Ceramics International 31 (2005) 791–794

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Influence of post-sintering annealing on relaxor behaviour of $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics

M. Adamczyk*, Z. Ujma, L. Szymczak, J. Koperski

Institute of Physics, University of Silesia, 40-007 Katowice, ul. Uniwersytecka 4, Poland

Received 12 July 2004; received in revised form 9 August 2004; accepted 9 September 2004
Available online 9 December 2004

Abstract

The dielectric and relaxor properties of lead–barium–zirconate–titanate (PBZT) ceramics of composition Ba/Zr/Ti:25/70/30 has been studied as-prepared (unannealed) as well as after annealing at 1000 °C for 20, 40 and 60 min, respectively. After the annealing treatment the Pb deficiency for the studied ceramics was found. The influence of a post-sintering annealing on the values of characteristic parameters describing a relaxor behaviour of the studied ceramics (ε'_{max}, T_m, T_f, T_B) was determined. The temperature T_m shifts towards the lower value and the dielectric constant increases after annealing. The general trend seems to indicate that the annealing broadens the temperature region of the specific relaxor properties occurrence.

Keywords: C. Dielectric properties; Relaxor ferroelectrics; Annealing conditions; Ceramics

1. Introduction

Dielectric properties of the system (Pb,Ba)(Zr,Ti)O_3 were broadly investigated by Li and Heartling [1]. The solid solutions containing about 25–35% of Ba and the ratio of Zr/Ti equal 70/30 exhibit the relaxor behaviour. It was also confirmed by our previous measurements [2]. Especially the composition 25/70/30 lead–barium–zirconate–titanate (PBZT, 25/70/30) exhibited the strong relaxor properties [3]. Relaxor ferroelectrics (RF) are characterised by the existence of a non-Debye dielectric dispersion in the radio frequency range. The peak of dielectric constant (ε'_{max}) and the corresponding temperature T_m move towards higher temperatures with the increasing frequency. Various models have been proposed to explain the polarisation mechanism and to describe the frequency dependence of the dielectric constant maximum temperature for RF [4]. It is widely accepted by many authors [4,5] that the dielectric properties of RF are associated with the behaviour of the polar regions (nanoclusters) which appear at temperatures much higher than T_m (at the temperature T_B). For this reason, the $\varepsilon'(T)$ deviates from the Curie–Weiss law below T_B and obeys this law above T_B. The dynamics of the polar regions associated with the thermally activated flips is considered to be responsible for the relaxor behaviour. That is why, the dielectric properties of RF ceramics are dependent on a grain structure (grain boundaries) and a screening process of the local dipole moments by point defects and ion or electron space charges. The influence of the La additives on grain structure and relaxor behaviour of PBZT 25/70/30 ceramics was reported in our earlier paper [6]. The results of the influence of the post-sintering annealing on these properties will be briefly shown at the present paper. We expected that the post-sintering annealing should cause a creation of the Pb vacancies in the A-site and a bigger disorder of atoms in A-site and B-site of the ABO_3 perovskite structure. It should influence the dynamics of the polar regions and change the temperature and frequency dependence of the dielectric response [7].

2. Sample preparation

The PBZT ceramics of composition 25/70/30 was prepared using conventional mixed–oxide processing

* Corresponding author. Tel.: +48 32 3591134; fax: +48 32 2588431.
E-mail address: madamczy@us.edu.pl (M. Adamczyk).

0272-8842/$30.00
doi:10.1016/j.ceramint.2004.09.005

technique. Thermal synthesis of blended and pressed mixture of PbO, $BaCO_3$, TiO_2 and ZrO_2 oxides was carried out at 925 °C for the period of 2 h. Crumbled, milled and sieved material was pressed again in the form of cylinders and then sintered at 1250 °C for 4 h. This procedure was repeated again before the final sintering at 1300 °C for 7 h. These sintering processes were performed in a double crucible with interior $PbO + ZrO_2$ atmosphere in order to maintain the established composition and especially to avoid the loss of PbO caused by its sublimation. The Archimedes displacement method with distilled water was employed to evaluated sample density. Sample bulk density was 6.8 g/cm^3.

The obtained ceramic cylinders were cut into 0.6 mm samples that were subsequently polished and divided into two parts. One part of samples was left as-prepared and the others were subjected to the high-temperature (1000 °C) annealing treatment in air for 20, 40 and 60 min, respectively.

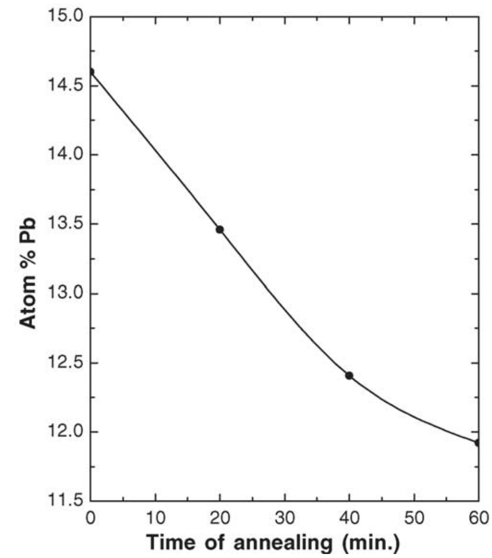

Fig. 2. Pb content in PBZT 25/70/30 ceramics after annealing treatment.

3. Results

The scanning electron microscope JSM-5410 equipped with an energy dispersion X-ray spectrometer (EDS with Si/Li X-ray detector) was used for investigation of the grain structure and the atomic composition of the obtained ceramics. The samples were broken in air, then covered with gold and placed in the vacuum (10^{-5} Torr) chamber of the electron microscope. A typical scanning electron micrograph of the fracture surface of the investigated unannealed ceramics is shown in Fig. 1. The average grain size was about 15 μm. No significant changes in the average grain size of the annealed samples were noticed.

The microanalysis of unannealed and annealed samples was performed with ISIS-300 SEMQuant program and all the analysed elements were normalised to 100%. The EDS analysis, performed for individual grains of annealed samples, indicates that average content of lead decreases from 14.6 to 11.9 at.% with time of annealing (Fig. 2). (The nominal content of the Pb in PBZT 25/70/30 ceramics should be equal to 15 at.%.) The average concentration of the other elements after annealing remains unchanged.

Samples 0.6 mm thick were used for measurements of the dielectric constant (ε') as a function of temperature. All the samples—unannealed and annealed—were coated with electrodes using a silver paste drying at room temperature. Impedance analyzer HP4192A was used to measure $\varepsilon'(T)$ at several frequencies in the range 0.1–100 kHz of the measuring field. These measurements were carried out on heating with constant rate 2 K/min. The comparison of $\varepsilon'(T)$ curves, obtained at the measuring field of frequency 1 kHz for the samples before and after annealing in air at 1000 °C for 20, 40 and 60 min, respectively, is given in Fig. 3. It is

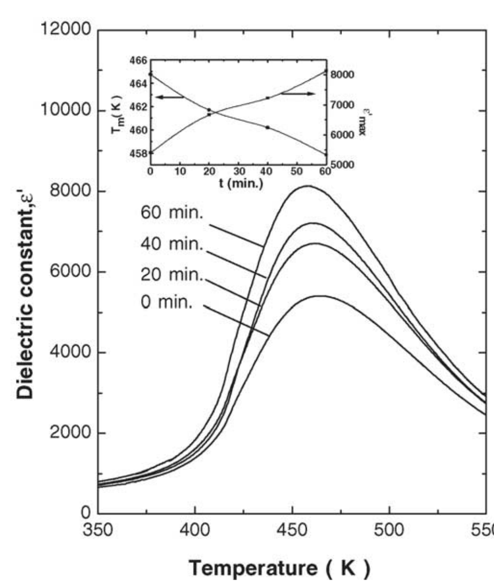

Fig. 3. Dielectric constant as a function of temperature, measured on heating at frequency of measuring field 1 kHz for ceramics with different time of annealing. The maximum in $\varepsilon'(T)$ and the corresponding temperature T_m vs. the annealing time are shown in the inserted figure.

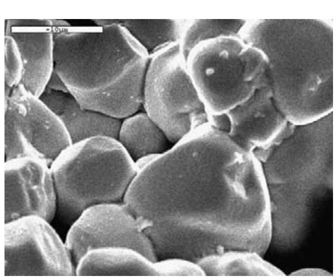

Fig. 1. SEM image of the fracture surface of unannealed PBZT 25/70/30 ceramics.

found that the longer is annealing period the higher is dielectric constant (see the inserted plot in Fig. 3). The temperature T_m, corresponding to the broadened maximum in the $\varepsilon'(T)$ curves, also depends on time of annealing. Similar trends were noticed after annealing treatment for other lead containing RF, for example PMN and PFN [8] or PZN–PT–BT ceramics [9].

The $\varepsilon'(T)$ curves presented for unannealed ceramics show a strongly diffuse character of FE–PE phase transition. Diffusivity insignificantly decreases for annealing ceramics. The quantitative assessment of the diffusivity (γ) in the paraelectric phase was evaluated using the expression given by Martirena and Burfoot [10]

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_{max}} = \frac{(T - T_m)^{\gamma}}{2\delta^2} \tag{1}$$

where γ and δ are constants. It is known that the value of γ ($1 \leq \gamma \leq 2$) is the expression of the degree of dielectric relaxation in a RF. The coefficient γ really insignificantly decreases with the time of annealing (from 1.94 to 1.91 for unannealed and annealed for 60 min ceramics, respectively). The Curie–Weiss law ($\gamma = 1$) was observed only at temperatures much higher than T_m.

The observed behaviour of $\varepsilon'(T)$ in the range of paraelectric phase can be also described by the Curie–Weiss formula, modified by Kirkpartick and Sherrington [11]

$$\varepsilon' = \frac{C\{1 - q(T)\}}{T - \theta\{1 - q(T)\}} \tag{2}$$

where θ is the Curie–Weiss temperature, C is the Curie–Weiss constant and $q(T)$ is the temperature dependent local order parameter which is equal to zero at the temperature where the polar clusters begin to appear on cooling (T_B). The characteristic parameters: θ, C and T_B calculated from the Eq. (2) for unannealed and annealed samples are listed in Table 1. One can notice the significant increase in the temperature T_B after annealing process.

All the investigated PBZT ceramics (unannealed and annealed) show behaviour typical for ferroelectric relaxors. The $\varepsilon'(T)$ curves measured at various frequencies show namely the reduction of ε'_{max} and shift of the corresponding temperature (T_m) towards the higher values with frequency increase. This behaviour is more distinct for the annealed ceramics. Fig. 4 shows dependences of $\Delta\varepsilon'_{max}$, defined as difference between ε'_{max} measured at 0.1 kHz and 100 kHz, and ΔT_m, defined in similar manner, versus time of annealing. The values of $\Delta\varepsilon'_{max}$ and ΔT_m significantly increase with increasing of annealing time. To describe the frequency dependence of the dielectric constant maximum temperature (T_m) the well known empirical Vogel–Fulcher relationship was used

$$f = f_o \exp\left(\frac{-E_a}{k(T_m - T_f)}\right) \tag{3}$$

where T_f is the freezing temperature of polarisation fluctuations, E_a is the activation energy, and f_o is the pre-exponential factor. The values of T_f and E_a calculated from above relationship versus time of annealing are shown in Fig. 5.

Table 1
Temperatures T_m, T_B, θ and Curie–Weiss constant C determined from measurements of $\varepsilon'(T)$ at $f = 20$ kHz

Time of annealing (min)	T_m (K)	T_B (K)	θ (K)	$C \times 10^5$ (°)
0	468	575	504	1.6
20	466	613	533	0.95
40	465	623	536	0.96
60	462	637	537	1.04

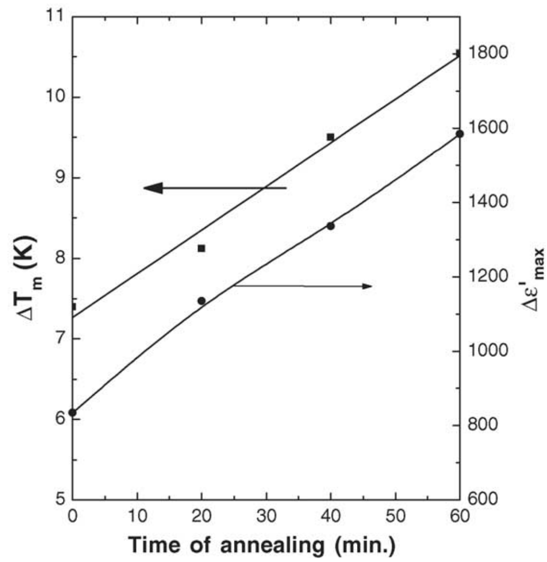

Fig. 4. Degree of frequency dispersion $\Delta T_m = T_m$ (100 kHz) $- T_m$ (0.1 kHz) and $\Delta\varepsilon'_{max} = \varepsilon'_{max}$ (0.1 kHz) $- \varepsilon'_{max}$ (100 kHz) vs. time of annealing.

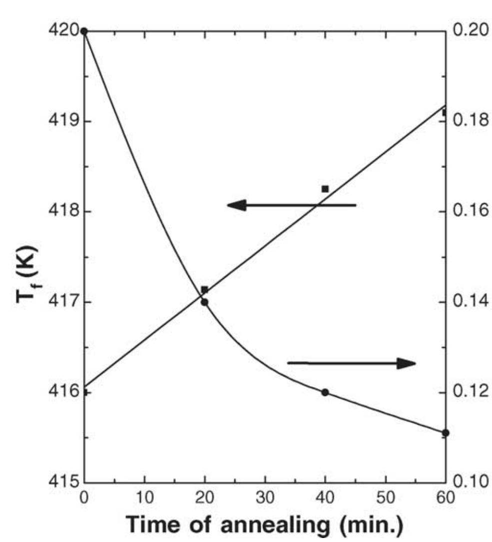

Fig. 5. Freezing temperature (T_f) and activation energy (E_a) calculated from the Vogel–Fulcher relationship vs. time of annealing.

The value of freezing temperature increases and activation energy decreases with the annealing time. It indicates that the point defects and connected with them electric fields made the flipping mechanism of polarisation inside the polar clusters easier. It is worth noting that the value of f_o is too high for unannealed PBZT 25/70/30 ceramics [6] ($f_o = 2.8 \times 10^{23}$ Hz) but it significantly diminishes for annealed samples ($f_o = 7.5 \times 10^{17}$ Hz for the 60 min annealed sample).

4. Discussion

The experimental results presented above show that the post-sintering annealing in air at 1000 °C does not introduce significant changes in the grain structure of PBZT 25/70/30 ceramics but causes Pb deficiency, which is dependent on the annealing time. After the annealing process, the changes of parameters characteristic for relaxor behaviour of studied ceramics can be noticed. The temperature T_B, at which polar regions appear on cooling, significantly increases and the temperature T_m determining the maximum of $\varepsilon'(T)$ insignificantly decreases with the increase in annealing time. The freezing temperature T_f exhibits also an insignificant increase. The behaviour of the characteristic parameters described above, can be understand if the occurrence of two kinds of the disorder in Pb containing relaxor ferroelectrics ceramics of $(A'A'')(B'B'')O_3$-type is taken into consideration: compositional (chemical) disorder of A- and B-site and A-site dynamical disorder caused by the unharmonic motion of Pb [5]. Therefore, two kinds of the polar regions (compositionally ordered and correlated dynamic regions) can exist. The annealing influences both the chemical clusters and correlated dynamic clusters related to the Pb disorder because the additional point defects in A sublattice are created. It is known that the Pb containing perovskite type ceramics are very often non-stoichiometric because of the PbO sublimation occurring during the thermal synthesis process. The Pb deficiency was also determined by us in the as-prepared PBZT 25/70/30 ceramics (14.6 at.% of Pb instead of 15 at.% was registered). The Pb concentration become much lower in the annealed samples and achieved 11.9 at.% after the annealing for 60 min. It follows that the presence of Pb vacancies plays an important role in the polar region creation in Pb containing ferroelectric relaxors. The high-temperature annealing leads also to the increase in chemical (structural) disorder in the polar regions which causes the decrease of T_m (for example in PIN [12]).

The studied PBZT ceramics subjected to the post-sintering high-temperature annealing demonstrated the significant increase of the dielectric constant at T_m. In normal displacive-type ferroelectrics ε'_{max} is mainly dependent on polar phonons. In the relaxor ferroelectrics polar phonons contribution into the dielectric constant is the most significant at temperatures higher than T_B [5]. Dielectric constant connected with the polar phonon mechanism achieves the highest value at T_B. In the temperature region between T_B and T_f the polar cluster flipping and cluster boundary fluctuations contribute to the dielectric response reaching its maximum at T_m. Both mechanisms depend on the vacancies in the Pb sublattice. Simultaneously, the annealing process causes decreasing of the activation energy (Fig. 5) of thermally activated flips of the polar regions, which also leads to the increase in the dielectric constant at T_m.

References

[1] G. Li, G. Haertling, Dielectric, ferroelectric and electric field-induced strain properties of $(Pb_{1-x}Ba_x)(Zr_{1-y}Ti_y)O_3$ ceramics, Ferroelectrics 166 (1995) 31–45.

[2] J. Hańderek, M. Adamczyk, Z. Ujma, Dielectric and pyroelectric properties of $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$ [$x = 0.25$–0.35] ceramics exhibiting the relaxor ferroelectrics behaviour, Ferroelectrics 233 (1999) 253–270.

[3] Z. Ujma, M. Adamczyk, J. Hańderek, Relaxor properties of $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics, J. Eur. Ceram. Soc. 18 (1998) 2201–2207.

[4] Z.Y. Cheng, R.S. Katiyar, X. Yao, A.S. Bhalla, Temperature dependence of the dielectric constant of relaxor ferroelectrics, Phys. Rev. B 57 (1998) 8166–8177.

[5] V. Bovtun, J. Petzelt, V. Porokhonskyy, S. Kamba, Y. Yakimenko, Structure of the dielectric spectrum of relaxor ferroelectrics, J. Eur. Ceram. Soc. 21 (2001) 1307–1311.

[6] M. Adamczyk, Z. Ujma, J. Hańderek, Relaxor behaviour of La-modified $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics, J. Appl. Phys. 89 (2001) 542–547.

[7] H. Gui, B. Gu, X. Zhang, Dynamics of freezing process in relaxor ferroelectrics, Phys. Rev. B 52 (1995) 3135–3142.

[8] D. Mohan, R. Prasad, S. Banerjee, Effect of post-sinter annealing on dielectric constants of PMN and PFN, Ceram. Int. 27 (2001) 243–246.

[9] X. Wang, H. Chen, Effect of annealing on dielectric properties of PZT–PT–BT ceramics, Mater. Sci. Eng. B99 (2003) 36–40.

[10] H.T. Martirena, J.C. Burfoot, Grain-size effects on properties of some ferroelectric ceramics, J. Phys. C: Solid State Phys. 7 (1974) 3182–3192.

[11] S. Kirkpartick, D. Sherrington, Infinite ranged models of spin-glasses, Phys. Rev. B 17 (1978) 4384–4403.

[12] A.A. Bokov, I.P. Rayevskii, V.G. Smotrakov, O.I. Prokopalo, Kinetics of compositional ordering in $Pb_2B'B''O_6$ crystals, Phys. Stat. Sol. (a) 93 (1986) 411–417.