Минно-геоложки университет "Св. Иван Рилски"
Годишник, том 47, свитък II, Добив и преработка на минерални суровини, София 2004, стр.99-101

Properties of $Ba_{0.7}Sr_{0.3}Ti_{1-x}Sn_xO_3$ Ceramics Obtained by the Peroxomethod

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ABSTRACT. The system $Ba_{0.7}Sr_{0.3}Ti_{1-x}Sn_xO_3$ has been obtained by the peroxomethod. The paper studies the temperature dependencies of the dielectric permittivity ε_r and the dielectric losses tan δ at a frequency of 1 kHz for the following temperature conditions of ceramics calcination: 1250°C, 1300°C, and 1400°C. The ceramic material composed of $Ba_{0.7}Sr_{0.3}Ti_{0.8}Sn_{0.2}O_3$ and calcinated at 1400°C in the temperature interval 20-120°C has a temperature coefficient of dielectric permittivity $TK\varepsilon_r \rightarrow 0$ and low dielectric losses. These properties make it suitable for manufacturing thermally stable capacitors of low dielectric losses.

СВОЙСТВА НА $Ba_{0.7}Sr_{0.3}Ti_{1-x}Sn_xO_3$ КЕРАМИКА ПОЛУЧЕНА ПО ПЕРОКСОМЕТОД
РЕЗЮМЕ. Получена е по пероксо метод системата $Ba_{0.7}Sr_{0.3}Ti_{1.}xSn_xO_3$. Изследвани са температурните зависимости на диелектричната проницаемост ε_r и диелектричните загуби tan δ при честота 1кHz за следния температурен режим на изпичане на керамиката: 1250, 1300, 1400 °C. Керамичния материал със състав $Ba_{0.7}Sr_{0.3}Ti_{0.8}Sn_{0.2}O_3$ изпечен при 1400 °C за температурния интервал от 20 до 120 °C има температурен коефициент на диелектричната проницаемост $TK\varepsilon_r \rightarrow 0$ и ниски диелектрични загуби. Тези данни го правят подходящ за производството на термостабилни кондензатори, както и за кондензатори с ниски диелектрични загуби.

Introduction

The ceramics obtained on the basis of $BaTiO_3$ of perovskite structure is one of the most important materials in using multilayer ceramic capacitors, thermistors of positive temperature coefficient, etc. It should be noted that the electric properties of the $BaTiO_3$ ceramics can be controlled by slight modifications by means of doting substances as $SrTiO_3$ (Tsuzuki et al.,1998), Nd_2O_3 (Kohler et al., 1996), La_2O_3 (Natsuko and Makoto, 1997) and others or depressor agents as $MgTiO_3$, $NiTiO_3$, $ZnTiO_3$ (Parvanova and Andreev 2002), Bi_2O_3 (Yi Zhi et al., 1998), SnO_2, ZrO_2 and others. The paper presents the results of the study on the dielectric properties and resistivity of the solid solutions $Ba_{0.7}Sr_{0.3}Ti_{1-x}Sn_xO_3$ where x=0.05; 0.10; 0.15; 0.20 mol. The materials were prepared by using the peroxomethod. Technologically, it has certain advantages over standard ceramic technologies: the titanates obtained are characterized by higher purity and homogeneity; no preliminary grinding of the input materials is required; the synthesis temperature is considerably lower.

Sample Preparation and Measurements

The input titanates $BaTiO_3$, $SrTiO_3$ were prepared by using the peroxomethod (Genov et ai., 1988; Maneva and Parvanova, 1995) based on the interaction of a $TiCl_4$ and Me-salt (Ba^{2+}, Sr^{2+}) solution with H_2O and alkalization with NH_3 to a fixed pH value. The synthesized peroxo-compounds were sintered at T=600°C and T=650°C, respectively, until metatitanates were obtained. The later were identified by an X-ray phase analysis by using a TUR-U-62 device. SnO_2 has 99% purity. The following compositions were synthesized: $Ba_{0.5}Sr_{0.5}Ti_{1-x}Sn_xO_3$ where x=0.05, 0.10, 0.15 and 0.20 mol. The powders were pressed under $P=200x10^5$Pa. 10% polyvinyl alcohol was used as plasticizer. The resultant product was disks 7mm in diameter and 4mm in thickness. They were calcinated at T_{cal}=1250, 1300, 1400°C for 3 hours, with a 0.5-hour retention at 360°C and 400°C to gradually evaporate the plasticizer. In order to make the contact required for the electric measurements, the disks were metallized on both sides using silver paste.

The temperature dependence of the capacity and dielectric losses (tanδ) were tested at a frequency of 1 kHz by using a Gener*al* Radio impedance meter (model 1687). The temperature dependence of the capacity was measured in a Heraeus Votsch temperature chamber in a temperature range from -40°C to +120°C at steps of 5°C.

Results and Discussion

Figs. 1 and 2 show the dependencies of the dielectric permittivity ε_r and the dielectric losses tan δ of the materials on the concentration of Sn^{4+} ions. For all three compositions ε_r increases smoothly, passes through a broad maximum and decreases at a concentration of Sn^{4+} ions higher than 0.1 mol. The permittivity has the highest values for materials calcinated

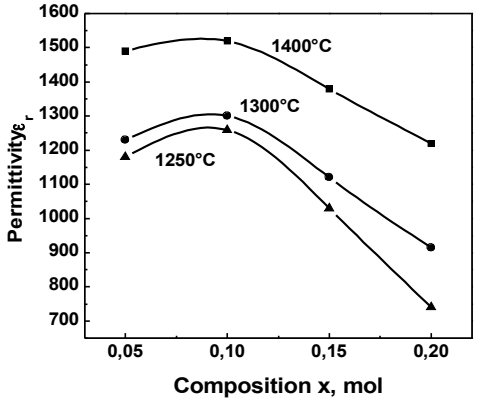

Fig. 1. Dependence of the dielectric permittivity ε_r of the materials on the concentration of Sn

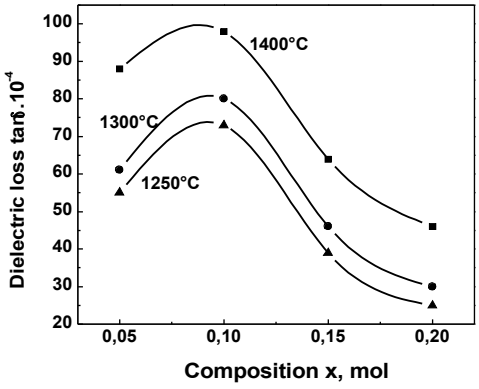

Fig. 2. Dependence of the dielectric losses tan δ of the materials on the concentration of Sn

at the highest temperature. A similar dependence is also observed in the composition studied by Parvanova in which the depressor agent is Mg^{2+}. The character of change in the curves of tan δ is the same as that for ε_r [Fig. 2].

The resistivity ρ_v of the compositions decreases with increasing the concentration of Sn^{4+} ions and reaches its peak value for the material calcinated at the lowest temperature.

The properties of $BaTiO_3$ ceramics in which the ions (Ba^{2+}) and (Ti^{4+}) are replaced simultaneously with other ions of suitable valence and ionic radii, depend on the influence of each admixed ion. By replacing Ba^{2+} ions in the solid solutions with Sr^{2+} ions, the phase transition temperature T_c decreases inearly, the ceramics (Ba, Sr) TiO_3 having higher peak values of permittivity than pure $BaTiO_3$ (Cava et al., 1996; Parvanova, 2002; Tavata and Kawai, 1997).

In the system $BaO\text{-}TiO_2\text{-}SnO_2$ small amounts of SnO_2 stabilize two new phases of barium titanate – $Ba_2Ti_5O_{12}$ and $Ba_2Ti_9O_{12}$ (Jaffe et al., 1971). With increasing the concentration of Sn^{4+} ions the contribution of these phases to permittivity increases and reaches its peak value at x=0.1 mol, whereas ε_r and tan δ pass through a broad maximum.

The dependence of the resistivity ρ_v of materials on the concentration of Sn^{4+} ions is presented in Fig. 3. The resistivity

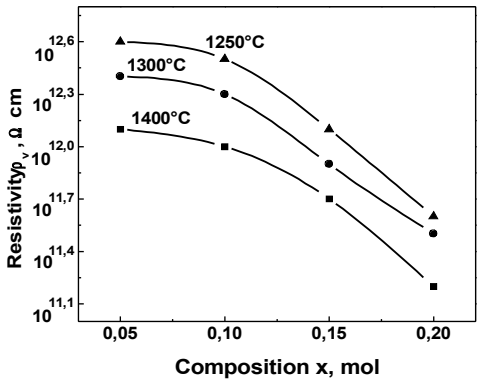

Fig. 3. Dependence of the resistivity ρ_v of materials on the concentration of Sn

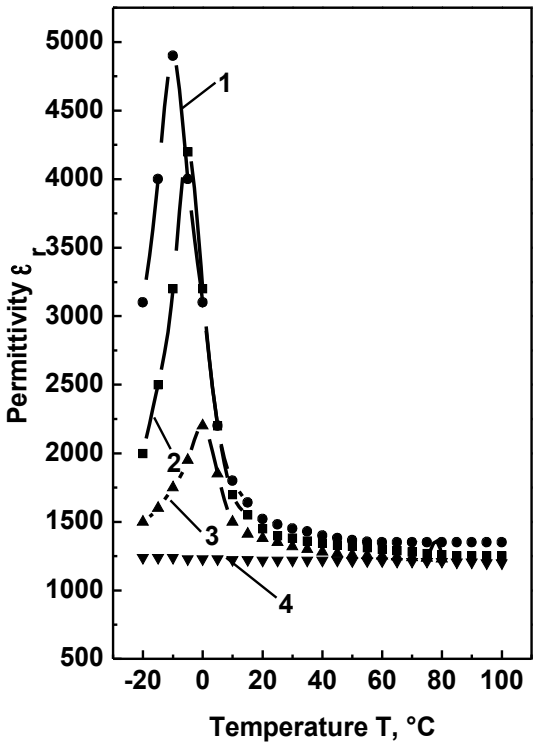

Fig. 4. Dependence of the dielectric permittivity ε_r on the composition of the material calcinated at a temperature of 1400°C; 1) x=0.05 mol; 2) x=0.10 mol; 3) x=0.15 mol; 4) x=0.20 mol

decreases with increasing the concentration of Sn^{4+} ions and reaches its peak value for the material calcinated at the lowest temperature. When calcinating the titanates of Ba and Sr oxygen vacancies occur which participate in the material conductivity (J. lin and T. Wu, 1990). The concentration of

these vacancies increases with increasing the concentration of Sn^{4+} ions and as a result the strength of materials decreases (Fig. 3). The fact that the material calcinated at the lowest temperature has the highest ρ_v shows that the concentration of the oxygen vacancies in it has the lowest value.

The dependence of the permittivity ε_r of the material calcinated at 1400°C on the temperature is shown in Fig. 4.

With increasing the concentration of Sn^{4+} ions the peak values of ε_r of the material decrease and the phase transition region expands. The temperature of the tetragonal rhombic phase transition increases, the rhombic phase stabilizes and ε_r remains constant in the temperature interval under study.

The experimental dependencies of permittivity and dielectric losses obtained can also be related to the various polarizabilities of the ions Ti^{4+} and Sn^{4+}. Sn^{4+} has a higher electronic polarizability that causes an increase in the spontaneous deformation of the elementary cell. As a result ε_r and tan δ decreases with increasing the concentrations of the ions Sn^{4+}, i.e. the ferrohardness of the materials increases.

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