Bulgarian Chemical Communications, Volume 46, Number 1(pp. 56 – 61) 2014

Phase composition and microstructure of sodium-alumoborosilicate glasses and glass-ceramics in the system $Na_2O/BaO/TiO_2/Al_2O_3/B_2O_3/SiO_2/Fe_2O_3$

R. Harizanova[1*], L. Vladislavova[1], C. Bocker[2], C. Rüssel[2], I. Gugov[1]

[1]*University of Chemical Technology and Metallurgy, 8, Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*

[2]*Institut für Glaschemie "Otto-Schott-Institut", Friedrich-Schiller-Universität, Fraunhoferstr. 6, 07743 Jena, Germany*

Received January 2, 2013; Revised February 2, 2013

The present work reports on the synthesis, phase formation and microstructure of glasses and glass-ceramics, obtained in the system $Na_2O/TiO_2/BaO/Al_2O_3/B_2O_3/SiO_2/Fe_2O_3$. The characteristic temperatures of the samples are determined by differential thermal analysis. X-ray diffraction is used for phase identification. Scanning electron microscopy, combined with energy dispersive X-ray analysis, is used for microstructural characterization and determination of the chemical composition of the formed crystals. All investigated compositions were amorphous. The annealing of the obtained glasses results in formation of spherical $BaTiO_3$ particles with sizes in the range from 100 nm to several μm.

Keywords: invert glass; barium titanate; nanocrystallisation; microstructure

1. INTRODUCTION

Barium titanate is a well-known dielectric material which possesses multiple polymorphic modifications. The tetragonal modification is stable at room temperature and is the predominantly observed one, which results in ferroelectric properties. Tetragonal barium titanate is used for the preparation of powerful capacitors and as a substitute of the magnetic RAM, e.g. as FRAM [1-5]. However, the cubic modification of $BaTiO_3$ which is stable at temperatures above the Curie temperature (~120 °C) is also characterized by a high dielectric constant and due to the lack of ferroelectricity, by isotropic dielectric properties [1, 4, 5]. Thus, it finds application in multilayered capacitors for energy storage [1, 3, 4] and depending on its optical properties, it may be a promising candidate for UV laser preparation for optoelectronic applications [5]. Different experimental techniques are used to obtain barium titanate as bulk material [1, 2, 4, 5]. The preparation of $BaTiO_3$ thin films is also reported in the literature [3, 6].

The different allotropic modifications of $BaTiO_3$ can be stabilized at room temperature by addition of dopants of different type and concentration. The various crystallite sizes will also lead to stabilization of one or another modification of barium titanate. This enables to control the properties of the resulting materials [2, 3]. In the literature, the addition of 3d-transition metal oxides (for example iron oxides) to systems in which $BaTiO_3$ crystallizes is reported [2]. Conventional barium titanate ceramics are prepared by the chemical reaction of barium carbonate and titanium oxide to barium titanate, subsequent milling and sintering [2]. Also, the preparation of barium titanate nanorods by means of a hydrothermal method is reported in [5]. These nanorods show light emission in the blue part of the visible spectrum if irradiated with UV light.

In the literature, also advanced glass melting techniques for the preparation of barium titanate and magnetite nanoparticles are reported. The materials prepared in this way are promising candidates for application in spintronics [7, 8]. Recent studies were carried out in the system $(24\text{-}y)Na_2O/yAl_2O_3/14B_2O_3/37SiO_2/25Fe_2O_3$ with y = 8, 12, 14 and 16 [9] while other investigations were performed on compositions derived from this system [10-12]. It was reported that primarily phase separation occurs in the prepared glasses and droplets with sizes in the range from 100 to 800 nm enriched in B_2O_3 and FeO_x are formed. Subsequently, magnetite crystals with sizes in the range from 25 to 40 nm precipitate within these droplets [12]. The materials prepared in this way may be suitable for applications as multicore magnetic nanoparticles.

* To whom all correspondence should be sent:
E-mail: ruza_harizanova@yahoo.com

This paper reports on the synthesis and characterization of glasses and glass-ceramics in the system (23.1-x)Na_2O/23.1BaO/23TiO_2/7.6B_2O_3/17.4SiO_2/5.8Fe_2O_3/xAl_2O_3. The reported glasses contain less than 30 mol % glass-forming oxides. The occurrence of droplet-like regions in which cubic barium titanate crystallizes is observed after annealing of samples from all glass compositions in the system.

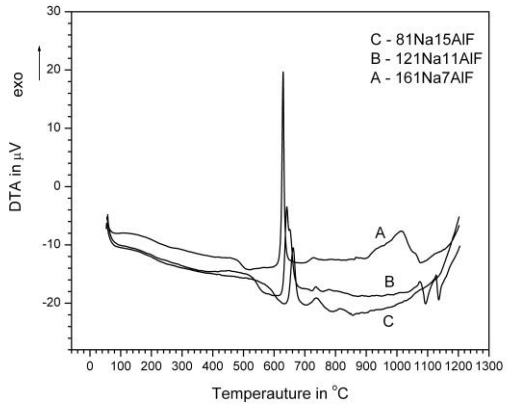
2. EXPERIMENTAL

Samples with the mol % compositions (23.1-x)Na_2O/23.1BaO/23TiO_2/7.6B_2O_3/17.4SiO_2/5.8Fe_2O_3/xAl_2O_3, x = 0, 3, 7, 11, 15 (batch composition) are melted from the following reagent grade raw materials: Na_2CO_3, $BaCO_3$, TiO_2, $Al(OH)_3$, $B(OH)_3$, SiO_2 and Fe_2O_3. The glasses are melted in 60 g batches for 1 h at 1250 °C in air using Pt crucibles in a furnace with SiC heating elements. The melts are quenched on a copper block without pressing. Then, in order to increase the mechanical stability and to minimize internal stresses, the glass is transferred to a pre-heated graphite-mould and held for 15 min at 450°C in a muffle furnace. Subsequently, the furnace is switched off and the sample is allowed to cool to room temperature. Crystallization of the samples is carried out at 550°C in a muffle furnace for different times.

The phase compositions of the samples from all melted compositions are studied by X-ray diffraction (XRD), *Siemens D5000* using Cu-Kα radiation (λ = 1.5406 Å) and Ni filter. The glass transition and crystallisation temperatures are determined on bulk samples by differential thermal analysis (DTA), *Perkin Elmer Diamond TG/DTA*. The microstructure and the elemental composition of the prepared glasses and subsequently, of the crystallised samples is further analysed by scanning electron microscopy (SEM) in combination with energy-dispersive (EDX) analysis, (*JSM-7001F, JEOL Ltd., Japan*). Imaging of the crystallised samples is performed on polished samples, or if this did not result in a good contrast, on samples etched for 5 s in 1% HCl solution. The topography of selected samples is studied on polished surfaces by atomic force microscopy (AFM), *Zeiss Ultra Objective, Carl Zeiss GmbH, Germany*.

3. RESULTS AND DISCUSSION

The samples show a dark brown coloration after quenching on the copper plate. Some parts of the surface are slightly crystallised and formation of droplet-like light brown regions is observed. The bulk of all samples is, as seen at a fractured surface, glassy. The XRD patterns of the bulk specimens prove that the samples are amorphous, which indicates that the quantity of crystals is negligibly small and they are mainly observed at the surface.



The DTA profiles of the melted glasses, as shown for three of them in Fig. 1, allow to determine the glass transition and the crystallisation temperatures of the prepared materials. They further help to choose appropriate time-temperature annealing regimes in order to study the crystallisation behaviour of the samples. In Figure 1 DTA profiles for the samples with 16.1 mol% Na_2O and 7 mol% Al_2O_3 (sample A), 12.1 mol% Na_2O and 11 mol% Al_2O_3 (sample B) and 8.1 mol% Na_2O and 15 mol% Al_2O_3 (sample C) are shown. As seen in the Figure, the glass transition temperature of sample C with the smallest alkali and highest alumina concentration increases to about 580°C in comparison to samples A and B with glass transition temperatures of 480°C and 530°C, respectively. The crystallisation temperatures follow the same trend. The effect of the varied Na_2O and Al_2O_3 concentrations on the glass transition temperature has already been reported by other authors for sodium alumosilicate glasses of various compositions [13-18]. It has been observed that with increasing the alumina concentration, the viscosity and the glass forming ability also increase and the maximum value of viscosity is achieved for a ratio $[Na_2O]/[Al_2O_3]$ = 1 [11, 13-18]. A similar observation is reported in our

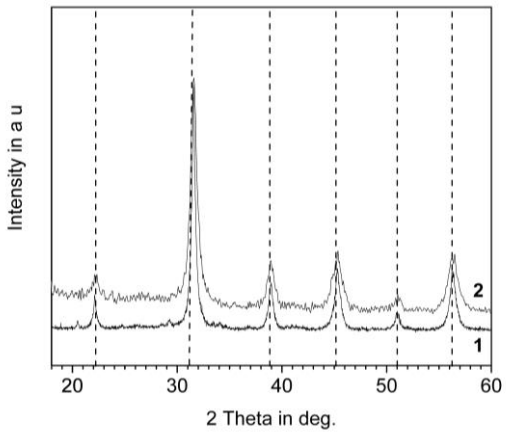


Fig. 2 XRD-patterns of samples with 23.1 mol% Na_2O and 0 mol% Al_2O_3 (1) and with 20.1 mol% Na_2O and 3 mol% Al_2O_3 (2), annealed respectively for 4h and 3h at 550°C - formation of cubic $BaTiO_3$; dashed line – lines of $BaTiO_3$.

study – the melts with equimolar alumina and sodium oxide concentrations showed a glass transition temperature about 50 K higher than that of the sample with 16.1 mol% Na_2O and 7 mol% Al_2O_3 and 100°C higher than that of the sample with 0 mol% Al_2O_3.

In order to investigate the crystallisation behaviour of the prepared glasses with the compositions (23.1-x)Na_2O/23.1BaO/23TiO_2/7.6B_2O_3/17.4SiO_2/5.8Fe_2O_3/xAl_2O_3 with x = 0, 3, 7, 11, pieces from the bulk were chosen and annealed for 3 or 4 h at 550°C, i.e. above or near Tg. The annealing times were chosen in such a way that the average crystallite size hardly changes when increasing the time of thermal treatment. Thus, the crystals precipitated in specimens with different compositions may be compared. The resulting samples are visually well-crystallized in the bulk and the XRD-patterns show only the formation of cubic $BaTiO_3$, (JCPDS Nr. 01-079-2263), as shown in Figure 2. The obtained $BaTiO_3$ phase is recognized as the cubic modification since there is no visible splitting in the characteristic peak at about 45.3° – as it should be in the case of the tetragonal $BaTiO_3$ modification [1, 19].

Some authors report that the change in the symmetry of barium titanate from cubic to tetragonal depends on the size of the precipitated crystals [1, 19] or even discuss the formation of a tetragonal core and a cubic shell

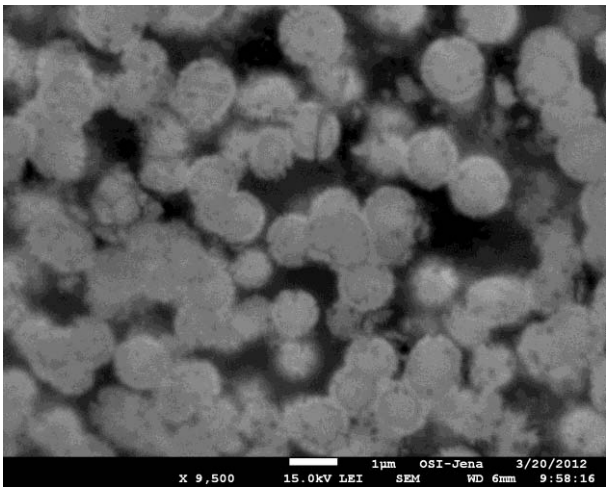


Fig. 3 SEM-micrograph of a sample with 23.1 mol% Na_2O and 0 mol% Al_2O_3 crystallised for 4h at 550°C

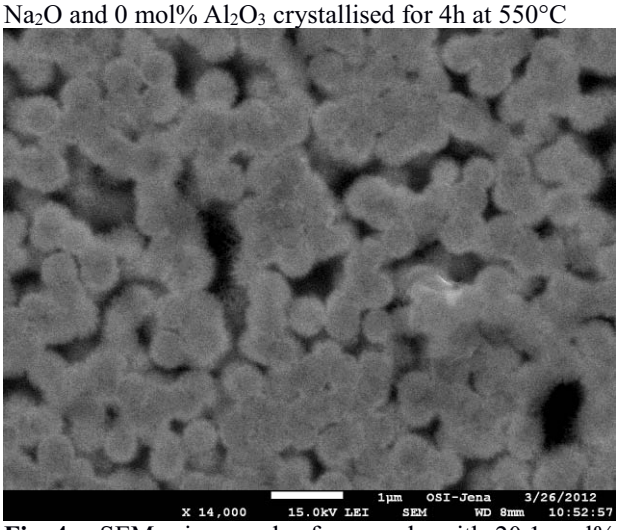


Fig. 4 SEM-micrograph of a sample with 20.1 mol% Na_2O and 3 mol% Al_2O_3 crystallised for 3h at 550°C.

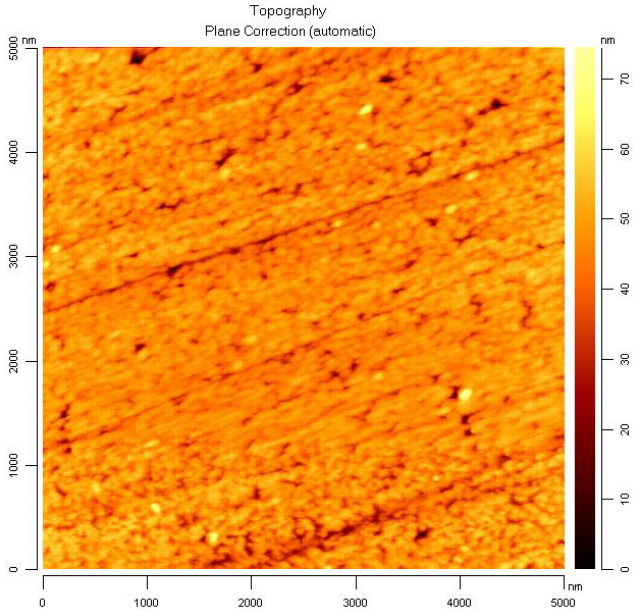


Fig. 5 AFM image (topography mode) of a sample with 16.1 mol% Na_2O and 7 mol% Al_2O_3, annealed for 3h at 550°C – average size of the spherical $BaTiO_3$ crystals about 150 nm.

for the growing barium titanate particle [1]. In our work, however, we did not observe up to now such a dependency and the crystallised $BaTiO_3$ is always cubic. Similar observations are done when imaging the microstructure of the annealed samples (see Figures 3 to 5) – only one morphological type of crystals is present. The SEM imaging of samples with different thermal history and composition suggests that for annealing times $t \geq 3$ h the mean size of the formed globular crystals only slightly changes. In Figure 3 a SEM micrograph of a sample without Al_2O_3 is shown. It is observed that spherical crystals with a mean size of about 1μm are formed. The same crystal morphology is already seen in other, similar as chemical composition, glass-ceramic materials [9, 12] and suggests the idea that first phase separation and subsequently crystallisation in the droplets may occur in the present set of compositions. The brighter appearance of the formed crystals serves as an evidence that they contain the heavier elements of the initial composition, e. g. Ba, Ti and probably, also some Fe. The addition of transition metal oxides as dopants, in the present study Fe and Ti, is a well-known method for changing the modification and thus, the properties of the resulting crystals. This has already been reported for other Fe- and (Ba,Fe,Ti)-containing glass systems [2,7,11]. The successful combination of two or more transition metals may result in the formation of core-shell structures composed by both, ferroelectric and ferromagnetic crystals. This will enable to combine the properties of the two phases formed, which may result in multiferroic properties and the synthesis products can find unique applications in electronics [7, 8]. Anyway, the presented XRD data, as seen in Fig. 1, support the presence of only Ba and Ti and no Fe in the crystals. The total lack of Fe in the barium titanate crystals, or its presence in concentrations too small to be detected, may be attributed to the relatively low Fe_2O_3 concentration. This is in contrast to the data from other authors, who by sintering powders obtained Fe-doped barium titanate [2]. According to these reports, however, the Fe-doped barium titanate crystals change their symmetry from tetragonal to hexagonal. This effect occurs in parallel to the incorporation of iron and is undesired because the hexagonal phase is not ferroelectric and furthermore, in comparison to the cubic modification it possesses worse dielectric parameters.

The SEM-micrograph of a sample with 20.1 mol% Na_2O and 3 mol% Al_2O_3 (see Figure 4) shows crystals with an average size of about 500 nm. The higher magnification in Figure 4, compared to that in Figure 3, allows seeing that the separate spherical crystals are in close contact with each other, which constrains their further growth. These crystals are smaller than the ones shown in Figure 3, which represents a SEM micrograph of the composition with 0 mol% Al_2O_3. The same trend – decrease of the average size of the crystals formed with increasing alumina concentration - is also observed in the XRD patterns of Figure 2. Here the peaks of the sample with 3 mol % Al_2O_3 are wider than those with 0 mol% Al_2O_3. The latter observation might be explained by the higher glass transition temperature and hence, the higher viscosity of the glass with a higher Al_2O_3 concentration when annealed at the same temperature (550°C) as the glass without alumina.

The microstructure of the samples shown in Figures 3 and 4 proves the existence of spherical crystals with core-shell structure. Similar observations are done by other authors who report the combination of two modifications of $BaTiO_3$, coexisting in one core-shell crystal – tetragonal core and cubic shell [1]. In [1] they report that the size of the formed barium titanate crystals determines the allotropic modification present and that the process of crystallite growth leads to transition within one and the same particle from cubic to tetragonal barium titanate. In our investigation, however, we could not conclude if this is the reason for the formation of core-shell structure in the growing crystals and further investigation of the particles is needed in order to elucidate this problem. In general, the imaging of the samples with increasing Al_2O_3 content is difficult due to the decreasing size of the crystals. Actually, the crystal morphology in the sample with 7 mol% Al_2O_3 crystallised

for 3 h at 550°C could only be investigated by AFM – the size of the crystals was found to vary from about 100 to 150 nm, as seen in Figure 5. From Figures 3 to 5 it can be concluded that the volume concentration of crystals in the samples is high – there is almost no glassy phase remaining between the crystals. The separate particles tend to aggregate and form larger complexes which grow together – as seen in Figure 3 and already observed in other systems where the crystallisation is preceded by droplet-like phase separation [9, 12].

The observed morphology of the formed crystals, as well as the resulting size variation depending on the composition of the initial glasses, may affect the dielectric properties of the obtained barium titanate glass-ceramics and will be a subject of further investigation.

4. CONCLUSIONS

A set of invert glass compositions $(23.1-x)Na_2O/23.1BaO/23TiO_2/7.6B_2O_3/17.4SiO_2/5.8Fe_2O_3/xAl_2O_3$ is melted and subsequently quenched on a copper block, which leads to glass formation. Annealing above or near Tg results in the crystallisation of crystals of cubic $BaTiO_3$ gathered in spherical particles in the amorphous matrix, whose mean sizes vary from 100 nm to 1 μm for the different compositions. The X-ray diffraction studies and the SEM investigations of the spherical particles allow concluding that these are mainly enriched in barium and titanium oxide and formation of cubic $BaTiO_3$ occurs without the participation of Fe in the crystals. With increasing alumina and decreasing sodium oxide concentrations, the average particle sizes decrease.

Acknowledgements: *This work was financially supported by contract № D02-797/28.08.2012, index: P-5-22/2012, project: BG051PO001-3.3-05/0001 «Science-business», funded by Operational program «Development of human resources».*

REFERENCES

1. J.F. Capsal, E. Dantras, L. Laffont, J. Dandurand, C. Lacabanne, *J. Non-Cryst. Solids,* **356,** 629 (2010).
2. G.P. Du, Z. J. Hu, Q. F. Han, X. M. Qin, W.J. Shi, *Journal of Alloys and Compounds,* **492,** L79 (2010).
3. T.J Jackson, I. Jones, *J. Mater Sci.,* **44,** 5288 (2009).
4. Z. Libor, S.A. Wilson, Q. Zhang, *J Mater Sci.,* **46,** 5385 (2011).
5. R. Vijayalakshmi, V. Rajendran, *Digest Journal of Nanomaterials and Biostructures*, **5,** 511 (2010).
6. S.F. Mendes, C.M. Costa, C. Caparros, V. Sencadas, S. Lanceros-Mendez, *J. Mater. Sci.,* **47,** 1378 (2012).
7. R.P. Maiti, S. Basu, S. Bhattacharya, D. Chakravorty, *J. Non-Cryst. Solids,* **355,** 2254 (2012).
8. A.K. Zvezdin, A.S. Logginov, G.A. Meshkov, A.P. Pyatakov, *Bull. Russian Acad. Sci.: Physics,* **71,** 1561 (2007).
9. R. Harizanova, G. Völksch, C. Rüssel, *J. Mater. Sci.,* **45,** 1350 (2010).
10. W. Vogel in: *Glasschemistry*, 3 Ed. Springer-Verlag, Berlin-New York-London-Paris-Tokyo-Hong Kong-Barcelona-Budapest, 1992.
11. R. Harizanova, I. Gugov, C. Rüssel,, D. Tatchev, V. S. Raghuwanshi, A. Hoell, *J. Mater. Sci.: Size Dependent Effects* **46,** 7169 (2011).
12. C. Worsch, P. Schaaf, R.Harizanova, C. Rüssel, *J. Mater. Sci.,* **47,** 5886 (2012).
13. K. El-Egili, *Phys., B* **325,** 340 (2003).
14. S. Hornschuh, B. Messerschmidt, T. Possner, U. Possner, C. Rüssel, *J. Non-Cryst. Sol.,* **347,** 121 (2004).
15. L. Hong, P. Hrma, J.D. Vienna, M. Qian, Y. Su, D.E. Smith, *J. Non-Cryst. Sol.,* **331,** 202 (2003).
16. D. Benne, **C.** Rüssel, M. Menzel, K. Becker, *J. Non-Cryst. Sol.,* **337,** 232 (2004).
17. H. Schirmer,R. Keding, C. Rüssel, *J. Non-Cryst. Sol.,* **336,** 37 (2004).
18. D. Benne, C. Rüssel, D. Niemer, M. Menzel, K. Becker, *J. Non-Cryst. Sol.,* **345-346**, 203 (2004).
19. S.D. Vacche, F. Oliveira, Y. Leterrier, V. Michaud, D. Damjanovic, J.E. Manson, *J. Mater. Sci.,* **47,** 4763 (2012), DOI 10.1007/s10853-012-6362-x.

ФАЗОВ СЪСТАВ И МИКРОСТРУКТУРА НА НАТРИЕВО-АЛУМОБОРОСИЛИКАТНИ СТЪКЛА И СТЪКЛОКЕРАМИКИ В СИСТЕМАТА $Na_2O/BaO/TiO_2/Al_2O_3/B_2O_3/SiO_2/Fe_2O_3$

Р. Харизанова[1*], Л. Владиславова[1], Кр. Бокър[2], Кр. Рюсел[2], И. Гугов[1]

[1]Химикотехнологичен и металургичен университет, бул."Кл. Охридски" № 8, 1756 София, България
[2]Ото Шот институт по химия на стъклото, Университет „Фридрих Шилер", ул. „Фраунхофер" № 6, 07743 Йена, Германия

Получена на 2 януари, 2013 г.; коригирана на 2 февруари, 2013 г.

(Резюме)

Настоящата работа докладва данни за синтеза, фазообразуването и микроструктурата на стъкла и стъклокерамики, получени в системата $Na_2O/TiO_2/BaO/Al_2O_3/B_2O_3/SiO_2/Fe_2O_3$. Характеристичните температури на пробите са определени с помощта на диференциален термичен анализ. Методът на рентгеновата дифракция е използван за фазова идентификация. Сканираща електронна микроскопия, комбинирана с енергийно-дисперсивен рентгенов анализ, позволява характеризиране на микроструктурата и определяне на химичния състав на формираните кристали. Продуктите на синтеза за всички изследвани състави са аморфни. Темперирането на получените стъкла води до кристализацията на сферични $BaTiO_3$ частици с размери от 100 nm до няколко μm.