

**STUDY OF LABS-COMPOSITION GLASSES REMELTED IN RESISTANCE
FURNACE AND IN COLD CRUCIBLE INDUCTION MELTER**

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ABSTRACT

Searching for advanced prospective hosts for actinides waste (including weapon-grade plutonium) fixation an important problem of safe HLW management. Lanthanide borosilicate glasses (LaBS) designed in the U.S.A. are known to be one of the prospective vitreous matrices for actinides waste immobilization. In this study results of current study on composition and structure of remelted lanthanide borosilicate glasses have been focused on. The samples were prepared by repeated melting of initial LaBS-glass precursor. Both conventional high-temperature resistive furnace and inductively heated melter with cold crucible were employed for fabrication of the glasses. Five samples were produced and researched in detail. Three of them were obtained in high-temperature furnace (remelted LaBS-glass, LaBS+10% CeO₂, and LaBS+20% CeO₂). The other two samples produced with inductive melting in cold crucible were remelted initial LaBS-glass differed on material (SiC or metallic Al) initiated heating and melting of the initial batches. The specimens were studied by optical microscopy, XRD, and SEM/EDS methods. All specimens produced in resistance furnace even with the highest cerium content are homogeneous glasses. The samples fabricated by inductive melting among with glass contain some crystalline phases (1-2 vol.%), including metallic Si-silicon and borides of Zr and REE. Reasons for their appearance are discussed.

INTRODUCTION.

The development of optimum technology for solidifying radionuclides in immobilizing matrices is one of the most important problems concerning the disposal of radioactive wastes. A hot pressing, cold pressing followed by sintering, and melting are the main methods used for synthesizing waste forms. These methods are developed in different countries as applied to specific types of wastes. A hot pressing is used in Australia for production of Synroc polyphase ceramics. A melting and also cold pressing followed by sintering are applied at research centers

in Russia, Europe, North America, and Japan to the preparation of vitreous composites and ceramics. In recent years, the international cooperation between scientists in the field of waste management becomes progressively closer, which stimulates considerable interest in a comparative study of materials that have similar chemical composition and are prepared by different technologies. An example is investigations of hot-pressed and sintered [1] and also hot pressed and melted composites of the Synroc type [2, 3].

Similar explorations become especially topical in relation to the problem of efficient and ecologically safe immobilization of long-lived actinides including weapons plutonium. The utilization of actinide-containing wastes is the international problem and its solution requires joint efforts of scientists in different countries. This problem has arisen rather recently. On the one hand, its appearance is associated with devising methods for the fractionation of high-level wastes (HLW) into groups of elements, which allows one to search for composites intended for comparatively narrow range of isotopes (for example, for actinide-rare-earth waste fraction). On the other hand, the demand for these materials is caused by the necessity of producing matrices for the immobilization of the so-called weapons plutonium formed in dismantling of nuclear arsenals in Russia and United States.

Modern technologies of immobilizing radioactive wastes are designed for liquid HLW formed at radiochemical plants [4, 5]. The major portion of uranium and plutonium is extracted from these HLW for reuse. Relatively small amounts of actinides remaining in HLW can be completely dissolved in aluminophosphate or borosilicate glass. Note that, on the whole, a low solubility of actinides is characteristic of these glasses. As a rule, the solubility of plutonium in typical glasses of these types is no more than 1 - 2 wt % [6 - 9]. At high contents of elements, they precipitate in the form of oxide phase. An increase in the solvent action of a melt can be achieved by increasing the concentration of alkali and alkali-earth elements; however, this leads to a decrease in the chemical durability of glasses and makes them unsuitable for a long-term storage of plutonium and actinide fractions. This fact has given impetus to the development of various ceramic materials consisting of crystalline phases isomorphously capacious with respect to actinides, among them zirconolite, phosphates, zircon, zirconium oxide, and others [10 - 14]. A comparative characterization of the above materials is given in [11 - 12]. At the same time, the attempts to design special glasses characterized by both a high capability for solving actinides and a good chemical durability have been also in progress. Alkali tin-silicate (ATS) or lanthanide borosilicate (LaBS) [15 - 17] glasses were proposed as matrices that potentially possess suitable properties.

In this work, we considered the features of structure and composition of glasses obtained by remelting of the LaBS glass frit in a resistance furnace and also in an induction melter with a cold crucible (CCIM). The initial glass frit was received from experts of the Lawrence Livermore National Laboratory (USA) for the performance of works in the framework of the UTA96-0330 Contract.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The first group of samples based on the LaBS glass frit was prepared in a high-temperature furnace in platinum crucibles at 1500°C. This group involves remelted initial frit (LaBS⁰) and also glasses obtained by melting of the initial frit with addition of actinide simulators (cerium).

These samples are designated as LaBS¹ (without cerium), LaBS² (10% CeO₂), and LaBS³ (20% CeO₂). Only the initial glass frit LaBS⁰ was melted by the CCIM method (T = 1600 - 1800°C). Two samples differing in the features of starting heating were synthesized: LaBS⁴ (starting heating with SiC and addition of metallic aluminum powder) and LaBS⁵ (starting heating with metallic aluminum powder). The prepared materials were investigated by optical and electron microscopy and also X-ray powder diffraction analysis.

EXPERIMENTAL RESULTS

The composition of the initial frit differs substantially from the early composition of the LaBS glass (Table 1) and is close to that of the last modified version of this glass [17]. The samples melted in a high-temperature furnace consist of a homogeneous glass. All cerium oxide additionally introduced into the frit is completely dissolved in the melt (Table 2). As the cerium content increases, the glass color changes from light brown (LaBS²) to dark brown (LaBS³). Note that the initial glass frit (LaBS⁰) and cerium-free sample (LaBS¹) are deep pink in color.

Table 1. Compositions of glasses for plutonium immobilization

Oxide, wt %	(1) ATS	(2) LaBS*	(3) LaBS**	(4) LaBS ⁰	(5) LaBS ¹	(6) LaBS ²	(7) LaBS ³	(8) LaBS ⁴	(9) LaBS ⁵
SiO ₂	41.4	34.6	17.4	29.1	27.6	25.1	24.1	29.4	26.1
B ₂ O ₃	12.0	5.1	9.9	11.7	nd	nd	nd	nd	nd
Al ₂ O ₃	2.3	9.0	17.8	21.5	17.1	15.5	14.5	17.8	21.4
ZrO ₂	5.3	0.1	0.8	1.3	1.2	1.4	1.1	0.9	0.6
La ₂ O ₃	-	9.3	Σ Ln ₂ O ₃ =30.0	12.4	13.2	11.6	10.7	12.9	13.3
Ce ₂ O ₃	-	-		-	-	9.5	18.3	-	-
Nd ₂ O ₃	-	-		12.8	13.4	11.9	11.4	13.0	12.8
Sm ₂ O ₃	-	18.4		-	-	-	-	-	-
Gd ₂ O ₃	3.2	-		8.6	8.4	7.4	7.4	8.0	8.3
SrO	-	-	3.6	2.5	2.6	2.6	2.7	3.8	3.6
AnO ₂	11.4 (Pu)	6.9 (Pu)	20.0 (Th)	-	-	-	-	-	-
PbO	-	13.0	-	-	-	-	-	-	-
BaO	-	3.8	-	-	-	-	-	-	-
Other	23.6								

Glasses: (1) ATS [15], (2) early LaBS version [16], (3) optimum composition of LaBS glass [17], (4) initial frit LaBS⁰ (LLNL), (5 - 7) glasses after remelting in Pt crucibles in a high-temperature furnace, (8, 9) glasses remelted by the CCIM method upon starting heating with SiC+Al (8 - LaBS⁴) and metallic aluminum (9 - LaBS⁵).

Table 2. As-analyzed compositions of the synthesized glasses LaBS¹, LaBS², and LaBS³

Material Type	Oxide content, wt %							
	SrO	ZrO ₂	La ₂ O ₃	CeO ₂	Gd ₂ O ₃	Nd ₂ O ₃	SiO ₂	Al ₂ O ₃
LaBS ¹ *	2.4	1.2	12.2	-	8.4	12.4	27.2	16.8
LaBS ¹ *	2.7	1.4	12.7	-	8.4	12.8	26.9	16.1
LaBS ¹ **	2.9	1.5	12.9	-	8.2	13.9	26.8	17.2
LaBS ¹ **	2.8	1.1	13.9	-	8.0	13.6	28.1	17.2
LaBS ¹ **	2.2	1.2	13.9	-	8.9	13.5	27.8	17.4
LaBS ² *	2.8	1.6	11.9	9.3	6.8	12.5	25.8	16.1
LaBS ² *	2.0	1.1	11.4	9.3	7.8	11.4	24.1	14.5
LaBS ² **	2.7	1.5	11.7	9.6	8.1	10.8	25.5	15.8
LaBS ² **	2.9	1.4	11.7	9.6	6.7	12.8	25.0	15.8
LaBS ³ *	2.6	1.2	10.4	18.7	6.7	11.4	24.8	14.8
LaBS ³ *	2.6	1.3	10.8	17.9	8.1	11.3	24.3	14.2
LaBS ³ **	2.8	0.9	10.8	18.1	7.0	11.3	23.5	14.6
LaBS ³ **	2.7	1.0	10.9	18.5	7.9	11.5	24.0	14.4

B₂O₃ – not determined

* Electron probe diameter, 2 μm.

** Analysis over the site, 20×20 μm.

Different situation is observed for glasses remelted by the CCIM method. From micrographs (optical and electron) of the LaBS⁴ and LaBS⁵ glasses (Figs. 1, 2), one can see that both samples exhibit an inhomogeneous phase structure. They are predominantly comprised of glass phase that involves tiny crystals in the form of flattened hexagonal prisms observed throughout the entire glass bulk. These particles are characterized, depending on the section plane, by hexagonal or elongated prismatic shape. The crystalline phase is more or less uniformly distributed over the entire glass bulk. In some cases, the particle aggregates have the form of stripes indicating the lines of streams of melt upon its convective stirring in a cold crucible (Fig. 1). The crystals are composed dominantly of zirconium (Table 3) and, to a smaller extent, of rare-earth elements, silicon, and aluminum. The content of elements varies in such a way that, as the zirconium concentration decreases, the amounts of all the other elements increase approximately in the equal proportion.



Fig. 1. Micrograph of thin section of the sample prepared by the CCIM method (optical microscopy; transmitted light; parallel nicols; magnification, 15^x, grey regions – glass, small black crystals – inclusions of zirconium phase)

Table 3. Compositions of crystalline phases in the glass remelted by the CCIM method

Oxide, wt %	Zr phase	Corundum (Al ₂ O ₃)	Element, wt %	Metallic Si	I/ZrB ₂ /ZrB*	II/(La,Nd)B ₆ **
SiO ₂	4.7	0.6	Si	100.4	0.5	<0.1
B ₂ O ₃	nd	nd	B	nd	nd/19.2/10.6	nd/31.4
Al ₂ O ₃	2.8	98.6	Al	<0.1	<0.1	<0.1
ZrO ₂	82.7	<0.2	Zr	<0.2	85.7/80.8/89.4	<0.2
La ₂ O ₃	<0.4	<0.2	La	<0.2	<0.2	34.5/33.7
Nd ₂ O ₃	1.5	0.5	Nd	<0.2	<0.2	32.5/34.9
Gd ₂ O ₃	2.8	<0.3	Gd	<0.2	<0.2	2.9
SrO	<0.3	0.6	Sr	<0.3	<0.3	0.7
Σ	94.5	100.3	Σ	100.4	86.2/100/100	70.6/100

nd – not determined; I – as-analyzed composition of zirconium boride phase; II – as-analyzed composition of REE boride phase; * – calculated compositions of phases with ideal stoichiometries ZrB₂ и ZrB; ** – calculated compositions of phases with ideal stoichiometries (La_{0.5}Nd_{0.5})B₆.

It can be assumed that, since particles are very small in size that does not exceed several microns and is comparable with the electron probe diameter, the probe partially covers surrounding glass in measurement of the particle composition. Therefore, the as-analyzed compositions correspond to a mixture of crystals and a glass, which explains the presence of silica and alumina in the obtained compositions. The shape of particles suggests the hexagonal (trigonal) symmetry of their crystalline lattice. We failed to find the analog of this compound neither in the nature nor among synthetic phases. It closest to zirconium oxide (ZrO₂) in composition, but the latter compound exhibits another (tetragonal or monoclinic) crystal system. The formation of phase under consideration brings about a decrease in concentration of zirconium in the glass as compared to its initial content in the frit (from 1.3 to 0.6 - 0.9 wt % ZrO₂). Reasoning from this difference, the fraction of the zirconium-containing phase in the sample is less than 1 vol %.

Another type of inhomogeneity is also observed in both glasses remelted by the CCIM method. This inhomogeneity manifests itself as a small number of spherical inclusions with diameter from 50 to 200 μm (Figs. 2a-2c). At the surface of area 1.5 × 2 cm, there are from 2 to 4 such globules. Their fraction in the total volume of samples amounts to approximately 0.2 - 0.4%. Spheres have very similar internal structure and are constituted predominantly by metallic silicon and, to a lesser extent, by phases of zirconium borides (elongated bipyramidal crystals) and rare-earth element borides (crystals with quadratic sections). Moreover, in the sample obtained upon starting heating with a SiC+Al mixture (LaBS⁴), spherical silicon inclusions are fringed with corundum (Al₂O₃) particles (Figs. 2a-2c, Table 3).

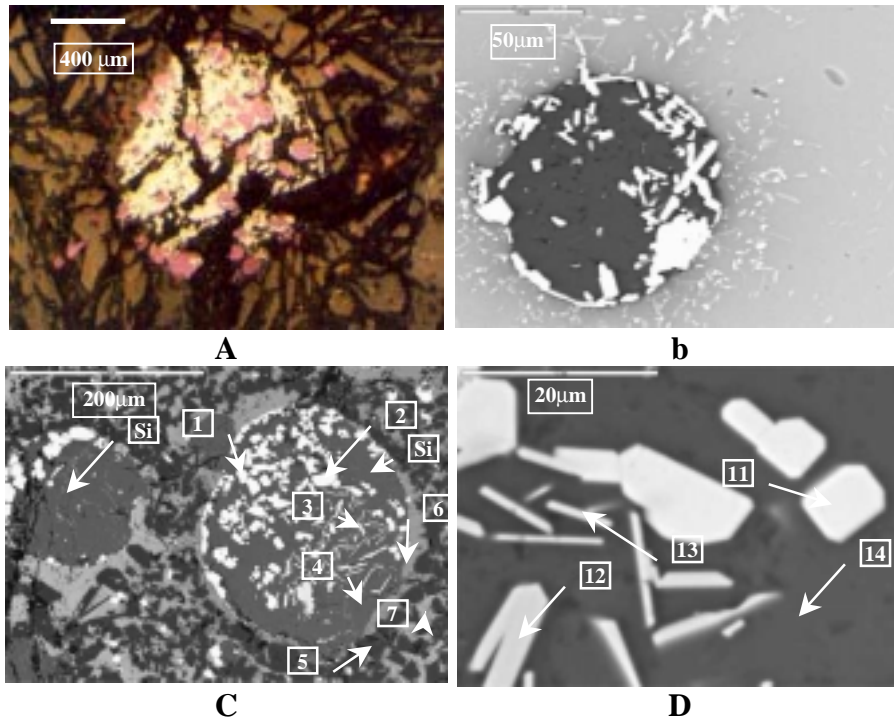


Fig. 2. Optical and SEM micrographs of LaBS materials

- a -optical microscopy, LaBS⁴ glass sample; reflected light; parallel nicols; magnification, 25^x.
 b - SEM micrograph of the LaBS⁵ glass sample
 c, d - SEM micrographs of the LaBS⁴ glass sample: (1, 2, 11) REE borides (LnB₆),
 (3, 12, 13) zirconium boride (ZrB₂), (4, 14) metallic silicon (Si_{met}), (5) corundum (Al₂O₃), and (6, 7) glass.

For the most part, boride particles are localized in the boundary regions of inclusions. The composition of boride particles was not completely identified, because the "light" element - boron - cannot be quantitatively determined by the SEM/EDS technique. Qualitatively, the ratio between elements in phases can be revealed from their energy-dispersive spectra. In particular, it can be seen that the boron content in zirconium boride is appreciably lower than that in rare-earth boride. Assuming that the boron content in phases is equal to the difference between 100% and the total of the other analyzed elements (Table 3), one obtains that the phase compositions are closest to the ZrB₂ (or ZrB) and LnB₆ stoichiometries. In rare-earth boride, La and Nd are dominant, and Gd is present in a smaller amount. The La:Nd atomic ratio is equal to 1.7-1.4:1 for the LaBS⁴ sample and decreases to 1.1-1.0:1 for the LaBS⁵ sample. The ZrB₂ and LnB₆ phases are typical high-temperature compounds of boron with zirconium and rare-earth elements, respectively [18]. The assumption on the above stoichiometry of the phases found in the samples agrees with the shape and color of boride particles and is corroborated by the data of X-ray powder diffraction analysis. This study was carried out for samples with the largest number of spherical inclusions. The reflections of metallic silicon (the main reflections are at 3.12, 1.92, and 1.63 Å) clearly manifest themselves in the corresponding diffraction patterns. Weaker reflections (at 2.77, 2.16, 1.58, and 1.48 Å) are attributed to the ZrB₂ phase. The reflections associated with rare-earth boride are not observed, which is explained by a small amount of this phase.

According to the electron microscopic data, both samples of the LaBS glass remelted by the CCIM method more than by 98% consist of glass close in composition to the initial frit. One of

the most notable difference is a decreased content of zirconium in the samples. As shown above, this is connected with the precipitation of zirconium oxide and zirconium boride phases. The content of rare-earth elements in the glass is virtually identical to that in the initial frit, which confirms the conclusion on a very low content of rare-earth element boride. The LaBS⁴ and LaBS⁵ glasses differ predominantly in the content of SiO₂ and Al₂O₃ (Table 1), which is likely associated with passing a some amount of these elements from a starting material. Note also that the glass compositions near and far from metallic silicon inclusions are different (Table 4).

Table 4. Glass compositions in the LaBS material remelted by the CCIM method

Oxide, wt %	Glass LaBS ⁴		Glass LaBS ⁵	
	far from	near	far from	
	metallic silicon inclusions			
SiO ₂	29.4	33.7	45.2	26.1
B ₂ O ₃	nd	Nd	nd	nd
Al ₂ O ₃	17.8	20.3	17.8	21.4
ZrO ₂	0.9	0.8	0.7	0.6
La ₂ O ₃	12.9	15.4	10.5	13.3
Nd ₂ O ₃	13.0	14.5	12.0	12.8
Gd ₂ O ₃	8.0	9.6	8.0	8.3
SrO	3.8	4.1	5.1	3.6
Σ	85.8	98.4	99.3	86.1

nd – not determined

As follows from the analytical data, the total content of elements in the glass near inclusions (at a distance of several tens of microns) is almost 100%. This indicates that boron content is very low due to the formation of zirconium and rare-earth element borides. Far from inclusions, the sum of element oxides decreases almost by 14%, which likely corresponds to the boron content in the glass matrix.

DISCUSSION

The feature of the LaBS glasses remelted by the CCIM method is the disturbance of their homogeneity. Aside from the dominant glass phase, the final product involves a small amount (1 - 2%) of additional phases in the form of microspherical silicon inclusions with zirconium and rare-earth element borides and also tiny crystals of zirconium-containing phase distributed throughout the bulk of the glass. A some amount of aluminum oxide (corundum) spatially arranged near metallic silicon spheres is formed in the LaBS⁴ material prepared upon starting heating with a SiC+Al mixture. The amount of all these phases is very small, and their formation virtually does not affect the composition of base glass. The sole exception is zirconium whose content in the remelted glass is reduced by approximately twice as compared to that in the glass frit. All the above-mentioned phases (especially, zirconium and rare-earth element borides) exhibit a high chemical durability [18]. It is likely that their appearance does not deteriorate the durability properties of glasses. It should be noted that actinide group elements also react with boron to yield a number of compounds of the AnB_n type (where n = 1, 2, 4, 6, 12). On the other hand, it is not improbable that the formation of all the above phases can be prevented by correcting the melting technology. To do this requires analysis of factors responsible for the formation of these phases. The arising of zirconium-rich phase distributed throughout the glass is likely connected with substantial local overheating of melt upon starting heating of the glass frit.

The formation of metallic silicon and boride phases unambiguously demonstrates that redox reactions attended by a change in the valence of elements proceed in local regions of melt. This process is associated with the use of strong reducing agents such as silicon carbide and, especially, metallic aluminum for the starting heating. In order to estimate the oxidation potential upon melting of the glass frit by the CCIM method, the T - P_{O2} diagram with lines separating the stability fields for compounds of elements occurring in the system were constructed using the data from [19, 20] (Fig. 3). Some reference equilibria important for the comparative evaluation of synthesis conditions with the use of the CCIM and hot pressing methods are also depicted in Fig. 3. At melting temperatures of 1600 - 1800°C, the formation of both metallic silicon and aluminum oxide is observed in the narrow P_{O2} range ~ 10⁻¹⁴ - 10⁻¹⁶ bar, which corresponds to approximately the middle of the range typical of matrix synthesis by the hot pressing method [20].

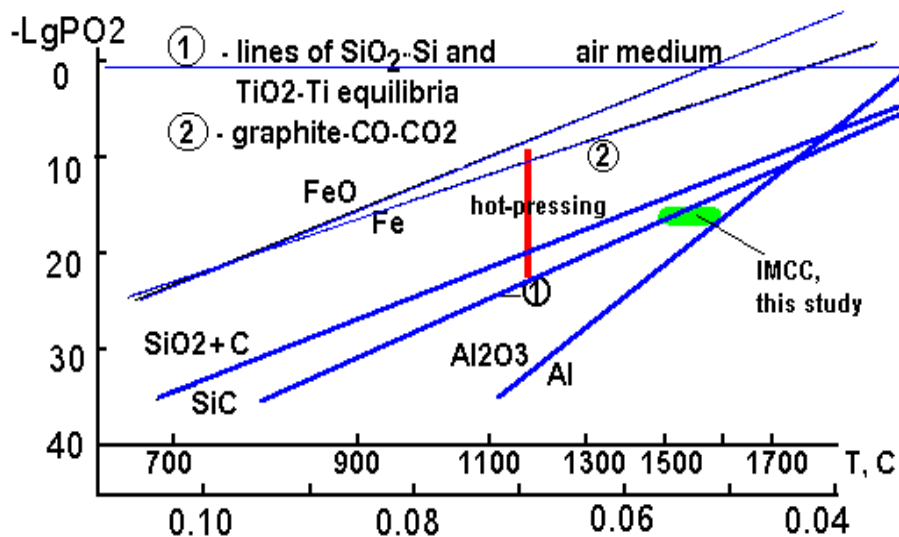


Fig. 3. Lines of solid-phase redox reactions and the most probable parameters T-P_{O2} for the CCIM and hot pressing methods.

It is possible that replacement of starting material with a weaker reducing agent permits one to decrease the rate of reduction processes in borosilicate melt and to prevent the formation of borides. At the same time, the role of these phases should not be overestimated, because, owing to small amounts, their influence on the matrix properties should not be essential. Furthermore, the discharge of the first melt portion containing inclusions of silicon and boride phases provides a way of eliminating their presence in products of subsequent melting. Therefore it can be concluded that the CCIM method is suitable for the actinide immobilization into the LaBS glass. The main direction of further investigations is the structural study of these glasses involving actinides or their simulators.

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