We also plan to continue studying some borates such as the cesium system (laser recrystallization studies have already begun successfully on this system).

1. c) Physical properties and atomic structure of multicomponent borosilicates

Radioactive waste containment from nuclear power plants remains a key issue for the nation's future use of fission as a source of energy. We have been developing models and making careful measurements of key structural indicators of stability in complex borosilicates. The parameters include the abundance of non-bridging oxygens on silicate Q^i tetrahedra and the fraction of four-coordinated borons [22, 23, 24]. Shown below in Figure 3 is an example from this work: a comparison of the fraction of Q^3 groups in multi component simulated borosilicate waste glasses as determined from NMR and Raman spectroscopies; note the good agreement.

We plan to continue this work on more realistic glasses. Basically we want to form practical models that are highly predictive of short-range structure while increasing the complexity or number of components of the glasses we examine. This work is done with Prof. Diane Holland of Warwick University as NMR is done to determine the amount of key structural parameters such as the fraction of tetrahedral borons and of the silicate Q^i units.

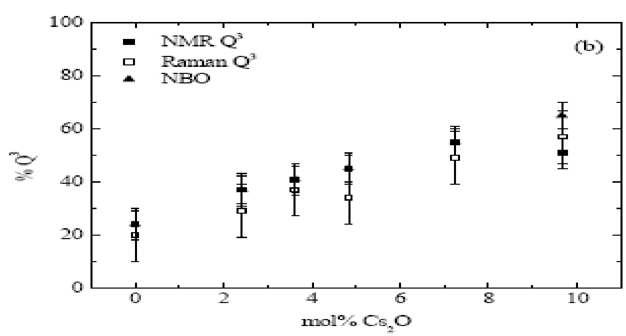


Fig. 3: Comparison of ^{29}Si MAS NMR derived Q^3 abundances with Raman spectroscopy [23].

Another part of this work compares properties and structure of ternary alkali and alkaline-earth borosilicates. We've made much progress recently on topic and presented two papers on structural modeling and packing in these glasses at the recent Borate VI meeting in Japan [25, 26]. This work is crucial in formulating models of the more complex waste glasses. We have found, for instance, that the alkaline–earth borosilicates require considerably different modeling than the alkalis (example: the Dell model from sodium borosilicates is poorly predictive of property trends). Further, we have found that the packing fraction is a powerful dimensionless measure of glass structure in these glasses. To date we have studied calcium and barium and compared them to the alkali counterparts (Li-Na-K-Rb-and Cs) borosilicates. Much more work is needed here. We will move on to magnesium and strontium borosilicates (each family requires 30-40 samples to see structural changes affecting properties and to map out glass forming ranges) and then to more complex borosilicate glasses that are combinations of alkali and alkaline-earth borosilicates. Our new thermal suite (DTA and hyper DSC) will be of enormous help with this work as will Raman spectroscopy.

2. The construction of a new generation of digitally controlled roller quenchers

Last winter and summer the first of our sixth generation twin-roller quenchers was designed, built, tested, and put into operation [6] (see broader impacts section for photos of the new quencher). It was sold to Corning, Inc who also funded its development. It is capable of cooling liquids at near 10^6 K/s and is fully digital. We propose to build a new roller-quencher, for our own use, that will add a few key capabilities to our previous machines including:

a) dry nitrogen flow in the sample collection volume,
b) a custom-designed attached furnace for ease of sample thermal control before and to the point of quenching,
c) development of software for computer control of the whole quench process including automatic gap control and computer operation of the rollers.

This will be a wonderful project for students. It is eminently practical and the students will work with local engineering expert, Morgan Karns. Autocad® drawings will be a key documentation and will constitute machining instructions. This is also an excellent student-learning opportunity as students become expert at Autocad®; this was shown by Coe junior Amanda Havel (physics and Art major) last summer. It is a way to more broadly involve students in our research.

Once samples are prepared we plan to do a thorough study of the glasses the roller quencher can produce. We will see how we can expand glass forming ranges in borates, silicates, and vanadates to begin with. These very rapidly-cooled glasses will be characterized by thermal properties and density.

3. Study of novel glass systems

We routinely use rapid cooling and a solution approach to glass formation to make new glasses. We then characterize property and structure. Examples are plentiful [27, 28, 29] and include new vanadate glasses [27], heavy metal oxide glasses [30], glasses with extremely high levels of alkali or alkaline-earth modification, [5, 7, 9, 31, 32, 33] new germanate glasses [34] and more [35, 36, 37, 38]. We discuss here, as a representative case study, an example of new exploratory work we will do. We will study glasses with low packing in bismuth-containing glasses (one use is H storage in glass). These include bismuth silicates, their ternary and quaternary cousins, and bismuth vanadates and their extended family of related glass systems. Both systems have relatively low packing, thermal stability, and in the case of the vanadates relatively low fabrication temperatures.

a) Glasses based on Bismuth Silicates

The bismuth glass systems are remarkable for their relativity low packing efficiencies. Shown below in Figure 4 are the packing fractions for bismuth silicate glasses as a function of bismuth oxide content. Near 40 molar percent bismuth oxide there is a very interesting local minimum at a remarkably low 36 % packing. Given this, such glass maybe be suitable "containers" for the storage of hydrogen or other fuels.

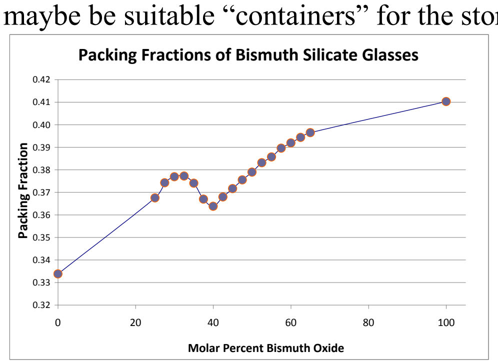


Fig. 4: Packing fractions in bismuth silicate glasses (after Bansal and Doremus [39])

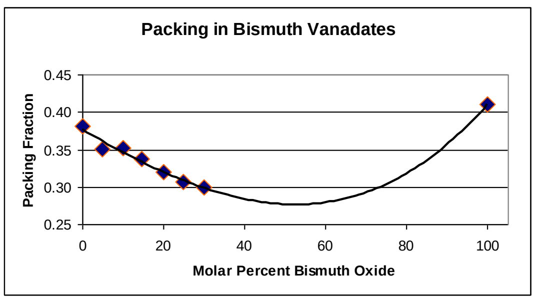
By way of comparison glasses containing large alkalis have much larger packing, approaching 64% for comparable compositions. Further, recent work from our lab at Coe College that has employed laser desorption-time-of-flight mass spectroscopy has shown that bismuth glasses have a tendency to form nanoclusters. While we have seen this tendency in some heavy metal oxide glasses, the area of research is novel and much remains to be done. Specifically we will:

1) prepare and characterize the physical properties of thermal stability, density, packing, and glass transition temperatures of binary, ternary, and quaternary glasses near the packing minimum around 40 molar percent bismuth oxide. Examples of glasses 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. Such glasses are likely to have increased stability against crystallization with lower Tgs and, therefore, lower thermal demands upon manufacture.

2) determine the ease of nanoparticle formation. This would involve variations in thermal processing followed by detailed spectroscopic analyses by laser desorption time-of-flight mass spectroscopy, Raman spectroscopy, XRD, and FTIR.

b) Glasses Based on Bismuth Vanadates

Bismuth vanadate glasses have remarkably small packing fractions and low glass transitions temperatures (See Figures 5 and 6) while maintaining high thermal stability. As a result they present a reasonable possibility that such glass might also be useful for energy storage.



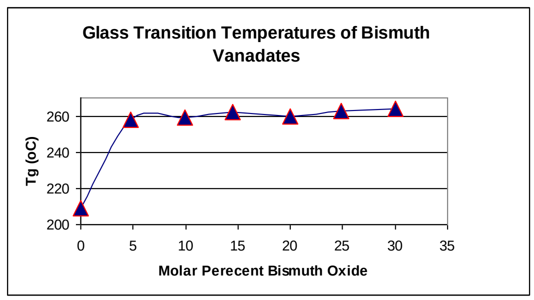


Fig. 5: Packing in bismuth vanadate glasses   Fig. 6: Glass transition temperatures of bismuth vanadate glasses

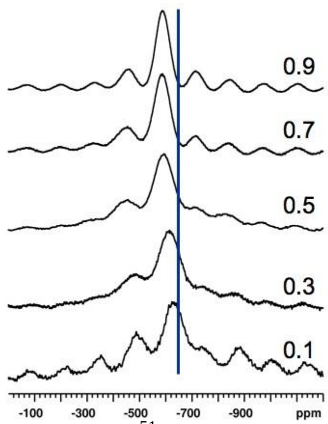
These glasses have many unsolved problems. Foremost amongst these are the glass forming limits (not fully mapped out) and knowledge of the structure. Speculations persist about the structural groups present from both the conditional glass former V_2O_5 at low bismuth oxide contents (tetrahedral vanadium, pentahedral, or octahedral and in what quantities) and both vanadate and bismuthate structures at high bismuth content. The physical properties need to be mapped out more thoroughly. While the packing decreases until at least 33 molar percent bismuth oxide and the packing of binary bismuth oxide is 11 % higher than that of these glasses (30% versus 41%), what happens at intermediate concentrations of bismuth oxide is not known.

Furthermore, derivative ternary and quaternary glasses are essentially unstudied. We have done some work on lithium borovanadates [40] and some other alkali borovanadate systems. However, glass families such as bismuth borovanadates, bismuth silicate vanadates, and bismuth phosphate vanadates remain unstudied and are of potential use for this project. In each system we will comprehensively study the properties over a wide range of compositions.

c) ^{11}B and ^{51}V NMR work with Prof. Scott Kroeker's group at University of Manitoba

We plan to do study the lead, barium, and bismuth vanadates using NMR since the structure is not presently known and because of their practical implications described in sections 1a) and 1b). We have already begun to study the ternary lithium borovanadate system. Figures 7 and 8 below depict promising NMR results from the calcium vanadate and lithium borosvaandate systems, respectively. Figure 7 shows ^{51}V NMR spectra and clear structural changes with composition (0.1 through 0.9

represent R in the relation $RCaO.V_2O_5$). Figure 8 shows new N_4 values from lithium borovanadate glasses compared with lithium borates; it is indicative of the sharing of lithium oxide between the borate and vanadate structures [40]. This will be used to form structural models once a full set of spectra are obtained from the system $RLi_2O.B_2O_3.KV_2O_5$. We plan to extend the work to various ternary vanadate systems including finishing the alkali systems and moving on to lead and bismuth borovanadates.



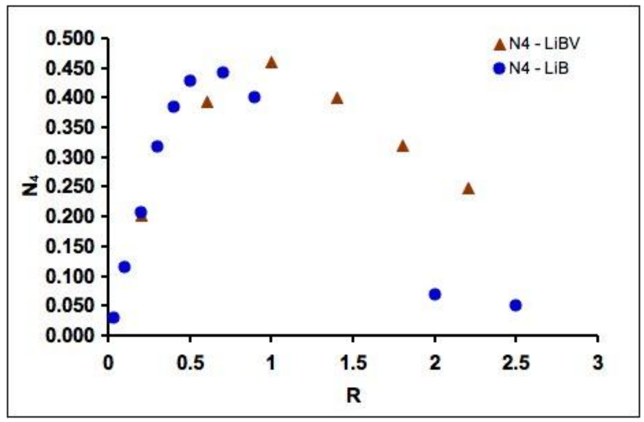


Fig. 7: [51]V NMR spectra in $RCaO.V_2O_5$ glasses Fig. 8: N_4 fractions in LiB and LiBV glasses.

d). ESR studies of vanadate glasses

Since vanadate glasses contain sizable quantities of paramagnetic V^{+4} we have launched an ESR study of rapidly cooled vanadium-containing glasses as a supplemental structure probe. Excellent spectra have been obtained; see representative sodium vanadate glass spectra shown in Figure 9 [41]. Such spectra yield information of the separation between the paramagnetic species as well as the local electronic structure. Indeed, in the spectra shown in Figure 9 we can see the transition from mostly isolated vanadium ions at low R values to strong dipolar broadened spectra as the concentration of vanadium and hence V^{+4} increases.

This study goes hand in hand with the laser modification study described above since we can easily monitor the spectra changes that take place with crystallization. We'd also like to study the electronic structural changes taking place in the microspheres we are forming. We are capable of making alkali, alkaline-earth, lead and bismuth vanadates, and alkali borovanadates using rapid cooling.

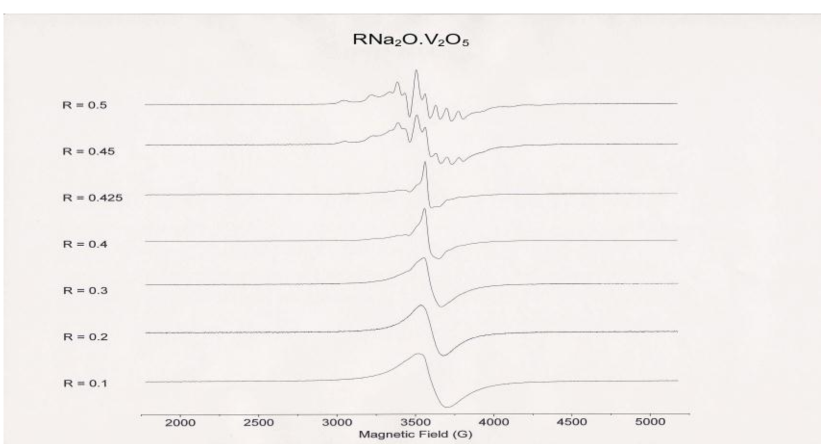


Fig. 9: ESR spectra obtained from sodium vanadate glasses as a function of R, the molar ratio of Na_2O to V_2O_5.

4. EXAFS spectroscopy on heavy metal oxide vanadate glasses

Mario Affatigato spent a semester performing EXAFS on leaded glasses with Prof. Dalba's group at the University of Trento (Italy). This technique is complimentary to our other structural probes and is especially good at looking at the heavy metal ions, lead for example, as a probe of its local structure. We propose to continue this work to heavy metal oxide vanadates, specifically to lead vanadate and barium vanadate glasses and benchmark crystals within these systems (examples: crystalline vanadium pentoxide, lead metavanadates, lead pyrovanadate and lead orthovanadate. Our new XRD will provide key purity information on these crystals). This will complement our NMR studies of the same systems with Prof. Scott Kroeker's group, see section 3 above. These are glasses we are modifying using laser recrystallization (Figure 10), see discussion above. Coe students and faculty will participate at the University of Trento (Italy) as well as at the experiments in Grenoble, France at the ILL synchrotron source. Further, students and faculty from Prof. Dalba's group will be coming to Coe College to learn rapid glass forming techniques.

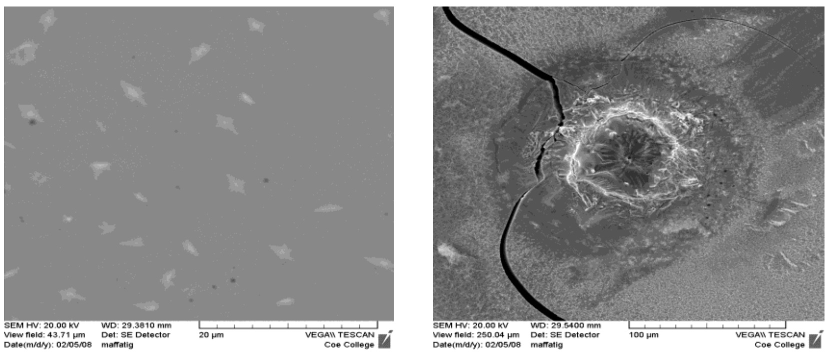


Fig.10: Lead metavanadate glass, before (left) and after laser irradiation.

The Coe undergraduate student will be responsible for the manufacturing of the samples during the time period preceding the trip, which includes three weeks of full time work. This will allow plenty of time for manufacturing the glasses and for the preliminary measurements (Raman, SEM). The student will then spend seven weeks with the Italian group, taking the XRD spectra, learning about the EXAFS analysis with specialized software (*e.g.* EXTRA, EDA, FEFF, GNXAS), and, depending on the scheduled beamtime, participating in the EXAFS data acquisition in Grenoble (F) or in Trieste (I). The Italian student (or postdoc) will spend seven weeks at Coe. During this time she/he will develop greater expertise in glassmaking, especially with the roller quenching cooling technique, and will make Raman and SEM measurement on the samples they make. It is likely that during the first year the student will also focus on the crystals made by devitrification. We note that a brand new state-of-the-art roller quencher will be in place by then, allowing for further pushing of the limits of glass formation.

5. Intermediate range order studies of glassy and crystalline borates using ^{10}B NMR (with Professor Diane Holland of University of Warwick, UK).

We propose to continue a very successful and original study using ^{10}B NMR to obtain detailed information on the rich intermediate range order found in modified borate glasses [2,3]. To date we've studied a number of compounds and glasses to first establish what sensitivity ^{10}B NMR has in discerning subtle structural changes occurring in borate rings. Table 1 below describes some atomic environments studied to date and Table 2 gives the quadrupole parameters obtained through third-order perturbation fitting of the powder pattern (done by a Coe student). The spectra are exceedingly sensitive to the quadrupole parameters (30 times more sensitive than ^{11}B on the average) and this allows us to study structure at a level of organization that encompasses 10-15 atoms. Note for instance the variation in the asymmetry parameter from 0.035 to about 0.30 among trigonal borons with all bridging or all non-bridging oxygens in borate rings and isolated triangles. Also, note in Table 2 ^{10}B NMR's ability to "see" distributions in the quadrupole parameters. This opens up many possible studies of the degree of randomness present in borate glasses prepared under differing cooling rates. We will do just this with boron oxide glass and combine it with a neutron scattering study of the same glasses.

We propose to further this work in two ways. We will study other important ring and related structures such as the pentaborate ring with four trigonal borons and one tetrahedral boron, the tetraborate group (actually composed of two smaller rings) with trigonal borons three times more populated than tetrahedral borons, the pyroborate short range structure (with two non-bridging oxygens and one bridging oxygen) and more. In short, we wish to perform a complete mapping of the borate intermediate and short-range structures by ^{10}B pulsed NMR.

Sample	**Short-Range Structures**	**Superstructural Group**
c-Li_3BO_3	Symmetric $[BO_3]^{3-}$	None, isolated trigonal borate units
c-$LiBO_2$	Asymmetric $[BO_3]^-$ with two bridging and one non-bridging oxygens	Long-chain
v-B_2O_3	Symmetric $[BO_3]$	Boroxol ring
c-CsB_3O_5 v-CsB_3O_5 v-23Rb_2O-77B_2O_3 v-Cs	trigonal borons with three bridging oxygens and tetrahedral borons with four bridging oxygens and $N_4 = 1/3$ ~ as c- CsB_3O_5 trigonal borons with three bridging oxygens and tetrahedral borons with four bridging oxygens and $N_4 \sim 0.3$	Triborate ring ? ?

Table 1: Some selected borate glasses and crystals studied by ^{10}B NMR 2,3].

	B3		B4	
Sample	C_Q and (σC_Q) simulation (MHz)	η and (σ_η) simulation	C_Q and (σC_Q) simulation (MHz)	η and (σ_η) simulation
c-Li_3BO_3	5.50 (0.10)	0.035 (0.013)	-	-
c-$LiBO_2$	5.14 (0.50)	0.50 (0.02)	-	-
c-CsB_3O_5	5.50 (0.60)	0.23 (0.02)	0.40 (0.15)	0.50
v- CsB_3O_5	5.30 (0.80)	0.25 (0.20)	0.55 (0.4)	0.50 (0.01)
v-B_2O_3	5.50	0.12 (0.12)	-	-
v-B_2O_3 [15]	5.51 (0.21)	0.12 (0.043)	-	-
v-23Rb_2O-77B_2O_3	5.50 (0.20)	0.27 (0.20)	0.80 (0.60)	0.60 (0.3)
V-$Cs_2B_4O_7$	5.30(0.30)	0.30(0.40)	1.15(0.80)	0.50(0.40)

Table 2: Quadrupole parameters, along with distributions, found from our ^{10}B NMR spectra [2, 3].

We'd also like to investigate more complex structures such as crystalline reedmergnerite (BSi_4O_{10}) as found in the sodium borosilicate system; a unit with each of its tetrahedral borons surrounded by four silica tetrahedra.

Secondly, we'd like to study the cesium borate glass system to see if we can identify the intermediate range structures present in these glasses as a function of composition. We'd like to quantify these structures and form a more sophisticated quantitative model of structural evolution, that includes intermediate range structure, than is known today. We have shown in our previous work that we can form cesium borate glasses from boron oxide continuously even to cesium concentrations greater than 75 mol% cesium oxide (using our own state-of-the art roller quenching and our employment of a new chemical solution method of forming glasses from hydroxides instead of carbonates). We hope to also resolve some long-standing questions of structure such as what short-range units the invert cesium borate glasses contain (glasses greater than 50 mol.% cesium oxide). Figures 11 a) and b) present representative spectra as proof-of-principle. Note the excellent fits which give the quadrupole parameters and their distributions.

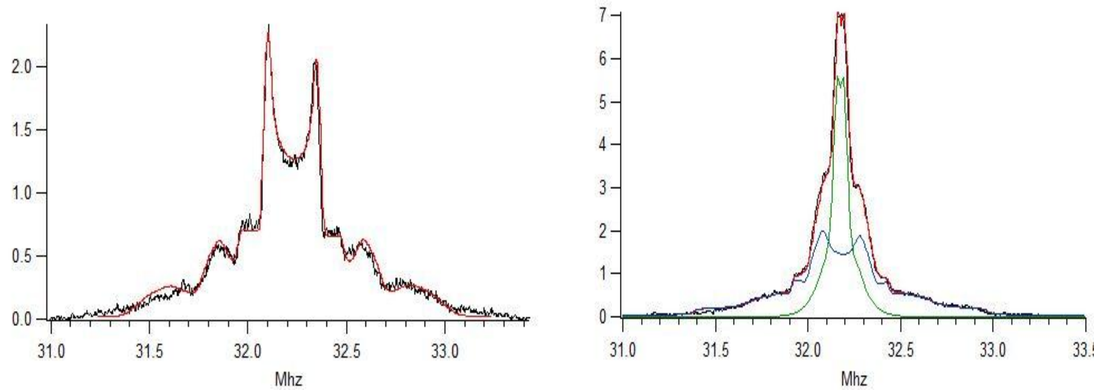


Fig.11 a and b: Representative ^{10}B NMR spectra from B_2O_3 and glassy cesium diborate (x = 1/3).

6. ^{11}B study of short range order in highly ionic conducting alkali thioborate glasses.

For many years Prof. Steve Martin at Iowa State University (ISU) has studied structure and properties of the sulfide analogues to the borate glasses we have studied at Coe College [42, 43, 44]. We propose to join efforts and study, in detail using modern solid state NMR, the short and intermediate range order in these glasses. A most unusual aspect of these glasses is the rate at which the fraction of four-coordinated borons increases with modification. They form at rates that are many multiples of the alkali borates. For example, in sodium thioborates (sulfide analogous of the borates) the rate is about 8 four-coordinated borons formed for each added sulfur whereas in the sodium borates the rate is just two for each added oxygen. We plan to do ^{11}B MAS NMR to determine the fractions of tetrahedral borons as well as fractions of trigonal borons with increasing numbers of non-bridging sulfurs. For this, careful deconvolution of the lineshape will be needed. Ultimately we'd like to form structural models of these glasses, compare them with the oxide analogues from the alkali borate system, and then compare to physical property measurements previously determined at ISU.

7. Neutron scattering and X-Ray studies of borates, borosilicates, and lead silicates

Elastic neutron scattering is particularly effective at determining coordination numbers, bond angles, and the presence of ring structures whereas inelastic neutron scattering is adept at finding vibrational modes from the density of states [15, 16, 17, 18]. We have much experience (with Adrian Wright) studying alkali borate and borosilicate glasses using both elastic and inelastic scattering.

We will do both elastic and inelastic scattering to examine borate superstructural groups in cesium borate glasses and crystals (to match the ^{10}B NMR study described above). For example, the presence of superstructural groups with different breathing mode energies has been seen by us using inelastic scattering in the cases of boroxol rings, cesium enneaborate crystal, and cesium triborate crystals Elastric scattering will give us coordination number bond lengths, including those in intermediate range order structures. We will study cesium diborate, cesium pentaborate glasses and crystals. This work will be done with Prof. Adrian Wright of Reading University (UK), one of the world's experts on neutron scattering studies of glasses.

Further, we propose to study lead silicate glasses by neutron scattering over an exceptional compositional regime. We do so for a number of reasons. Lead silicates are the base glass for many practical glasses and we have a long-established interest in the structural role of heavy-metal cations such as Pb in glasses. Lead oxide can be incorporated to very high concentrations in oxide glasses, to the point where it must constitute part of the network by forming Pb-O-Pb links. We have demonstrated that roller quenching is able to be used to form glasses in the lead silicate system, $xPbO \bullet (1-x)SiO_2$, to x = 0.83. Previous studies, including our own laser desorption TOF mass spectroscopic studies have suggested the formation of edge-shared dimeric units $[Pb_2O_4]$ which are bonded into the silicate network at high values of x. We wish to confirm their presence by determining the atom distribution in the glasses, and particularly by measuring the Pb-Pb distance using neutron and x-ray diffraction. At the very highest values of x, near 0.83, there is evidence that the silicate “network” must consist almost entirely of isolated [SiO_4] and [Si_2O_7] units, and we also wish to attempt to resolve the Si-Si distance by the difference method. This work will be done in association with Prof. Diane Holland of Warwick Univ. (UK) and Dr. Alex Hannon, neutron spectroscopist at ISIS (Rutherford Lab, UK).

F. Broader Impacts

We consider broader impacts to be a very important and serious responsibility arising from the privilege of having an NSF research grant. We adopt a multipronged approach to serving broader needs.

1. The Coe College Model of the Role of Undergraduate Students in Research:

The principal broader impact of this research is the sustained and substantial faculty research work with undergraduates [45]. This amounts to a significant and important form of teaching that augments classroom instruction. Each summer 20-25 students participate in glass science work at this college and at a number of our collaborating labs. This occurs in a number of ways.

a) The standard model here is to begin research with students during their first academic year and summer. Typically, these students are teamed with one of the PIs and with one or more older students. The students then do two or three years of work in glass science with us and then explore additional aspects and approaches at a collaborator’s lab or they join another group in another field. This is typically one or two years of additional research. Thus, our typical student has done three to four years of solid research *before* they go on to graduate school.

b) Another track is for students to begin doing research the summer before their first year. We have established, a special get-started-early program (The First Year Research Experience, *FYRE*,) in all the sciences. This, in effect allows students an additional summer of research during their undergraduate career. After an external grant paid for the program for three years (2003-2006), the College recognized its importance and fully took on the responsibility to fund it.

c) A final track is the REU one. We are a REU site in physics and chemistry with the joint theme of spectroscopy. This results in two to three students per year (out of seven REU participants) doing research on glass with us. These students come from another college. These tend to be first generation students from research inactive institutions.

We wish to point out that we actively encourage inclusion by all groups including specifically women and underrepresented groups. Nearly 200 students have been a part of the Coe College Glass Research Program. About one third of our research students have been women. To date we’ve had participation by African-Americans, Hispanics, and a high fraction of first-generation college students. About 15% of our researchers have been international students from Africa, Europe, Asia, and South America. Domestically, we are one of the most diverse program on campus with participation from about 25 states. This diversity enriches our program and we will certainly continue. We actively recruit students nationally in an inclusive manner. We want participation by all.

We are communicating this undergraduate research approach ever more widely [44]. Due to the unusually active undergraduate research program we have built up we give frequent talks on what and how we do things. Under the current grant we have given 23 talks at college, universities, and conferences on specifically how our program works.

2. Coe College Students Going to Graduate School in Science and Engineering

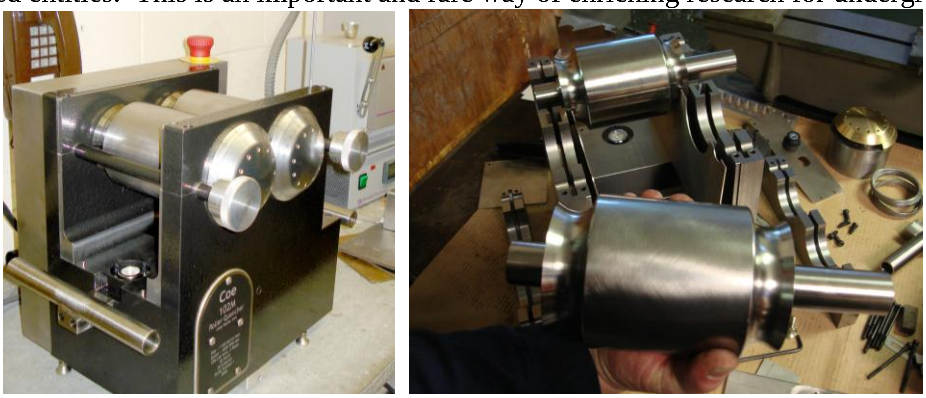
Almost 80 % of our research students over the past 25 years have moved on to graduate school. This serves the nation in a number of ways since these students go to graduate school in a wide variety of technical areas. Further, our students succeed at some of the nation’s best graduate schools. Recent examples include Harvard Univ. (Applied Physics), MIT (Nuclear Engineering), Stanford Univ. (Geology and Materials Science), Univ. of Minnesota (Materials Science), Northwestern Univ. (Physics and Materials Science), Univ. of Iowa (Physics), Iowa State Univ. (Electrical Engineering and Materials Science), Missouri Institute of Technology at Rolla (Ceramic Engineering), Penn State Univ. (Materials Science and Engineering), and Lehigh Univ. (Materials Science).

3. Sustained Research Work with Pre-College Students

As we have under the current grant we will work with both high school students, including those in the federally funded *Upward Bound* program. This occurs in two principal ways. First, we routinely invite local high school students to do glass research with us each summer; we average 2-4 such students per summer. Over half of these students have then joined our department. Work with the Coe College *Upward Bound* program brings additional diversity into our group. Last summer upward bound student Cimone Wright joined us and continued work into the fall. Secondly, we invite students in the summer before they matriculate, see *FYRE* program above.

4. Construction of State-of-the-Art Twin Roller Quenchers for the Field of Glass Science

With the completion of a new roller quencher design we expect to produce several for the field. Corning, Inc is already using one of our new quenchers to produce metallic glasses. We know of several other interested entities. This is an important and rare way of enriching research for undergraduates.



Figs.12a and b: The new Coe College-produced twin roller quencher

5. Teaching Courses on Glass Structure by Spectroscopy and on Glass Properties.

Mario Affatigato prepared a series of lectures on Raman spectroscopy and delivered them through a consortium online course offered through Clemson University. Steve Feller just prepared three lectures on volume properties in glass for the second course in the series on properties. These lectures are now archived on the *NSF IMI: New Functionalities in Glass* website for use by students learning about glass at either the beginning graduate level or the senior undergraduate level.

6. Service to the Glass Community Beyond Research

Mario Affatigato continues to serve in leadership roles within the *Glass and Optical Material Division of the American Ceramic Society*. He just ended service as the chair of the division. He has served as secretary and vice-chair as well. Undoubtedly, this leadership service will continue. For example, Mario has joined the AcerS Committee for a new glass journal and we have put in a bid to edit it. Steve Feller also helped organize sessions at conferences including the recent MS&T conference in Pittsburgh (2008). He also serves on the Cooper Committee for an undergraduate award in glass science through AcerS. Steve Feller serves on the International Organizing Committee of the Borate Conference Series. He helped organize all six borate conferences including the recent Borate VI meeting held in Himeji, Japan and he will participate on the committee for Borate VII to be held in Halifax, Nova Scotia in 2011. Along these lines Mario and Steve brought six students to Japan as part of an NSF grant to encourage student participation at the conference.

7. Service to the Physics Community Beyond Research

Steve Feller is extremely active within the AIP. He recently served four years as national president of the honor society in physics, *Sigma Pi Sigma*. He is currently the lead organizer of this society's quadrennial congress to be held at Fermilab in Fall 2008. This service within AIP will continue. Mario Affatigato is active within the REU community. He serves as director of Coe's innovative REU site on spectroscopy jointly housed in the physics and chemistry departments. He also is active at the national level on the NSF steering Committee for REU sites. This group has organized poster sessions at

Congress, for example. His presentation at the APS 2009 meeting in Pittsburgh is on the benefits to students of the REU programs.

8. Collaborations as a means of Educating Students on modern Methods of Research

a) We hosted three students from the University of Warwick (Emma Barney, Robin Orman, and Nathan Barrow; all of Prof. Holland's group). Emma did wonderful work roller quenching tellurium borate glasses as well as lead aluminates. Robin roller quenched several new oxide glasses including amorphous antimony oxide. Nathan did quite a bit of Raman spectroscopy on borates he is studying by DAR NMR at Warwick; he also prepared doped (to reduce relaxation times) lithium borate samples.
b) We hosted two graduate students from the University of Tsukuba (Japan). They were from Prof. Seiji Kojima's group. They rapidly cooled several silicate glasses for optical spectroscopy back in Japan.
c) In summer 2006, winter 2007, and summer 2007 we sent three students to Professor Holland's group to do ^{29}Si and ^{11}B NMR on the alkaline-earth borosilicates. These are precursors to glasses of interest for radioactive waste incorporation. These students also did ^{29}Si MAS NMR studies of mixed Li-Cs glasses and ^{10}B NMR studies of intermediate range order in borate crystals and glasses enriched in ^{10}B.
d) We prepared a large sample of hygroscopic cesium metaborate glass enriched with ^{11}B for an inelastic neutron scattering experiment at the Rutherford Appleton Lab with Prof. Adrian Wright's group. Tyler Mullenbach of our group went there in fall 2007 for the experiment. In fall 2006 Biswas Rijal of our group did another set of neutron scattering experiments with Prof. Wright's group.
e). We sent three students to William Jewell College to do ESR experiments on glassy alkali and alkaline –earth vanadates. Two William Jewell students along with Prof. Pat Bunton came to Coe College to learn to prepare vanadate glasses by rapid cooling.
f) Two students did IR and Raman studies of mixed alkali silicate glasses as well lead silicate glasses at the National Hellenic Research Foundation in Athens.
g.) In December 2008 we are sending two students: Maranda Franke and Mike Huff to University of Warwick to do NMR experiments on calcium and barium borosilicates.

9. Outreach to the Cedar Rapids Regional Community

Students and faculty involved with our research also participate in a very active outreach program to bring our science to schools and students to our college. We bring several classic physics demonstrations, including making glass with a small electric muffle furnace, to school groups ranging from an entire grade of hundreds of students, to classes of 25, to after school programs for 5 students. Also, we frequently host elementary and high school students at the college for hands-on-science sessions and tours of our glass research facilities.

Our largest on-campus event is the ***Coe Playground of Science*.** Held every October the event now draws between 1500 and 2000 students and their parents. We are the main organizers of this extensive open house and night of demonstrations. Other departments that join us include chemistry, biology, mathematics, nursing, and psychology. Our entire building and the immediate outside grounds are used to house about 50 science activities.


Fig.13 a and b: The 2007 Coe Playground of Science

Mario Affatigato and Steve Feller also give forums on science related–topics, including reporting on our research, at Coe's Thursday Forum Program. Typically, 200 community people, many of whom are senior citizens, attend these forums. These forums run four weeks and we offer one or two per year.