SYNTHETIC RESEARCH REPORT 2019

Report on project achievement in the period January-December 2019

Stage 2: Obtaining and characterization of $4PbO-B_2O_3$ glasses and vitroceramics co-doped with samarium and terbium ions

The objectives of the stage

1. The synthesis of lead-borate glasses and vitroceramics based on **$4PbO-B_2O_3$** co-doped with samarium and terbiu ions (*products PbB-Wastes*) by melt quenching method;
2. Investigation of structural, spectroscopic, optical and magnetic properties of obtained products;

Expected results to achieve the phase objectives:

- Lead-borate glasses and vitroceramics in vitrous system with composition **$xSm_2O_3\cdot(100-x)[4PbO\cdot B_2O_3]$**, where x=0-40 mol % Sm_2O_3, respectively **$xTb_4O_7\cdot(100-x)[4PbO\cdot B_2O_3]$**, where x=0-25 mol % Tb_4O_7;
- Structural characterization of glasses and vitroceramics by X-ray diffraction (**XRD**), Fourier Transform Infrared spectroscopy (**FTIR**) , **Raman** spectroscopy, Photoluminescence (**PL**), Ultraviolet-Visible spectroscopy (**UV-Vis**), Electron Spin Resonance spectroscopy (**ESR**) and X-ray absorption spectroscopy (**XAS**) (with chinese parteners).

Contents of the scientific and technical report (RST)

Summary of the phase

At the moment, vitrification is the preferred solution for the low, medium and high level of waste, because their radioactive emissions are reduced. On the other hand, the development of new materials and their use as materials with optical or luminescent properties, is a component of the management of industrial ecology.

The goal of the phase consists of: **a) the synthesis** by melt quenching method of two vitrous sistems with composition **$xSm_2O_3{\cdot}(100-x)[4PbO{\cdot}B_2O_3]$**, where x=0-40 mol % Sm_2O_3, respectively **$xTb_4O_7{\cdot}(100-x)[4PbO{\cdot}B_2O_3]$**, where x=0-25 mol % Tb_4O_7; **b) structural characterisation** of obtained samples by: XRD, FTIR, Raman, PL, UV-Vis, ESR and XAS spectroscopy (with chinese parteners) in order **to test** their **capacity to immobilize radioactive waste** and **revaluate the obtained products** for **technological applications.**

X-ray diffraction analysis revealed the amorphous nature of the samples, containing up to x=10 mol % of Sm_2O_3, respectively x= 1 mol % of Tb_4O_7. In vitroceramics samples, for higher dopant concentrations than previously mentioned, the presence of orthoborate crystalline phases of rare earth ions ($SmBO_3$ și $TbBO_3$) and crystalline phases PbO_2 with ortorombic structure was detected.

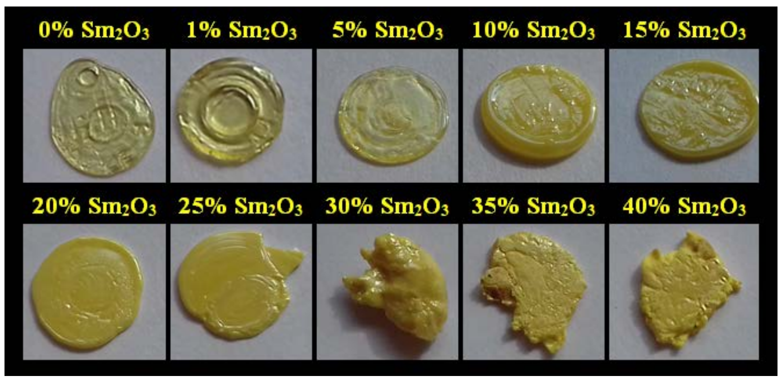
The **FTIR** and **Raman** data analysis indicates some important structural changes that occur in the **$4PbO{\cdot}B_2O_3$** host matrix by introduction a high content of rare earth oxide, namely: structural unit conversions [BO_4] into [BO_3] triangle units and formation of [PbO_4] structural units.

The **XANES** data results indicate that the lead atom is found in several oxidation states. The **EXAFS** data analysis indicates that the sample with x = 0 and 5 mol % of Sm_2O_3 are the most ordered around the lead atom which is tetracoordinated with oxygen and have a local structure similar to that

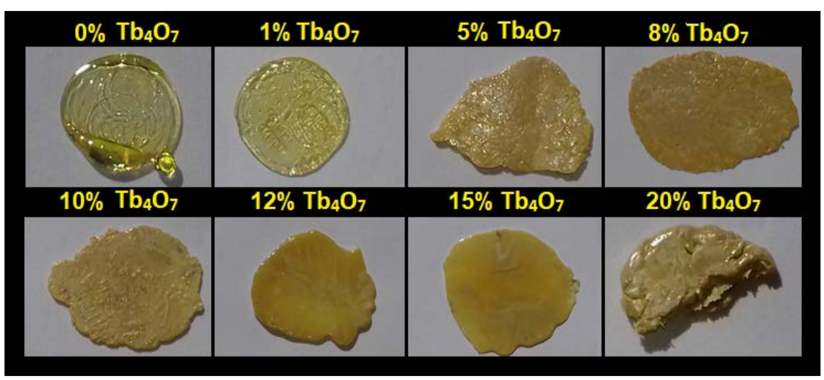
of lead dioxide. By increasing the dopant level the disorder increases around the lead atom and the excess oxygen causes the creation of BO_3^{-3} free orthoborous units that will lead to the formation of the $SmBO_3$ crystalline phase.

ESR data reveal the resonance lines characteristic of Sm^{3+} and Tb^{4+} ions. The intensity of the resonance lines changes with the dopant level. This evolution can be explained by the fact that by doping there is a tendency to convert Sm^{3+} ions into Sm^{2+} ions, respectively Tb^{3+} ions in Tb^{4+} ions.

The **UV-Vis** and **PL** spectra indicate the characteristic f-f transitions of rare earth ions and demonstrate the aplications of these materials in the field of optical devices: lasers, LEDs, diodes or efficient display devices.



$xSm_2O_3\cdot(100-x)[4PbO\cdot B_2O_3]$, where x=0-40 mol % Sm_2O_3



$xTb_4O_7\cdot(100-x)[4PbO\cdot B_2O_3]$, where x=0-20 mol % Tb_4O_7

Conclusions and proporsals for the future research directions of the project

New lead-borate materials doped with samarium and terbium ions: **$xSm_2O_3\cdot(100-x)[4PbO\cdot B_2O_3]$** where $0\leq x\leq 40$ mol % Sm_2O_3 and **$xTb_4O_7\cdot(100-x)[4PbO\cdot B_2O_3]$** where $0\leq x\leq 25$ mol % Tb_4O_7 were obtained by the melting and quenching method at **low temperature** as an alternative to immobilization of radioactive waste.

For the vitreous system with **$4PbO{\cdot}B_2O_3$** doped with **samarium ions**, **X-ray diffraction** analysis indicated the amorphous nature of the samples to a content of 10 mol % of samarium oxide. For the samples with x≥20 mol % of Sm_2O_3, the presence of orthoborate crystalline phases of $SmBO_3$ and crystalline phases PbO_2 with ortorombic structure was detected. X-ray diffractograms for the **$xTb_4O_7{\cdot}(100-x)[4PbO{\cdot}B_2O_3]$** system revealed the amorphous nature of the samples for x≤1 mol % terbium oxide, and in the vitroceramics was detected the crystalline phase $TbBO_3$ and crystalline phases PbO_2 with ortorombic structure was detected.

The analysis of **FTIR** and **Raman** data indicates that accommodating the host matrix with excess rare earth oxide is possible by deforming the Pb-O-Pb or O-Pb-O angles, converting the structural units [BO_4] into [BO_3] and forming free ortoborate structural units BO_3^{-3}.

Structural investigations by **UV-Vis spectroscopy** indicate the presence of f-f electron transitions of the Sm^{3+} and Tb^{3+} ions. Optical gap energy values are dependent on the concentration of rare earth oxide as dopant.

For $xSm_2O_3{\cdot}(100-x)[4PbO{\cdot}B_2O_3]$ system, the intensity of **the photoluminescence** bands does not change significantly with the increase of the Sm^{3+} ions concentration. In the case of lead-borate system doped with terbium, the PL spectra show the existence of emission bands associated with the $4f^8 \rightarrow 4f^8$ transitions from $^5D_3$ to $^7F_{4,5}$. The increase in the terbium ion concentration does not involve major changes in the intensity of the photoluminescence bands.

XAS data analysis indicates that by doping with high levels of samarium trioxide, the lead atom is found in several oxidation states and the local disorder around the lead atom increases because the Pb-O interatomic distance in the first coordination sphere increases.

ESR data indicates resonance lines characteristic of Sm^{3+} and Tb^{4+} ions. By increasing the level of dopant, the resonance line corresponding to the Sm^{3+} ions decreases what indicates the conversion of $Sm^{3+} \rightarrow Sm^{2+}$ ions. The intensity of the resonance signal attributed to the Tb^{4+} ion increases by doping, indicating the conversion of ions $Tb^{4+} \rightarrow Tb^{3+}$.

Glasses and vitroceramics studied are good hosts for **incorporating radioactive waste** due to **the low processing temperature** (700 ° C) and "**imitation**" of actinide behavior, simplifying working conditions in research projects. Therefore, at this stage of implementation of the project, the following were achieved: a) the ability to contain up to 10 mol % of Sm_2O_3 and 1 mol % of Tb_4O_7 in a matrix based on **$4PbO{\cdot}B_2O_3$** was demonstrated; b) the spectroscopic properties of obtained samples for their testing to immobilize the radioactive waste were investigated; c) photoluminescence properties demonstrate the value of products obtained for applications in optical devices such as high density optical storage, color displays, lasers, LEDs, diodes or efficient display devices.

As **future directions of research**, for the final storage of glasses doped with rare earth ions, the durability tests and the mechanical properties of the obtained products are required. In this regard, in the final stage of the project, investigations will be carried out by DTA / TG analysis to determine the crystalline phases that can occur by increasing the final storage temperature up to 300^{o}C and hardness tests using **Digital MicroVickers Hardness Tester - NOVA 130**, purchased in the framework of this postdoctoral research project (www.itim-cj.ro/PNCDI/pd33/index.htm) to determine the fragility of the samples.

The comparative analysis of the obtained systems will be followed:

$xSm_2O_3{\cdot}(100\text{-}x)[4PbO{\cdot}B_2O_3]$, x=0-40 % moli Sm_2O_3

$xSm_2O_3{\cdot}(100\text{-}x)[4B_2O_3{\cdot}PbO]$, x=0-40 % moli Sm_2O_3

$xTb_4O_7{\cdot}(100\text{-}x)[4PbO{\cdot}B_2O_3]$, x=0-25 % moli Tb_4O_7

$xTb_4O_7{\cdot}(100\text{-}x)[4B_2O_3{\cdot}PbO]$, x=0-20 % moli Tb_4O_7

in order **to develop a theoretical model** for **the immobilization of radioactive waste** simulated in glass and vitroceramics. Also, a card with the characteristics of the most suitable matrix based on lead-boron trioxide which will immobilize radioactive waste will be realized.

Possibilities to capitalize on the obtained results

1. The production of **lead-borate** glasses and vitroceramics doped with **samarium** and **terbium** ions for **incorporating radioactive waste** has the following advantages:

a) low processing temperature (700 ° C), lower than the synthesis temperature of phosphate glasses

b) short processing time (10 minutes)

c) the solubility of glass waste (up to 10 mol % of Sm_2O_3 and 1 mol % of Tb_4O_7)

d) The obtained products have practical applications on optical devices (lasers, LEDs, diodes or efficient display devices)

2. The realization of the WEB of the project will open new opportunities for new research projects.

3. The acquisition from this project of equipment for measuring hardness by indentation of type NOVA 130 will allow the successful achievement of the objectives of the last stage of the present project, contributes to the increase of the degree of expertise in the field and has allowed the recent gain of a new project of mobility type MC with no. 2058/2019 with the title "***Microstructure and mechanical properties of zirconia-based ceramics stabilized with other oxides***", project manager CSI. Abil. Dr. **Rada Simona**.

Dissemination of the results obtained during this phase was done by:

1) **Project website** (www.itim-cj.ro/PNCDI/pd33/index.htm)
2) **CD** with the curent stage of knowledge in the field
3) **ISI articles: 1** (published): Adriana Dehelean, Adriana Popa, Simona Rada, Ramona Crina Suciu, Manuela Stan, Eugen Culea. *Spectroscopic investigation of new manganese tellurite glasses synthesized by sol-gel method***. Journal of Alloys and Compounds** 801 **(2019)** 181-187

   and **2 (**send for publication)

   A. Dehelean, S. Rada, C. Grosan, A. Popa, J. Zhang. *Peculiarities of local structure of the samarium ions in lead borate glasses and vitroceramics*

   A. Dehelean, S. Rada, M. Zagrai, C. Molnar. *Concentration dependent spectroscopic behavior of terbium ions doped lead-borate glasses and vitroceramics*
4) **Brevet**: 1 (in preparation): Procedeu de preparare, înglobare a deșeurilor radioactive in sticle pe baza de PbO-B_2O_3 si aplicarea lor ca materiale luminescente
5) Papers presented at **international conferences**:
   1. Adriana DEHELEAN, Simona RADA, Mioara ZAGRAI, Adriana POPA and Ramona SUCIU. **Spectroscopic studies of samarium ions in lead borate glass-ceramics.** *19th International Balkan Workshop on Applied Physics and Materials Science, Constanta, Romania 16-19 July 2019*. Book of abstracts. 19th International Balkan Workshop on Applied Physics. Issue 19/2019. Pag. 58-59.
   2. Adriana DEHELEAN, Simona RADA, Mioara ZAGRAI, Ramona SUCIU and Sergiu MACAVEI. **Influence of samarium ions concentration on structural and optical properties of lead borate glasses and vitroceramics.** *19th International Balkan Workshop on Applied Physics and Materials Science, Constanta, Romania, 16-19 July 2019*. Book of abstracts. 19th International Balkan Workshop on Applied Physics. Issue 19/2019. Pag. 59-60.
   3. Adriana DEHELEAN, Simona RADA, Ramona SUCIU, Mioara ZAGRAI and Sergiu MACAVEI. **XRD, UV-Vis and photoluminescence studies of terbium ions doped 4PbO-B_2O_3 glasses and**

vitroceramics. *21st Romanian International Conference on Chemistry and Chemical Engineering, Constanta-Mamaia, Romania, September 4-7, 2019.* Poster No. S6_216.

4. Adriana DEHELEAN, Simona RADA, Mioara ZAGRAI, Camelia GROSAN Adriana POPA. **Influence of samarium ions on structural properties of lead-borate glasses and vitroceramics.** *21st Romanian International Conference on Chemistry and Chemical Engineering, Constanta-Mamaia, Romania, September 4-7, 2019.* Poster No. S6_211.

Data	Director de proiect
28.11.2018	Cercetător științific II Augusta-Adriana Dehelean