

## DIELECTRIC PROPERTIES OF (100-x)BaTiO<sub>3</sub>.x(In<sub>2</sub>O<sub>3</sub>.SnO<sub>2</sub>) CERAMICS

V. PARVANOVA

*Department of Inorganic Chemistry  
University of Chemical Technology and Metallurgy  
8 Kliment Ohridski Str., 1756 Sofia, Bulgaria*

M. NADOLIISKY

*Department of Physics  
University of Architecture, Civil Engineering and Geodesy  
1 Hristo Smirnenski Blvd, 1421 Sofia, Bulgaria*

**Abstract.** A new system (100-x)BaTiO<sub>3</sub>.x(In<sub>2</sub>O<sub>3</sub>.SnO<sub>2</sub>) was synthesized using the peroxide method. The influence of the additive In<sub>2</sub>O<sub>3</sub>.SnO<sub>2</sub> on the relative dielectric constant  $\epsilon_r$ , the dielectric losses  $\tan \delta$  and the specific resistivity  $\rho_v$  were studied. The experiments were conducted with values of  $x = 0.5, 1.0, 1.5, 2.0$  mol and at temperatures of calcination of the materials  $T_{\text{calc}} = 1200, 1300, 1400$  °C. These parameters indicated good applicability of these materials for the manufacturing of high capacity condensers.

**PACS number:** 77.84.Dy

### 1. Introduction

Barium titanate BaTiO<sub>3</sub> has a ABO<sub>3</sub>-type structure in which A sites are occupied by Ba<sup>2+</sup> ions and B sites by Ti<sup>4+</sup> ions. The doping effect and the thermal treatment in these ceramics lead to changes in the physical properties and give wider opportunities for their practical use. A number of papers have studied the substances added to BaTiO<sub>3</sub> that improve their dielectric permittivity, Curie temperature and influence the diffuse phase transitions of ceramic materials. Some of the additives of this type are MgO [1-4], Bi<sub>2</sub>(SnO<sub>2</sub>)<sub>3</sub> and NiSnO<sub>3</sub> [5], Nb [6-8], ZrO<sub>2</sub> [9-12], Nb<sub>2</sub>O<sub>5</sub> and Co<sub>3</sub>O<sub>4</sub> [13-15]. Kumar et al [16] have investigated the effect of addition Bi<sup>3+</sup> at the A site and Fe<sup>3+</sup> addition at the B site on the phase transition and ceramic dielectric properties. The

effect of substitution of  $\text{Y}^{3+}$  for  $\text{Ti}^{4+}$  on the ceramic dielectric properties has been studied by Zhi Jing et al [17]. The dielectric and ferroelectric properties of  $\text{BaTiO}_3$  ceramics doped by  $(\text{Li}^+ - \text{Nd}^{3+})$  and  $(\text{K}^+ - \text{Nd}^{3+})$  have been investigated by Kumar and Rao [18].

The authors have pointed that the preparation of ceramic dielectrics with temperature-stable characteristics of the dielectric constant is obtained by the suppression of grain growth and stabilization of microstructure with chemical inhomogeneity.

The present paper describes a new system  $(100-x)\text{BaTiO}_3 \cdot x(\text{In}_2\text{O}_3 \cdot \text{SnO}_2)$ , obtained using the peroxide method and its dielectric properties are studied also. The additive  $\text{In}_2\text{O}_3 \cdot \text{SnO}_2$  is used to obtain materials with high dielectric permittivity, preserving the value in a wide temperature interval, and having low dielectric losses which can be used for the manufacturing of condensers.

## 2. Sample Preparations and Measurements

A new system  $(100-x)\text{BaTiO}_3 \cdot x(\text{In}_2\text{O}_3 \cdot \text{SnO}_2)$ , where  $x = 0.5, 1.0, 1.5, 2.0$  mol was synthesized using the peroxide method [19, 20]. The input raw materials for the synthesis of  $\text{BaTiO}_3$  were  $\text{TiCl}_4$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  in molar ratio 1:1:10 at temperature 10–12 °C and pH = 9. The resulting substance was an intermediate peroxide compound having the following composition:  $\text{Ba}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4] \cdot 4\text{H}_2\text{O}$ .

From it, through hardening at temperature 600 °C for a period of 6 hours, we obtained fine-crystal  $\text{BaTiO}_3$  with size of the particles less than 1  $\mu\text{m}$ .

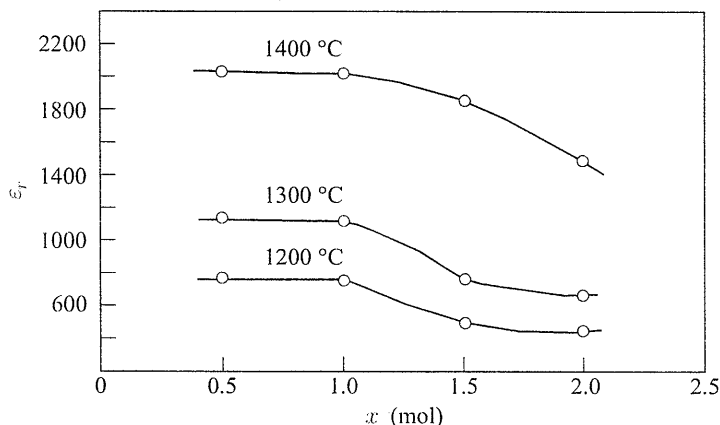
To obtain the tablets, dusts containing the additive  $\text{In}_2\text{O}_3 \cdot \text{SnO}_2$  were put under pressure of  $4.9 \times 10^7$  Pa. The plasticizing agent used was a 10 % solution of polyvinyl alcohol. The prepared disks were hardened at temperature of calcination  $T_{\text{cal}} = 1200, 1300, 1400$  °C for a period of 2 hours. The experimental samples, 9 mm in diameter and 2 mm thick, were metallized with silver paste.

The capacity  $C$  and the dielectric losses  $\tan \delta$  were measured at a frequency of 1 kHz with a digital LCR-meter type E7-15, produced by Belvar, Belarus. Temperature dependence of the capacity and the dielectric losses were registered in a Heraeus Vötsche temperature chamber at an interval of 3 °C. The size of the grains (the crystallites) was measured by means of a scanning electronic microscope, IXA-SOA type.

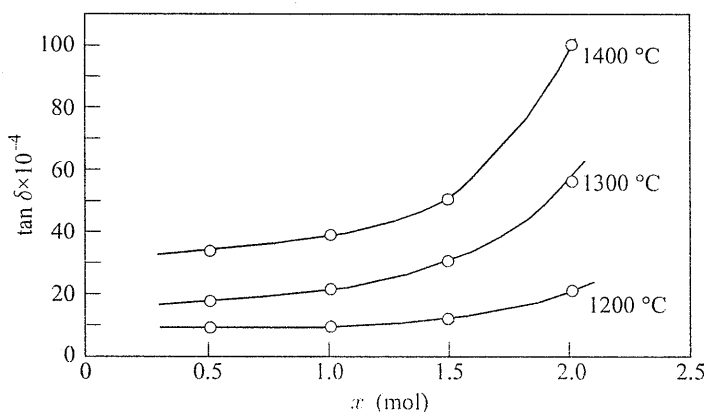
## 3. Results and Discussion

The dependence of the relative dielectric constant  $\epsilon_r$  (for  $T = 20$  °C) on the composition of the system studied and the temperature of calcination is shown in Fig. 1. Permittivity increases as  $T_{\text{cal}}$  increases; and decreases as the concentration of  $\text{In}_2\text{O}_3 \cdot \text{SnO}_2$  increases. When  $x = 1$  mol, the additive practically

has no effect on the values of  $\varepsilon_r$ . Such behavior of permittivity is caused by the increased density of the materials and the increased grain size when  $T_{\text{cal}}$  is increased. At  $T_{\text{cal}} = 1200^\circ\text{C}$  the grain size is  $0.8\text{--}1.6\ \mu\text{m}$ , whereas at  $T_{\text{cal}} = 1400^\circ\text{C}$  it is up to  $2.5\text{--}4.2\ \mu\text{m}$ .



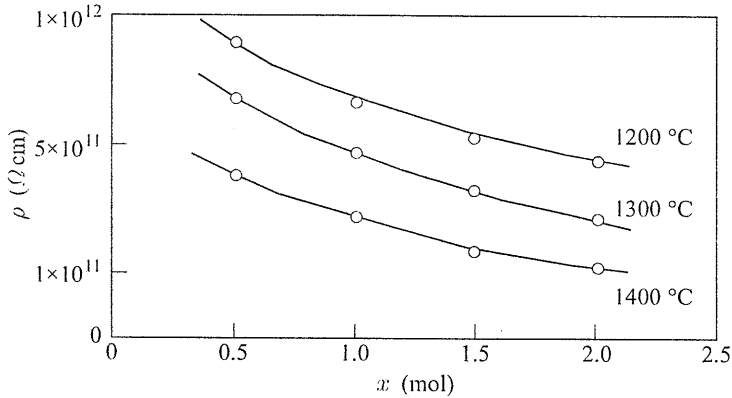
**Fig. 1.** Dependence of  $\varepsilon_r$  (for  $T = 20^\circ\text{C}$ ) on the composition of system  $(100-x)\text{BaTiO}_3 \cdot x(\text{In}_2\text{O}_3 \cdot \text{SnO}_2)$  at different calcination temperatures



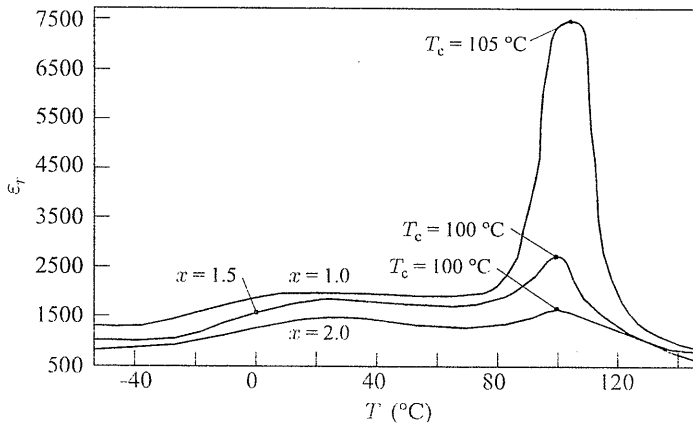
**Fig. 2.** Dependence of  $\tan \delta$  (for  $T = 20^\circ\text{C}$ ) on the composition of the system  $(100-x)\text{BaTiO}_3 \cdot x(\text{In}_2\text{O}_3 \cdot \text{SnO}_2)$  at different calcination temperatures

Figure 2 shows the dependence of dielectric losses  $\tan \delta$  on the composition of the system and on  $T_{\text{cal}}$ . Losses increase as  $T_{\text{cal}}$  and the relative part of  $\text{In}_2\text{O}_3 \cdot \text{SnO}_2$  increase. The increase of the size of the grains at higher temperatures of calcination creates more favorable conditions for the creation of new domain walls that further add to the total measured losses. On the other hand,

the increased  $\tan \delta$  under higher  $T_{\text{cal}}$  is due to the higher conductivity because of the decreased specific resistivity  $\rho_v$  of the various compounds (Fig. 3).



**Fig. 3.** Dependence of the specific volume resistivity  $\rho_v$  (for  $T = 20^\circ\text{C}$ ) on the composition of the system  $(100-x)\text{BaTiO}_3 \cdot x(\text{In}_2\text{O}_3 \cdot \text{SnO}_2)$  at different calcination temperatures

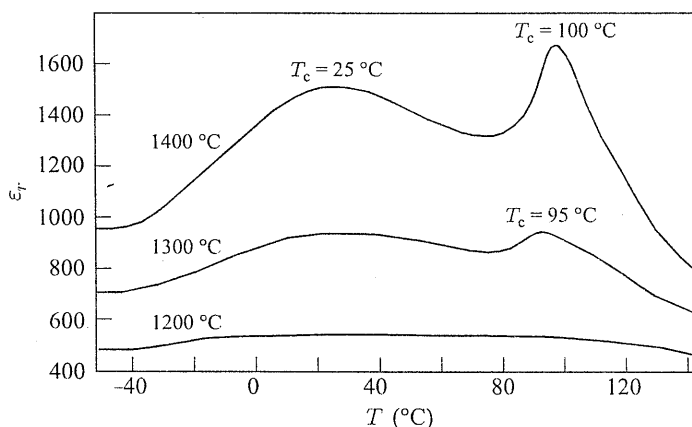


**Fig. 4.** Temperature dependence of  $\epsilon_r$  for the system  $(100-x)\text{BaTiO}_3 \cdot x(\text{In}_2\text{O}_3 \cdot \text{SnO}_2)$  at  $T_{\text{cal}} = 1400^\circ\text{C}$

Figure 4 shows the temperature dependence of  $\epsilon_r$  for different values of  $x$  at  $T_{\text{cal}} = 1400^\circ\text{C}$ . For ceramics containing  $x = 1.5$  mol and  $x = 2.0$  mol, the dielectric permittivity at Curie temperature  $T_c$  has considerably lower values. A second maximum is observed for  $\epsilon_r$  at temperature of  $25^\circ\text{C}$ . For  $x = 1.0$  mol, the system has a definitely expressed temperature interval  $5\text{--}75^\circ\text{C}$ , in which  $\epsilon_r$  retains its value and has excellent qualities, very suitable for manufacturing condensers with high values of their capacity.

The conclusion may be drawn that the effect of the additive  $\text{In}_2\text{O}_3 \cdot \text{SnO}_2$  is evident when  $x = 1.5$  mol. As the curve path is similar to that of pure  $\text{BaTiO}_3$  for values lower than  $x = 1.5$  mol, the data for composition with  $x = 0.5$  mol has not been presented graphically.

The effect of  $T_{\text{cal}}$  on  $\epsilon_r$  at  $x = 2.0$  mol is investigated and shown in Fig. 5. For  $T_{\text{cal}} = 1300^\circ\text{C}$  and  $1400^\circ\text{C}$  a double maximum has appeared at wide temperature interval, which prevents sudden loss of the ferroelectric properties of the materials. This property of the system could be explained with the formation, during high-temperature heating, of two phases possessing different Curie temperatures  $T_c$ , as well as with different values of their dielectric permittivity. Similar results have been obtained by Okazaki and Kawahima [5], Bussem and Kahn [7], Kahn [6], Chazomo and Kishi [14, 15], who studied ceramic materials prepared using the standard ceramic technology with the additives mentioned above. The identification of the two phases by means of a roentgen structure analysis is difficult, as the parameters of their crystal lattices are too close. However, they could be indirectly identified on the basis of the relatively precise data from the measurements of their electric characteristics.



**Fig. 5.** Temperature dependence of  $\epsilon_r$  for the composition  $98\text{BaTiO}_3 \cdot 2(\text{In}_2\text{O}_3 \cdot \text{SnO}_2)$  at different calcination temperatures

The  $\text{Sn}^{4+}$  ions replace the  $\text{Ti}^{4+}$  in the crystal lattice and lead to lower Curie temperature  $T_c$  [21, 22]. On the other hand, the  $\text{In}^{3+}$  ions most probably replace the  $\text{Ti}^{4+}$  ions, which results the creation of oxygen vacancies in the ceramics. Increasing the relative share of the additive  $\text{In}_2\text{O}_3$  leads to increasing the concentration of oxygen vacancies, that restricts the domain mobility of walls. Thus results the decrease of dielectric constant  $\epsilon_r$  when  $x > 1$  mol (Fig. 1).

## References

1. P. Baxter, N. Hellicar and B. Lewis. *J. Am. Ceram. Soc.* **42**(10) (1959) 465.
2. Y. Sakabe. *Am. Ceram. Soc. Bull.* **9** (1987) 1338.
3. K. Okazaki. *Ceramic Engineering for the Electricians*. 4th edn, Publishing Co Ltd, Japan, Gakken-sha 1992, p. 281.
4. T. Nagai, K. Iijima, H. Hwang, M. Sando, T. Sekino and K. Niihara. *J. Am. Ceram. Soc.* **1** (2000) 107.
5. K. Okazaki and S. Kawashima. *J. Ceram. Assoc. Jap.* **1** (1965) 106.
6. M. Kahn. *J. Am. Ceram. Soc.* **9** (1971) 455.
7. W. Buessem and M. Kahn. *J. Am. Ceram. Soc.* **5**(9) (1971) 458.
8. E. Burn. *Electrocomponent Sci. Technol.* **2** (1976) 241.
9. T. Armstrong, K. Young and R. Buchanan. *J. Am. Ceram. Soc.* **3** (1990) 700.
10. H. Lu, J. Bow and W. Deng. *J. Am. Ceram. Soc.* **12** (1990) 3562.
11. P. Gallagher. *J. Am. Ceram. Soc.* **46** (1963) 359.
12. D. Hennings. *Int. J. High Technol. Ceram.* **3** (1987) 91.
13. D. Hennings and B. Schreinemacher. *J. Eur. Ceram. Soc.* **14** (1994) 463.
14. H. Chasomo and H. Kishi. *J. Am. Ceram. Soc.* **10** (1999) 2689.
15. H. Chasomo and H. Kishi. *J. Am. Ceram. Soc.* **1** (2000) 101.
16. M. Mahesh Kumar, K. Srinivas and S. Suryanarayana. *Appl. Phys. Lett.* **76** (2000) 1330.
17. Zhi Jing, Chen Ang, Zhi Yu and P. Vilarinho, J. Baptista, *J. Appl. Phys.* **84** (1998) 983.
18. P. Kumar and K. Rao. *Ferroelectrics* **94** (1989) 299.
19. *Jap. Pat. No 51 80 C1 23/00.*
20. L. Genov, M. Maneva and V. Parvanova. *J. Therm. Anal.* **44** (1988) 727.
21. B. Jaffe, W. Kook and H. Jaffe. *Piezoelectric Ceramic*. Academic Press, London 1971.
22. J. Lin and T. Wu. *J. Appl. Phys.* **68** (1990) 985.