

DIELECTRIC PROPERTIES OF $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{1-x}\text{Ce}_x\text{O}_3$ CERAMICS OBTAINED BY THE PEROXOMETHOD

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ABSTRACT

The samples of the system $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{1-x}\text{Ce}_x\text{O}_3$ are synthesized by the peroxomethod with $x = 0.025, 0.050, 0.075$ and 0.100 mol at calcination temperatures $T_{\text{cal}} = 1300, 1350$ and 1400 °C and calcination time 2.5 h. The following important dielectric properties of the system are investigated at frequency of 1 kHz: permittivity ϵ_r , dielectric losses $\tan \delta$ and conductivity σ . At increasing the concentration of CeO_2 the dielectric constant ϵ_r is reduced but the thermal stability of the capacitors investigated is improved. The composition $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.925}\text{Ce}_{0.075}\text{O}_3$ demonstrates a zero temperature coefficient of the dielectric constant $T C \epsilon_r = 0$ and $\tan \delta = 58 \times 10^{-4}$.

Keywords: dielectric properties, $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{1-x}\text{Ce}_x\text{O}_3$.

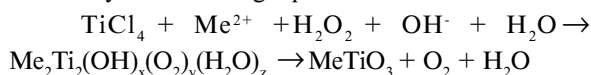
INTRODUCTION

Multicomponent metatitanates are of a definite practical interest because they offer the possibility for controlled variations of the parameters of passive electronic components. Perovskite type BaTiO_3 ceramics are one of the most important electronic materials for use in multilayer ceramic capacitors, positive temperature coefficient thermistors and piezoelectric transducers [1-5]. More importantly, the electrical conductivity of BaTiO_3 system ceramics can be controlled by minor modifications of dotents or variation of sintering conditions without seriously affecting other properties; ranges from ferroelectricity to semiconductivity [6]. Materials suitable for manufacturing of thermostable

capacitors with low dielectric losses are investigated in this work. Such materials based on the systems BaTiO_3 - MgTiO_3 [7-9], $(\text{Ba,Sr})\text{TiO}_3$ [10-12] and $(\text{Ba,Sr,Mg})\text{TiO}_3$ [13] are discussed in the literature and they demonstrate valuable characteristics. The main intent of this work is the investigation of ceramic materials on the base of $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{1-x}\text{Ce}_x\text{O}_3$ applicable for the production of thermal stability capacitors with low dielectric losses. However no data are reported about the possible depressor behavior of CeO_2 included in such systems. It is assumed that introducing CeO_2 into the starting material $(\text{Ba,Sr,Mg})\text{TiO}_3$ would result in smoothening of the temperature-dependence maximum of ϵ_r around the Curie temperature and in reduction of the dielectric losses.

EXPERIMENTAL

In this work the metatitanates of Ba^{2+} , Sr^{2+} and Mg^{2+} are obtained by the peroxomethod [14-17], as described by the following equation:



H_2O_2 is added to a solution of TiCl_4 and a Me-salt ($\text{Me} = \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Mg}^{2+}$). Then the solution is alkalinized with NH_4OH to pH = 9 and 12. The synthesized peroxocompositions are calcined at temperatures of 600 °C and 650 °C respectively, upto obtaining metatitanates with grain size under 1 μm . BaTiO_3 , SrTiO_3 and MgTiO_3 are identified by X-ray analysis [18-20], with a TUR-62 apparatus. CeO_2 is of 99.0 % purity. The following compositions: $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{1-x}\text{Ce}_x\text{O}_3$, where $x = 0.025, 0.050, 0.075$ and 0.100 mol are synthesized. The powders obtained are homogenized in a planetary ball mill for 30 min. They are pressed at a pressure $P = 150 \times 10^5$ Pa. 10 % polyvinyl alcohol is used as a binder. Pellets with diameter of 9 mm and thickness of 4 mm are obtained. They are calcined at $T_{\text{cal.}} = 1300, 1350$ and 1400°C for 2.5 h. At $T = 360^\circ\text{C}$ the temperature was maintained constant for 0.5 h in order to achieve a gradual evaporation of the binder. The pellets are metalized on both sides by means of a silver paste.

The capacitance C and the dielectric losses are measured at a frequency of 1 kHz on a General Radio 1687 system. The temperature dependence of the capacitance C and the dielectric losses is investigated with an Heraeus Votsh temperature chamber. The resistance is measured on a Terohm meter TR-2201 at a voltage of 50 V applied.

RESULTS AND DISCUSSION

The dependence of the permittivity on the composition of the system (x) and the calcination temperature $T_{\text{cal.}}$ observed at $T = 20^\circ\text{C}$, is shown in Figure 1. It is seen from the Figure that at $T = 20^\circ\text{C}$, ϵ_r of the samples strongly depends on the composition and to some lower degree on the temperature $T_{\text{cal.}}$. ϵ_r has it's a maximum value at $x = 0.025$ mol. It falls down at greater values of x . This could be explained by the enhanced concentration of CeO_2 featuring lower ϵ_r . It is seen also from Figure 1 that ϵ_r (measured at 20°C) is increasing

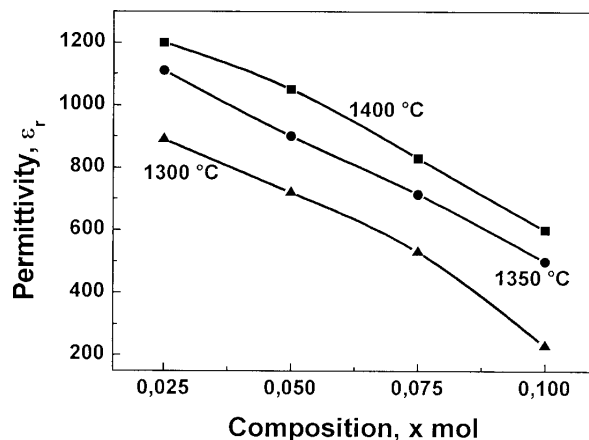


Fig. 1 Dependence of the permittivity ϵ_r on the composition x mol at three different calcinations temperatures ($T_{\text{cal.}} = 1300, 1350$ and 1400°C).

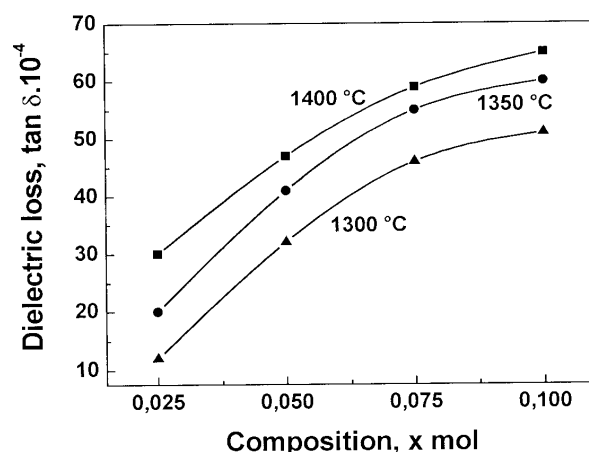


Fig. 2. Dependence of the dielectric losses $\tan \delta$ on the composition x mol at three different calcinations temperatures ($T_{\text{cal.}} = 1300, 1350$ and 1400°C).

with higher $T_{\text{cal.}}$ and for $x = 0.025$ mol, $T_{\text{cal.}} = 1400^\circ\text{C}$ the value of ϵ_r is 1200 (for the same $x = 0.025$ mol and $T_{\text{cal.}} = 1300^\circ\text{C}$, $\epsilon_r = 920$). This behavior could be explained by the higher degree of formation of the isomorphic structure and the higher density of the ceramics ($\rho_{1300^\circ\text{C}} = 5000 \text{ kg m}^{-3}$ for the composition $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.975}\text{Ce}_{0.025}\text{O}_3$). It is seen from the figure that the $T_{\text{cal.}} = 1300^\circ\text{C}$ is not high enough for formation of a domain structure.

In Figure 2 the dependence of the dielectric losses $\tan \delta$ on x and $T_{\text{cal.}}$ is illustrated. Dielectric losses in-

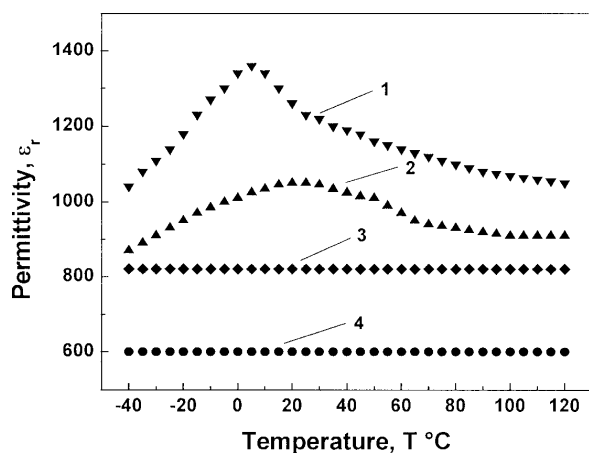


Fig. 3. Temperature dependence of the permittivity ϵ_r (1- $x = 0.025$ mol, 2- $x = 0.050$ mol, 3- $x = 0.075$ mol, 4- $x = 0.100$ mol).

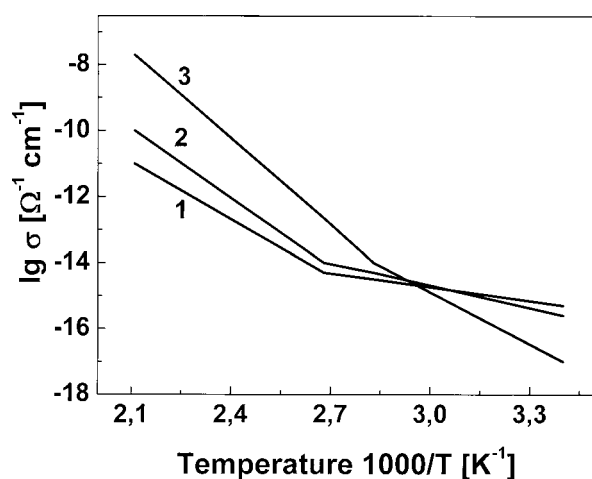


Fig. 4 Temperature dependence of the conductivity $\lg \sigma$ (1- $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.975}\text{Ce}_{0.025}\text{O}_3$, 2 - $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.950}\text{Ce}_{0.050}\text{O}_3$, 3 - $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.900}\text{Ce}_{0.100}\text{O}_3$)

crease at greater concentrations of CeO_2 in the samples. For composition $x = 0.025$ mol $\tan \delta = 30 \times 10^{-4}$ and for $x = 0.100$ mol $\tan \delta = 65 \times 10^{-4}$. As a reference the pure composition $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{TiO}_3$ (1400°C) features $\tan \delta = 37 \times 10^{-4}$ [13]. Increasing of $\tan \delta$ at higher T_{cal} is also observed. A probable reason for this is the higher concentration of defects in the crystal lattice at $T_{\text{cal}} = 1400^\circ\text{C}$.

The temperature dependence of ϵ_r at $T_{\text{cal}} = 1400^\circ\text{C}$ and at different compositions x is represented in Figure 3. At higher concentrations of CeO_2 the maxi-

mum of this dependence is smoothed resulting in higher temperature stability of the capacitors. At $x = 0.075$ mol the permittivity has a constant value in the range $-40 \div 120^\circ\text{C}$ ($\text{TC} \epsilon_r = 0$).

From the experimental data represented above a conclusion may be drawn that the ceramic material with composition $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.925}\text{Ce}_{0.075}\text{O}_3$ produced at $T_{\text{cal}} = 1400^\circ\text{C}$ demonstrates a zero temperature coefficient ($\text{TC} \epsilon_r = 0$) and low enough dielectric losses ($\tan \delta = 58 \times 10^{-4}$), within an wide temperature range ($-40 \div 120^\circ\text{C}$). This material could be used successfully for the production of thermostable capacitors with low dielectric losses.

In Fig. 4 the temperature dependence of the measured conductivity σ of the materials investigated is represented in a logarithmic scale. As it is seen from Fig. 4 each of the curves describing the temperature dependence of σ in a logarithmic scale consists of two linear parts corresponding to different activation energies (ΔE). For the compositions $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.95}\text{Ce}_{0.05}\text{O}_3$ and $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.925}\text{Ce}_{0.075}\text{O}_3$ the activation energies within the temperature range $20 - 100^\circ\text{C}$ are 0.28 eV and 0.36 eV respectively. Within the higher temperature range $100 - 200^\circ\text{C}$ these energies are 0.96 eV and 1.21 eV. For the composition $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.9}\text{Ce}_{0.1}\text{O}_3$ the activation energy for the range $20 - 80^\circ\text{C}$ is 0.9 eV and for the range $80 - 200^\circ\text{C}$ - it is 1.48 eV.

These energies correspond to an impurity character of the conductivity. In the lower-temperature range the conductivity is limited mainly by the interlayers between the grains (crystallites) while in the higher-temperature range it is determined by the intrinsic defects. Predominant are oxygen vacancies created during the high temperature calcination of the materials. These defects are compensated electrically by lowering the degree of oxidation of the nearest-neighbor ions [21].

CONCLUSIONS

Samples of the system $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{1-x}\text{Ce}_x\text{O}_3$ are synthesized by the peroxomethod with $x=0.025, 0.050, 0.075$ and 0.100 mol at calcination temperatures $T_{\text{cal}} = 1300, 1350$ and 1400°C and calcination time 2.5 h.

At increasing the concentration of CeO_2 the stability of the produced sample capacitors is improved but this improvement goes together with lower values

of ϵ_r and higher values of $\tan \delta$. A successful trade-off is the composition $\text{Ba}_{0.5}\text{Sr}_{0.3}\text{Mg}_{0.2}\text{Ti}_{0.925}\text{Ce}_{0.075}\text{O}_3$ with $\text{TC}\epsilon_r = 0$ and low dielectric losses, $\tan \delta = 58 \times 10^{-4}$. Due to these parameters this material could be applied successfully in the production of thermally stable capacitors with low dielectric losses.

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