SYNTHETIC RESEARCH REPORT 2018

Report on project achievement in the period May 2st 2018-December 31st 2018

Stage 1: Obtaining and characterization of $4B_2O_3$-PbO 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 **$4B_2O_3$-PbO** 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 $xSm_2O_3 \cdot (100-x)[4B_2O_3 \cdot PbO]$, where x=0-40 mol % Sm_2O_3, respectively $xTb_4O_7 \cdot (100-x)[4B_2O_3 \cdot PbO]$, where x=0-20 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**) and Electron Spin Resonance spectroscopy (**ESR**).

Contents of the scientific and technical report (RST)

1. **The preparation of lead-borate vitreous systems with composition $4B_2O_3 \cdot PbO$ co-doped with samarium and terbium ions**
2. **Glasses and vitroceramics in the composition $4B_2O_3 \cdot PbO$ doped with samarium ions**
   - 2.1. **X-ray diffraction** analysis
   - 2.2. Structural investigation by Fourier Transform Infrared Spectroscopy (**FTIR**) and **Raman** Spectroscopy
   - 2.3. Structural investigation by Ultraviolet-Visible spectroscopy (**UV-Vis**)
   - 2.4. Optical band gap energy (**E_g**)
   - 2.5. Structural investigation by Photoluminescence (**PL**). CIE chromaticity diagram.
   - 2.6. Structural investigation by Electron Spin Resonance spectroscopy (**ESR**)
3. **Glasses and vitroceramics in the composition $4B_2O_3 \cdot PbO$ doped with terbium ions**
   - 3.1. **X-ray diffraction** analysis

3.2. Structural investigation by Fourier Transform Infrared Spectroscopy (**FTIR**) and **Raman** Spectroscopy
3.3. Structural investigation by Ultraviolet-Visible spectroscopy (**UV-Vis**)
3.4. Optical band gap energy (**E_g**)
3.5. Structural investigation by Photoluminescence (**PL**). CIE chromaticy diagram.
3.6. Structural investigation by Electron Spin Resonance spectroscopy (**ESR**)

Summary of the phase

In recent years, there has been an increased interest in the immobilization of radioactive wastes by the vitrification process, because it reduces radioactive waste emissions and has the advantage of reducing waste reactivity. Vitrified wastes is very durable, highly stable and incorporates a wide variety of contaminants. Beside this, glasses and vitroceramcs co-doped with rare earth attract attention dur to optical, electrical and magnetic properties, giving them important technological applications in fields, such as laser technology, telecommunication, optical fibers, etc.

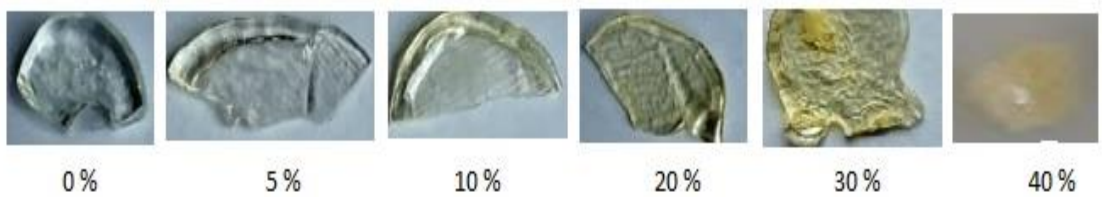
The goal of the phase consists of: **a) the synthesis** by melt quenching method of two vitrous sistems with composition **$xSm_2O_3 \cdot (100-x)[4B_2O_3 \cdot PbO]$,** where x=0-40 mol % Sm_2O_3 , respectively **$xTb_4O_7 \cdot (100-x)[4B_2O_3 \cdot PbO]$,** where x=0-20 mol % Tb_4O_7; **b) structural characterisation** of obtained samples by: XRD, FTIR, Raman, PL, UV-Vis and ESR spectroscopy 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=30 mol % of Sm_2O_3, respectively x= 8 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 was detected.

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

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 and TV screens due to green-yellow emission.



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

xTb_4O_7·(100-x)[4B_2O_3·PbO], 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·(100-x) [4B_2O_3·PbO] where $0 \leq x \leq 40$ mol % Sm_2O_3 and xTb_4O_7·(100-x) [4B_2O_3·PbO] where $0 \leq x \leq 20$ mol % Tb_4O_7 were obtained by the melting and quenching method as an alternative to immobilization of radioactive waste.

For the vitreous system with 4B_2O_3·PbO doped with samarium ions, **X-ray diffraction** analysis indicated the amorphous nature of the samples to a content of 30 mol % of samarium oxide. For the sample with x = 40 mol % of Sm_2O_3, a ceramic glass containing the $Sm(BO_3)_3$ crystalline phase was obtained. X-ray diffractograms for the xTb_4O_7·(100-x) [4B_2O_3·PbO] system revealed the amorphous nature of the samples for $x \leq 8$ mol % tertium oxide, and the higher crystalline phase in the vitro ceramic was detected with the crystalline $TbBO_3$ phase.

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 structural units [PbO_4]. These structural developments lead to the formation of orthobored crystalline phases of rare earth ion for high dopant levels.

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.

The intensity of **the photoluminescence** bands increases with the increase of the Sm^{3+} ions concentration, at low samarium oxide levels there is a luminescence extinction effect. 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 $^5D_3$ and $^5D_4$ to ^7F_J multiplexes. The increase in the terbium ion concentration does not involve major changes in the intensity of the photoluminescence bands.

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 glass ceramics are good hosts for **incorporating radioactive waste** due to **the low processing temperature** (1000 ° C) and "**imitation**" of actinide behavior, simplifying working conditions in research projects. Radioactive waste disposal technology requires the storage of waste as much as possible. Therefore, at this stage of implementation of the project, the following were achieved: a) the ability to contain up to 40 mol % of Sm_2O_3 and 8 mol % of Tb_4O_7 in a matrix based on **$4B_2O_3 \cdot PbO$** 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, optical fibers, etc.

As **future research directions**, we propose detailed characterization of the products obtained for their long-term storage - in this sense, **the hardness and chemical stability tests** will be carried out at **temperatures up to 300 °C as well as tests to monitor absorption capacity the water**.

For the purpose of comparative analysis, glasses and glass ceramics with $4PbO \cdot B_2O_3$ doped with samarium and terbium ions will be obtained and will be characterized in terms of their structural, optical and magnetic properties.

Possibilities to capitalize on the obtained results

1. The production of glasses and glass ceramics doped with samarium and terbium ion for incorporating radioactive waste has the following advantages:

a) low processing temperature (1000 ° C) similar to phosphate glasses

b) short processing time (10 minutes)

c) high solubility of glass waste (up to 30 mol % of Sm_2O_3 and 8 mol % of Tb_4O_7)

d) The obtained products have practical applications on optical devices (LEDs, color displays, lasers, optical fibers, etc.)

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

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) Papers presented at **national** and **international conferences**:

1. Adriana DEHELEAN, Simona RADA, Marius RADA, Ramona SUCIU. **The change of the local environment of samarium ions in lead-borate glasses and vitroceramics.** 22nd Conference "*New Cryogenic and Isotope Technologies for Energy and Environment*" - *EnergEn* 2018 Băile Govora, Romania, October 24 - 26, 2018. Book of abstract Vol 1/2018, pag. 163.

2. Adriana DEHELEAN, Simona RADA, Marius RADA, Ramona-Crina SUCIU and Sergiu MACAVEI. **Optical absorption and photoluminescence studies of Tb_4O_7 doped B_2O_3-PbO glasses and vitroceramics.** 22nd Conference "*New Cryogenic and Isotope Technologies for Energy and Environment*" - *EnergEn* 2018 Băile Govora, Romania, October 24 - 26, 2018. Book of abstract Vol 1/2018, pag. 254.

3. Adriana DEHELEAN, Simona RADA, Adriana POPA, Ramona SUCIU, Sergiu MACAVEI, Maria SUCIU. **UV-Vis, photoluminescence, SEM and EPR investigations of samarium (III) oxide-lead oxide-borate glasses and vitroceramics.** *International Conference for Engineering and Technology*, University of London Union, Malet Street, London WC1E 7HY, UK, 6 - 9 November 2018. Research ID: U8K811.

4. Adriana DEHELEAN, Adriana POPA, Maria SUCIU, Sergiu MACAVEI, Camelia GROSAN and Simona RADA. **XRD, SEM, FTIR, Raman and EPR Studies Of Lead Borate Glasses And Vitroceramics Containing Terbium Ions.** *International Conference for Engineering and Technology*, University of London Union, Malet Street, London WC1E 7HY, UK, 6 - 9 November 2018. Research ID: U8K812.