Glasses and Nanocomposites for Hydrogen Storage

2012 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

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DOE Hydrogen Program

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3/16/2012

Project ID #st085

Overview

Timeline

- Start: Jan. 2010
- Project delayed
- New End Date: Oct. 2012
- ~70% complete

DOE Barriers

- Congressionally Directed Project in basic sciences that involves fundamental research in physics and chemistry of glasses with potential interest in H-storage
- Project does not directly address hydrogen storage Technical Barriers in terms of *numbers*
- However, the anticipated outcomes could potentially be of interest for section 3.3, such as (A) System Weight and Volume, (B) System Cost (D) Durability/Operability

Budget

- Total project funding
  - DOE: $523,325
  - UNLV: $130,831

Project Lead and Collaborators

Independent Project:

- Research Professor Kris Lipinska, PI
- Research Professor O. Hemmers, co-PI
- Post-Doctoral Scholar
- some collaborations in materials science-microstructural characterization (Coe College, APS-ANL, Illinois Institute of Technology)

Relevance - Objectives

Relevance

- This is a fundamental research project in physics and chemistry of glasses and glass-based nano-crystalline materials
- Numerically, this project does not directly address any H-storage Technical Barriers. In particular, H-sorption and desorption tests or kinetics measurements are not part of the project
- The insights gained from these studies could **help to answer fundamental questions necessary for considering glass-based materials as H-storage media**

Global Objectives

This Congressionally Directed Project is aimed at:

- **jump-starting**, at UNLV, **glass and ceramic composites research** in light of hydrogen-storage materials and other renewable energy-related materials
- 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

Objectives for March 2011-March 2012

- Complete remaining instrumentation set-up
- Continue glass materials synthesis and processing
- Carry out microstructural characterization studies
- Synthesize glass-based nanocrystalline composites

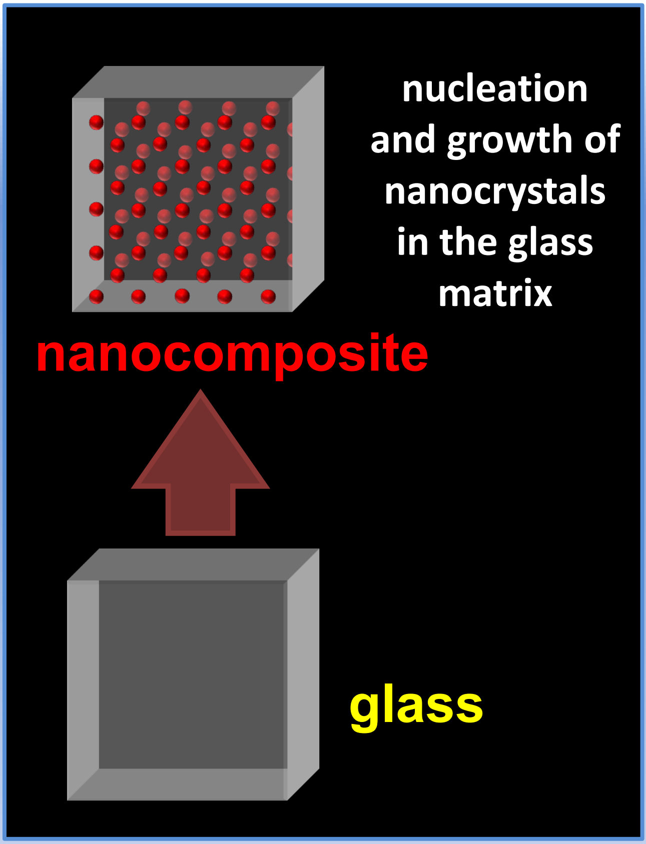
Approach – Uniqueness

Unique Concept 1: Glass-ceramic composite that could host hydrogen

- *Glass-ceramic composite* = glass with nucleated nanocrystals that can interact with hydrogen
- By growing "functional" **nanocrystals** within the glass we modify glass' interaction with hydrogen
- In our opinion this approach could open doors for **new glass materials functionalities** in respect to interactions with hydrogen

Unique Concept 2: Glass with increased free volumes that could host hydrogen

- *Voids or Structural Free Volume* = the disordered structure of glass has ample free spaces that can host hydrogen
- *Voids* can be modified by glass composition and by adding functional dopants etc.
- Glass with large amount of *Voids* could act either as sponge to host hydrogen or as a matrix material for the above composite



Approach – Plan

100% Complete

Task 1.0: Equipment Purchase, Laboratory Setup and Personnel Hiring

- Adaptation of laboratory space
- Equipment purchase, installation and testing, hiring of personnel

Milestone M.1: Lab and equipment setup

70% Complete

Task 2.0: Synthesis and Processing of Glass Materials

- Fabrication of glasses
- Characterization of glasses by Thermal Analysis

Milestone M.2: Fabrication of glasses, determination of glass thermal properties

70% Complete

Task 3.0: Micro-structural and Nano-structural Studies

- Raman Scattering Spectroscopy
- X-Ray Diffractometry, Micro/Nanoscale Imaging and Synchrotron X-Ray Absorption Spectroscopy

Milestone M.3: Understanding of glass structure

50% Complete

Task 4.0: Task 4.0 Synthesis of Glass-Based Nanocrystalline Composites

- Fabrication of Composites
- Raman Scattering Spectroscopy
- X-Ray Diffractometry
- Micro/Nano-scale Imaging
- Synchrotron X-ray Absorption Spectroscopy

Milestone M.4.1: Fabrication of nanocomposites
Milestone M.4.2: Determination of Microstructure
Milestone M.4.3: Determination of local structural environment

Changes to baseline schedule

Planned: Jan. 2010 – Oct. 2011

Delayed by ~12 months: necessary laboratory adaptation work and installation of new instrumentation

New End Date: 31 Oct. 2012

Previous Accomplishments

This Congressionally Directed Project is aimed at **adding instrumental capabilities** to UNLV and **jump-starting glass and ceramic composites research** related to H-storage and other renewable energy-related research projects.

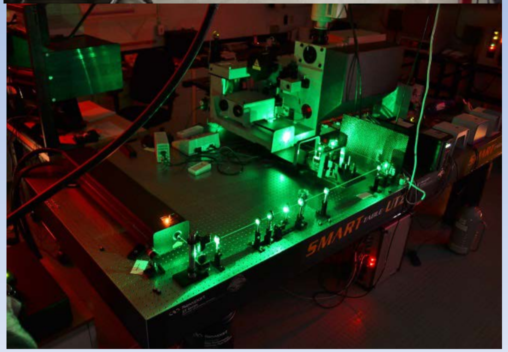
March 2010/March 2011: Instrumentation Purchase, Lab. Setup

- **New equipment was purchased, installed and tested**
  - materials synthesis and characterization capabilities are: Raman spectrometer, with confocal Raman microscope and motorized stage -*DOE funds*, optical tables -*other funds*, multi-wavelength gas laser -*other funds*, two high-T research furnaces: 1700^{o}C & 1400^{o}C -*UNLV funds*, stereo-microscope -*UNLV funds*
- **New research labs were established** (including reconstruction-adaptation of lab space -*UNLV funds*:
  - **Materials Synthesis Lab.**
  - **Materials at Extreme Environments Lab.**
  - **Laser Spectroscopy Lab.**

March 2010/March 2011: Experimental work started:

- Started synthesis and processing of new glass materials
- Started synthesis of glass-based nanocrystalline composites
- Started micro-structural studies



Technical Accomplishments & Progress

Setup of 2 new labs and of instrumentation was completed

- Finished installation of the Raman Spectroscopy System:
  - a motorized Z-stage for Raman mapping was installed and the entire optical path of the spectrometer was re-aligned
- Solved technical issues:
  - the Laser beam divergence issue: an external optical setup was built and the high-reflector mirror in the laser cavity was replaced
  - replaced the defective 2100F furnace; laid-in new electrical wiring for this furnace
- Completed setup of Materials Synthesis Lab
- Completed setup of Materials at Extreme Environments Lab
- Completed setup of Laser Spectroscopy Lab

Task 1: Equipment Purchase, Installation and Lab. Setup
→ 100% completed

Milestone M.1 (completed)

Technical Accomplishments & Progress

Glasses: best Glass Systems and Glass Chemical Compositions were identified

KS126

KS1212

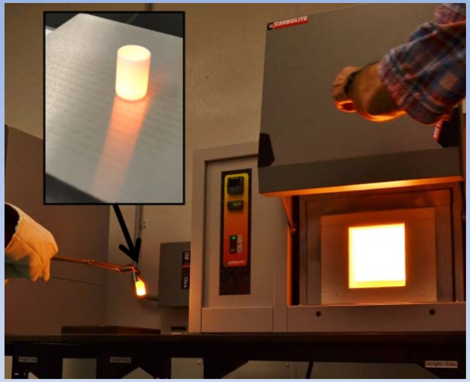
KS168

KS2010

these new glasses add to the pool of previously synthesized (2010-11) based on silica doped by titanium and tantalum.

Synthesized glasses:

- ***glass systems*** based on silica differently doped by IIIB oxides
- different ratio of glass **network formers** to the **network modifiers**
- different glass micro-structures: voids, bridging/non-bridging oxygens
- different glass ability to nucleate nanocrystals
- all glasses are homogeneous, optically transparent, do not have macro-crystalline inclusions

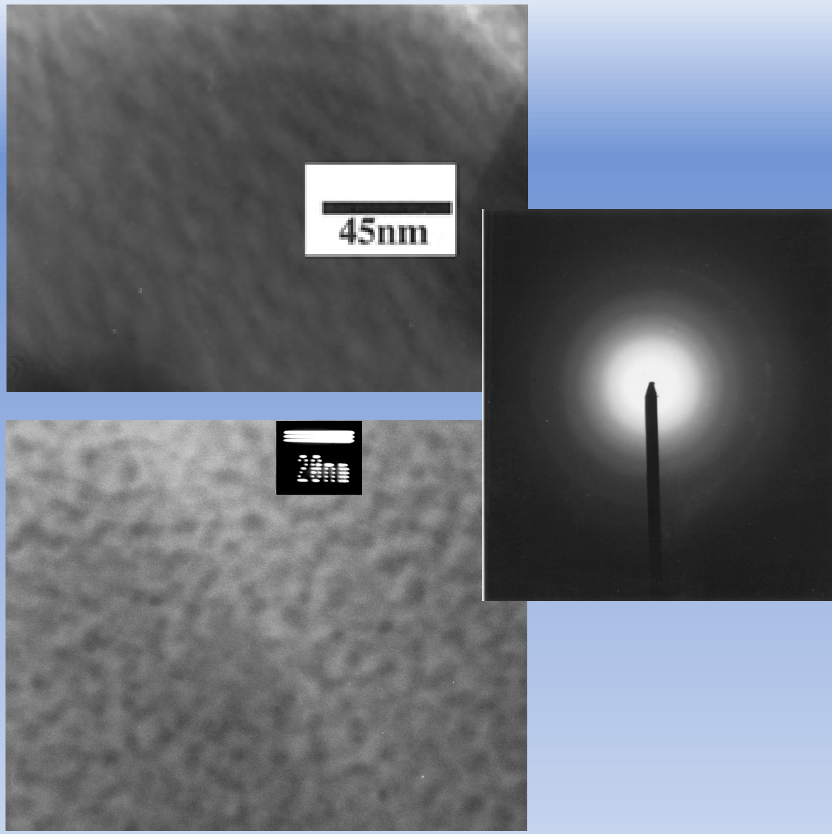


Task 2: Synthesis of Glass Materials → 70% completed

Milestone M.2

Technical Accomplishments & Progress

High Resolution Transmission Electron Microscopy - HRTEM:
best glasses were selected for nanocrystallization study



HRTEM images were collected through wedges of glass fragments, which are transparent to electrons:

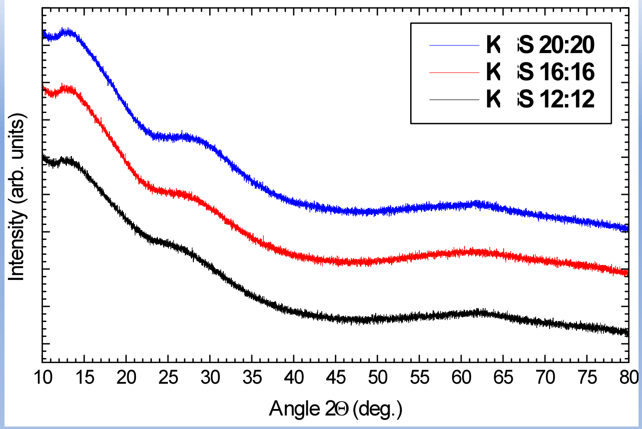
- HRTEM images of as-quenched glasses showed that they are homogeneous
- selected area diffraction (SAD) patterns did not reveal any crystalline reflections

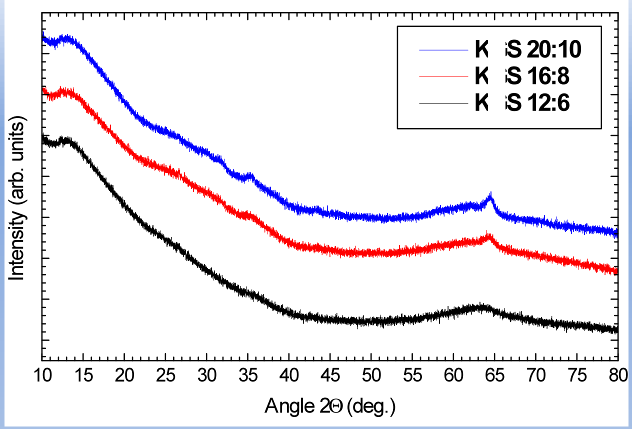
Task 3: Micro-structural and Nano-structural Studies of Glasses
→ 70% completed

Milestone M.3

Technical Accomplishments & Progress

X-Ray Diffraction studies - XRD:
best glasses were selected for nanocrystallization study





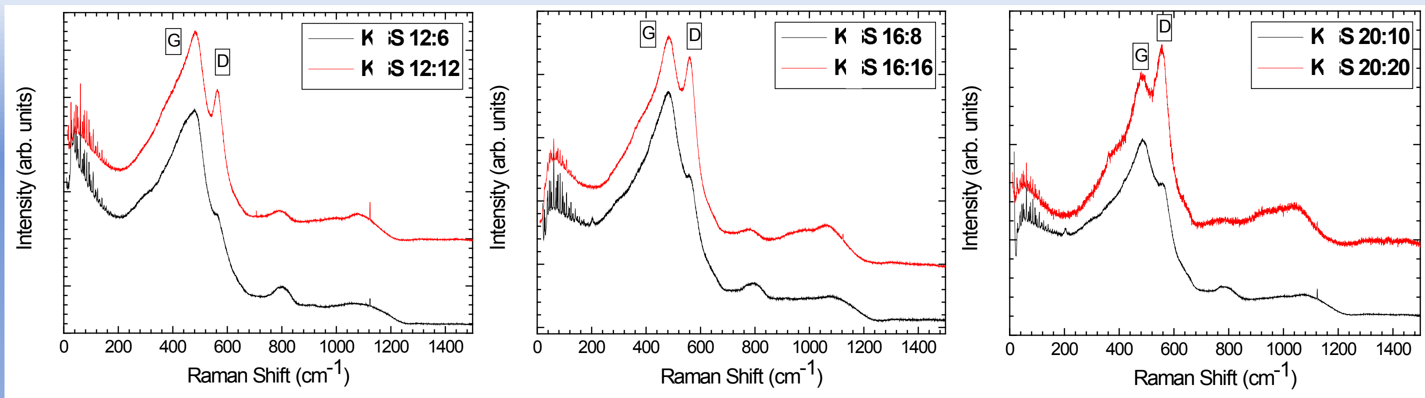
- XRD patterns of glasses with variable ratio of network formers to network modifiers
- glass ***systems*** based on IIIB oxides-doped silica compositions
- very broad bands (20º-70º) are characteristic of glasses
- in few cases, the diffraction patterns indicated early stages of long-range order that could be related to a phase-separation or beginning of nanocrystallization

Task 3: Micro-structural and Nano-structural Studies of Glasses
→ 70% completed

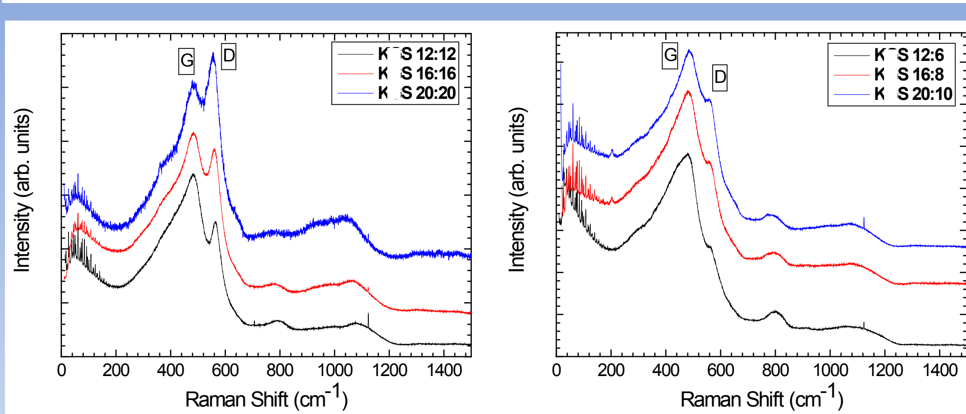
Milestone M.3

Technical Accomplishments & Progress

Raman Scattering Spectroscopy:
glass microstructure can be tuned by ratio of network formers to modifiers



- Raman bands change according to ratios of network formers to network modifiers



- synthesized glasses have different network ordering
- **2012** – what is the local structure of the glass? how are voids influenced?

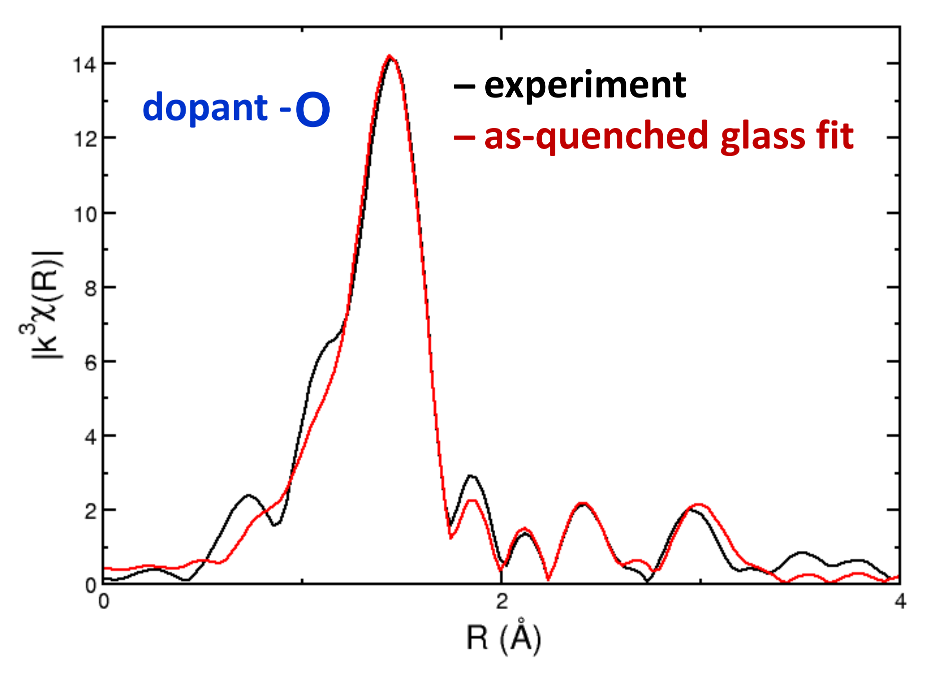
Task 3: Micro-structural and Nano-structural Studies of Glasses
→ 70% completed

Milestone M.3

Technical Accomplishments & Progress

X-Ray Absorption Fine Structure - XAFS:
all glass networks are built of interconnected SiO_4 and dopant tetrahedra

- XAFS experiments at the Advanced Photon Source of Argonne National Lab
- XAFS data fitting: dopant-edge in glass
- dopant near-neighbors are O's at R=1.83 Å, in four-fold coordination (tetrahedra)
- XAFS showed that in all as-quenched glasses dopant atoms are in tetrahedral environment with O's



dopant atoms in tetrahedral environment with O's

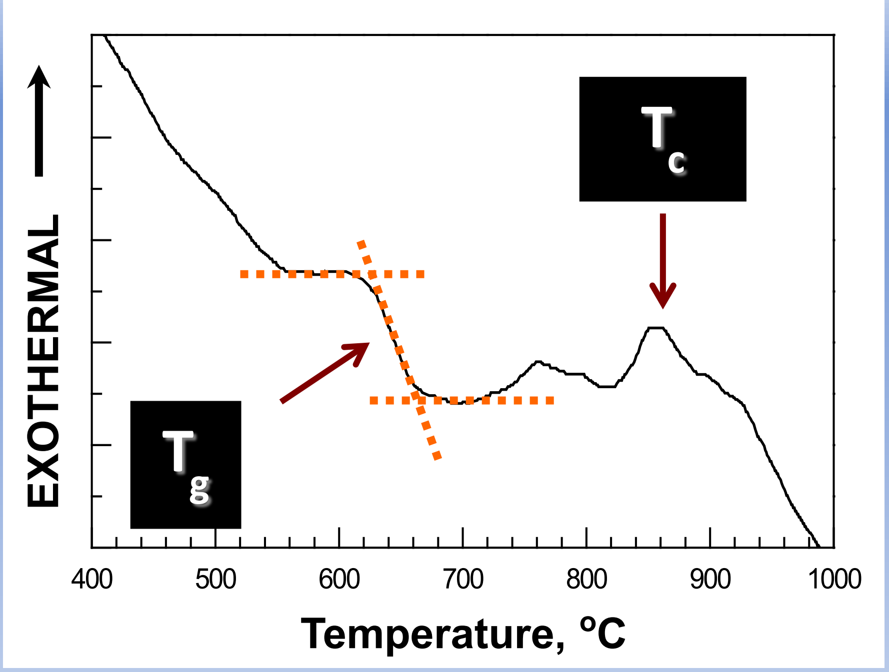
Subtask 3.3: is completed

Task 3: Micro-structural and Nano-structural Studies of Glasses
→ 70% completed

Milestone M.3

Technical Accomplishments & Progress

Differential Thermal Analysis:
glass transformation T can be tuned by concentration of network modifiers.



Glass Sample	Glass Transformation Temperature T_g
KS 126	687 °C
KS 168	680 °C
KS 2010	676 °C
KS 1212	544 °C

- glass transformation T – beginning of nucleation in glass – established for each glass composition
- T_g ranges from ~540°C to ~690°C
- full glass crystallization T is ~200°C higher than T_g for each case
- **2012**: influence of T-treatments on nucleation progress in glass?

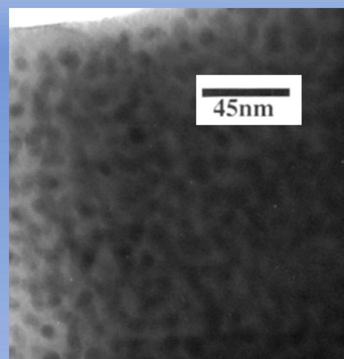
Task 3: Micro-structural and Nano-structural Studies of Glasses
→ 70% completed

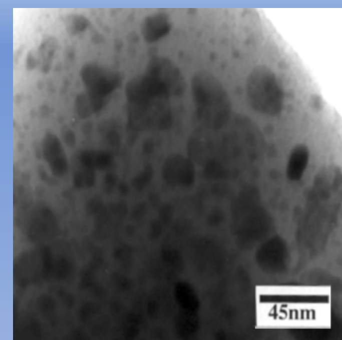
Milestone M.3

Technical Accomplishments & Progress

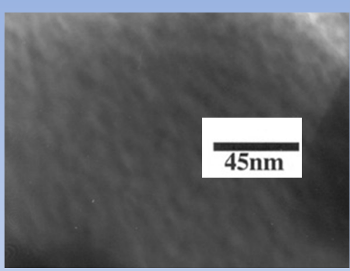
High Resolution Transmission Electron Microscopy - HRTEM:
successful synthesis of few nano-composites with variable size of nanocrystals.
NOTE: there exist only very few glasses compositions capable of nucleating single-phase nanocrystals in their matrices

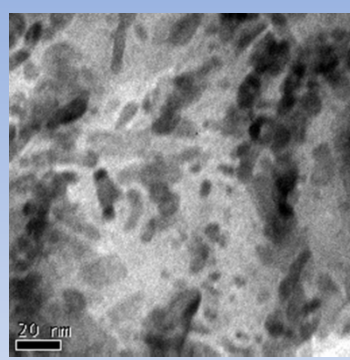
- HRTEM images of an as-quenched glass and of four composites

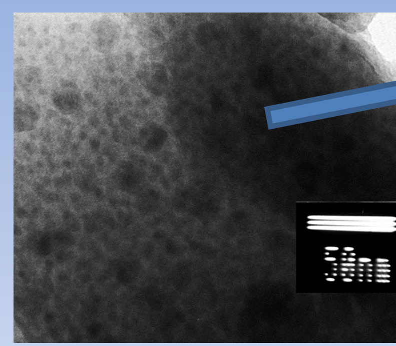


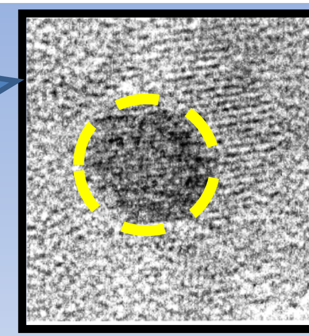


- processing can change: size, shape, density, distribution of nanocrystals
- **2012**: how to promote specific type of nanocrystallization in glass?









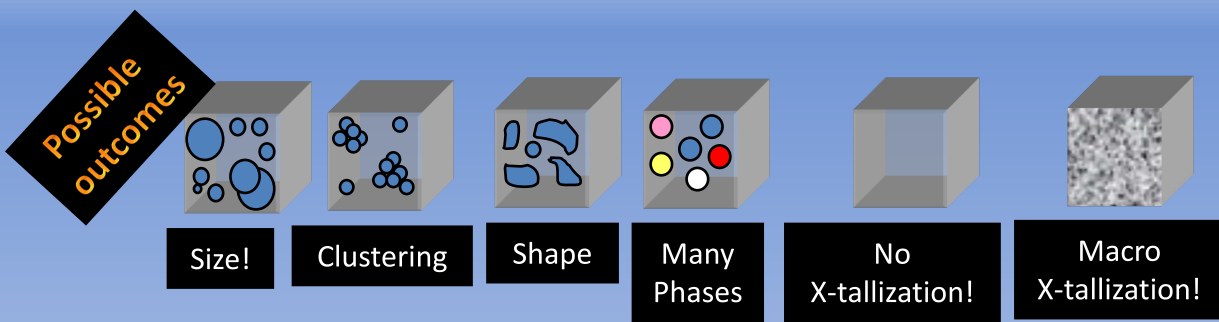
Task 4: Synthesis of Glass-Based Nanocrystalline Composites
→ 50% completed

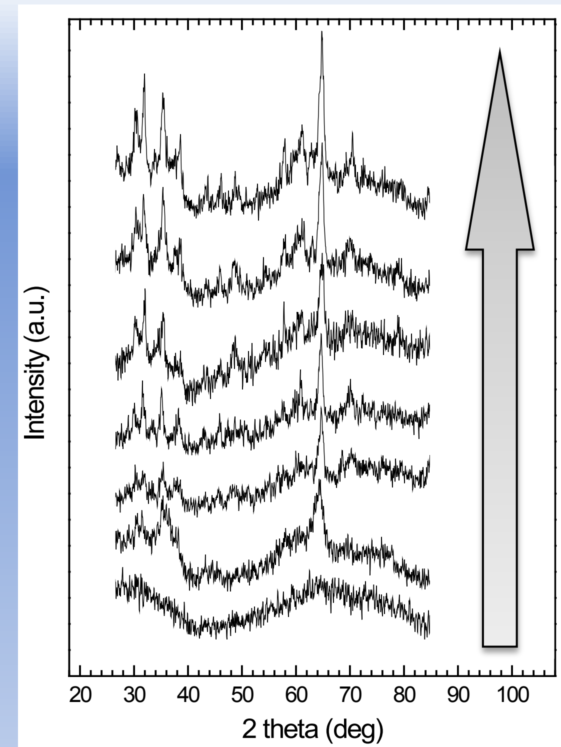
Milestone M.4.1 and M.4.2

Technical Accomplishments & Progress

X-Ray Diffraction studies:
successful synthesis of glass-based composites with variable size of nanocrystals.

NOTE: there exist only very few glasses compositions capable of nucleating single-phase nanocrystals in their matrices





as-quenched glass and few nanocrystalline composites

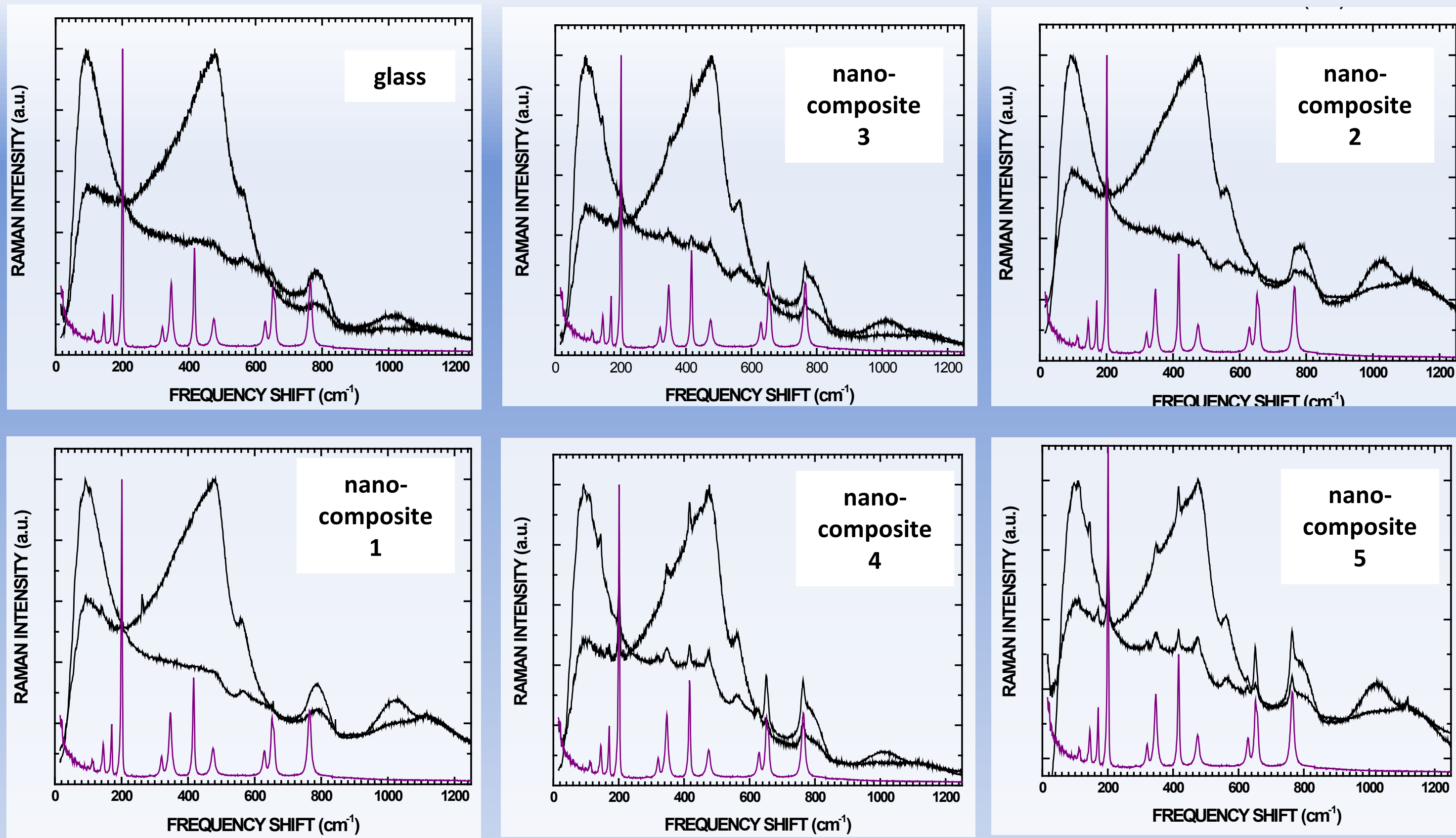
- nanocrystals are of single crystalline phase
- no secondary crystalline phases detected!
- processing conditions can change: size, shape, density, distribution and type of nanocrystals
- **2012**: how to promote specific type of nano-crystallization?

Task 4: Synthesis of Glass-Based Nanocrystalline Composites
→ 50% completed

Milestone M.4.1 and M.4.2

Technical Accomplishments & Progress

Raman Scattering Spectroscopy:
concentration of nanocrystals in glass can be adjusted by processing conditions



- Raman reveals the dual nature of composites = amorphous + nano-crystalline
- VV and HV polarized Raman spectra showing nucleation of nanocrystals
- no secondary crystalline phases detected!

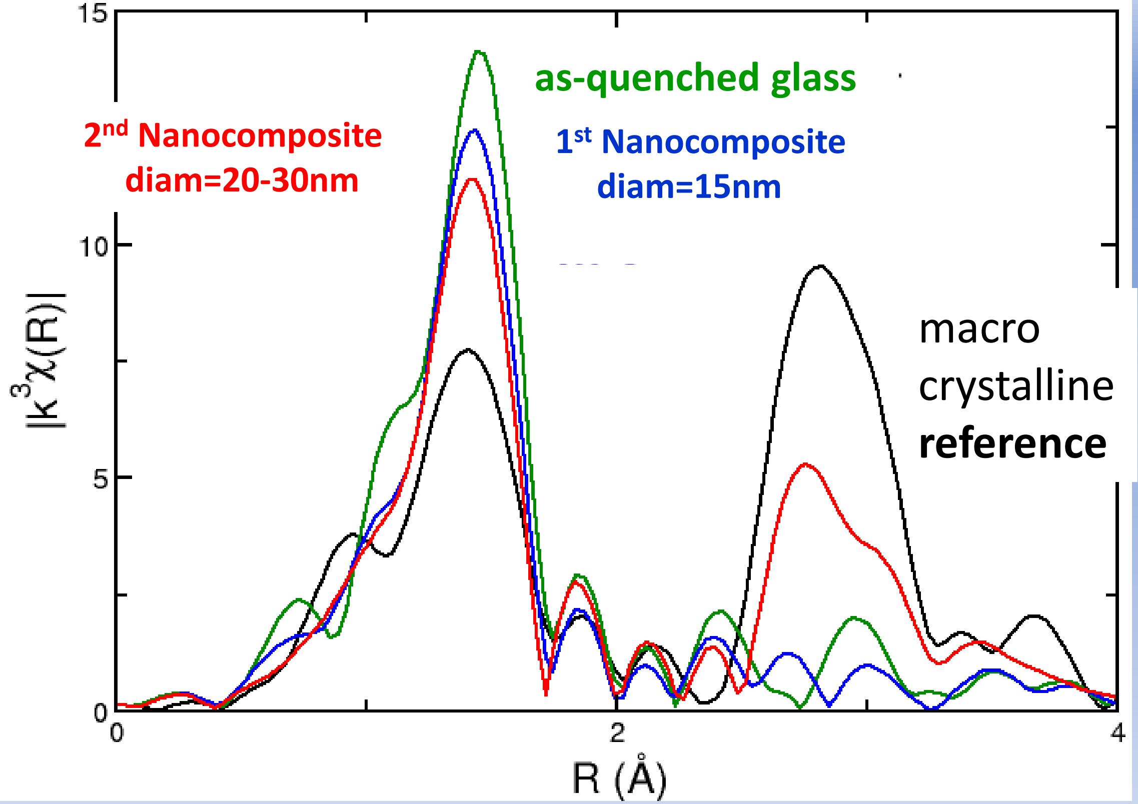
Task 4: Synthesis of Glass-Based Nanocrystalline Composites
→ 50% completed

Milestone M.4.1 and M.4.2

Technical Accomplishments & Progress

X-Ray Absorption Fine Structure - XAFS:
in nanocrystalline composites dopant atoms are shared between glass and nanocrystals

- XAFS done at the Advanced Photon Source of Argonne National Lab
- transition from as-quenched glass to nano-crystalline composite involves change of coordination number of dopant atoms from 4 to 6 as an effect of nanocrystallization process



Subtask 4.3: is completed

Task 4: Synthesis of Glass-Based Nanocrystalline Composites
→ 50% completed

Milestone M.4.1 and M.4.3 (completed)

Collaborations

- **Coe College, Physics Dept. Glass Laboratory**
  - differential thermal analysis of glasses
  - estimation of glass characteristic temperatures

- **ANL and Illinois Institute of Technology**
  - synchrotron X-ray absorption spectroscopy
  - calculation of local structural environment in glasses and composites

- **Purdue University, School of Aeronautics and Astronautics, Hydrogen Systems Lab.**
  - Hydrogen absorption studies: characterization of glasses and glass-nanocrystalline hybrid materials at pressures and temperatures expected for vehicle operation

Proposed Future Work

FY 2012

- complete synthesis and microstructural characterization of glasses; determine the best glass compositions (M.2 and M.3)
- complete synthesis and microstructural characterization of glass-based nanocrystalline composites (M.4.1, M.4.2)

Additional work recommended by reviewers – but outside of the project objectives:

- perform H-sorption measurements at collaborator facility, on selected glass materials
- using Raman spectroscopy study hydrogen interaction with glass: H_2, Si-OH and Si-H vibrational bands
- For further studies, select best glass-based materials as a function of H-sorption measurements and outcome of spectroscopy measurements

Summary

- **Relevance:**
  - answer fundamental questions necessary for considering glass-based materials as H-storage media
- **Approach:**
  - develop glasses and glass-ceramic composites with "functional" nanocrystals capable to interact with hydrogen
- **Technical Accomplishments and Progress**:
  - demonstrated fabrication of glasses and nanocrystalline composites
  - performed multi-techniques microstructural studies
  - demonstrated tunability of size & density of nanocrystals in glass matrices
  - improved UNLV research infrastructure through instrumentation acquisition
  - established 2 new labs and jump-started glass and glass-ceramic composites research on campus
- **Proposed Future Research**:
  - complete materials synthesis and characterization and select the most promising materials further exploration in the H-storage field
  - *as recommended by reviewers*: carry out H_2-sorption studies