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Crystallization and dielectric properties of $BaTiO_3$-containing invert aluminoborosilicate glass-ceramics

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The synthesis of invert glasses is possible in the oxide system $Na_2O/TiO_2/BaO/Al_2O_3/B_2O_3/SiO_2/Fe_2O_3$ for glass-former concentrations less than 30 mol%. The prepared glasses are further annealed at different temperatures above the glass transition temperature for different periods of time. This resulted in the simultaneous crystallization of cubic and tetragonal $BaTiO_3$ as shown by x-ray diffraction. The scanning electron microscopy imaging shows precipitation of globular crystals with sizes varying from some ten nanometers to 1-2 micrometers. The dielectric properties of the glass-ceramic samples are investigated by the method of impedance spectroscopy as a function of frequency. High dielectric constants of the order of 1000 at room temperature and frequency 13 Hz are obtained.

Key words: barium titanate, invert glass, crystallization, impedance spectroscopy, dielectric constant.

INTRODUCTION

Oxide glasses and glass-ceramics, containing less than 50 mol% glass-forming oxides have high tendency to crystallization and are known as invert glasses [1]. These systems, although difficult to obtain as amorphous solid, can be crystallized using an appropriate thermal treatment in order to obtain crystalline phases with distinct physical properties. In an ideal case, the obtained glass-ceramic materials combine advantageous properties of the amorphous and of the crystalline phase. The precipitation of crystalline phases with extremely high melting temperature from such invert glasses allows to decrease the synthesis temperature of the corresponding material and to obtain high volume fraction of the crystals. This technique can also be applied to the preparation of dielectric materials such as barium titanate. Barium titanate, $BaTiO_3$ is a well-known dielectric which possesses numerous allotropic modifications. In most cases, the tetragonal modification of $BaTiO_3$ is preferred since it is ferroelectric up to about 120°C and may be utilized for the preparation of capacitors due to its high dielectric constant and as a substitute of the magnetic RAM, e.g. as ferroelectric RAM (FRAM) [2-6]. The cubic modification of $BaTiO_3$ also possesses high dielectric constant and due to the lack of ferroelectricity has isotropic dielectric properties [2, 5, 6]. So, it can be applied for the preparation of different types of electronic elements, for example as multilayered capacitor for energy storage [2, 4, 5]. Depending on its optical properties, the cubic modification may be a promising candidate for UV laser preparation for optoelectronic applications [6]. Multiple experimental techniques are used for the preparation of barium titanate as bulk material, [2, 3, 5, 6]. There are also reports dedicated to the preparation of $BaTiO_3$ in the form of thin films [4, 7].

Some authors report on the addition of 3d-transition metal oxides, for example Fe, to systems in which $BaTiO_3$ is crystallized [3]. Often, the crystallization of $BaTiO_3$ with or without the addition of iron oxide is achieved by treatment at high temperatures [3]. Other investigations are devoted to the preparation of barium titanate nanorods with cubic symmetry showing emission in the blue part of the visible spectrum [6] using hydrothermal methods or, however, of the tetragonal modification with potential application in electronics [8]. There are also authors who prefer traditional glass melting techniques to precipitate core-shell nanoparticles composed of barium titanate and magnetite which are promising candidates for application in spintronics [9, 10]. The as obtained modifications of barium titanate exhibit numerous interesting properties, i.e. electric, optical and piezoelectric [6, 8, 11] which promotes the further interest in their investigation.

Another important aspect in the preparation of barium titanate or core/shell particles composed of barium titanate and magnetite is the proper choice of the initial glass composition, so that a tailored

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size of the precipitated crystals and large enough volume fraction may be achieved. Studies carried out using the composition $12Na_2O/12Al_2O_3/14B_2O_3/37SiO_2/25Fe_2O_3$ [12] or similar oxide systems [13-19] show that the varied ratio of the alkaline and alkaline earth oxides leads to controlled viscosity of the melt. This allows controlling the crystallite size and volume fraction in the corresponding materials.

This work reports the results from the synthesis of glasses from invert compositions with less than 30 mol % glass-forming oxides in the system $(23.1-x)Na_2O/23.1BaO/23TiO_2/7.6B_2O_3/17.4SiO_2/5.8Fe_2O_3/xAl_2O_3$ and the resulting microstructures. Further, it shows the possibility to crystallize $BaTiO_3$ with varying particle sizes from glass compositions with different ratios $[Na_2O[/[Al_2O_3]$. The dielectric constants of the synthesized glass-ceramic materials are determined by impedance spectroscopy.

EXPERIMENTAL

The ratio $[Na_2O]/[Al_2O_3]$ is varied and a series of compositions with the formula $(23.1-x)Na_2O/23.1BaO/23TiO_2/7.6B_2O_3/17.4SiO_2/5.8Fe_2O_3/xAl_2O_3$ x = 0; 3 in mol% (batch composition) are melted from reagent grade raw materials: Na_2CO_3, $BaCO_3$, TiO_2, $Al(OH)_3$, $B(OH)_3$, SiO_2 and Fe_2O_3. All glasses are melted in 60 g batches for 1 h at 1250 °C in air using a Pt crucible in a furnace with SiC heating elements. Then, the melts are quenched (without pressing) on a copper block and, in order to reduce the mechanical stresses in the glass, transferred to a pre-heated C-mould and held for 10-15 min at 450°C in a muffle furnace. Then, the furnace is switched off and the samples are allowed to cool to room temperature.

The phase compositions of the samples from all melted compositions are studied by x-ray diffraction (XRD), *Siemens D5000*, using Cu-Kα radiation (λ = 1.541874 Å) and Ni-filter. The microstructure and the elemental composition of the prepared glasses and subsequently, of the crystallised ones is further analysed by scanning electron microscopy (SEM), combined with energy-dispersive (EDAX) analysis, (*JSM-7001F, JEOL Ltd., Japan*). Imaging of the crystallised samples is performed on both polished and if no good contrast is achieved – on etched surfaces (5 s in 1% HCl solution). The dielectric properties are investigated by impedance spectroscopy at room temperature in the frequency range from 1 Hz to 130 kHz. First the impedance modulus and the phase angle are measured as function of frequency and then an appropriate equivalent circuit is proposed (impedance meter *Zahner IM6, Kronach, Germany*). The capacitance derived from the equivalent circuit is determined at several frequencies and the dielectric constant is calculated.

RESULTTS AND DISCUSSION

All prepared glasses after quenching on a copper plate possess dark brown coloration. There are some parts of the surface which seems to be slightly crystallised. Here, the formation of droplet-shaped light brown regions is observed. The bulk of all samples appears glassy, as seen at a fractured surface and as concluded from XRD patterns and SEM imaging. The XRD patterns of the untreated glass and samples annealed at 550°C for different periods of time are shown for the composition with 20.3 mol% Na_2O and 3 mol% Al_2O_3 in Figs. 1 and 2 (samples G1 to G7).

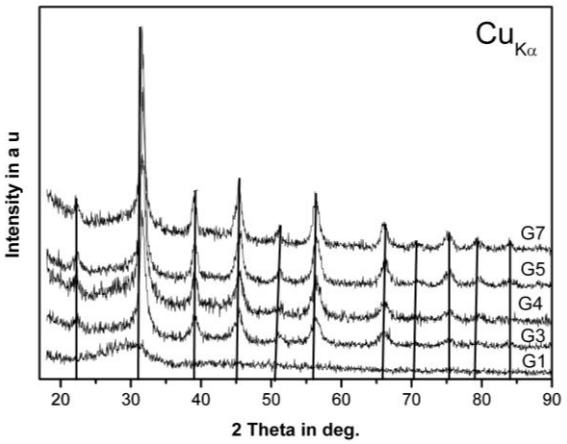

Fig. 1. XRD patterns of samples with 5,8 mol% Fe_2O_3 and 3 mol% Al_2O_3 – glass as prepared (G1) and crystallization of $BaTiO_3$ (JCPDS 1-74-1962) after annealing for 30 min (G3), 1 h (G4), 2 h (G5) and 5 h (G7) at 550°C; lines – peaks of $BaTiO_3$.

Increasing annealing times lead to peaks of larger intensity and to a larger volume fraction of crystalline phase. The same results are observed earlier for the same system [20] and for similar borosilicate glasses from which $BaTiO_3$ can also subsequently be crystallized [21]. In the present study and from our previous work [20], we have the idea that with increasing Al_2O_3 concentration, the crystallization tendency on the surface decreases up to the ratio $[Na_2O]/[Al_2O_3]$ = 12.1/11. For a concentration of 15 mol% Al_2O_3, already spontaneous and sporadic crystallisation occurs in the bulk, although in the XRD-pattern no distinct lines are observed. The average size of the crystals

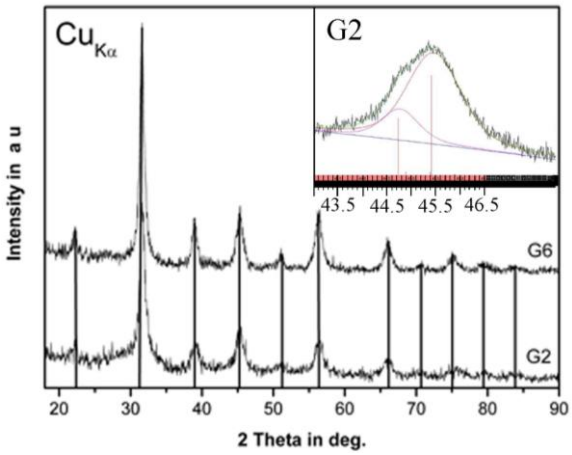

Fig. 2. XRD patterns of samples from the system $Na_2O/BaO/TiO_2/B_2O_3/SiO_2/Fe_2O_3$ with 5.8 mol% Fe_2O_3 and 3 mol% Al_2O_3 – crystallization of $BaTiO_3$ after annealing for 15 min (G2) and 3 h (G6) at 550°C; lines – peaks of $BaTiO_3$; inset: magnified peak at 45.3° with peaks of the tetragonal phase fitted.

formed during annealing at 550°C and for equal periods of time show that an increasing ratio sodium oxide/alumina leads to an increase in the average crystallite size – as already reported in [20]. Such a dependency of the size of the formed crystals on the ratio $[Na_2O]/[Al_2O_3]$ is attributed to the increase in the viscosity with decreasing ratio and was already observed in other non-transition metal containing aluminoborosilicate glasses [14-16] or in glasses containing minor quantities of polyvalent elements, e.g. tin or iron [17-19]. However, the same dependency on the viscosity and thus, of the size of the precipitated crystalline phase on the ratio between the alkali and aluminum oxides is also seen for borosilicate glass melts with higher Fe_2O_3 concentration (between 14 and 25 mol%) [12]. The same situation is observed for the crystallization products in the present study – see Figs. 3 and 4. Here the formed crystals for compositions without Al_2O_3 are of the order of 1 micrometer while the crystals precipitated under the same annealing schedule but for an alumina concentration of 3 mol% are less than 600 nm. The XRD analyses show that for both compositions always one and the same crystalline phase – cubic $BaTiO_3$, JCPDS 1-74-1962, is formed. The same observation was already reported in our earlier works [20, 21]. The Rietveld refinement of the peak at 45.3°, however, shows that the peak may be represented as a combination of two peaks – see the inset in Fig. 2, i.e. in the annealed samples with 3 mol% Al_2O_3 obviously also the tetragonal modification of barium titanate is present. This type of analysis has already proved to be a trustful way to establish the presence of cubic or/and tetragonal $BaTiO_3$ [2, 8]. Usually, the size of the formed particles and the preparation conditions are decisive for the formation of either cubic or tetragonal barium titanate [2, 4-8, 11]. The fit in Fig. 2, however, suggests that here simultaneously cubic and tetragonal $BaTiO_3$ are present. The simultaneous presence of the tetragonal modification which is ferroelectric but also of the cubic one – paraelectric with isotropic dielectric properties – may have an interesting impact on the dielectric properties of the resulting glass-ceramics. As seen in Figs. 3 and 4, the prepared glass-ceramic materials are characterized by a high degree of crystallization in the bulk and thus, high dielectric constants are expected for them as already observed in the work of other authors concerning barium titanate based glass-ceramics [23].

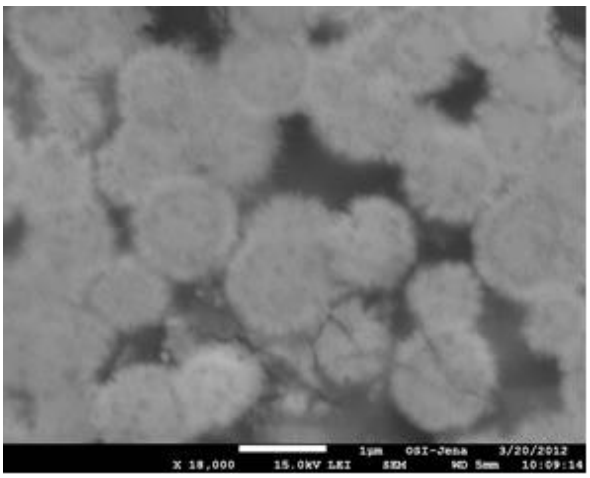

Fig. 3. SEM of a polished and C-covered sample with 5.8 mol% Fe_2O_3 and no Al_2O_3 – formation of spherical core-shell crystals after annealing for 4 h at 550°C

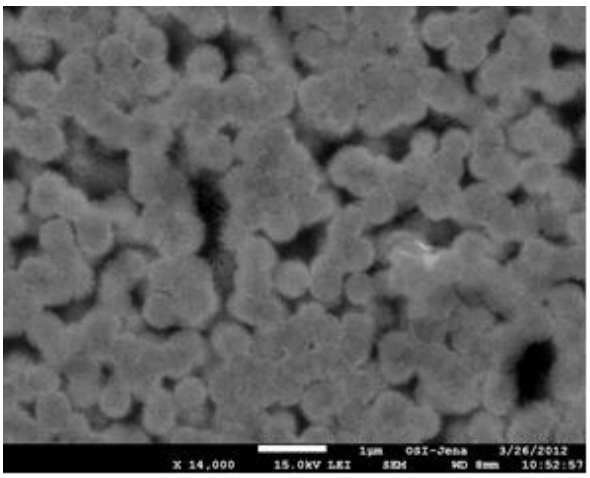

Fig. 4. SEM of a C-covered sample with 3 mol% Al_2O_3 and 5.8 mol% Fe_2O_3, annealed for 3 h at 550°C - crystallization of globular $BaTiO_3$ in the bulk [20].

The tendency of combining different transition metals – here Fe and Ti – is a well-known method for changing the type and the properties of the

resulting crystals and is already observed in other (Ba,Fe,Ti)-containing glass systems [3, 9]. The simultaneous presence of two or more transition metals in the composition of an oxide glass can result in formation of core-shell structures consisting of ferroelectric and ferromagnetic crystals [9]. Such structures may combine the properties of the two phases formed, which results in a multiferroic property and finds novel and interesting practical applications in electronics [9, 10]. Anyway, from the presented XRD data, as seen in Figs. 1 and 2, and as concluded from the elemental EDAX analyses performed on the crystals from Fig. 3, only Ba and Ti are present in the formed crystals, however, Fe is not detected in the crystals. One reason for the total lack of Fe or only undetectable minor Fe concentrations incorporated in the $BaTiO_3$ crystals might be the relatively low Fe_2O_3 concentration. This is in contrast to the results reported by other authors, who by sintering routes obtain Fe-doped barium titanate [3] or by applying appropriate annealing programs crystallize core-shell multiferroic particles from a borosilicate amorphous matrix with a comparable iron oxide concentration [9]. It should be noted, that the Fe-doped barium titanate crystals from Ref. [3] change their symmetry from tetragonal into hexagonal due to the incorporation of Fe in the crystals. This effect is disadvantageous because the hexagonal phase exhibits no ferroelectricity and also, possesses worse dielectric parameters, in comparison to the cubic one as reported in [3].

In order to evaluate the dielectric constants of the obtained barium titanate based glass-ceramics, impedance measurements were performed. Samples from both compositions are prepared by roughly polishing two plane parallel surfaces and sputtering gold electrodes at them. Then, two points measurement was done using an impedance analyzer, first measuring the impedance modulus and phase angle as function of frequency. Then, after attributing the electrical behaviour at room temperature to an RC-circuit in parallel, the capacity is measured at a fixed frequency. The results from the performed measurements at a fixed frequency allow, for a known geometry of the samples, to calculate the dielectric constants as a function of the frequency at room temperature. Data for two annealed samples are shown in Fig. 5. It is to be mentioned that the samples show a dependency of the dielectric constant on the frequency typical for all dielectric materials – no matter what the crystalline phase is [22].

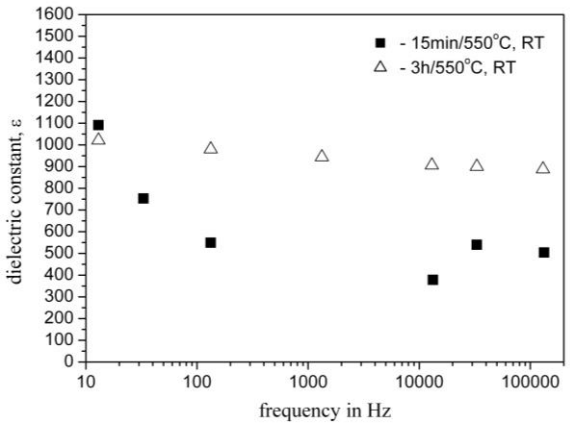

Fig. 5. Dielectric constant as function of frequency at room temperature for samples with 20.1 mol% Na_2O and 3 mol% Al_2O_3 – annealed for 15 min (G2) and 3 h (G6) at 550°C.

However, in the present case a very high dielectric constant in the whole frequency region is obtained – results comparable to the results reported by other authors in case of purely ferroelectric barium titanate [23]. From Fig. 5 in the present work it becomes clear that a longer annealing time and the same annealing temperature lead to a higher dielectric constant at one and the same frequency. This fact can be explained by the larger degree of crystallization of the sample annealed for 3h compared to that crystallized for 15 min, though both are well-crystallized since in the XRD-patterns almost no glassy halo is seen, cf. Fig.2. The data in Fig. 2 also suggests that the volume fraction and the size of the crystals in the sample annealed for 15 min at 550°C, are smaller with respect to those for the sample crystallized at the same temperature but for 3h. In Fig. 5 it is also shown that the decrease in the dielectric constant with increasing frequency is steeper for the sample crystallized for 15 min. One possible reason could be the higher losses in comparison to those in the sample crystallized for 3h for which the dielectric constant shows only a slight variation with the frequency. The explanation of this phenomenon for the present system is still not clear.

CONCLUSION

The quenching of melts from the studied compositions results in glass formation in the bulk and slight crystallization at the surface. Annealing of samples from the bulk above Tg leads to the crystallization of spherical particles of cubic $BaTiO_3$ for all ratios $[Na_2O]/[Al_2O_3]$. The Rietveld refinement of the x-ray diffraction data reveals simultaneous crystallization of the tetragonal and the cubic $BaTiO_3$ phase. No influence of Fe on the crystal phase composition and symmetry is

observed. The dielectric constant, calculated at room temperature, is about 1000 at 13Hz and its decrease with the increasing frequency depends on the annealing time applied.

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КРИСТАЛИЗАЦИЯ И ДИЕЛЕКТРИЧНИ СВОЙСТВА НА ИНВЕРТНИ АЛУМО-БОРОСИЛИКАТНИ СТЪКЛОКЕРАМИКИ, СЪДЪРЖАЩИ БАРИЕВ ТИТАНАТ

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(Резюме)

В системата $Na_2O/TiO_2/BaO/Al_2O_3/B_2O_3/SiO_2/Fe_2O_3$ е възможен синтезът на инвертни стъкла за концентрации на стъклообразувателите по-малки от 30 мол%. Получените стъкла са подложени на термично третиране при различни температури над температурата на стъклообразуване за различно време. Резултатът е едновременната кристализация на кубичен и тетрагонален $BaTiO_3$, както свидетелстват данните от рентгеновата дифракция. Анализите с помощта на сканираща електронна микроскопия показват образуването на глобуларни кристали с размери, вариращи от няколко десетки нм до 1-2 микрометра. Диелектричните свойства на стъклокерамичните проби са изследвани по метода на импедансната спектроскопия в зависимост от честотата. Определени са високи диелектрични константи от порядъка на 1000 при стайна температура и честота 13 Hz.