Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 789–792
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Electret state in $Bi_4Ti_3O_{12}$ ceramics

Č. Jovalekić [a,*], M. Zdujić [b]

[a] Institute for Multidisciplinary Research, Kneza Višeslava 1a, Belgrade, Serbia
[b] Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35, Belgrade, Serbia

Received 17 June 2009; received in revised form 23 June 2009; accepted 14 July 2009

Abstract

The effect of thermal treatment atmosphere (argon, air or oxygen) on the electret behavior of bismuth titanate ($Bi_4Ti_3O_{12}$) ceramics was investigated. Polycrystalline ferroelectric ceramics were prepared by reactive liquid phase sintering. Sintered samples were polarized applying an electric field, $E_p = 1\ \mathrm{MV\ m^{-1}}$ at 100 °C for 60 min. Effective surface density, σ_{eff} of free charges was determined by compensation voltage measurements. Thermally treated samples in oxygen atmosphere exhibit a significant decrease of σ_{eff} while those treated in argon exhibit an increase of σ_{eff} accompanied by the improvement in stability of electret charge. In all cases homocharge with a time independent sign was obtained.

Keywords: A. Sintering; C. Electrical properties; D. $BaTiO_3$ and titanates; E. Sensors

1. Introduction

Systematic investigation of electret effect has begun in 1920s [1]. Since then, electrets passed a long way from barely an interesting natural phenomenon important only to solid state physics, to presently extensive use in technical application. Electrets are used for the manufacturing of transducers (e.g. microphones, headphones and loudspeakers), motors and generators, air filters [2], electret floppy disc for storing digital information [3], as well as dosimeters, implants for medicine and even for the desalination of water [4]. Although the applications are mainly restricted to polymer electrets, there is also a considerable interest in nonorganic electrets since they exhibit better mechanical properties and may operate in a wider temperature range, as well as in aggressive atmospheres [5].

Bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT) is a well known ferroelectric material with unique dielectric behavior. It belongs to the family of perovskite compounds with layer structure (family of Aurivilius compounds) with general formula $Bi_2O_2^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$ where A and B are cations, and m corresponds to the number of perovskite-type units between the bismuth oxide layers. The crystal structure of bismuth titanate consists of $Bi_2Ti_3O_{10}^{2-}$ layer formed by two $BiTiO_3$ layers [6,7]. At room temperature, bismuth titanate has a crystallographic point symmetry C_{1h} = m (monoclinic), characterized by ferroelectric properties. Vector of spontaneous polarization lies in the monoclinic plane *ac*, at the angle of 4–5° in respect to the main crystal axis. The intensity of spontaneous polarization is $P_a = 50\ \mu\mathrm{C\ cm^{-2}}$ along the *a*-axis, and $P_c = 4\ \mu\mathrm{C\ cm^{-2}}$ along *c*-axis. Above the Curie temperature ($T_c = 675\ ^\circ\mathrm{C}$) $Bi_4Ti_3O_{12}$ transforms to the paraelectric state. Such high temperature of phase transformation permits its application over a broad temperature range.

Furthermore, electret properties, such as stability of electret charge, depend on the structure and phase composition, as well as condition of polarization (i.e. intensity of applied electrical field, temperature, atmosphere, etc.) [8]. The purpose of this work is to study intensity and stability of electret charge of the polycrystalline bismuth titanate ceramics. The change of electret charge was followed by compensation voltage measurements, i.e. effective surface density, σ_{eff} dependence on time.

2. Experimental

The polycrystalline BIT ceramics were prepared by the method of reactive sintering. The initial powders were Bi_2O_3 (Bismuth Institute) and TiO_2 (GmbH Ventron), both at a purity of 99.8%. The powders were mixed in the stoichiometric ratio (2:3), as required by the balance equation for a synthesis of

---

* Corresponding author. Tel.: +381 112085841; fax: +381 113055289.
E-mail addresses: jovalek@cms.bg.ac.yu, jovalek@imsi.rs (Č. Jovalekić).

doi:10.1016/j.ceramint.2009.09.019

desired compound. The mixture was homogenized in a planetary ball mill for 2 h and then cold pressed under a pressure of 500 MPa. After compression, the samples were sintered isothermally in air at 1100 °C for 4 h. BIT samples of 9 mm diameter and 1 mm thickness were obtained. The density was 7.52×10^3 kg m^{-3} or 93.5% of the theoretical density. Subsequent thermal treatment on the sintered samples was done at 850 °C for 1 h in air, oxygen and argon atmospheres. The microstructure of the chemically etched surface of the BIT ceramics pellets has been examined by light microscopy and scanning electron microscopy (JEOL JSM4300). The polarization was done at a temperature of 100 °C in an electric field of 1 MV m^{-1} over 90 min. The time for isothermal polarization was 60 min. The polarization current was measured by galvanometer. Prepared polarized samples were stored in air. Surface charge density was determined by compensation method, and was followed during two weeks. The effective surface density of free charge, σ_{eff} (C m^{-2}) of polarized samples was calculated from the following relation:

$$\sigma_{\text{eff}} = \frac{\varepsilon_{\text{r}}\varepsilon_{\text{o}}V_{\text{k}}}{l}$$

where ε_{r} is the dielectric permittivity, ε_{o}-the permittivity of free space (8.85×10^{-12} F m^{-1}), l-the sample thickness (m) and V_{k}-the measured compensation voltage (V).

3. Results and discussion

The ceramics sintered at 1100 °C was characterized by X-ray diffraction (XRD) in order to check if reaction of Bi_2O_3 and TiO_2 has been completed. All peaks observed in obtained XRD diagram in Fig. 1 belong to polycrystalline $Bi_4Ti_3O_{12}$ compound. This demonstrates that a synthesis has been successfully accomplished. Also, the micrograph of sample surface illustrates the presence of randomly distributed piles of thin plates of the crystallites (Fig. 2a). The BIT crystallites preferentially grow into platelike shapes, similar in morphology to mica due to large anisotropy in surface energy (Fig. 2b).

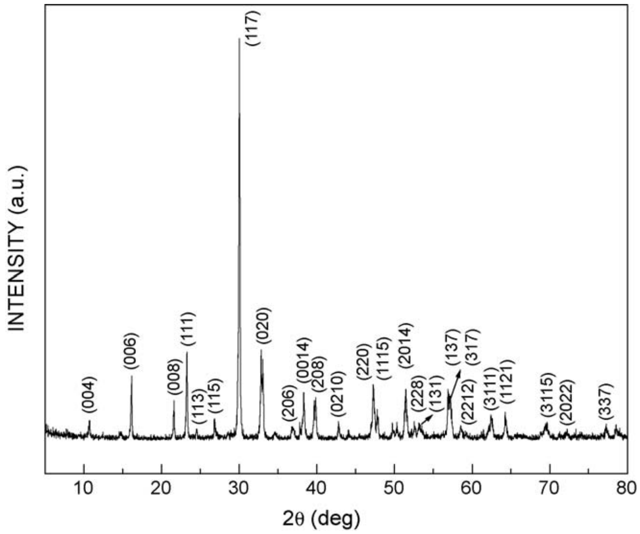

Fig. 1. XRD pattern of $Bi_4Ti_3O_{12}$ sintered at 1100 °C for 4 h.

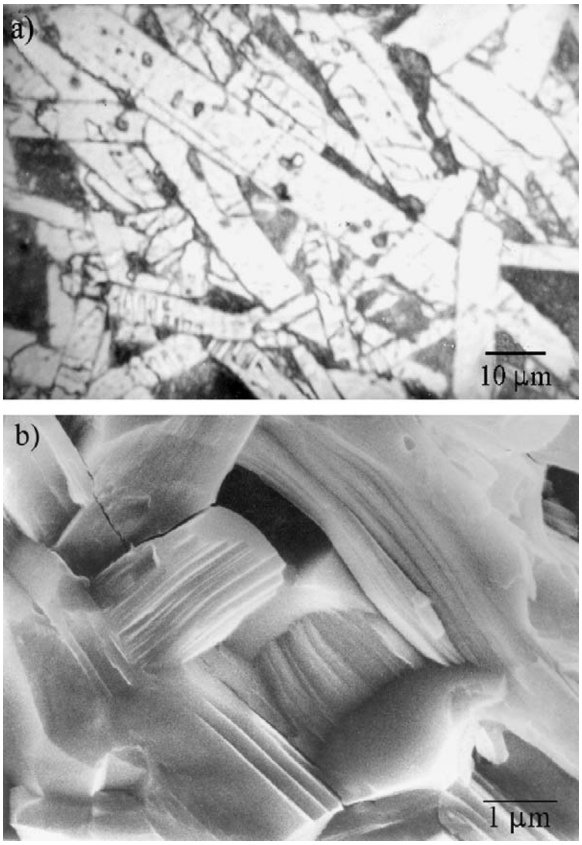

Fig. 2. Optical (a) and SEM (b) micrographs of the surface of BIT ceramics.

During electret formation, polarization current was measured as a function of time and temperature. In the first stage of polarization (during heating from room temperature to 100 °C) current decreases for all investigated samples regardless of the thermal treatment atmosphere (air, argon or oxygen). One can see from Fig. 3 that the effect is most pronounced for a sample treated in argon, having a value of specific resistivity of 2.15×10^{11} Ω cm, while for air and oxygen its value is 1.63×10^{11} and 0.53×10^{11} Ω cm, respectively. During cooling in an applied electric field, the mobility of free electric carriers decreases while, owing to the ferroelectric nature of

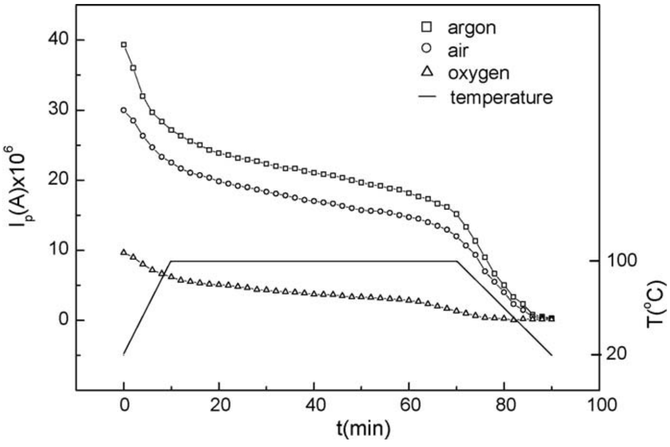

Fig. 3. Polarization current *vs* time for various thermal treatment atmospheres.

bismuth titanate, ‘‘freezing’’ of dipoles in polycrystalline grains take place. As a result, the polarization current decreases. Minimum current after polarization depends on the conduction of the polycrystalline sample, and also on the thermal treatment atmosphere. Considerably smaller values of polarization current for the samples thermally treated in oxygen in comparison to that treated in argon and air indicates that the main role of oxygen vacancies are in conducting processes rather than in polarization.

Effective surface density of free charges, σ_{eff} as a function of time for samples thermally treated in argon, air and oxygen is given in Fig. 4a. Thermal treatment in argon gives the maximum value of $\sigma_{\mathrm{eff}} = 180\ \mu\mathrm{C\ m^{-2}}$, while after 15 days decreases to $\sigma_{\mathrm{eff}} = 104\ \mu\mathrm{C\ m^{-2}}$ (Fig. 4a). The samples treated in argon atmosphere have a stable surface charge density after 7 days of polarization, and considerable better stability than the samples treated in air. For samples treated in air, the maximum value of σ_{eff} is $170\ \mu\mathrm{C\ m^{-2}}$. As one can see, σ_{eff} decreases with time and after 15 days it reaches the value of $67\ \mu\mathrm{C\ m^{-2}}$. In comparison to the thermal treatment in air, samples treated in oxygen exhibit significantly lower values of σ_{eff} (40, and $22\ \mu\mathrm{C\ m^{-2}}$ after 15 days), indicating that the atmosphere has an important influence on the formation of the electret properties (Fig. 4a). In this case, substantially smaller value of the surface charge density should be the consequence of reducing oxygen defects. For all the investigated samples, time independent homocharges were found. Absolute value of the electric charge on one or the other side of the sample differs slightly (Fig. 4b).

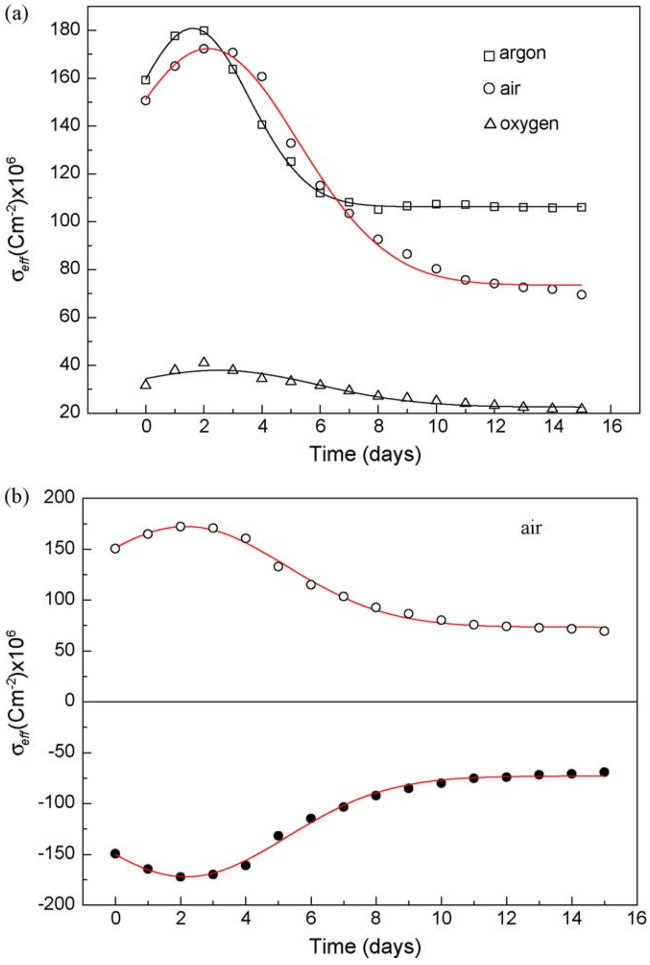

Fig. 4. Surface charge density, σ_{eff} *vs* time for various thermal treatment atmospheres (a); homocharges on the both side of electret *vs* time (b).

The properties of ceramic electrets were found to depend on the defects [9]. The presence of defects promotes the formation of specific quasi dipoles formed by ions located in lattice points and vacancies of opposite electric sign. Orientation of quasi dipoles is chaotic without the applied field, while in its presence, quasi dipoles are oriented in the direction of applied field. At higher temperatures, more vacancies were generated, allowing their transport into the regions near the electret surface. The formation of oxygen vacancies is dominant via migration of oxygen ions from the crystal lattice point to the gaseous phase. Therefore, the concentration of oxygen vacancies can be varied by the oxygen partial pressure [10]. The increase of the oxygen partial pressure decreases the concentration of oxygen vacancies, and thereby the quasi dipole polarization. In contrast, when the oxygen partial pressure decreases, concentration of oxygen vacancies increases. Under the influence of the polarization field at higher temperatures, either the reordering of dipoles and quasi dipoles in the direction of the applied field, or their destruction takes place. In the latter case, isolated vacancies move into the electret surface, forming heterocharges. Hetero- and homocharge are additive so that the sign of the electric charge depends on their absolute value as well as on their relaxation time. After removing polarization field, depolarization of the electret occurs by two mechanisms: the vacancy concentration through the bulk of the electret tends to become homogeneous; and the release of the injected electric charge from the trap and movement through the volume of the electret. A final result is the charge decay in the time which was revealed by the measurement of effective surface density of free charges.

4. Conclusion

The influence of thermal treatment atmosphere on the intensity and stability of electret charge of bismuth titanate ceramics was investigated. Polycrystalline samples remain polarized in time. The heat treatment atmosphere has an important effect on effective surface density of free charge. Inert atmosphere promotes creation of oxygen defects, which have a significant role in the formation of dipole polarization, and also on the intensity and stability of electret states in polycrystalline bismuth titanate ceramics.

Acknowledgements

This work was financially supported by the Ministry of Science of the Republic of Serbia, Grants No. 141027 and 142030.

References

[1] M. Eguchi, On the permanent electret, Philosophical Magazine 49 (1925) 178–192.

[2] G.M. Sessler, J.E. West, Applications, in: G.M. Sessler (Ed.), Electrets, second ed., Springer-Verlag, Berlin/Heidelberg/New York/London/Paris/Tokyo, 1987, pp. 347–453.

[3] H. Amjadi, C.-P. Franz, An electret floppy disk for digital information storage, Journal of Electrostatics 50 (2001) 265–277.

[4] H. Ni, R.C. Amme, Y. Jin, Desalination by electret technology, Desalination 174 (2005) 237–245.

[5] A.N. Gubkin, G.I. Skanavi, On inorganic electrets problem, Solid State Physics (Fizika Tverdovo tela) 3 (1961) 297–304 (in Russian).

[6] B. Aurivilius, Mixed bismuth oxides with layer lattices, Arkiv för Kemi 1 (1949) 499–512.

[7] J.F. Dorian, R.E. Newnham, D.K. Smith, M.I. Kay, Crystal structure of $Bi_4Ti_3O_{12}$, Ferroelectrics 3 (1971) 17–27.

[8] Č. Jovalekić, M. Pavlović, P. Osmokrović, M. Zdujić, Polarization behaviour of ferroelectric $Bi_4Ti_3O_{12}$ ceramics, IEEE Transactions on Electrical Insulation 2 (3) (1995) 409–412.

[9] A.N. Gubkin, G.I. Skanavi, Fabrication and behaviour of new electrets from inorganic dielectrics, Solid State Physics 22 (1958) 330–342 (in Russian).

[10] G.D. Mahan, Intrinsic defects in ZnO varistors, Journal of Applied Physics 54 (1983) 3823–3825.