CLSI PROPOSAL SUBMISSION

GENERAL USER

Proposal #26-8611
11ID-2 (VLS-PGM)
Sector

Date Created: 2017-02-18
Cycle 26 (July 2017 - December 2017)

Title of Proposal:	Investigation of glass-ceramic composites for nuclear waste immobilization applications
Type of Proposal:	General User
Proposal Duration:	3 cycles (18 months)
Subject of Research	Material and Chemical Sciences
Industrial Partners Involved?	No
Five Key Words	XANES, nuclear waste sequestration, glass, ceramics, composite materials
Funding Sources	
Additional Support?	No

RESEARCH TEAM

First Name	Last Name	Email	Institute/Affil.	Department	Classification	Status
Spokesperson						

INVOICING DETAILS

Name	Address	City	State / Province	Postal / Zip Code	Country

BRIEF DESCRIPTION

summarizes: (1) the importance and goal of the research project; (2) what experiments will be carried out during the requested beam time and (3) how the acquired data will contribute towards achieving the goal explained in (1).

Nuclear energy is considered to be a green technology compared to power facilities that use fossil fuels; however, nuclear waste is produced, which needs to be dealt with. Current strategies for dealing with nuclear waste involve vitrification of the waste or storage of the entire spent fuel bundle. Geologic sequestration is another strategy that is under development and involves incorporating the nuclear waste elements in ordered crystalline structures. Pyrochlore-type oxides (e.g., $Gd_2Ti_2O_7$) and zirconolite-type oxides (e.g., $CaZrTi_2O_7$) have received considerable attention, as these materials can remain crystalline for long periods of time even as the waste elements undergo radioactive decay. The choice of wasteform can be (partially) related to the solubility of the waste elements in the materials. Some fission products (e.g., K) can dissolve in high concentrations in glasses while the solubility of actinides is much lower. It is possible to synthesize glass-ceramic composites where the waste elements are distributed between the glass and the ceramic. Developing direct synthetic methods to form these composites materials (instead of the normal two-step method) will be important to the application of these materials in the nuclear waste management industry. This study will focus on the direct synthesis of these materials, including the optimization of these synthetic methods. The composition, structure, and morphology of these materials will be studied using X-ray diffraction, X-ray absorption spectroscopy, and electron microscopy. One objective of this study is to understand how the local structure of the composites are affected by the synthetic method used to form them through the collection of Si L2,3-, Al L2,3-, and B K-edge XANES spectra.

SOCIETAL AND ECONOMIC IMPACT

Describe how the exploitation of the project results will benefit the Canadian and/or world economy within a reasonable time, as well as any additional economic, social, and/or environmental benefits that will or could be realized in Canada/the world.

A sustainable nuclear power industry plays an important role in providing Canada with a safe and reliable source of electricity. Canada has some of the largest and highest-grade uranium deposits in the world and the mining industry has significant impact on the Canadian economy. Uranium mining has created approximately 5000 jobs in Canada, and, in 2010, uranium exports generated $150 million in tax/royalty revenues for the Province of Saskatchewan. It is important to investigate various strategies to sequester nuclear waste if we are to increase our development and use of nuclear power.

VALUE OF THE RESULTS AND INDUSTRIAL RELEVANCE

Describe the anticipated value of the project results, highlighting the industrial relevance of the scientific or technical advances, or the innovative techniques, processes, or products that will be developed.

The development of materials for the safe sequestration of nuclear waste is important to the advancement of nuclear energy. The objective of this research project is to understand how the method used to synthesis glass-ceramic composite nuclear waste sequestration materials affects their long- and short-range structure. The glass-ceramic materials that will be investigated here are being examined for the sequestration of nuclear waste from UK, Europe, and USA nuclear facilities. The results of this research will be applicable to the nuclear industry as it will provide direct information on the ability to directly synthesize composite materials that can sequester nuclear waste elements for the long term.

SCIENTIFIC MERIT

describes: (1) what is to be studied and the importance of it; (2) what hypothesis would be tested; (3) how the results will impact the field and (4) what is the likelihood of success? Evaluation Criteria

The continued development of nuclear energy as an alternative power source to fossil fuels requires the development of materials to sequester nuclear waste so as to limit the environmental impact of this technology. Multiple strategies are under use or under development to deal with low-, medium-, and high-level nuclear waste, including: water pools, storage casks, vitrification, deep geological storage of spent fuel rods, and incorporating waste elements in crystalline structures [1]. The variety of elements that represent high-level waste from a spent nuclear fuel pellet makes it difficult to incorporate this waste in materials for long-term storage using only one technology. While many atoms can be incorporated in high concentrations in glasses for containment, larger elements (e.g., U, Pu, Cs) have a lower solubility in glasses and may require the use of other materials to sequester them [1,2]. Crystalline materials like those adopting the pyrochlore-type structure (e.g., Gd2Ti2O7) have been studied for the sequestration of actinide elements as they can substitute for Gd on the 8-coordinate site in this structure [1]. Other oxide structures have also been examined for this application. For example, hollandite (BaAl2Ti6O16) has been investigated for the sequestration of Cs as this element can substitute for Ba in the structure [3]. Spent nuclear fuel pellets contain a range of radiotoxic elements that need to be stored for the long-term. Separation of these elements for the incorporation in different materials can be a costly endeavour. The objective of this research proposal is to develop direct synthetic strategies to form glass-ceramic composite materials [4-6].

Glasses are an important class of materials that can have a wide range of compositions and many applications. For example, the addition of ceria (CeO2) can limit the ability of UV rays to penetrate through window glass and glasses containing hafnium oxide (HfO2) have been proposed for use as gate dielectrics in the next generation of computer chips. Further, composite materials containing ceramic crystallites dispersed in a glass matrix have been proposed for the immobilization of nuclear waste. This project will focus on studying glass-ceramic composite materials containing brannerite- (e.g., CeTi2O6), zirconolite- (e.g., CaZrTi2O7), and pyrochlore- (e.g., Gd2Ti2O7) phase crystallites dispersed in a borosilicate glass matrix. These (or similar) composite materials have been produced previously by combining the already formed crystalline oxide species and glasses followed by heating to form a composite; however, these composites have not been formed from the direct reaction of the binary oxide constituents that make up these materials, and this will be the focus of this investigation. Developing direct synthetic methods to form these composites materials (instead of the normal two-step method) will be important to the application of these materials in the nuclear waste management industry. This study will focus on the direct synthesis of these materials, including the optimization of these synthetic methods. The composition, structure, and morphology of these materials will be studied using X-ray diffraction, X-ray absorption spectroscopy, and electron microscopy. The primary objective of the beamtime applied for here is to understand how the local structural environment of Si, Al, and B changes depending on the composition and the method used to synthesize the composite materials using X-ray absorption near-edge spectroscopy (XANES). The glass matrix is amorphous, and because of this, it is necessary to use XANES to investigate the local change in the structure, as this information cannot be easily determined by diffraction-based techniques [7]. Si L2,3-, Al L2-3-, and B K-edge XANES spectra from the composite materials will be collected during this study using the VLS PGM beamline. The spectra that will be collected are very sensitive to changes in the local structure of these atoms and will provide important information on how the structure of these materials is affected by changes in composition and synthetic method [8,9]. Along with the spectra to be collected using the VLS PGM beamline, Ti K-edge XANES spectra will also be collected using the SXRMB beamline at the CLS or the 20BM beamline at the APS to study how the local structure of Ti in these composite materials.

REFERENCES:

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EXPERIMENT PROCEDURE

describes sample procedures and explains the basis for the estimate of the amount of beam time needed as well as who will perform the measurements and how the data will be analyzed.

Glass-ceramic composites will be made by combining different amounts of SiO2, B2O3, Na2O, CaCO3, MgO, Fe2O3, Al2O3, Gd2O3, TiO2, ZrO2, CeO2 followed by heating at temperatures ranging from 1300 C to 700 C. A co-precipitation method involving the digestion of oxides and nitrates in nitric acid followed by precipitation by the addition of excess amounts of ammonium hydroxide will also be used. The long-range structures of all materials are being studied by powder X-ray diffraction and the distribution of the pyrochlore grains in the glass matrix is being studied by electron microprobe imaging. The synthesized materials will be mounted on double sided carbon tape and loaded into the vacuum chamber of the VLS PGM X-ray absorption endstation. Si L2,3-, Al L2,3-, and B K-edge XANES spectra will be collected from these materials to determine how the composition and synthesis method affects the local structure of these materials. Standard spectra from materials having Si, Al, and B in different coordination environments will be collected to aid interpretation of the spectra from the as-synthesized and ion implanted glass-ceramic composites. All spectra will be analysed using the Athena software program.

It is anticipated that as many as 20 glass-ceramic composite materials (and 6 standards) will be studied with ~90 Al L2,3-, Si L2,3-, and B K-edge spectra being collected in total. Previous experience by this research group using the VLS PGM beamline to collect XANES spectra suggests that 1.5 hours will be required to collect each spectrum. As such, we estimate that we will require 135 hours to collect the spectra along with time to load the samples into the absorption chamber. We request 19 shifts over three cycles to complete the experiments described in this proposal.

SUITABILITY

identifies (1) why a third generation synchrotron such as the CLS and the particular beamline/endstation is more suitable than others; (2) comments on whether complementary measurements will be made and (3) justifies the amount of beamtime requested in terms of the required development and number of samples. Evaluation Criteria

The focus of this proposal is a study of how the structure of glass-ceramic composites changes depending on the glass:ceramic ratio, the type of glass, and the method used to synthesize these materials. This experiment requires a local probe (e.g., XANES) to examine the coordination environment of the atoms that make up the glass. Si L2,3-, Al L2,3-, and B K-edge XANES spectra will be collected during this study. The VLS PGM beamline is the only beamline at the CLS that can be used to collect these spectra. It is anticipated that a total of 90 XANES spectra will be collected from ~26 glass-ceramic composite and standard materials. A total of 19 shifts over three cycles will be required to complete this project with each spectrum taking ~1.5 hours to collect.

PAST PRODUCTIVITY - Evaluation Criteria

a) Briefly discuss results from previous shifts received at CLS. The table below identifies shifts received in the past two years if you were the spokesperson.
b) New User to CLS - comment on your research team's recent synchrotron experience and evidence of capability. If you have no synchrotron experience, give evidence of productivity in other fields.

Access Mechanism	Cycle 23	Cycle 24	Cycle 25	Cycle 26
General User	9	15	6	0
Special Requests	0	6	0	0
Total Shifts	9	21	6	0

a) Our recent studies that have been performed with the use of the VLS PGM beamline have focussed on studying the local structure of glass and ceramic materials proposed for the sequestration of nuclear waste. In the first study, composite materials formed using two step synthetic process were studied to understand how the local structure of Si and Al ions in these materials were affected by composition (weight % loading of ceramic and glass) and annealing temperature used to form the materials. A manuscript that describes this study was recently accepted for publication in the Canadian Journal of Chemistry (E. Paknahad, A. P. Grosvenor, Can. J. Chem., 2017, accepted). In the second study performed during the last cycle, we used the VLS PGM beamline to understand how the local structure of rare-earth phosphate materials changes after exposure to water for extended periods of time. The solubility of potential nuclear waste forms needs to be studied so as to determine how the material would behave during long-term storage if there was a containment breach and the materials were exposed to water. This study is now complete and a thesis chapter (and manuscript) that describes the results of this study is currently being prepared.

b) n/a

BEAMLINE REQUIREMENTS

Beamline:	11ID-2 (VLS-PGM)

Preferred Beamline:	
CLS Staff Contacted:	Lucia Zuin
Endstation:	Absorption Chamber
Technique:	X-ray Absorption Spectroscopy (XAS)
Wavelength / Energy Range:	40 - 180 eV
Spotsize on Sample:	1x1 mm
Energy Resolution:	10000 E/deltaE

SCHEDULING REQUIREMENTS	
Total # shifts for entire proposal:	19

Specific scheduling requirements:	As we are located at the U of S, we would prefer to have beamtime allocated in 3-4 shift blocks so that we may optimize our experimental methods between beamtime.
Preferred dates (current cycle)	2017-10-22 to 2017-12-31 2017-07-01 to 2017-08-05
Unacceptable dates (current cycle)	2017-08-13 to 2017-09-05

SAFETY AND MATERIALS

LOW RISK

A. BIOLOGICAL SECTION

1) Does this research involve living human participants, human biological materials derived from living or deceased individuals, or cell lines?	No
2) Does this research use animal tissue or biological fluids from animals?	No
3) Does this research involve live animals?	No
4) Does your work involve Genetically Modified Organisms/Microorganisms or Transgenic Organisms?	No
5) Are you bringing/using any other biological materials?	No

B. CHEMICAL SECTION

1) Are you bringing/using any nanomaterials?	No
2) Are you bringing/using pesticides?	No
3) Are you bringing/using any other hazardous chemical materials?	No

C. RADIOACTIVE SECTION

1) Are you bringing/using anything radioactive?	No

D. NON-HAZARDOUS SECTION

1) Are you bringing/using any non-hazardous samples/standards/materials? Yes

Name	State	Quantity per item (include unit)	Total # of items
Ca/B/Mg/Si/Al/Fe-glass	solid	50 mg	5
CaZrTi2O7-Ca/B/Mg/Si/Al/Fe-glass	solid	50 mg	5
Gd2Ti2O7-Ca/B/Mg/Si/Al/Fe-glass	solid	50 mg	5
CeTi2O6-Ca/B/Mg/Si/Al/Fe-glass	solid	50 mg	5
B2O3	solid	50 mg	1
Al2O3	solid	50 mg	1
SiO2	solid	50 mg	1

a) Will any sample preparation with non-hazardous items, that has not already been disclosed, be performed while at the CLS?* Yes

b) Briefly describe the sample preparation procedure:

Materials to be studied will be powders or pellets. The powders or pellets will be attached to the PGM sample holder using double-sided carbon tape. Latex gloves will be worn when preparing the samples.

You have indicated that you will not be bringing any heavy atom solutions or other hazardous/biohazardous substances to CLS.

EQUIPMENT	
Are you bringing any equipment to the CLS to assist you with this experiment?	No