SYNTHETIC RESEARCH REPORT 2020

Report on project achievement in the period January-October 2020

Stage 3: Testing and validation of *PbB-Wastes* products

The objectives of the stage

1. Testing of the chemical durability and mechanical hardness of the obtained products (*PbB-Wastes*);
2. Development of a theoretic model for the immobilization of simulated radioactive waste in glasses and glass ceramics

Expected results to achieve the phase objectives:

- Experimental study on the **chemical durability** of the obtained lead-borate glasses and glass ceramics
- **Mechanical hardness** tests of the obtained products
- **Card** with the best matrix characteristics suited to immobilize radioactive wastes

Contents of the scientific and technical report (RST)

1. **The temperature effect** on **the structure** of *PbB-Wastes* products
   - 1.1. **X-ray diffraction** analysis
   - 1.2. Structural investigation by Fourier Transform Infrared Spectroscopy (**FTIR**) and **Raman** Spectroscopy
   - 1.3. Structural investigation by Ultraviolet-Visible spectroscopy (**UV-Vis**)
   - 1.4. Optical band gap energy ($\mathbf{E_g}$)
   - 1.5. Structural investigation by Photoluminescence (**PL**)
2. **Chemical durability testing of *PbB-Wastes* products**
   - 2.1. **Weight loss**
   - 2.2. **Dissolution** in deionized water
   - 2.3. The concentrations of **Pb, B, Sm and Tb** in **leachate** measured by ICP-MS
3. Testing of **the microhardness** of *PbB-Wastes* products
4. **Card** with the best matrix characteristics suited to immobilize radioactive wastes
5. **Results dissemination**

Summary of the phase

The purpose of the phase consists in: A) the investigation of **temperature effect** on **the structure** of *PbB-Wastes* products; B) **chemical durability** testing of PbB-Wastes products and C) **mechanical hardness** testing of *PbB-Wastes* products. In this sense, the following *PbB-Wastes* products were subjected to the mentioned research: **$4B_2O_3 \cdot PbO$ (P1); $4PbO \cdot B_2O_3$ (P2)**; **$xSm_2O_3 \cdot (100-x)[4B_2O_3 \cdot PbO]$**, unde x= 5 moli Sm_2O_3 **(P3)**; **$xSm_2O_3 \cdot (100-x)[4B_2O_3 \cdot PbO]$**, unde x= 30 moli Sm_2O_3 **(P4)**; **$xTb_4O_7 \cdot (100-x)[4B_2O_3 \cdot PbO]$**, unde x=8 % moli Tb_4O_7 **(P5)**; **$xSm_2O_3 \cdot (100-x)[4PbO \cdot B_2O_3]$**, unde x= 10 moli Sm_2O_3 **(P6)**; **$xTb_4O_7 \cdot (100-x)[4PbO \cdot B_2O_3]$** unde x=1 % moli Tb_4O_7 **(P7)** as potential products for the immobilization of radioactive waste. These investigations are necessary to identify the matrix with the best characteristics to immobilize radioactive waste based on uranium and plutonium.

A) For the final storage of radioactive waste in designed specially places (eg deep caves) it is known that it must be stable (not to undergo structural changes) up to temperatures of 200 - 300 ^oC. **To investigate the effect of temperature on the structure** of *PbB-Wastes* products, the vitreous system with the composition **$xSm_2O_3 \cdot (100-x)$ $[4B_2O_3 \cdot PbO]$**, **x = 10, 20, 30 mol % Sm_2O_3** was treated at different temperatures: 200, 300 , 450, 500 and 520 ^oC. **XRD**, **FTIR**, **Raman**, **UV-Vis** and **PL** methods were used for structural investigations of new products. **XRD analysis** revealed the amorphous nature of all the samples. **FTIR spectra** indicate a trend of displacement of IR bands attributed to $[BO_3]$ structural units (1200-1500 cm^{-1}) towards higher wave numbers, which increases with the temperature. This structural evolution can be explained by considering reorganizations in the structural units [BO3]. Also, the structural changes can be observed in the **Raman spectra** (variations in the intensity of the Raman bands attributed to $[BO_3]$ structural units between 1100 and 1470 cm^{-1}). In addition, the Raman spectra show increases in the intensity of Raman bands centered at 270 cm^{-1} attributed to the deformation vibrations of the Pb-O-Pb angles. **UV-Vis spectra** indicate important structural changes for samples treated at 520 ^oC and new UV-Vis bands appear in 300-560 nm region. The samarium ions have a pronounced affinity for $[BO_3]$ structural units and will compensate for their charge in their vicinity. By reorganizing of the $[BO_3]$ structural units (according to FTIR and Raman data) some samarium ions become free and thus increase the intensity of UV-Vis bands due to their electronic transitions (320-560 nm). According to UV-Vis data, the intensity of the **PL** bands increases with the temperature due to the mobility of samarium ions.

B) The *PbB-Wastes* products proposed for **chemical durability testing** are given in Fig. 1. The chemical durability of samples was evaluated by mass loss measurement after exposure to **deionized**

water at **90 °C** for **7 days**. This test conforms to the standard procedure described by ASTMĂ MCC-1 [1, 2] which is suitable to simulate the chemical dissolution of glassy materials in an accelerated manner.

The specific mass loss (SML) was calculated to monitor the chemical durability of glass as follows: SML=$(m_0-m_n)/S$, where SML is the total mass loss (g mm^{-2}), m_0 is the original unleached specimen mass (g), m_n is the specimen mass after each leaching (g), n=1, 2, 3, 4 and 7, S is the sample surface area (mm^2). The dissolution rates for each sample were calculated by dividing SML to leaching periods of 24 h (first day), 48 h (second day), …., 168 h (seventh day). These are values helpful to compare the dissolution rates of various samples in different stages.

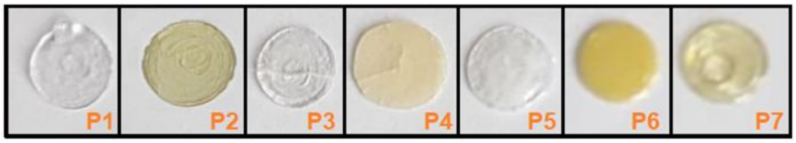

Fig.1. The *PbB-Wastes* products proposed for chemical durability testing

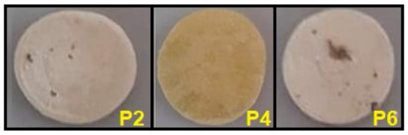

Fig. 2. The products after second day of chemical durability testing

Examination of the chemical durability test indicates that the samples xSm_2O_3·(100-x) [4PbO·B_2O_3], where x = 10 mol % Sm_2O_3 **(P6)** and xSm_2O_3·(100-x) [$4B_2O_3$·PbO], where x = 5 mol % Sm_2O_3 **(P3)** shows *low chemical durability* (due to high mass loss: P3 (0.4-3.0 gmm^{-2}) and P6 (1.8-7.7 gmm^{-2})), and *high chemical durability* (by low mass loss: P4 (0.1-0.4 gmm^{-2} and P7 (0.01-0.03 gmm^{-2})) of xTb_4O_7·(100-x) [4PbO·B_2O_3] where x = 1 mol % Tb_4O_7 **(P7)** and xSm_2O_3·(100-x) [$4B_2O_3$·PbO], where x = 30 mol % Sm_2O_3 **(P4)** products. The dissolution rate of P6 and P3 products does not remain constant, increases with increasing exposure time suggesting that no an experimental layer or that it is not sufficiently protective to prevent the diffusion of ions in the test solution. The experimental results obtained indicate that the evolution of the lead and boron leaching process is closely related to the composition of the host matrix, the rare earth ion and of exposure time.

Comparison of **ICP-MS results** for B in the test solutions at the end of the chemical durability tests indicate that much less B was dissolved from the high PbO glass sample (P7- xTb_4O_7·(100-x) [4PbO·B_2O_3] where x=1 mol % Tb_4O_7) when compared to low PbO glass (P5- xTb_4O_7·(100-x) [$4B_2O_3$·PbO], where x = 8 mol % Tb_4O_7). Also, much less Pb is found in the test solution for P4 product compared to P6 product. The alteration mechanisms at the interface of high and low PbO glasses are significantly different from each other; apparently in the latter one, the alteration layer is not effective enough to prevent B diffusion after the initial stage, while in high PbO glasses, the alteration layer is a very effective passivation layer.

As a result we can conclude that the chemical durability of the product **can be improved** by: incorporation of *1 mol % Tb_4O_7* in *[$4PbO\cdot B_2O_3$]* host matrix **(P7)**, incorporation of *30 mol % Sm_2O_3* in *[$4B_2O_3\cdot PbO$]* host matrix **(P4)**, respectively. The rare earth ions (Sm or Tb) are used in order to „imitate" the behavior of uranium or plutonium ions that represent an important segment of the nuclear wastes. **Tb ions** *increases the chemical durability* of the high PbO matrix **[$4PbO\cdot B_2O_3$]**, while **Sm ions** *improves the chemical durability* of the high B_2O_3 matrix **[$4B_2O_3\cdot PbO$]**.

C) Vickers **mechanical hardness tests** of *PbB-Wastes* products (P1 to P7 products, as mentioned at B) by indentation method were performed with NOVA 130 - Digital MicroVickers Hardness Tester (INNOVATEST certificate) purchased in the second stage of this project.

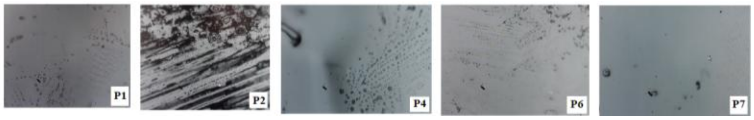

Fig. 3. The photographs of samples visualized through a microscope attached to the NOVA 130 - Digital MicroVickers Hardness Tester

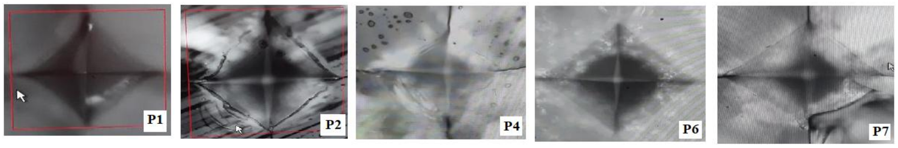

Fig. 4. Vickers indents made at 0.5 kgf

The glass with the composition [$4B_2O_3\cdot PbO$] has a higher hardness (423 MPa) compared to [$4PbO\cdot B_2O_3$] glass matrix (225 MPa). The hardness of the *PbB-Wastes* product with the composition [$4B_2O_3\cdot PbO$] is improved by doping with 30 mol % Sm_2O_3 (H_v=476 MPa) and 8 mol % Tb_4O_7 (H_v=512 MPa), respectively. The incorporation of 1 mol % Tb_4O_7 in the *PbB-Wastes* product with the composition [$4PbO\cdot B_2O_3$] improves the Vickers hardness (H_v=250 MPa) while the addition of 10 mol % Sm_2O_3 decreases the hardness (227 MPa) compared to the doping with terbium, but increases compared to the matrix host.

D) **Card** with the best matrix characteristics suited to immobilize radioactive wastes

In order to verify the ability to immobilize radioactive waste, the following glass systems were prepared:

M1a)-$xSm_2O_3\cdot(100-x)[4PbO\cdot B_2O_3]$, where x=0 and 10 mol % Sm_2O_3;

M2a)-$xSm_2O_3\cdot(100-x)[4B_2O_3\cdot PbO]$, where x=0, 5 and 30 mol % Sm_2O_3;

M1b)-$xTb_4O_7\cdot(100-x)[4PbO\cdot B_2O_3]$, where x=0 and 1 mol % Tb_4O_7;

M2b)-$xTb_4O_7\cdot(100-x)[\ 4B_2O_3\cdot PbO]$, where x=0 and 8 mol % Tb_4O_7

As a result of complex and detailed investigations of *PbB-Wastes* products, 2 cards were recommended for the immobilization of simulated radioactive waste, and their capitalization as luminescent materials, namely:

-for radioactive waste with a high content of volatile component, it is recommended to incorporate them in **M1** glass matrix having the composition **$4PbO•B_2O_3$**, at a temperature of **700 ^oC**, which will allow the immobilization of a content of up to **10 mol % of uranium** and **1 mol % of plutonium**;

- for radioactive waste with high levels of uranium and plutonium it is recommended to use **M2** glass matrix with the composition **$4B_2O_3•PbO$**, at a temperature of **1000 ^oC** when a high rare earth content of up to **30 mol % of uranium** and **8 mol % of plutonium**;

- M1 and M2 materials have applications in the field of lasers due to the luminescent properties of immobilized ions;

- **M2a)** ($4B_2O_3•PbO$ doped with 5 mol % Sm_2O_3) product and **M1a)** ($4PbO•B_2O_3$ doped with 10 mol % Sm_2O_3) product have **low chemical durability**;

- **M2a)** ($4B_2O_3•PbO$ doped with 30 mol % Sm_2O_3) product and **M1b)** ($4PbO•B_2O_3$ doped with 1 mol % Tb_4O_7) product has **high chemical durability**;

- **M2a)** ($4B_2O_3•PbO$ doped with 30 mol % Sm_2O_3) product and **M2b)** ($4B_2O_3•PbO$ doped with 8 mol % Tb_4O_7) product has **high mechanical hardness**;

- **M1a)** ($4PbO•B_2O_3$) product and **M1a)** ($4PbO•B_2O_3$ doped with 10 mol % Sm_2O_3) product has **low mechanical hardness**

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) **2 ISI articles: 1. A. Dehelean**, S. Rada, J. Zhang. *Determination of the lead environment in samarium - Lead oxide-borate glasses and vitroceramics using XANES and EXAFS studies*. Radiation Physics and Chemistry 174: 1-9 (2020)

   2. A. Dehelean, S. Rada. M. Zagrai, R. Suciu, C. Molnar. *Concentration dependent spectroscopic properties of terbium ion doped lead-borate glasses and vitroceramics*. Analytical Letters. DOI: 10.1080/00032719.2020.1723614 (2020)
4) The registration at **OSIM** of **a patent**: *Procedeu de preparare, înglobare și aplicare a deșeurilor radioactive în sticle pe bază de B_2O_3-PbO/ Preparation, incorporation and application of radioactive waste in glasses based on B_2O_3-PbO.* Registration No. A/00097 from 25.02.2020
5) **Participation** at **The International Exhibition of Research, Innovations and Inventions**, PRO INVENT, the 18th edition, 18-20 November 2020

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4. A.Dehelean, S. Rada, M. Zagrai, R. Suciu, C. Molnar, *Concentration dependent spectroscopic properties of terbium ion doped lead-borate glasses and vitroceramics*, Analytical Letters, 2020, doi.10.1080/00032719.2020.1723614
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9. A.Dehelean, S. Rada, J. Zhang. *Determination of the lead environment in samarium – Lead oxide-borate glasses and vitroceramics using XANES and EXAFS studies***.** Radiation Physics and Chemistry 174: 108927 (2020)
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Data	Director de proiect
28.11.2018	Cercetător științific II Augusta-Adriana Dehelean