

Studies on immobilization of thorium in barium borosilicate glass

R.K. Mishra ^a, Pranesh Sengupta ^b, C.P. Kaushik ^{a,*},
A.K. Tyagi ^c, G.B. Kale ^b, Kanwar Raj ^a

^a Waste Management Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

^b Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

^c Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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Abstract

The barium borosilicate glass (BBS) matrix has shown considerable solubility of ThO₂ at 1000 °C. As seen by X-ray diffractometry (XRD) and Electron probe micro analysis (EPMA) up to 15.86 wt% of ThO₂ could be dissolved in this matrix. The homogeneity of thorium loaded glass was convincingly ascertained by EPMA. Attempts to load more than 16 wt% ThO₂ led to the phase separation of crystalline phases identified as major phase of ThO₂ and minor percentage of ThSiO₄ phase with altogether different morphologies, as seen by XRD. Interestingly, the back scattered images of thorite crystals point towards the presence of chemical zoning. The results being reported in this paper are of interest especially with respect to immobilization of other actinides in borosilicate glass matrix.

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1. Introduction

Conditioning of metallic oxides in silicate glass is probably one of those few techniques that human being mastered since historic time. As a testimony for this, one can refer to the beautiful antique glass vessels recovered from various archeological pot across the world [1]. Besides, the product durability

properties e.g. homogeneity, toughness, strength, leach resistance etc of these materials, one that attracted most of the common people is the bright attractive coloration of some of these vessels. Among these glass articles, those exhibiting bright yellow to green colors and also fluorescence are particularly important in the context of nuclear waste vitrification. Detailed analytical studies of these antique items revealed that they contain uranium (U) of different valence states i.e. 4+, 5+ and 6+ in varying proportions [2]. Besides coloration, addition of uranium in silicate glass matrices is also found to be beneficial for the development of glass

* Corresponding author. Tel.: +91 22 2559 5528; fax: +91 22 2550 5185.

E-mail addresses: cpk@barc.ernet.in (C.P. Kaushik), aktyagi@barc.ernet.in (A.K. Tyagi).

to metal graded seals [3]. Like uranium, thorium (Th) is also known to have many important uses in glass industries in which the development of thoria (ThO_2) containing camera lenses is worthy of mention. Thus addition of actinides within glass for the development of various household articles is known since long and was practiced in industrial scale till the first-quarter of the last century when the radioactivity associated with such actinide containing glasses became a serious issue. Such awareness not only stopped the production of actinide glasses but also hampered the academic interest on this class of materials. However, recently with the advent of vitrification technology for long term conditioning of high-level nuclear waste (HLW) study on actinide containing glasses has been rejuvenated [4]. It may be mentioned here that HLW containing minor actinides generated during spent fuel reprocessing plants are currently planned to be incorporated in borosilicate glass matrices.

HLW vitrification technology, however, depends heavily on dissolution and immobilization of actinides and other metal oxides into suitable silicate or borosilicate glass matrix. Selection of a suitable glass matrix for conditioning of HLW is a challenging job as it is guided by various factors such as radio chemical composition of the HLW, limitation of plant scale vitrification (e.g. temperature), requirements of final disposal etc. Hence one has to carry out several investigations pertinent to process and product durability assessments before finalizing matrix composition. The easiest way to perform this herculean task is to properly utilize the vast scientific knowledge base and technological experiences already available in this regard. Keeping this in mind, a set of experiments have been designed at Bhabha Atomic Research Centre (BARC) to examine the feasibility of using barium borosilicate glass matrix (BBS, developed recently at BARC for vitrification of sulfate rich HLW) for conditioning actinide containing HLW [5,6]. The work discussed here is a part of a long term study on solubility of actinide in borosilicate glasses, undertaken (a) to assess actinide solubility limit in these glasses, (b) to understand the mechanisms controlling actinide solubilization, and (c) to determine the structural role of actinides in these glasses. As a part of this investigation, currently Th behavior in BBS glass having pouring temperature $\sim 1000^\circ\text{C}$ is being studied and the results are discussed as follows. It may be noted here that Th-containing HLW streams are expected during reprocessing of thoria-based fuels of Fast

Breeder Reactor and Advanced Heavy Water Reactor [7]. Besides nuclear waste disposal, study on Th solubility in silicate matrix is important for understanding Th distribution in crustal rocks as it has direct bearing to the 'front-end' of nuclear fuel cycle.

Solubility of actinide ions in silicate based glasses depends on various process parameters like base glass composition, temperature, oxygen fugacity etc. Each of these factors in turn can control the valence state of actinides and hence their solubility. Lopez et al. [8] have recently studied the solubility of actinide surrogates e.g. Ce_2O_3 (Ce as a surrogate for 4+ and 3+ actinides), HfO_2 (Hf as a surrogate for 4+ actinides) and Nd_2O_3 (Nd as a surrogate for 3+ actinides) in borosilicate waste glass to understand the effect of processing conditions (temperature and oxidizing versus reducing conditions) on their solubility. It is observed that at a given temperature among these three surrogates, Nd has the maximum solubility in borosilicate glass whereas Ce has intermediate and Hf has minimum solubility. In general, actinide ion solubilities in silicate matrices are greater for higher valence states [3]. Additionally, dissolution capability of silicate glasses increases with increase in alkali content [3]. Earlier, Eller et al. [9] reported solubility limits of about 2 wt% for oxides of Np, Pu and Am and ~ 10 wt% for U in complex borosilicate glasses melted under air atmosphere at 1000°C . In case of Th, a maximum solubility of Th $\approx 2\text{--}5$ wt% in borosilicate glasses quenched from near 1250°C has been reported [10]. In a separate investigation, Sonavane et al. [11] reported ~ 6 wt% thoria solubility in sodium borosilicate glass.

From the above data, it is clear that borosilicate glass matrix has low solubility of actinides and in all probability may act as 'waste load' limiting factor. Hence it is very important to assess the actinide solubility limit in different borosilicate matrices so as to make HLW vitrification technology economical and viable. As a step towards this direction, Th solubility limit assessment has been done in BBS matrix and the details are given below.

2. Experimental

2.1. Preparation of the thoria glass

BBS glass samples having thoria concentration varying from 0 (henceforth referred as base glass) to 23.7 wt.% (Table 1) were prepared by conven-

Table 1
Glass composition for thorium containing BBS glasses (wt%)

Code	SiO ₂	B ₂ O ₃	Na ₂ O	BaO	ThO ₂
SBTH-0	38.60	25.32	12.03	24.05	0.00
SBTH-1	35.98	23.59	11.21	22.41	6.81
SBTH-2	34.34	22.53	10.70	19.15	13.28
SBTH-3	32.47	21.30	10.13	20.23	15.87
SBTH-4	31.41	20.61	9.79	19.58	18.61
SBTH-5	29.43	19.31	9.18	18.33	23.75

tional melt quench method [5]. Stoichiometric amounts of glass forming chemicals like SiO₂, H₃BO₃, NaNO₃, Ba(NO₃)₂ of analytical reagent grade and hydrated thorium nitrate were mixed thoroughly and heated gradually in a fire clay siliminite crucible at 700 °C under oxidizing atmosphere in a resistance furnace (with a temperature controller to maintain the temperature within ±5 °C). Water of crystallization in thorium nitrate was determined by thermal analysis of hydrated thorium nitrate and corresponding corrections for the water is applied. The charge was kept at this temperature for 4 h to ensure complete calcination of the mixture. Subsequently, the mixture was crushed to fine powder using agate mortar and again heated in fire-clay crucible. This was repeated for three times and finally the calcined product was transferred into a platinum crucible kept inside a furnace. The temperature of the furnace was increased in step-wise fashion with an interval of 50 °C and kept for one hour at corresponding temperature. The glass melt was soaked for 4 h at 1000 °C and poured directly on clean stainless steel plate maintained at room temperature.

2.2. Microstructural characterization

The samples were observed under reflected optical microscope. Nature of the samples was assessed using Philips Diffractometer PW 1710. X-ray diffraction (XRD) patterns of the powdered glass samples were recorded from 2θ 10° to 70° at the step of 0.02° using monochromatic CuKα radiation at 40 kV excitation voltage and 30 mA tube current. Electron Probe Micro Analyzer (CAMECA SX 100) was used for assessing chemical homogeneity of the glass samples. An acceleration voltage of 20 kV and 4–100 nA stabilized beam current was used for secondary and back scattered electron (BSE) imaging (with atomic number (Z) contrast) and X-ray analysis respectively.

3. Results and discussion

3.1. Microstructural characterization of glass by EPMA

Typical optical and BSE images of base glass (glass without thoria, SBTH-0, Table 1) sample are shown in Fig. 1(a) and (b). Both the images show that the base glass is homogeneous in composition. The SiKα, BKα and BaKα X-ray images (Fig. 1(c)–(e)) also clearly show that these elements are homogeneously distributed in the glass.

Typical optical and back scattered electron (BSE) image of the Th containing barium borosilicate glass indicate homogeneous nature for samples even with addition of up to 15.87 wt% thoria (Fig. 2(a) and (b)), which is significantly higher compared to previously reported values of ~ 6 wt% thoria [11]. This observation probably indicates that barium plays an important role in increasing Th solubility in borosilicate matrix. Beyond 15.87 wt% thoria loading, transparent BBS glass gradually becomes translucent (18.61 wt% thoria) and finally opaque (23.75 wt% thoria) (Fig. 3(a)–(c)). This change in optical property of the glass is due to phase separation as can be seen from BSE images of samples containing 23.75 wt% ThO₂ (Fig. 4(a)). Two types of phases, having varying dimensions are seen in the matrix. Some are generally of large dimensions 10–30 μm and occur as clusters within the silicate glass matrix. These are designated as Type A phase. The BSE image at higher magnification clearly shows these phases. The outlines of the individual crystals are very sharp and each of them has a well defined shape, mostly hexagonal but some with rhombohedral outline are also seen. Another type of phases (namely type B) are very small in size (<1 μm) as seen in Fig. 4(b). This type B phases are irregular in outline and homogeneously distributed within the glass matrix. Volume fraction of type A phase is very small compared to type B phases. To identify the elements present within the phases, X-ray spectra were obtained using wavelength-dispersive X-ray spectrometer (WDS) attached to EPMA. The WDS spectra obtained from the core of type A phases (Fig. 5(a)) are shown in Fig. 5(b) and (c). These spectra indicate that type A phase consists of Th, Si and based on XRD studies, this phase has been identified as ThSiO₄. ThSiO₄ however, can occur as thorite (α-ThSiO₄: tetragonal, space group: I4₁/amd) or huttonite (β-ThSiO₄: monoclinic, space group: P2₁/n) depending on the

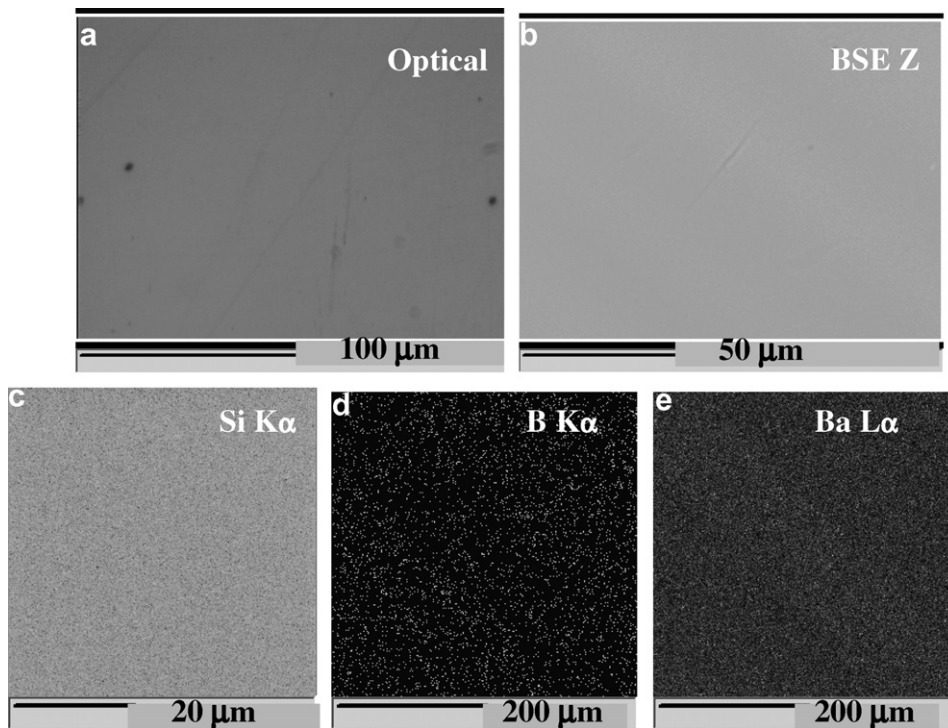


Fig. 1. (a) Optical, (b) BSE and (c) Si K α X-ray, (d) B K α X-ray and (e) Ba L α X-ray images showing homogeneous microstructure of the BBS base glass sample.

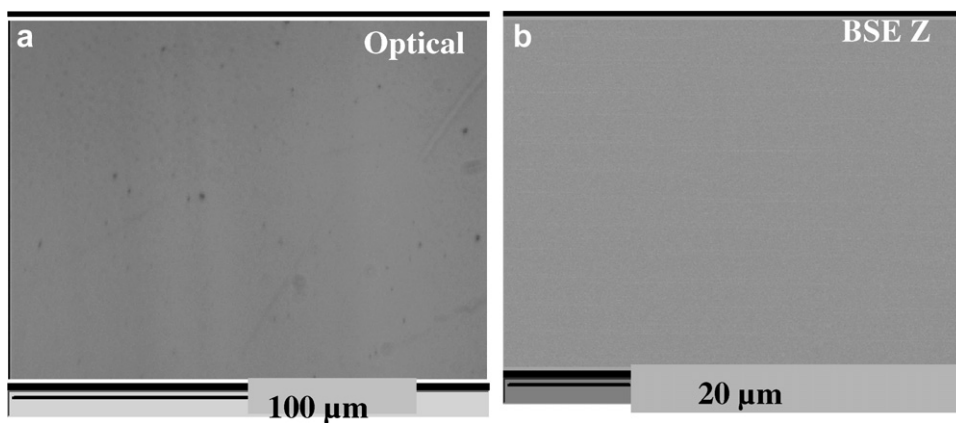


Fig. 2. (a) Optical and (b) BSE images showing homogeneous microstructure of the BBS glass sample with 15.87 wt% thoria.



Fig. 3. Hand specimens of thoria glass samples loaded with 15.87 wt%, 18.61 wt% and 23.75 wt% thoria respectively showing (a) transparent, (b) translucent and (c) opaque optical properties.

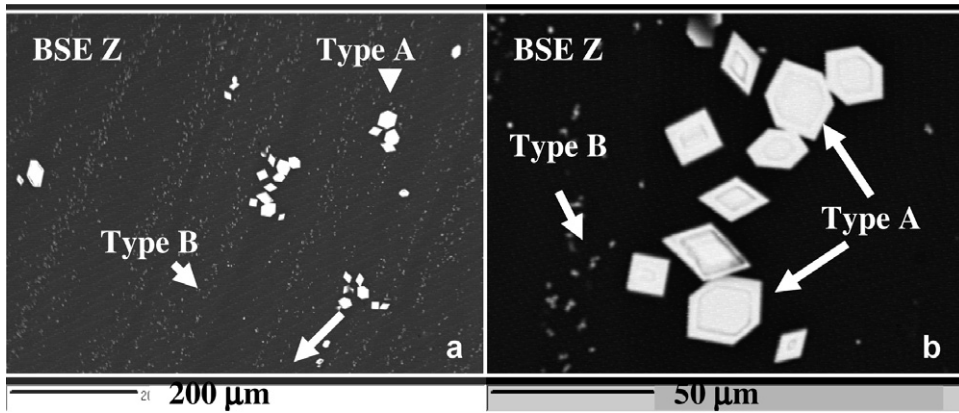


Fig. 4. (a) and (b) BSE images (taken at different magnifications) showing separation of regular shaped, coarse grained clustered type A and irregular shaped finer grained and homogeneously distributed type B phases within the matrix of BBS thoria glass containing 23.75 wt% thoria.

environment of crystallization [12]. Huttonite is confirmed to be isostructural with monazite, consisting of SiO_4 tetrahedral monomers and a compact arrangement of edge-sharing ThO_9 polyhedra. Tho-

rite is isostructural with zircon, consisting of SiO_4 tetrahedral monomers and an open arrangement of edge sharing ThO_8 polyhedra. Due to small volume fraction of ThSiO_4 in present case, proper

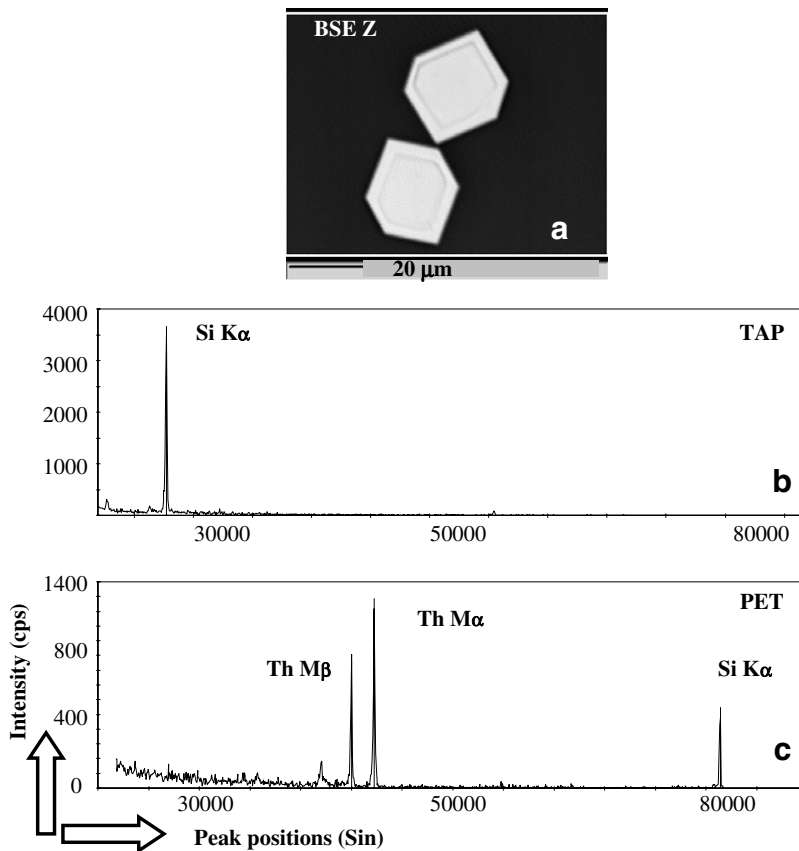


Fig. 5. (a) BSE image of thoria (crystallized in BBS glass containing 23.75 wt% thoria) showing hexagonal outline. (b) and (c) show the WDS spectrum obtained from the core of thoria crystals using synthetic TAP (thallium acid phthalate) and PET (pentaerithortol) crystals.

identification of thorite or huttonite from the X-ray diffraction (XRD) pattern was difficult. However, as two strongest peaks corresponding to thorite are present in the X-ray diffraction pattern obtained for the BBS glass containing 23.75 wt% of ThO_2 , it is believed that type A phase is thorite (discussed below, Fig. 6). This corroborates well with an earlier study [13] on polymorphism of ThSiO_4 that identified thorite as a low temperature polymorph and huttonite as a higher temperature polymorph with transition temperature around 1225°C . In the present experiment, glass was melted at 1000°C , hence, formation of thorite is most likely. Like in case of type A phase, WDS X-ray spectrum was also taken on type B phases. But due to its submicron size, proper identification of the type B phase could not be done as the probe diameter for the given analytical condition was roughly $1\ \mu\text{m}$. However, X-ray diffraction pattern obtained from the thoria glass (23.75 wt%) unequivocally identified phase B as thorianite (ThO_2 , Fig. 6).

The modes of occurrence of thorite and thorianite crystals in the present case are quite interesting. Thorite crystals are always coarse grained, euhedral (very regular) shaped and occur in clusters within the BBS matrix, whereas opposite is the case for thorianite which are small grained, anhedral shaped and homogeneously distributed in the BBS matrix. The first two features of thorite crystals indicate that this crystallization takes place at high temperature and

over a considerable time. The clustering nature of thorite crystals, however, is possibly due to the supply of ingredients from some isolated restricted pockets. Such restricted source of materials is probably not a case with thorianite and as a result it crystallizes homogeneously within the BBS matrix. Small grain size and anhedral shape of thorianite crystals hint that they crystallize very fast. It is to be noted that, within thorite clusters, no single grain of thorianite size is seen. This perhaps indicates that during high temperature treatment, i.e. at soaking stage, crystallization of thorite is preferred over thorianite crystallization, and this situation is reversed in subsequent quenching stage. Thus, microstructure of thoria glass bears signatures of two important phenomena that happened during its high temperature soaking and subsequent annealing of the samples i.e., (a) elemental diffusion is not homogeneous within the BBS melt and (b) phase stability fields change from soaking to cooling stages.

The best evidence of inhomogeneous elemental diffusion even within a restricted region is found to be preserved within thorite grains. A closer look at the BSE images of the thorite crystals shows the presence of some regular band structures as defined by variation in BSE Z intensity running parallel to the boundary. The widths of these bands are found to vary from sub-micron to one micron. Such feature probably indicates the presence of chemical zoning, a phenomenon which is commonly found

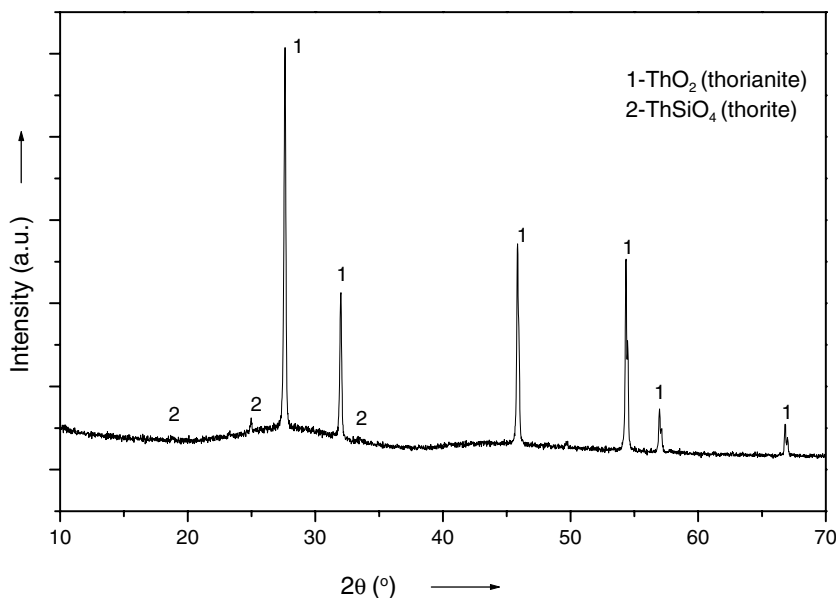


Fig. 6. X-ray diffraction pattern obtained for (a) BBS base glass and (b) thoria glass with 23.75 wt% thoria loading.

in natural silicate crystals formed during cooling of magma. To confirm this, X-ray images and line scans (marked on corresponding BSE image) for ThM α and SiK α across the phases were taken and are shown in Fig. 7(a)–(e). Although some variations in ThM α and SiK α signals are seen across the thorite but quantification of the same could not be done due to broader probe size. Explanation of the observed Th–Si zoning phenomenon in terms of Th⁴⁺–Si⁴⁺ elemental exchange or in terms of available ThO₂–SiO₂ binary phase diagram [14] is difficult. Owing to large ionic size mismatch between Si⁴⁺ and Th⁴⁺ or for that matter any An⁴⁺ ions, ionic substitution of Th⁴⁺ at Si⁴⁺ sites is not expected in any case. Application of ThO₂–SiO₂ binary phase diagram is limited in the present case due to the presence of multiple components. It is known that equilibrium phase relationships for any system can change substantially upon addition of other components, even in trace quantity. Zoning could be due to presence of other components in the glass. In the present case, thorianite and thorite are found to crystallize from silicate melt at a tempera-

ture at and below 1000 °C i.e. much lower than what is predicted by available ThO₂–SiO₂ phase diagram. This also could be due to multicomponent present in glass. Normalizing the experimental glass compositions only for ThO₂ and SiO₂ i.e. disregarding all other components, a ThO₂:SiO₂ composition close to 1:1 (in terms of wt%) is obtained. According to the phase diagram at this composition, thorianite is more likely to form initially and then get converted to thorite upon reaction with silicate melt. Due to slow interaction with silicate melt might have lead to low volume fraction of thorite.

Based on the ²⁹Si and ¹¹B solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) studies [15,16], it has been established that there is no interaction between borosilicate network and Th⁴⁺ ions in BBS glasses.

3.2. Microstructural characterization of glass by X-ray diffraction

XRD pattern of the BBS glass up to 15.87 wt% ThO₂ is amorphous in nature, whereas in case of

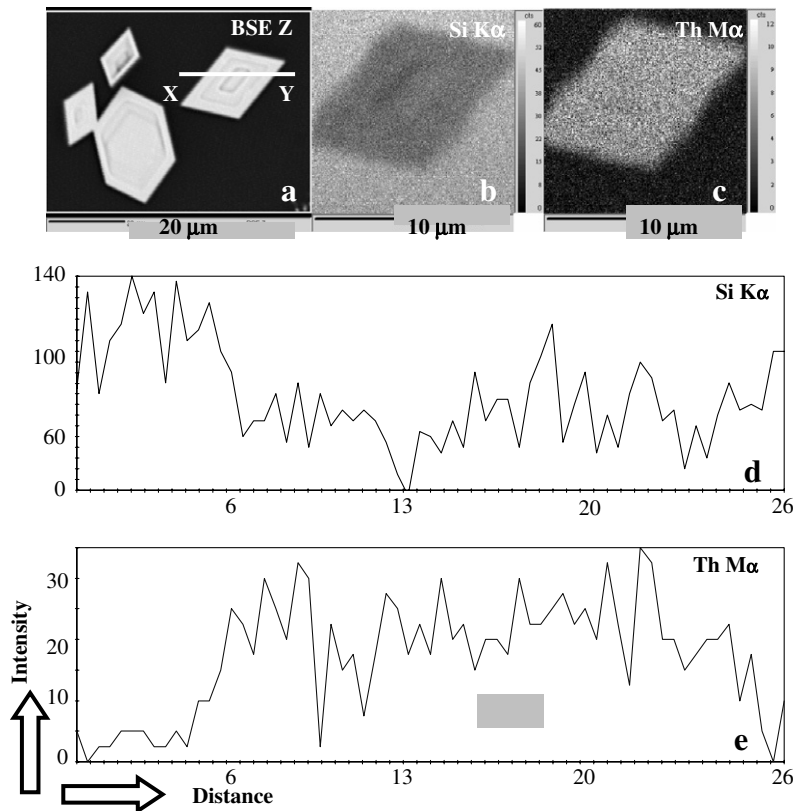


Fig. 7. (a) BSE image of thorite (crystallized in BBS glass containing 23.75 wt% thorium) showing hexagonal and rhombic outlines. SiK α and ThM α X-ray images and line scans (along X–Y line shown in (a)) across the rhombic phase are shown in (b)–(e), respectively.

glasses containing more than 15.87 wt% thoria showed the presence of crystalline phases (Fig. 6) identified as thorianite (JCPDS File number 42-1462) and thorite (JCPDS File number 18-1371).

4. Conclusion

The above study clearly shows solubility limit of thoria in borosilicate matrices increases with addition of barium as network modifier. It is noted that barium borosilicate glass matrix can contain up to 16 wt% thoria without phase separation. Beyond this limit, thorite and thorianite separates out within the matrix. The mode of crystallization of these phases is quite interesting and more detailed work need to be done to comprehend this in totality. MAS NMR studies done on the same experimental glass indicate that addition of thoria plays no significant role in modifying the BBS glass network.

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