

Microstructure of $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{TiO}_3$ based glass-ceramics doped by Mn

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Abstract. We studied microstructure, surface morphology, and domain structure of $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{TiO}_3$ based glass-ceramics with different amount of Mn additive (from 0 to 0.5%) prepared from melted and quenched mixed powders using several microscopic methods. The as-quenched sample was annealed and subjected to a controlled crystallization in air for 2h at temperatures 850 and 950°C. It was shown that the addition of the Mn up to 0.5% had no impact on morphology and domain structure. The dendrite structure was revealed in the samples crystallized at 850°C. The geometry of the clusters was analysed in terms of fractal approach. The faceted grains with size about 150 nm were found in ceramics annealed at 950°C. Individual grains demonstrated non-uniform piezoresponse, which could be attributed to existence of domain structure.

1. Introduction

Glass-ceramics representing ferroelectric grains embedded in a glass matrix are of significant interest for power electronic applications, especially for energy storage devices [1,2]. It has been shown that the application of the glass-ceramics based on the ferroelectric materials can improve energy storage properties by the utilization of a high dielectric constant of ferroelectrics and relatively high breakdown voltage of glass [2]. It is known that the aluminosilicate glass-ceramics based on $(\text{Ba,Sr})\text{TiO}_3$ (BST) are one of the most promising materials for the energy storage applications [3]. An addition of SrO is used for tuning the Curie temperature and increasing the dielectric constant at room temperature.

It has been shown that the energy storage properties of the BST glass-ceramics depend on their microstructure [4,5]. Different additives (AlF_3 , La_2O_5 , MnO_2 , etc.) were used to control the microstructure, thus optimizing the dielectric properties [5].

The effect of space charges (interfacial polarization) at the interphase boundaries between crystalline grains and glass on the breakdown voltage and the dielectric properties has been discussed [6-8]. At the same time, properties of the ferroelectric materials strongly depend on the domain structure, but little is known about the domain structure of the BST glass-ceramics. The purpose of the present paper is to study the domain structure and its relation with the microstructure of the BST glass-ceramics with different sintering conditions and concentrations of Mn additive.



2. Experimental

The samples of the BST based glass-ceramics with different concentrations of Mn additive were prepared from melted and quenched mixed powders. The compositions of the studied glass-ceramics are presented by a chemical formula $(27.75-0.75x) \text{BaCO}_3-(9.25-0.25x) \text{SrCO}_3-29 \text{TiO}_2-20 \text{SiO}_2-14 \text{Al}_2\text{O}_3 - x \text{MnO}_2$ (mol %) with $x = 0.1-0.5$. The compositions were prepared from well-mixed powders of BaCO_3 , SrCO_3 , TiO_2 , SiO_2 , Al_2O_3 , and MnO_2 . All raw materials were prepared by a ball milling in ethanol media using zirconia balls in polyethylene jars. After drying, the powder mixture was melted in a platinum crucible at 1550°C for 3 h. The melt was poured into a preheated $\text{Ø}30 \text{ mm} \times 20 \text{ mm}$ Cu mould. The casted glass was immediately annealed at 650°C for 3 h to relieve residual stresses. Finally, prepared samples with different Mn concentrations were subjected to a controlled crystallization in air at 850 and 950°C for 2h with the heating rate of $5^\circ\text{C}/\text{min}$ to convert the glass into the glass-ceramics. A detailed description of the BST glass-ceramics with Mn additives preparation and its dielectric properties was published [5].

The sample surface was polished by diamond paste with decreasing of grain sizes from 6 to $0.25 \mu\text{m}$. The final polishing was done by colloidal silica (SF1 Polishing Suspension, Logitech, UK). The sample thickness after polishing was about $400 \mu\text{m}$.

The microstructure of the glass-ceramic samples was studied by a scanning electron microscope (SEM, Merlin, Carl Zeiss, Germany) with field-emission using a secondary electron imaging with charge compensation.

P-E hysteresis loops were measured using FE module of AixACCT TF 2000 system (aixACCT Systems GmbH, Germany). Bipolar triangular voltage pulses were applied to the sample and the current was measured using a virtual ground transimpedance amplifier. For measurement, silver paste electrodes with area about 10 mm^2 were used.

The visualization of the domain structure with high spatial resolution was performed using piezoresponse force microscopy (PFM). The samples were mounted by conductive silver paste to metal disks. PFM measurements were realized by a scanning probe microscope NTEGRA Aura (NT-MDT, Russia). The silicon HA_NC/W2C tips (ScanSens, Russia) with a tungsten carbide conductive coating with a radius of curvature $R = 35 \text{ nm}$, resonance frequency $f = 140 \text{ kHz}$, and spring constant $k = 3.5 \text{ N/m}$ were used. Piezoresponse measurements were realized by the application 5 V AC far from contact resonance frequency to the SPM tip.

Polarization reversal was done using NI-6251 multifunction data acquisition board and high-voltage amplifier Trek-677B by application of rectangular DC pulses. The local switching was realized at the ambient conditions with relative humidity about 40% [9,10].

3. Results and discussion

Investigation of the BST glass-ceramics microstructure by SEM allowed revealing dendrite-like clusters of crystal phase in the samples annealed at 850°C (Fig. 1a,b). The clearly visible cluster boundaries resemble Voronoi diagram. The average cluster size about $5 \mu\text{m}$ (Fig. 1c) does not depend on doping level. The formation of dendrite structures in glass-ceramics with addition of AlF_3 and MnO_2 were reported [5,11], but not clearly identified. In contrast, the faceted grains with size about 150 nm were found in samples annealed at 950°C . The structure type and grain sizes did not demonstrate significant dependence on the doping level (Fig. 1d-e).

Detailed study of the samples annealed at 850°C allowed revealing the individual branches in clusters with width below 100 nm (down to 30 nm) (Fig. 2a,b). The structure of the crystal phase clusters is similar to the famous clusters formed by diffusion limited aggregation (DLA). The number of cluster particles on radius r from the centre is [11]:

$$N(r) = N_0 \left(\frac{r}{R_g} \right)^D f \left(\frac{r}{R_g} \right), \quad (1)$$

where N_0 is total number of particles, D is fractal dimension, $R_g = \left(N_0^{-1} \sum_i r_i^2 \right)^{1/2}$ is gyration radius, and $f(x) = \{1 \text{ for } x < 1, x^{-D} \text{ for } x > 1\}$ is transition function.

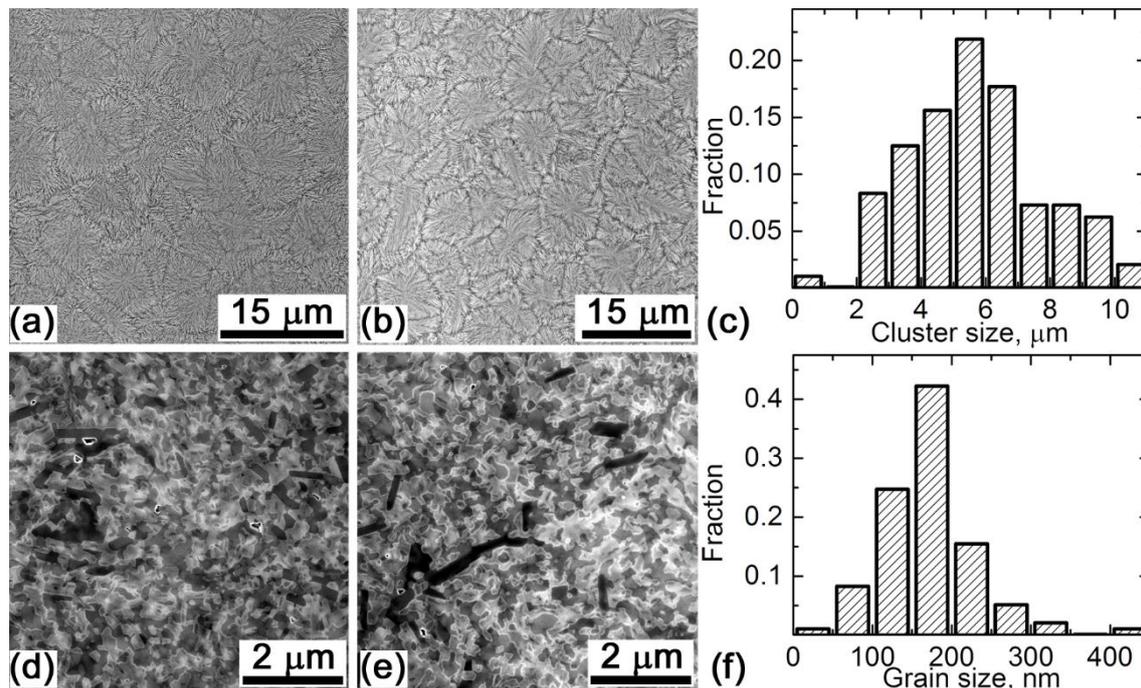


Figure 1. SEM images of BST glass ceramics doped by Mn annealed at 850°C: (a) 0.1%, (b) 0.5%, (c) histogram of cluster size distribution; at 950°C: (d) 0.1%, (e) 0.5%, (f) histogram of grain size distribution.

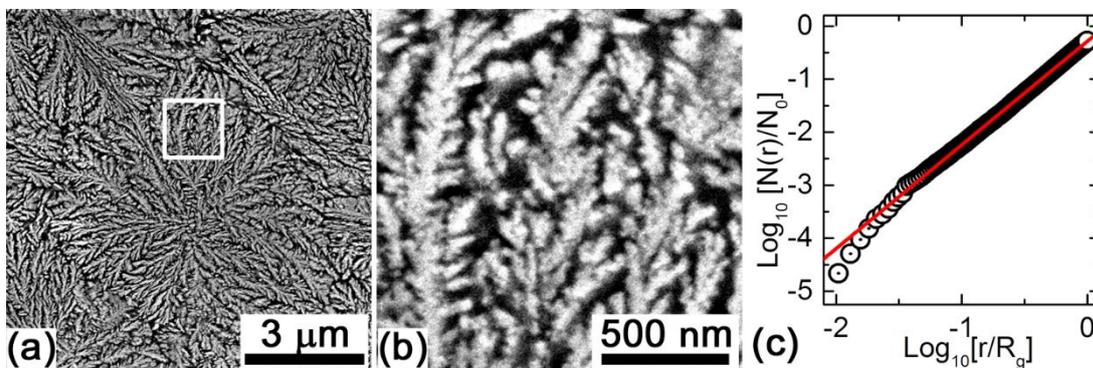


Figure 2. High resolution SEM images of BST ceramics doped by 0.1% Mn annealed at 850°C: (a) individual cluster, (b) zoomed region, (c) dependence of number of particles in cluster on radius.

Although dendrite clusters are three-dimensional, only the surface two-dimensional SEM image can be analysed (Fig. 2a). The analysis has been done after binarization of the image and fractal dimension was calculated using Eq. (1) (Fig. 2c). The obtained $D = 1.95$ is sufficiently larger than typical fractal dimension for DLA clusters ($D = 1.70$) [12]. The analysis of the same image by Box Counting [13] method gave the similar result ($D = 1.94$).

The P-E loops in the studied samples demonstrated different behaviour for different annealing temperatures (Fig. 3). The value of remnant polarization (P_r) increased significantly with annealing temperature. Hysteresis loop for sample annealed at 850°C was narrow with $P_r = 0.3 \text{ C/cm}^2$, whereas in sample annealed at 950°C the loop was wider with $P_r = 0.8 \text{ C/cm}^2$. The lower value of P_r in the sample annealed at 850°C can be attributed to lower fraction of the ferroelectric phase in this sample.

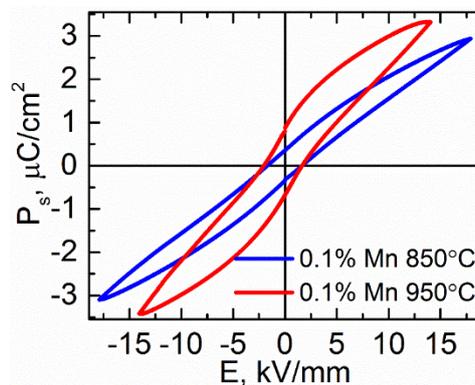


Figure 3. P-E hysteresis loops for the BST glass ceramics with different annealing temperatures. The measurements were made at 1 Hz.

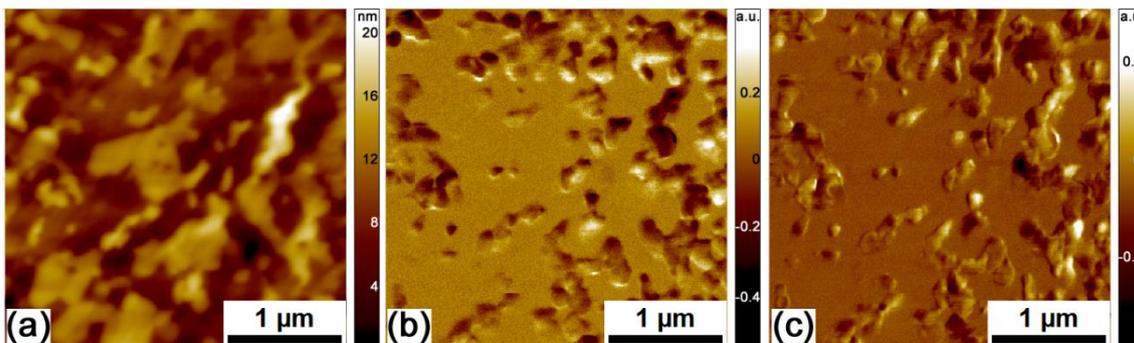


Figure 4. PFM images ($R \cdot \cos \theta$) of domain structure in BST glass-ceramics, annealed at 950°C: (a) topography, (b) out of plane, (c) in plane.

The PFM contrast was revealed only in the samples annealed at 950°C (Fig. 4). The non-polar glass matrix and polar grains associated with ferroelectric phase can be clearly distinguished on PFM images (Fig. 4). The individual grains demonstrated spatially non-uniform piezoresponse, which can be attributed to existence of the domain structure. The calculated fraction of the non-polar phase [14] averaged over several images was about 0.5.

No significant piezoresponse was measured in the samples annealed at 850°C. The obtained signals can be associated only with the surface relief (topography). Absence of piezoresponse contrast correlates with narrow P-E loops in these samples. Application of the single voltage pulse with amplitude up to ± 200 V and duration 60 s did not allow realizing local polarization reversal. This fact can be attributed to effective bulk screening [15] or domain wall clamping by glass matrix [16,17].

4. Conclusion

The statistical information about grain sizes was obtained for the BST glass-ceramics with different Mn concentrations. It was shown that the increase of the Mn concentration up to 0.5% did not lead to visible changes in morphology or domain structure. It was found that crystallization temperature had a critical role on ceramics morphology. The dendrite-like clusters with extremely high value of fractal dimension were found in glass ceramics crystallized at 850°C. The obtained information about the domain structure can be used for further improvement of the dielectric properties of BST glass-ceramics.

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