

Final Report:

IV.H.3 HGMS: Glasses and Nanocomposites for Hydrogen Storage.

Project Period: November 25, 2009 to October 31, 2012

Submitting Organization:

University of Nevada Las Vegas, Harry Reid Center for Environmental Studies, Las Vegas, NV 89154-4009

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Executive Summary

The primary goal of this project is to fabricate and investigate different glass systems and glass-derived nanocrystalline composite materials. These glass-based, two-phased materials will contain nanocrystals that can attract hydrogen and be of potential interest as hydrogen storage media. The glass materials with intrinsic void spaces that are able to precipitate functional nanocrystals capable to attract hydrogen are of particular interest. Proposed previously, but never practically implemented, one of promising concepts for storing hydrogen are micro-containers built of glass and shaped into hollow microspheres. The project expanded this concept to the exploration of glass-derived nanocrystalline composites as potential hydrogen storage media.

It is known that the most desirable materials for hydrogen storage do not interact chemically with hydrogen and possess a high surface area to host substantial amounts of hydrogen. Glasses are built of disordered networks with ample void spaces that make them permeable to hydrogen even at room temperature. Glass-derived nanocrystalline composites (two-phased materials), combination of glasses (networks with ample voids)

and functional nanocrystals (capable to attract hydrogen), appear to be promising candidates for hydrogen storage media.

Key advantages of glass materials include simplicity of preparation, flexibility of composition, chemical durability, non-toxicity and mechanical strength, as well as low production costs and environmental friendliness. This project encompasses a fundamental research into physics and chemistry of glasses and nanocrystalline composite materials, derived from glass. Studies are aimed to answer questions essential for considering glass-based materials and composites as potential hydrogen storage media. Of particular interest are two-phased materials that combine glasses with intrinsic voids spaces for physisorption of hydrogen and nanocrystals capable of chemisorption.

This project does not directly address any hydrogen storage technical barriers or targets in terms of numbers. Specifically, hydrogen sorption and desorption tests or kinetics measurements were not part of the project scope. However, the insights gained from these studies could help to answer fundamental questions necessary for considering glass-based materials as hydrogen storage media and could be applied indirectly towards the DOE hydrogen storage technical targets such as system weight and volume, system cost and energy density. Such questions are: Can specific macro-crystals, proven to attract hydrogen when in a macroscopic form (bulk), be nucleated in glass matrices as nanocrystals to create two-phased materials? What are suitable compositions that enable to synthesize glass-based, two-phase materials with nanocrystals that can attract hydrogen via surface or bulk interactions? What are the limits of controlling the microstructure of these materials, especially limits for nanocrystals' density and size?

Finally, from a technological point of view, the fabrication of glass-derived nanocomposites that we explore is a very simple, fast and inexpensive process that does not require costly or specialized equipment which is an important factor for practical applications.

Overarching Project Objectives

This research project was aimed at:

- (i) improving UNLV research infrastructure indispensable, but lacking, in materials science research through acquisition of state-of-the-art analytical instrumentation and establishing of new laboratories.
- (ii) fabricating and studying new types of glass-based materials that could be promising candidates for hydrogen storage media, and at the same time jump-starting, at UNLV, glass and ceramic composites research in light of other renewable energy-related materials science projects.

The project was composed of two parts: (1) Preparatory Part and (2) Experimental Part that are presented below.

1. Preparatory Part of the Project – Equipment Procurement and New Laboratory Setup

The initial stage of the project - formulated in Task 1.0 - involved new research equipment and instrumentation procurement as well as set-up of new materials science research laboratories. Only a portion of this award's DOE funds was used to acquire one state-of-the art instrument - the Raman Spectrometer - for improving UNLV research infrastructure. UNLV-HRC funds (~\$400k) were used to setup, from scratch, 2 research labs, including reconstruction and adaptation of space needed to host new instrumentation and purchase of minor instrumentation for these 2 labs. Other funding sources were used to purchase complementary instrumentation, such as the laser (light source for Raman), the furnaces (for materials synthesis) and optical table (to host the spectroscopy set-up). These 2 new labs will serve UNLV's students and faculty in materials science, physics, chemistry and engineering for many years to come.

Here are the outcomes of this effort, comprised of adaptation of laboratory space and new instruments acquisition and installation.

Two, research labs were set-up at UNLV, Harry Reid Center for Environment Studies (Fig.1a and Fig. 1b): the Materials Synthesis & Materials at Extreme Environments Labs (500 sq.ft.) and the Laser Spectroscopy Laboratory (1000 sq.ft.).

The laboratories were equipped with the following, state-of-the-art, materials synthesis and characterization capabilities: Raman Micro-Spectrometer, confocal Raman microscope and motorized Raman-compatible xyz stage (this project funds), vibration-control optical tables (other funds), multi-wavelength gas laser-light source for Raman Spectrometer (other funds) three high-temperature research grade furnaces: 1700°C & 1400°C 1200°C (UNLV funds), high-resolution Stereo-Microscope with video camera (UNLV funds) and Simultaneous Thermal Analyzer combining Differential Scanning Calorimetry with Thermogravimetry, DSC/TG (other funds).



Fig. 1 (a): Photographs of the two research labs that were set-up for this project: (a) the Laser Spectroscopy Laboratory.



Fig. 1 (b): Photographs of the two research labs that were set-up for this project: (b) the Materials Synthesis & Materials at Extreme Environments Laboratory.

1. Experimental Part of the Project – Materials Design, Synthesis and Microstructural Characterization

The experimental part of the project -formulated in Tasks 2, 3 and 4 – was composed of: synthesis of glass materials, micro-structural and nano-structural studies and synthesis of glass-based nanocrystalline composites.

2.1. Synthesis of Glass Materials

A conventional high-temperature melting and fast quenching method was used to synthesize glass materials. A series of glasses was fabricated with variable contents of network formers and network modifiers (dopants). All glasses were prepared using high purity analytical grade reagents to avoid spurious effects from impurities. The batch components were first sintered at low temperature then ground and checked for weight loss and afterwards melted at high temperatures in a resistance furnace in an air atmosphere. Liquid glass melts were cast onto metal molds and air cooled to obtain glasses.

2.2. Synthesis of Nanocrystalline Glass-Based Composites

Following the glass materials synthesis, this task of the project consisted of fabrication of several nanocrystalline composites based on the above mentioned glasses. To induce nucleation of nanocrystals in the glass matrices, time-controlled gradual isothermal heat treatments below and above the glass transition temperature were performed. By varying heat treatment conditions, a number of glass-based nanocrystalline composites with various types and different mean diameters of nanocrystals were fabricated.

2.3. Experimental Techniques Used

During the execution of this research project numerous experimental techniques were used and they are outlined below.

2.3.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed to find the characteristic glass temperatures: glass transformation temperatures (T_g), glass nucleation

temperatures (T_n) and glass crystallization temperatures (T_c). Samples were finely ground, weighed and placed in an aluminum micro-crucible with a perforated aluminum lid. They were heated in an argon atmosphere from room temperature up to a top temperature with a constant heating rate of 10 or 20 deg/min. Five metal references were periodically used to ensure correct temperature and sensitivity calibration. The DSC curves allowed to extrapolate the temperatures of interest (T_g , T_n , T_c). These temperature points are distinctive for a given glass system and composition. They allowed to establish the conditions needed to direct the processes of nucleation and nanocrystallization in glasses and to fabricate the glass-crystal composites.

2.3.2 High-Resolution Transmission Electron Microscopy (HRTEM)

HRTEM images were collected from the powdered samples spread over carbon coated copper grids. Transmission electron micrographs were collected through wedges of glass fragments, which were transparent to electrons. For each sample several particles of the glass or nanocrystalline material powder were sampled. Selected area diffractions patterns were also collected to check for presence or absence of crystalline zones.

2.3.3 Confocal Laser Raman Spectroscopy

Raman scattering spectra were collected for all synthesized materials. Raman data were obtained on a confocal micro-Raman spectrometer using the 514.5 nm line of an Ar-Kr laser operating at 40mW at the samples. The monochromator was used in its triple configuration with three grating of 1800 lines/mm. the Raman signal was detected by a liquid nitrogen cooled CCD detector. Silicon was used as a reference for calibration purposes. Signal integration was 100-600s per sample and multiple acquisitions were followed by an averaging procedure. Measurements were carried out at room temperature in air atmosphere. The Raman signal was analyzed in backscattering configuration using a Raman microscope. The samples were placed on a motorized xyz-stage. Special care was taken to obtain reliable relative intensities of the Raman lines in different samples. For this purpose, few regions of a given sample were probed with the objective of the Raman microscope in order to select the best region.

2.3.4 Synchrotron X-Ray Absorption Fine Structure Spectroscopy (XAFS)

The local structural environment of specific atoms in glasses and nanocrystalline composites were characterized with synchrotron radiation-based X-Ray absorption fine structure spectroscopy (XAFS). XAFS experiments were carried out at the Advanced Photon Source of Argonne National Lab. For experiments a Si (111) cryocooled

monochromator with harmonic rejection mirror was used and sample fluorescence was measured at a 45 degrees angle using a Lytle Detector with Ar gas in the ion chamber (300V). All studies were done at room temperature in continuous scan mode with a tapered undulator.

2.3.5 X-Ray Diffraction

X-ray diffractometry was used to investigate homogeneity of samples and to detect any traces of crystalline impurities in all as-quenched glasses as well as to identify nanocrystalline phases in composites. X-ray diffraction patterns were collected using a laboratory diffractometer in the Bragg-Brentano geometry, CuK α radiation and in 10°-80° 2 theta diffraction angles. The samples in a form of fine powders were placed on a spinning stage. All X-ray patterns were collected at room temperature.

2. Results and Discussion

3.1. Glasses Synthetized

We successfully synthetized multiple series of glass materials based on tetrahedral network formers.

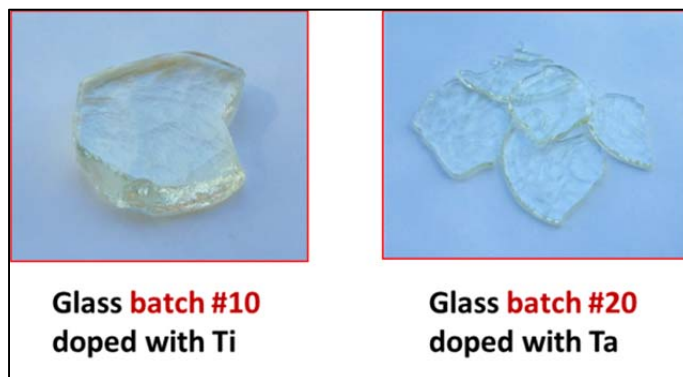


Fig. 2: Examples of fabricated glasses with different doping agents. All glasses are optically transparent and do not present any inhomogeneities.

Variable concentrations of glass network formers, modifiers and of functional dopants were studied to test glass forming ability and glass forming limits. In particular, ternary and quaternary glass systems were fabricated and tested with variable content of functional dopants, interesting for hydrogen storage applications.

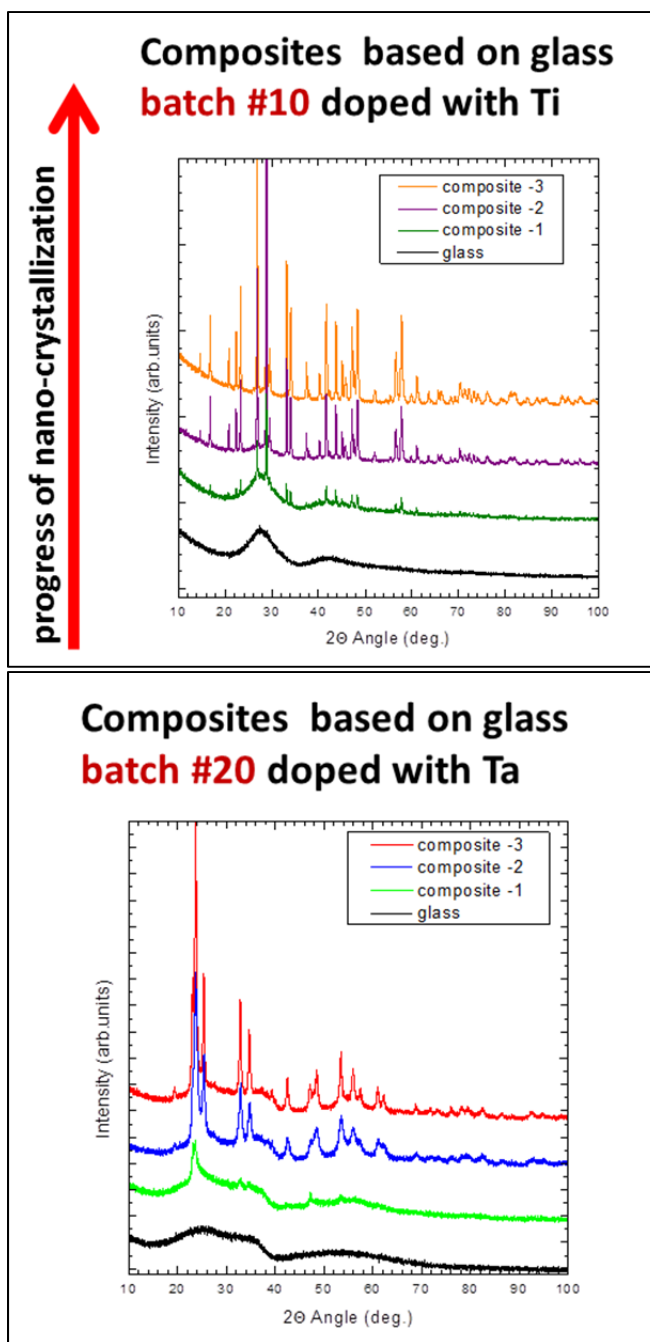


Fig. 3: X-ray diffraction patterns of two glasses (batch #10 and batch # 20) and of six nanocrystalline composites fabricated from those glasses. The process of nanocrystallization can be followed from bottom to top.

The first series of synthesized glasses were alkali-silica-based compositions doped with titanium, tantalum or niobium acting as network formers and/or network modifiers. The glasses were homogeneous, transparent and did not show signs of early nucleation, phase separation or presence of inclusions (Fig.2).

Progress of nucleation and crystallization was followed by X-ray diffractometry. Comparison of selected glasses and derived nanocrystalline composites are shown in Fig. 3. The wide bumps on the diffraction patterns (Fig. 3) correspond to the glass phase and the overlapped, increasingly sharp lines show the growth of nanocrystals inside the host glass.

Despite optical transparency, the nanocrystallization of the glasses of series #10 and #20 showed growth of multiple crystalline phases. These glasses were thus eliminated from further study in favor of other glass compositions displaying crystallization of single nanocrystalline phases.

The second series of glass batches synthesized were glass compositions based on silica and doped by IIIB oxides (proprietary compositions). All glasses were homogeneous, optically transparent, and colorless and did not display any macro-crystalline inclusions or phase separation (Fig. 4).

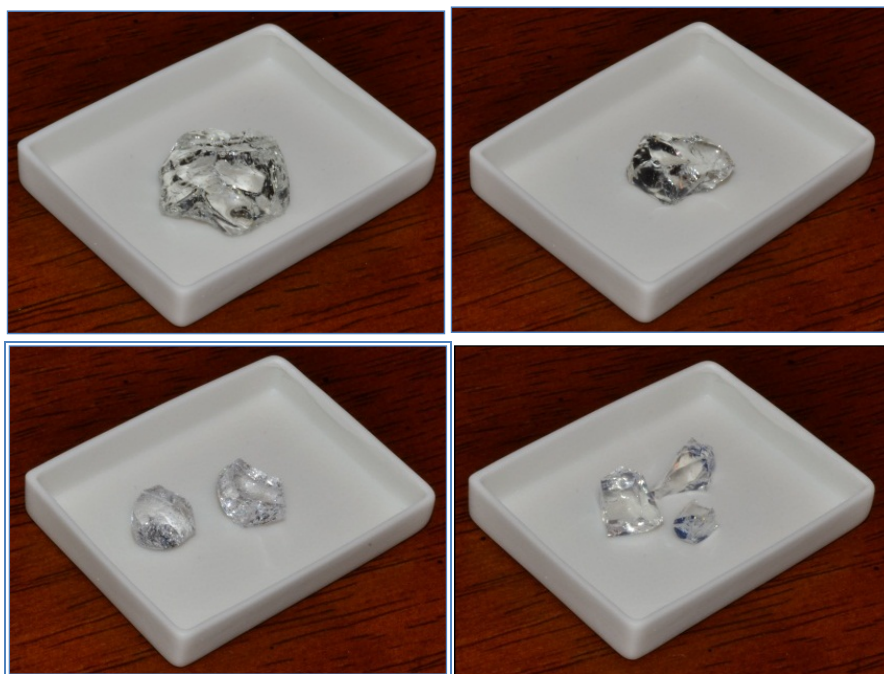


Fig. 4: The fabricated glasses from the series of proprietary batches #30, #40, #50 and #60 with variable content of IIIB oxides. The areas of darker color, visible in the photographs, are due to shadows on the irregularly faced glass fragments.

3.2. Differential Scanning Calorimetry of Glasses

We established the precise conditions needed to direct the nucleation and nanocrystallization processes in glasses and to fabricate the glass-crystal composites.

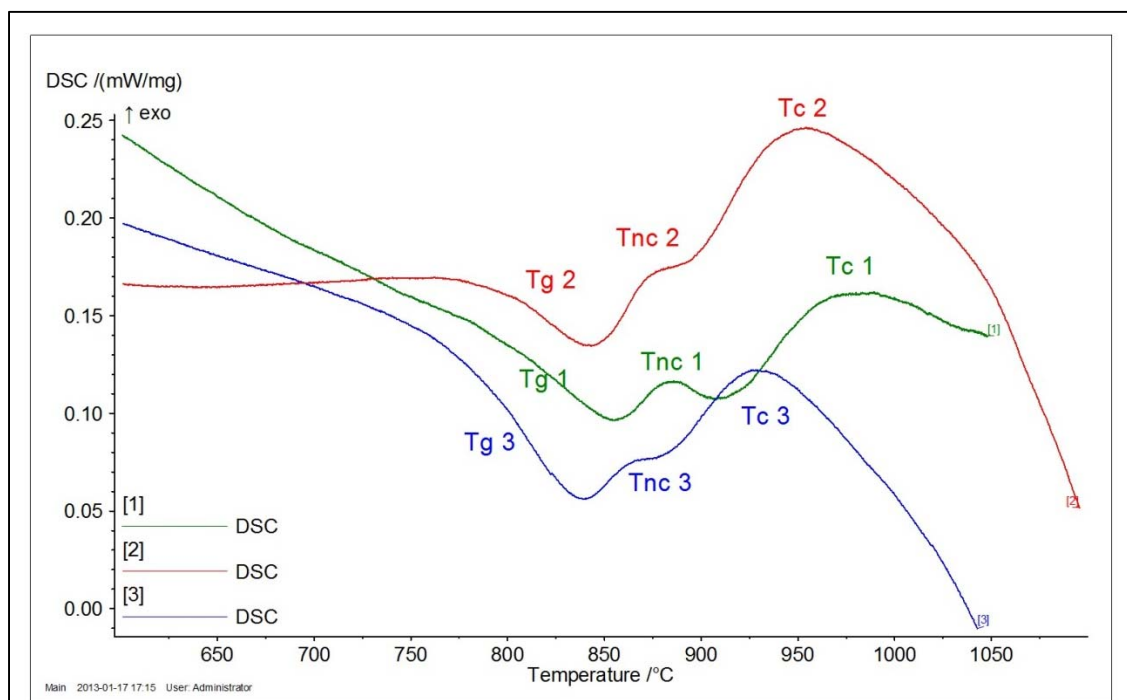
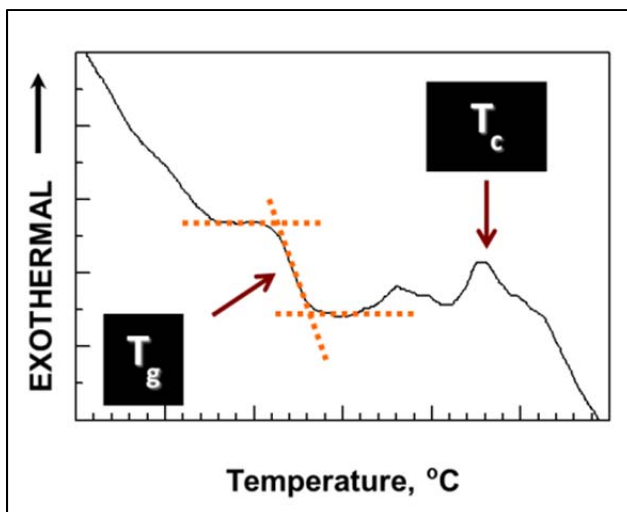


Fig. 5: *Top graph*: sketch showing how to read glass characteristic temperatures from a DSC measurements. *Bottom graph*: example of Differential Scanning Calorimetry (DSC) curve typical for the silica-based glasses doped by IIIB oxides (proprietary) fabricated in this project (proprietary glass batches #30, #40, #50).

Differential scanning calorimetry indicated a glass transformation temperature - T_g varying from 830°C to 850 °C, a glass nucleation temperature - T_n - varying from 870 °C to 960 °C and a glass crystallization- T_{cr} - varying from 950 °C to 1020 °C. These temperature points are distinctive for a given glass system and composition (Fig. 5).

Microstructural characterization of glasses was performed using Raman spectroscopy, synchrotron radiation-based X-Ray Absorption Fine Structure (XAFS), transmission electron microscopy (HRTEM) and X-ray diffraction.

3.3. X-ray Diffraction of Glasses

All series of glasses from different proprietary batches (#30, #40, #50 and #60) with variable content of IIIB oxide dopants were examined for disorder using x-ray diffraction. The XRD patterns (Fig. 6) showed very broad bands that are characteristic of amorphous systems without long-range order. In few cases, the diffraction patterns indicated very early stages of long-range order that could be related to a phase-separation or beginning of nanocrystallization.

3.4. Raman Spectroscopy of Glasses

The influence of glass compositional changes on its structure in the synthesized glasses was investigated using Raman spectroscopy. It was revealed that the main effect of compositional changes is the alteration of the medium-range order in the glass. It is associated with creation of new bonding in the network and can be seen from the modification of the low- and medium-frequency Raman vibrational modes. The Raman spectra of the fabricated glasses (Fig. 7) indicated that the glasses from different batches have different local structure. The spectra showed broad bands, characteristic for glasses and associated with their vibrational density of states. The band-widths reflected the structural disorder, typical of glasses. A low frequency band, called the Boson Peak is associated with librational-translational motions of rigid SiO_4 tetrahedra. The dominant feature of the Raman spectra is an intense, broad band located at about 480 cm^{-1} and called the G-band. The G-band is due to bending motions of oxygen atoms in Si–O–Si linkages, such as in large rings formed by more than four SiO_4 tetrahedra. The wide spread in the inter-tetrahedral Si–O–Si angle values translates into a large frequency distribution of the corresponding modes and thus a large inhomogeneous broadening of the G-band. Especially medium-range order of the glass network is different which is illustrated by the change in intensity and in energy position of the main glass bands (G-bands) and shift of position of the glass defect bands (D-bands). The results of Raman spectroscopic studies were analyzed from the point of view of capability of nucleation and growth of nanocrystals in glass matrices. The best glass candidates for the ensuing nanocrystallization treatments were selected.

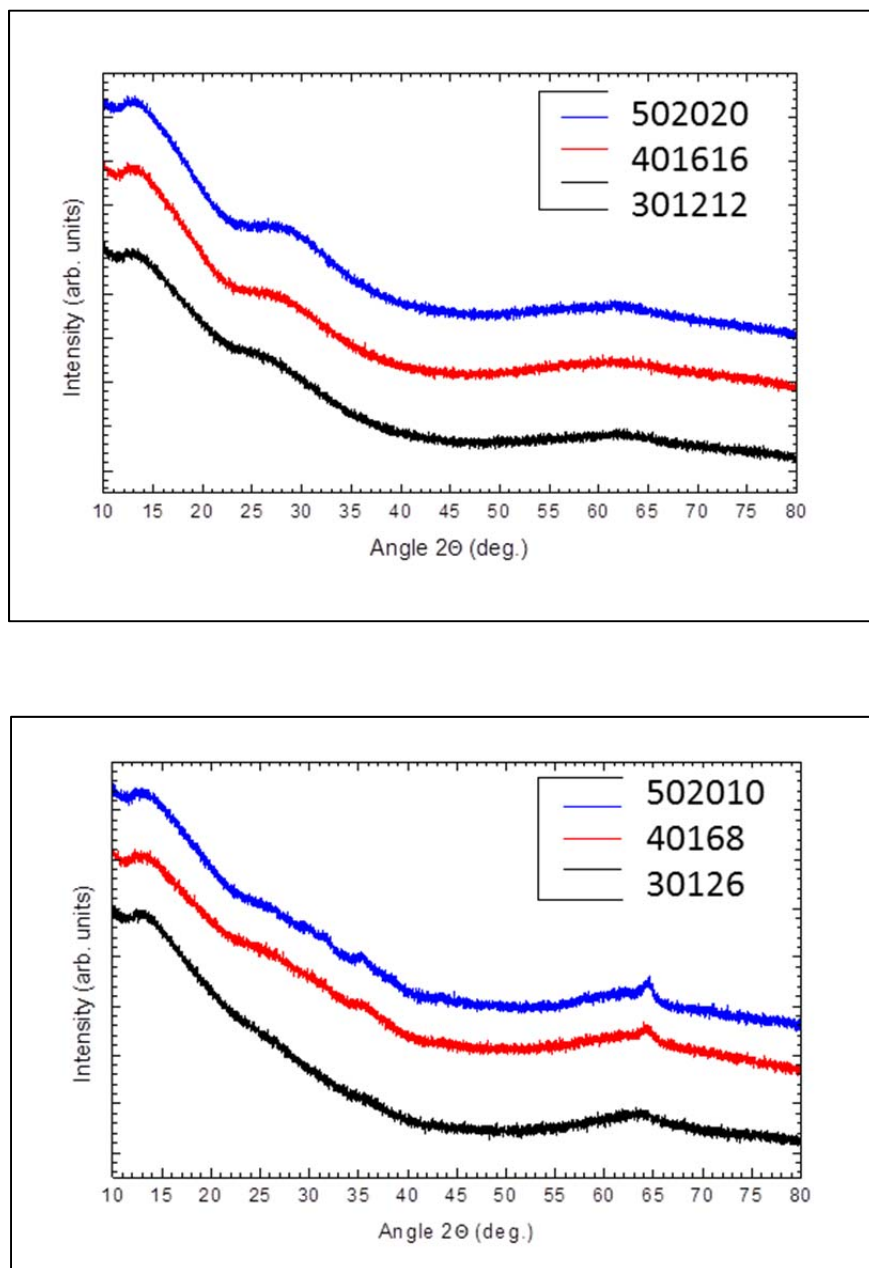
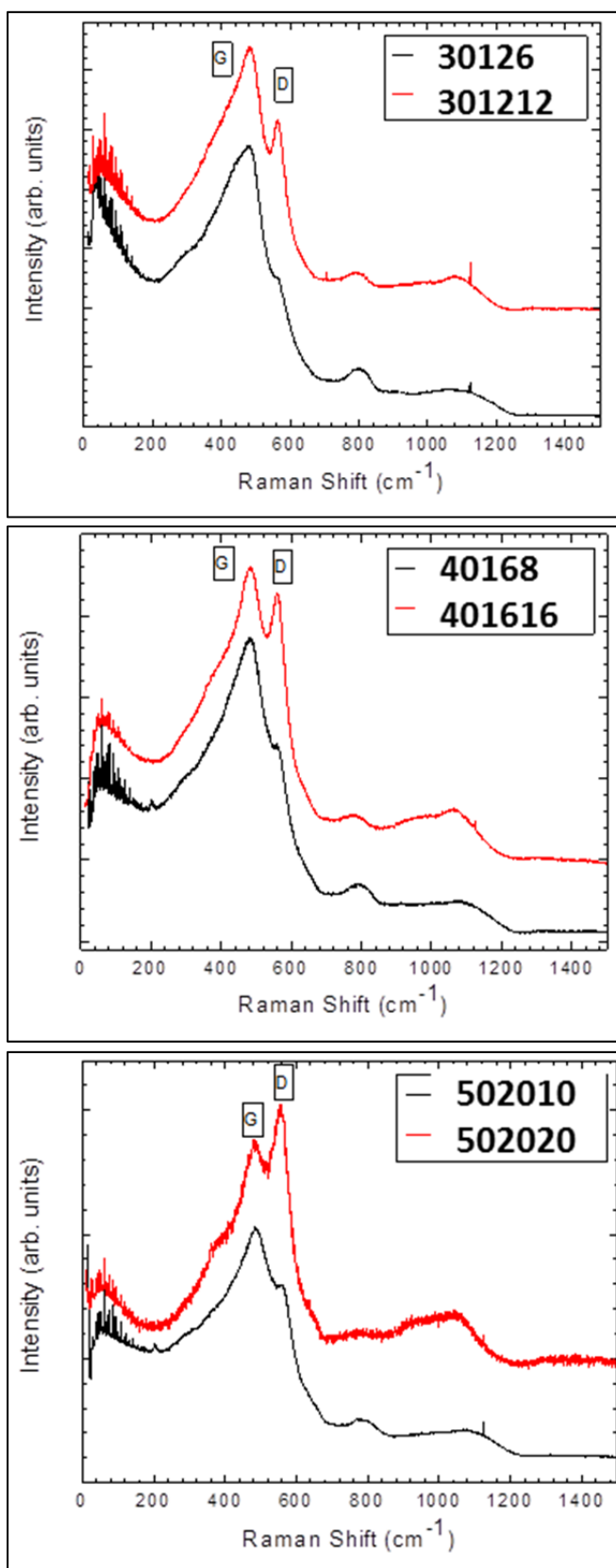


Fig. 6: Examples of X-ray diffraction patterns of silica-based glasses doped by IIIB oxides: batches #30, #40, #50 and #60 (proprietary) fabricated in this project. All patterns display a broad band typical of amorphous materials. In two patterns some trace of early crystallization or phase separation can be seen. At low angles some contribution due to the sample holder is also seen, overlapped with the amorphous background.



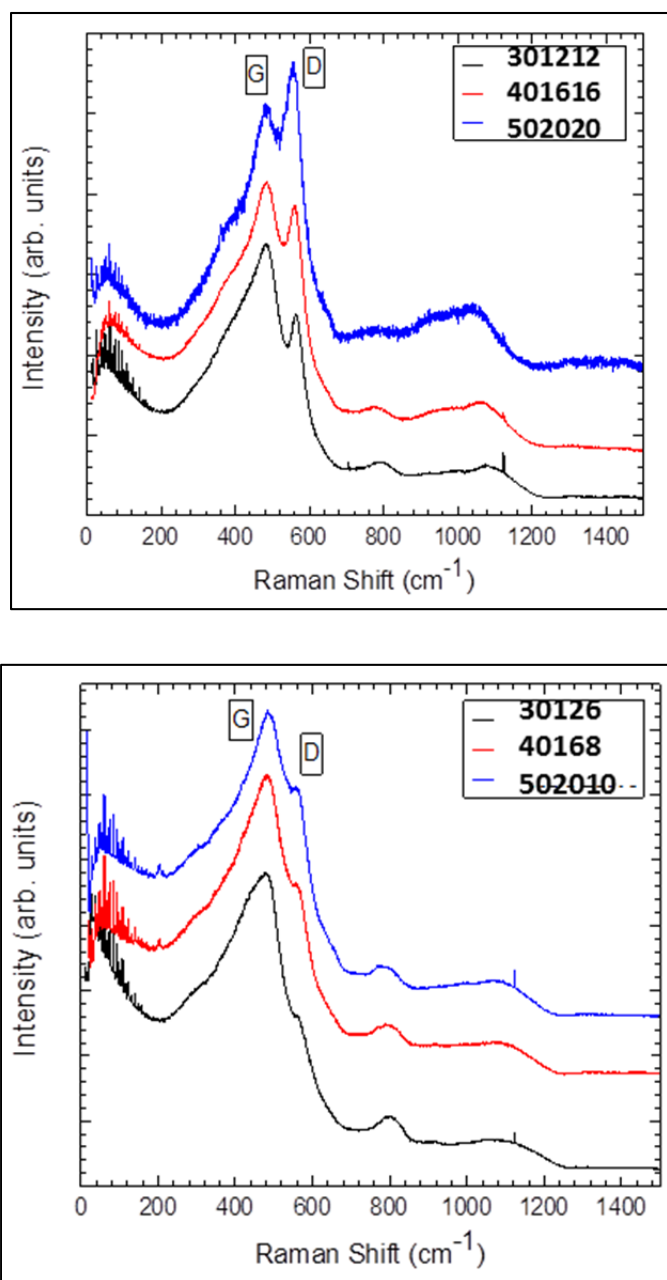


Fig. 7: Five plots with examples of Raman spectra of silica-based glasses doped by IIIB oxides (proprietary) fabricated in this project, batches #30, #40, #50 and #60. The band-widths reflect the structural disorder, typical of glasses. A low frequency band, called the Boson Peak is associated with librational-translational motions of rigid SiO₄ tetrahedra. The spectra also show the G-band and the D-band.

3.5. High Resolution Transmission Electron Microscopy (HRTEM) of Glasses

The microstructure of several samples of the as-quenched glasses doped by IIIB oxides (proprietary) were examined. HRTEM images were collected through wedges of glass fragments, which are transparent to electrons. HRTEM images showed that glasses are homogeneous without crystalline inclusions. Selected area diffractions (SAD) patterns (Fig. 8, bottom) did not reveal any crystalline reflection but the typical halo of amorphous systems.

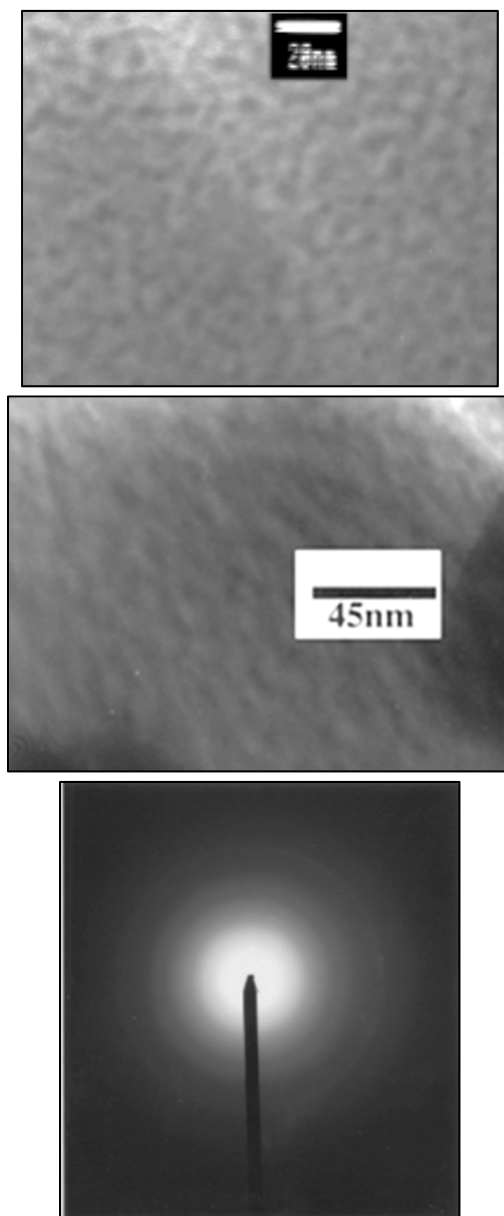


Fig. 8: Examples of HTREM and SAD of as-quenched (proprietary) silica-based glasses doped by IIIB oxides. All images confirm the amorphous nature of the materials.

3.6. Synchrotron X-Ray Absorption Fine Structure Spectroscopy (XAFS) of Glasses

The local structural environment of specific atoms in glasses was characterized by using synchrotron radiation-based X-Ray absorption fine structure spectroscopy (XAFS). XAFS data were collected at the relevant energy absorption edge of a given (proprietary) glass dopant (IIIB oxides) in order to probe the local structural environment, presence of near neighbors, calculate interatomic distances and coordination with oxygens in glass matrices. Results of XAFS (Fig. 9) allowed to conclude that all glass networks are built of interconnected SiO_4 and dopant tetrahedra.

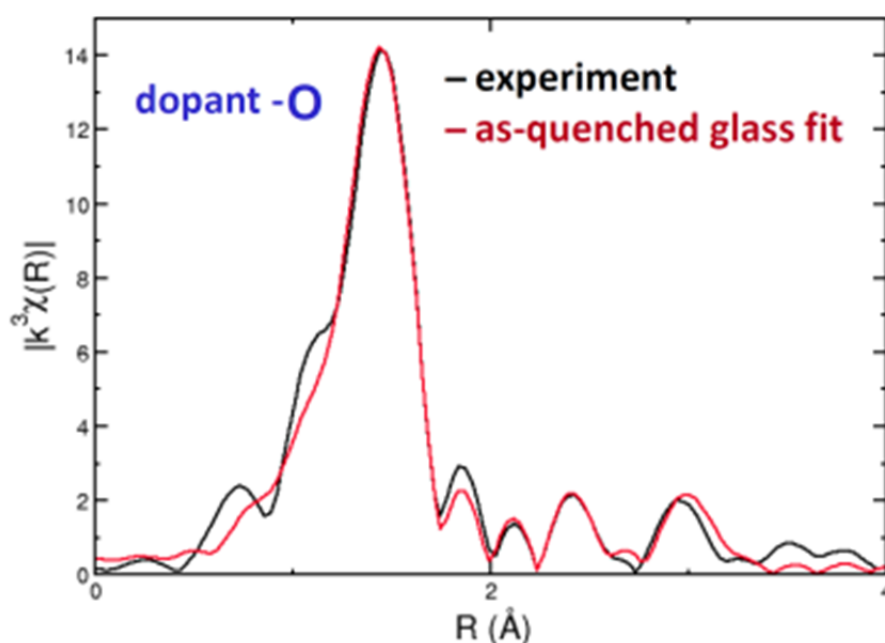


Fig. 9: Example of the X-Ray absorption fine structure (XAFS) spectra of one of the synthesized glasses doped with IIIB oxides (proprietary). XAFS shows that in all as-quenched glasses dopant atoms are in tetrahedral environment with oxygen atoms.

3.7. Glass-Ceramic Nanocrystalline Composites

3.7.1. Nanocrystallization Process in Glass

Glasses gain new functionality when they are transformed into nanocrystalline composites. Such transformation is achieved by nucleating nanosized crystallites inside the glass matrix. The resulting material, a glass-derived nanocrystalline composite, combines the best of the crystal and glass 'worlds', offering flexibility of composition, tunability of properties and providing a wide spectrum of technological advantages over

standard glasses or standard ceramics. Fig. 10 illustrates the process of transformation from glass to nanocrystalline composite.

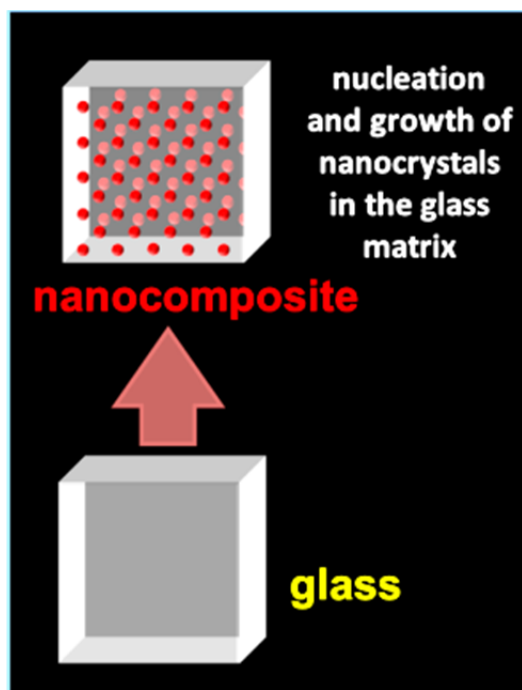


Fig. 10: Sketch showing transition from glass to nanocrystalline composite. Glass-ceramic composite corresponds to a glass with nucleated nanocrystals. By growing “functional” nanocrystals within the glass we modify the glass’ interaction with hydrogen.

The best glass compositions from the previous Task 2 of this project were selected for further processing in order to produce a series of glass-ceramic nanocrystalline composites. Not all glass compositions showed formation of desired functional nanocrystals. A number of glass-ceramic nanocomposites with variable density and size of nanocrystals precipitated in a host glass matrix were successfully fabricated. The nucleated nanocrystals were homogeneously distributed in glass matrix, were composed of a single crystalline phase and the diameters of those nanocrystals was controlled by fabrication conditions.

The synthesis of nanocrystalline composites presents many challenges (Fig. 11) such as: no crystallization occurs at all or immediate and complete transformation from 100% glass $\rightarrow$ 100% crystal, several phases may crystallize at once, the size and size distribution of crystals has a very wide range.

This is an important research achievement since there are only very few known glass compositions that allow for size-controlled and density-controlled formation of nanocrystals inside a glass matrix. We investigated how the controlled nucleation and

growth conditions are influencing the type, size, size distribution and concentration of nanosized crystals within the host glass matrix.

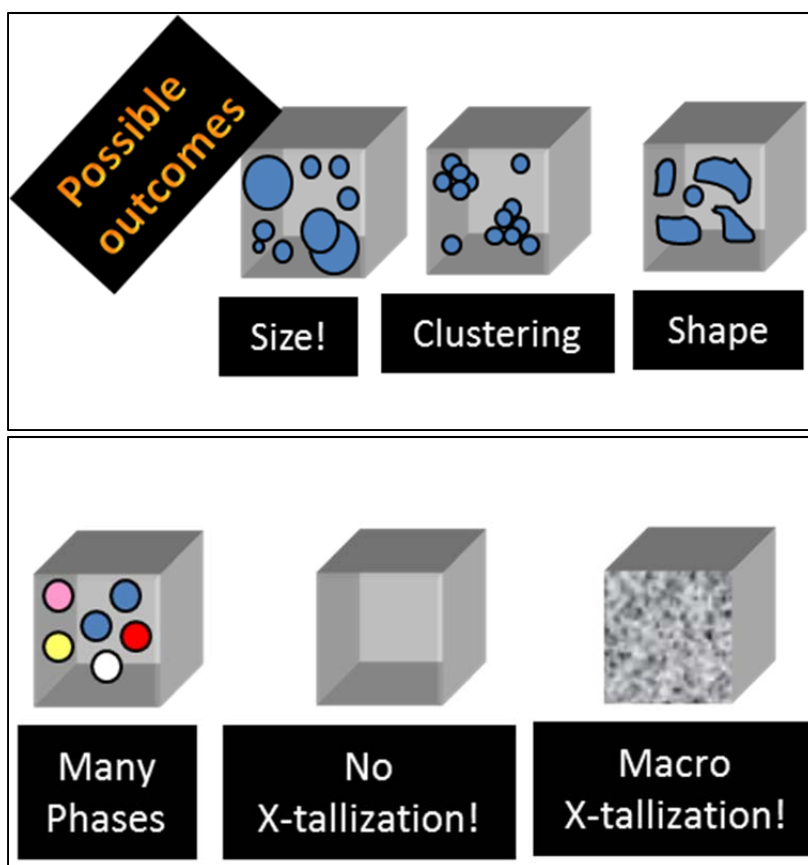


Fig. 11: Sketch illustrating the many problems associated with (nano)crystallization in glass matrices.

3.7.2. X-Ray Diffraction Study of Nanocrystalline Composites

We established procedures that allowed us to control the size and the quantity of nanocrystals precipitated inside glass matrices. Crystallization processes were monitored in selected glass samples. Fig. 12 shows X-ray diffraction patterns of few nanocrystalline composites fabricated from glasses of proprietary composition with variable content of IIIB oxides (batches # 30 and # 50). For each nanocrystalline composite the progress of crystallization is evidenced by the appearance and increase of intensity of diffraction lines of nanocrystalline phase. These lines are overlapped by the constantly present glass background. An example of the nanocrystallization progress for three series of composites fabricated from different glass batches (batches #30, #40 and #50) is shown on Fig. 13.

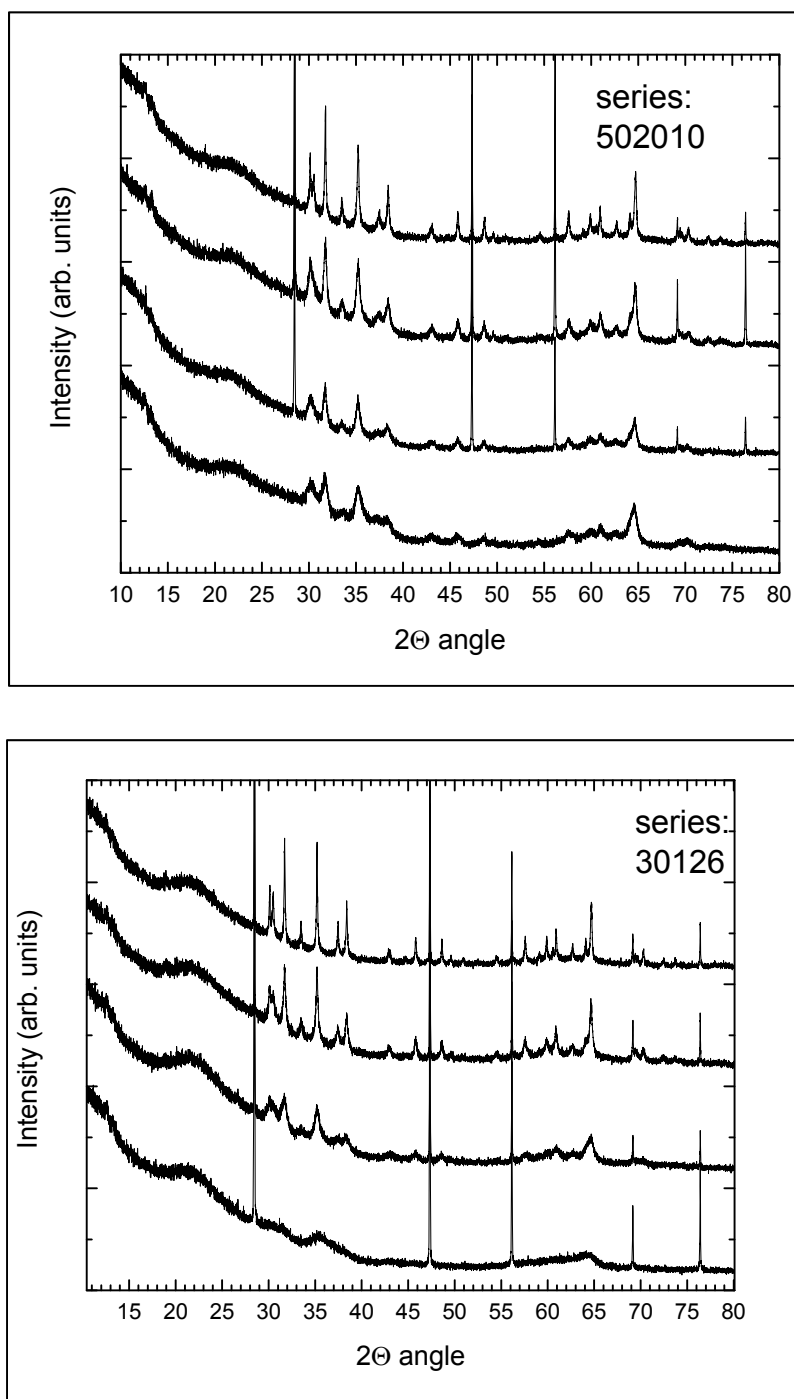


Fig. 12. Examples of X-ray diffraction patterns of nanocrystalline composites (glass batches # 30 and # 50) fabricated. The amount of nanocrystals increases from bottom to top. All diffraction patterns show that the broad glass background is overlapped with small peaks due to the presence of nanocrystals. The three very sharp and intense lines are due to internal standard.

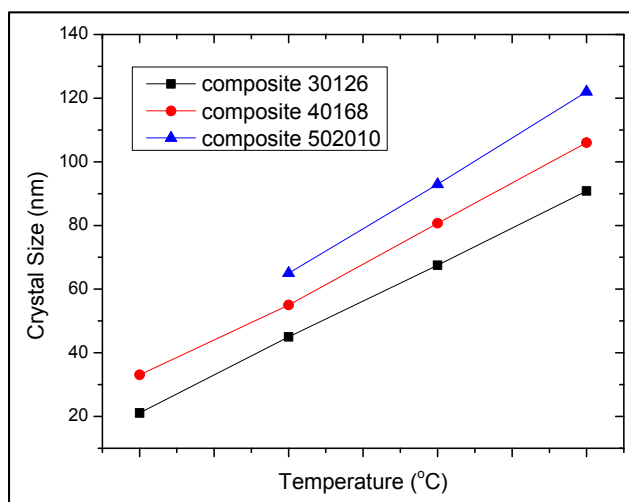


Fig. 13: Growth of nanocrystals inside matrices of selected glasses: the size of nanocrystals was tuned: from 20 nm to 90 nm (composite #30126); from 35 nm to 100 nm (composite #40168) and from 60 nm to 120nm (composite #502010).

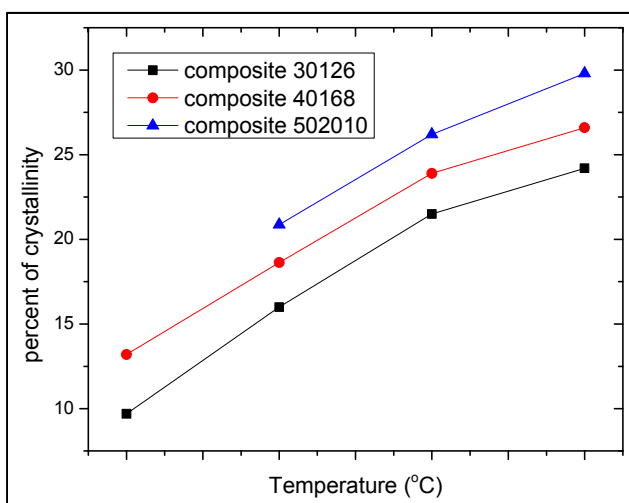


Fig. 14. Percent of crystallinity induced in glass matrices of few composites (derived from proprietary glasses). Crystallinity was altered: from 9% to 24% (composite #30126); from 13% to 27% (composite #40168) and from 20% to 30% (composite #502010).

We successfully synthesized a range of composites with nanocrystals as small as 20 nm and as large as 120 nm (Fig.13). The growth of nanocrystals can be controlled by temperature, since it is close to linear, as shown on the plot. The amount of crystalline phase precipitated in the glasses can also be controlled by temperature factor. Fig. 14 shows examples of synthesized nanocomposites (glass batches #30, #40 and #50) where the amount of nanocrystalline phase changes from 9% up to 30%.

3.7.3. Raman Spectroscopy of Glass-Ceramic Nanocrystalline Composites

We succeeded in combining two phases - nanocrystalline phase and glassy phase, - in one material for all nanocomposites that were fabricated. The nucleation and growth of nanocrystals in composites was monitored with Raman spectroscopy for several series of nanocomposites fabricated from the best glasses. Fig. 15 and Fig. 16 show comparison of the Raman spectra of as-quenched glass and of glass-derived composites. A nanocrystallization process was evidenced by the appearance and systematic increase of intensity of Raman peaks that prove the presence of nanocrystals in the glasses. These Raman peaks correspond to vibrational modes specific to those nanocrystals. The Raman peaks of nanocrystals are overlapped by the still present glass (amorphous phase) background.

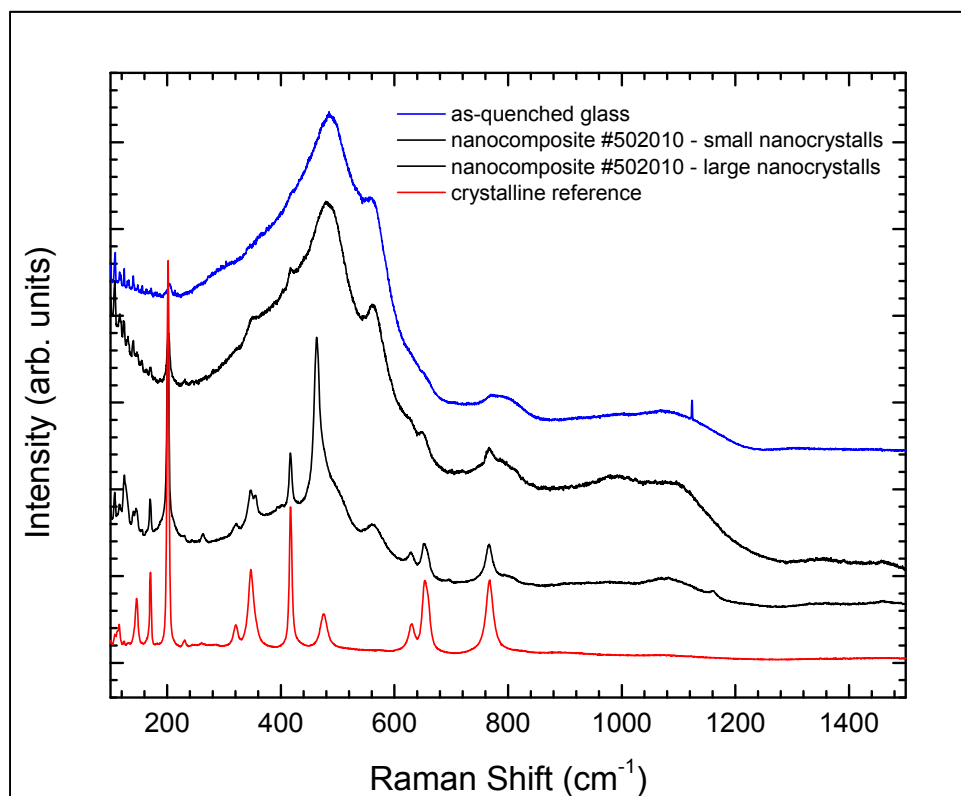


Fig. 15: Raman spectra: comparison of as-quenched glass (batch #502010, blue plot), with two nanocrystalline-composites derived from this glass (black plots) as well as a reference crystal of dopant - IIIB oxide (red plot). The progress of crystallization is evidenced by appearance of peaks assigned to IIIB oxide nanocrystals overlapped with the still present glass background.

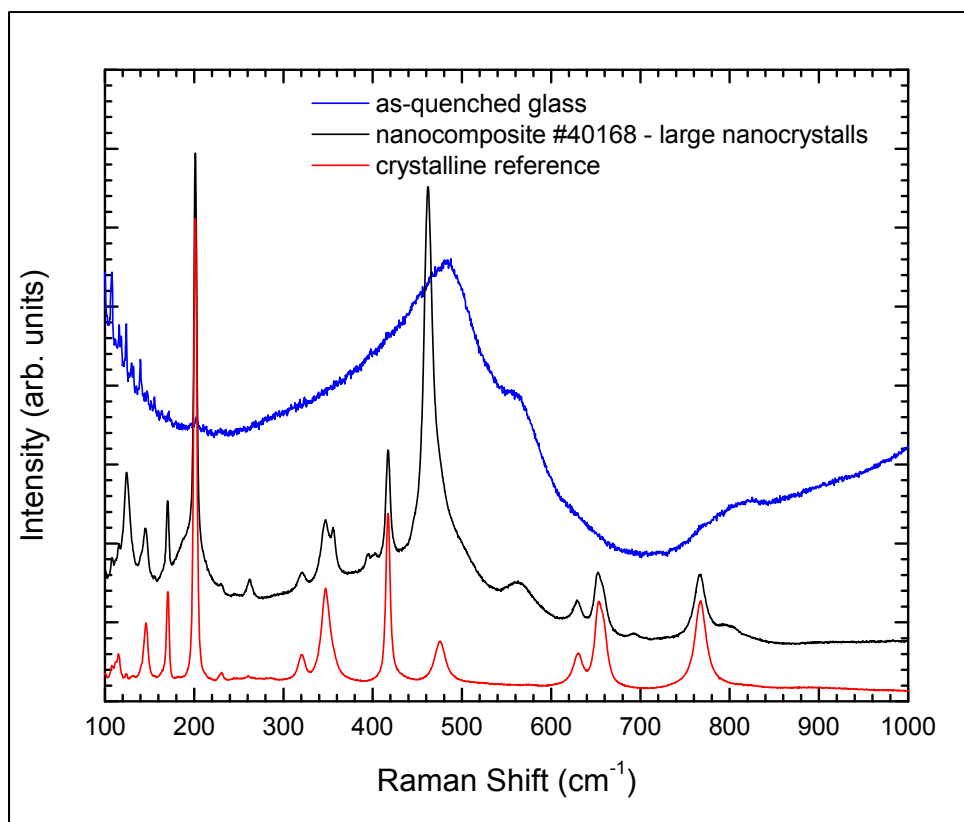


Figure 16: Raman spectra: comparison of as-quenched glass (batch #40168, blue plot), with one nanocrystalline-composite derived from this glass (black plot) as well as a reference crystal of dopant - IIIB oxide (red plot). The progress of crystallization is evidenced by appearance of peaks of assigned to IIIB oxide nanocrystals overlapped by the present glass background.

3.7.4. High Resolution Transmission Electron Microscopy (HRTEM) of Nanocrystalline Composites

The effective combination of two phases - nanocrystalline phase and glassy phase - in one material for all fabricated nanocomposites can be easily verified with HRTEM (Fig. 17). The micrographs illustrate the conversion from glass (amorphous material; leftmost image) to glass-based nanocomposites, where black spots on the images reflect the presence of nanocrystals. The black spots (coherently scattering domains) are more or less uniformly distributed inside the amorphous glass matrix. These scattering domains indicate that, at a given stage, either crystalline nucleation has already occurred within the sample or it is in a more advanced stage. The crystallite size can be tuned by adjusting the nucleation and growth conditions. The microstructure of the last composite (Fig. 17, right) reveals the presence of different sets of nanocrystals precipitated within the host glass matrix.

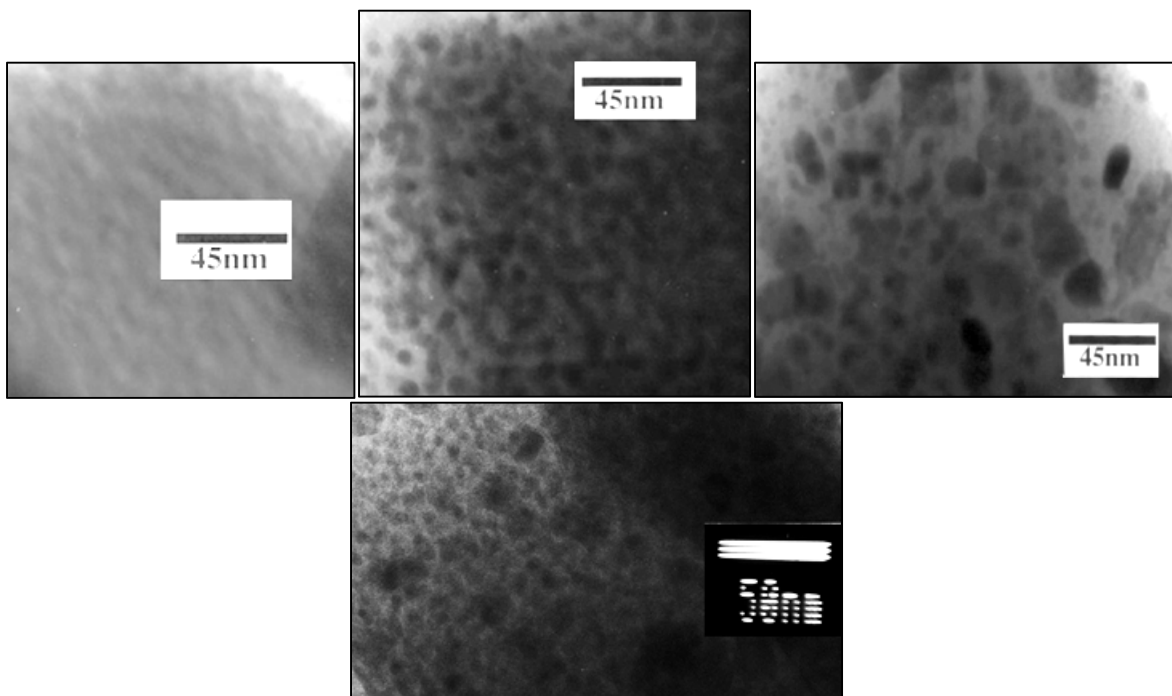


Fig. 17: Examples of HTREM images of nanocrystalline composites showing different stages of nanocrystallization in one of the proprietary silica-based glasses doped by IIIB oxides.

3.7.5. Synchrotron X-Ray Absorption Fine Structure Spectroscopy (XAFS) of Nanocrystalline Composites

The understanding of structural networks of nanocomposites was greatly improved by results of XAFS spectroscopy. It was revealed that dopant atoms (IIIB) advance gradually from a purely tetrahedral coordination in glass to a distribution among tetrahedral and octahedral sites in nanocomposites. Fig. 18 illustrates the structural transition from as-quenched glass to nanocrystalline composites. For initial glasses XAFS showed that dopant atoms (IIIB oxide atoms) are in tetrahedral environment with oxygen atoms (Fig. 18, green plot). As nanocrystals grow in the glass matrix and the nanocomposite is formed, the intensity of the first XAFS peak (1.4 Å; tetrahedral sites)) decreases as compared to the initial glass (Fig. 18, green plot) and a broad feature related to the nanocrystalline phase develops at 2.8 Å (octahedral sites; red plot) as contrasted with a macrocrystalline reference (black plot) that shows the coexistence of tetrahedral and octahedral sites. In summary, we demonstrated that nanocrystallization in our glasses causes IIIB oxide atoms to migrate from the glass matrix into the newly grown nanocrystalline phase and involves a change of

coordination number of dopant atoms (IIIB oxide atoms) from purely tetrahedral to a mix tetrahedral and octahedral environments with oxygen atoms.

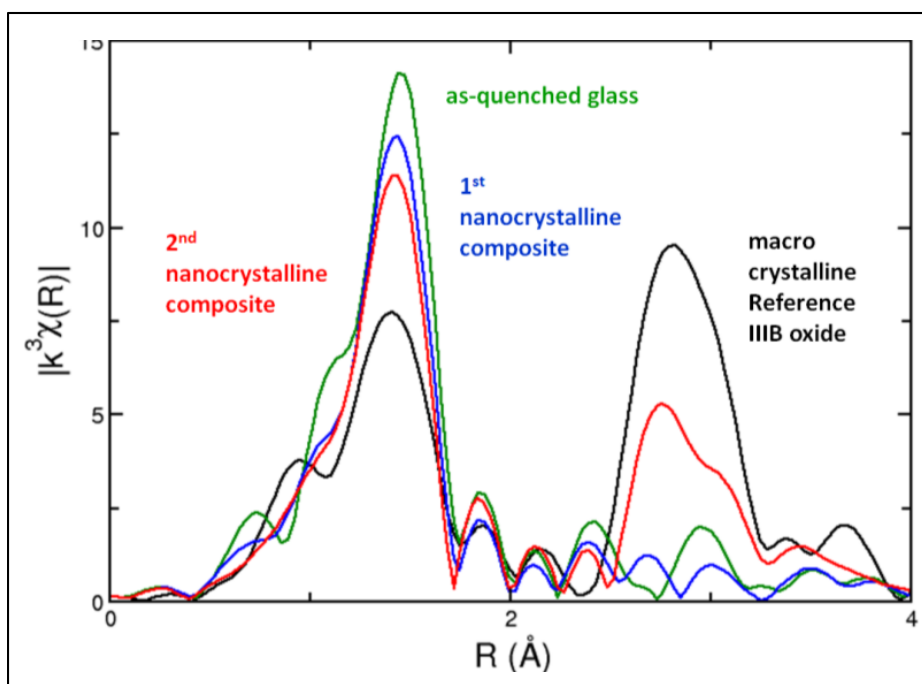


Fig. 18: XAFS spectra of as-quenched glass (green) doped with IIIB oxides (proprietary composition) and two nanocrystalline composites derived from this glass, marked “1st nanocrystalline composite” and “2nd nanocrystalline composite”. The black plot is a macrocrystalline reference.

3.8. Additional Work Executed Beyond the Project Objectives

Due to limitation of funding, the scope of this project did not include hydrogen sorption tests as part of its objectives. Therefore this project was not designed to directly address any hydrogen storage technical barriers.

Even though H-sorption and desorption tests were not part of the project, additional work was planned and was completed in terms of hydrogen sorption measurements on selected nanocrystalline composite at a collaborator’s facility. Hydrogen sorption studies were performed on one nanocrystalline composite, build of a silica glass host matrix with embedded IIIB oxide nanocrystals (proprietary composition). The overall content of IIIB oxide crystalline phase inside the glass matrix was evaluated to about 30%.

A facility for high-temperature absorption study was not available. Therefore the trial hydrogen sorption studies were performed:

- a. at room temperature only
- b. for a time of only 10 min of exposition to hydrogen at the final exposure pressure
- c. with hydrogen exposition pressures ranging only from 35 bar up to 180 bar

The hydrogen sorption studies done on one of the composites showed 0.04-0.05wt% of hydrogen in this material at room temperature at 300 bar with only 15 minutes of overall pressurizing. These results were within the error limit of the set-up and for that reason could be considered as inconclusive.

However, the measured values are actually consistent with those reported for pure silica glass, but only when it is hydrogenated at much higher temperatures and under higher pressures. Examples of hydrogenated silica glass include: hydrogenation at 800°C for 10h at 900 bar; or hydrogenation at 90°C at 850 bar for 2 weeks; or hydrogenation only at 90°C for 2 weeks. In this light, the low values obtained for one composite are actually encouraging. It is expected that if hydrogen sorption of composites equals that of silica glass, but is achieved at much lower temperatures and pressures, then the diffusivity of hydrogen in composites will dramatically increase with increasing temperature. Beyond simple diffusivity properties, our glass-ceramic composite materials are built of a mixture of glass and functional nanocrystals that are expected to interact with hydrogen because of their chemical composition. In fact, the glass-nanocrystal boundary can be a place where efficient interactions with hydrogen (in terms of bonding) may occur.

Further hydrogen sorption studies above room temperature will be subject of future studies, when additional funds will be secured. Addressing this important issue would be a step towards successful demonstration of sorption capabilities of fabricated materials.

3. Comparisons of Accomplishments with Project Goals

We achieved the two overarching goals of this project: (i) improving UNLV research infrastructure in materials science research in general, and renewable energy projects in particular, through acquisition of instrumentation and establishing of new labs; (ii) jump-starting, at UNLV, glass and ceramic composites research in light of hydrogen-storage materials and other renewable energy-related materials.

Task 1: Equipment Purchase and Laboratory Setup

All of the objectives of this task have been met. Two research labs were set-up as planned in this project: the Materials Synthesis & Materials at Extreme Environments Labs and the Laser Spectroscopy Lab, both equipped with state-of-the-art research instrumentation.

Task 2: Synthesis of Glass Materials

All of the objectives of this task have been met. We successfully synthesized multiple series of glass materials based on tetrahedral network formers. Variable concentrations of glass network formers, modifiers and of functional dopants were studied to test glass forming ability and glass forming limits. The fabricated ternary and quaternary glass systems had a variable content of network modifiers and functional dopants that were selected from the point of view of hydrogen storage applications

Task 3: Micro-structural and Nano-structural Studies of Glasses.

All of the objectives of this task have been met. Structural studies of the glass materials were accomplished with a multi-techniques approach using Raman spectroscopy, high-resolution transmission microscopy, x-ray diffraction, differential scanning calorimetry and synchrotron x-ray absorption spectroscopy. The influence of glass compositional changes on their structure was determined. It was revealed that the main effect of compositional changes is the alteration of the medium-range order in the glass. The study of local structural environment of specific atoms in glasses allowed to conclude that all the glass networks are built of interconnected silica and dopant tetrahedra. A number of glass compositions were investigated and the best of them were selected as starting materials for the synthesis of glass-derived nanocrystalline composites. The conditions needed to direct the nanocrystallization processes in glasses and to fabricate the glass-crystal composites were established.

Task 4: Synthesis and Microstructural Characterization of Glass-Based Nanocrystalline Composites.

Questions we intended to answer in this research project were: Can macro-crystals, proven to attract hydrogen when in a macroscopic form (bulk), be nucleated in glass matrices as nano-crystals to create glass-based two-phased materials? What are suitable glass compositions that enable to synthesize two-phase materials with nanocrystals that can attract hydrogen via surface or bulk interactions? What are the limits of controlling the microstructure of these materials, especially limits for nanocrystals' density and size?

Among possible routes to increase hydrogen sorption in glass-based, two-phase materials with nanocrystals that can attract hydrogen, we explored: at first the compositional effects on microstructure of glasses and secondly we focused on textural changes such as introduction of specific nanocrystals that hold promise to be capable to attract hydrogen.

All of the objectives of this task have been met. A number of nanocrystalline composites, with tunable diameter of single nanocrystalline phase, were successfully fabricated from glasses of proprietary composition. Structural studies of the glass samples were carried out using a multi-technique approach. The nucleated nanocrystals were of single nanocrystalline phase and homogeneously distributed in glass matrices. The density and size of nanocrystals in the glass matrix were successfully controlled by nucleation and growth conditions.

Fabrication of single crystalline phase nanocrystalline composites with tunable size/density of nanocrystals represents an important achievement of this project, since there are only very few known glass compositions that allow for size-controlled formation of nanocrystals inside a glass matrix.

In terms of glass compositions, we found that there is only restricted composition range that results in successful formation of nanocrystals, of single crystalline phase in a glass matrix, that are capable to attract hydrogen. The capability of interaction with hydrogen was not studied on glasses with embedded nanocrystals but was proved for macro-crystals of the same chemical composition (bulk form). Same or even enhanced properties are expected for nanocrystals.

In terms of materials microstructure, we found that growth of specific nanocrystals in glass matrices can be controlled on demand (Figs, 13, 14) so the next step would be to correlate the hydrogen sorption capability with the size and density of nanocrystals precipitated in the glass matrices of these two-phase materials. Hydrogen sorption tests should involve studies at variable temperatures, variable hydrogen pressures and variable time scales.

From a technological point of view the fabrication of nanocomposites that we developed is a very simple, fast and inexpensive process that does not require costly or specialized equipment which is an important advantage for practical applications.

A collaborator or a facility capable to perform hydrogen sorption studies on nanocrystalline composites at required elevated temperatures (above room temperature) could not be secured due to funding limitations. This issue represents a serious obstacle to the success of this project in terms of demonstrating of hydrogen sorption capabilities of the fabricated nanocrystalline composites.

Publications/Presentations generated as result of this project:

Kris Lipinska *et al*: “Glasses and Nanocomposites for Hydrogen Storage”, Presentation at 2012 DOE Annual Merit Review & Peer Evaluation Meeting, Washington DC, May 14-18, 2012.

Kris Lipinska *et al*: Presentation at DOE Annual Merit Review & Peer Evaluation Meeting, “Glasses and Nanocomposites for Hydrogen Storage”, Washington DC, May 9-13, 2011

Kris Lipinska *et al*: Presentation at DOE Annual Merit Review & Peer Evaluation Meeting, “Glasses and Nanocomposites for Hydrogen Storage”, Washington DC, April 9-13, 2010

Kris Lipinska *et al*: “EXAFS Study of Local Structural Environments of Glass-Ceramic Composites” in preparation, to be submitted to Journal of Applied Physics.

Kris Lipinska *et al*: “Nanocrystallization Processes in Glasses by Raman Spectroscopy” in preparation, to be submitted to Journal of Raman Spectroscopy.

Collaborations:

Illinois Institute of Technology and Advance Photon Source, ANL
Coe College, Physics Dept. Glass Laboratory
Purdue University, Hydrogen Systems Lab.