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Investigation of Dielectricl Properties of $(1\text{-}x)Ba_{0.7}Sr_{0.3}TiO_3 \cdot xMgZrO_3$ Ceramic Obtained by Peroxomethod

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ABSTRACT. The system $(1\text{-}x)Ba_{0.7}Sr_{0.3}TiO_3.x\ MgZrO_3$ where x=0.15; 0.20; 0.25; 0.30; 0.35 mol at calcination temperature T=1300; 1350; 1400°C for 4 hours was synthesized. The most important electric characteristics: relative dielectric permittivity (ε_r), dielectric losses (tan δ) and specific volume resistivity (ρ_v) were studiedat at frequency 1 kHz. The system $0.7Ba_{07}Sr_{0.3}TiO_3.035MgZrO_3$ has ε_r=1050, low dielectric losses tan δ=42.10^{-4}, in the temperature range 20-120°C temperature coefficient of the permitivity $TK\varepsilon_r \rightarrow 0$, and $\rho_v=10^8\ \Omega$ cm. Those values make it suitable for production of thermal stability capacitors as well as capacitors with low dielectric losses working at high frequencies.

ИЗСЛЕДВАНЕ ДИЕЛЕКТРИЧНИТЕ СВОЙСТВА НА $(1\text{-}x)Ba_{0.7}Sr_{0.3}TiO_3 \cdot xMgZrO_3$. КЕРАМИКА ПОЛУЧЕНА ПО ПЕРОКСОМЕТОД

РЕЗЮМЕ. Получена е по пероксо метод системата $(1\text{-}x)Ba_{0.7}Sr_{0.3}TiO_3 \cdot xMgZrO_3$. Изследвани са най-важните електрични характеристики: диелектричната проницаемост (ε_r) и диелектричните загуби (tan δ), обемно специфично съпротивление (ρ_v) при честота 1кHz за следния температурен режим на изпичане на керамиката: 1300, 1350, 1400°C за време 4 часа . Керамичния материал със състав $0.7Ba_{0.7}Sr_{0.3}TiO_3 \cdot 0.3MgZrO_3$ изпечен при 1400°C има ε_r=1050, ниски диелектрични загуби tan δ=42.10^{-4}, за температурния интервал от 20 до 120°C има температурен коефициент на диелектричната проницаемост $TK\varepsilon_r \rightarrow 0$ и $\rho_v=10^8\ \Omega$ cm. Тези данни го правят подходящ за производството на термостабилни кондензатори, както и за кондензатори с ниски диелектрични загуби.

Introduction

The investigation aims to study the materials suitable for the production of thermal stability capacitors with low dielectric losses. In many publications by substitution of $BaTiO_3$ with: $CaTiO_3$, $SrTiO_3$ (Tabata and Kawai, 1997; Cramer et al., 2003), $MgTiO_3$ (Parvanova, 2002), Nd_2O_3 (Kohler et al., 1996), Bi_2O_3 (Yi Zhi et al., 1998), $ZnTiO_3$, $NiTiO_3$ (Parvanova, 2002), La_2O_3, Cr_2O_3 (Fukunaga et al., 2003; Wang et al., 2001) it is achieved to smoothen the maximum of the dielectric permittivity (ε_r) in the range of the Curie temperature and decrease the dielectric losses.

The system $Ba_{0.7}Sr_{0.3}TiO_3$ is obtained by the peroxomethod. By adding different concentration of $MgZrO_3$ the last mentioned properties is aimed to be attained. In the reference data about the synthesis and the dielectric properties of the system (1-x) $Ba_{0.7}Sr_{0.3}TiO_3.x\ MgZrO_3$ is missing. The synthesized material is of scientific and practical interest to be studied as it has been obtained by peroxomethod. This method has a lot of advantages in comparison with the classical ones. The temperature of synthesis is considerably lower, the obtained titanates has higher purity, they are fine crystalline with homogeneous grain-size composition.

Experimental

The starting $BaTiO_3$ and $SrTiO_3$ were prepared by peroxomethod (Genov et al., 1988; Maneva and Parvanova, 1995). The peroxomethod is based the interaction of $TiCl_4$ solution and 17% solution of $BaCl_2$ and $Sr(NO_3)$ and H_2O_2 and NH_3 solution up to pH=9. The obtained intermediate peroxocompounds in the process of the reaction are amorphous precipitate. They were calcinated respectively at T=600°C for $BaTiO_3$ and T=650°C for $SrTiO_3$. The size of the particles is less than 1μm and no milling is needed. The titanates were proved by x-ray investigation with TUR-U-62 apparatus. $MgZrO_3$ is obtained by classical methods. MgO and ZrO_2 with 99% purity were used. The last mentioned were calcinated at 1400°C for 4 hours. The obtained $MgZrO_3$ was milled in planetary ball mill. A system with the composition $(1\text{-}x)Ba_{0.7}Sr_{0.3}TiO_3.x\ MgZrO_3$ where x=0.15; 0.20; 0.25; 0.30; 0.35 mol was obtained.

The powders were pressed at P=200.10^{5}Pa. 10% polyvinyl alcohol is used as a plastificator. 6 mm high discs with 10mm diameter were prepared. They were calcinated at T_{cal}= 1300; 1350 and 1400°C for 4 hours on air. The temperature T_{cal}=360°C was kept for half an hour to evaporate the plastificator. Aiming to provide a good contact during the electric measurements the discs were metaled with 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 20°C to +120°C at steps of 5°C.

Result and discussion

The dependence between the relative dielectric permittivity at T=20°C for the system composition and the calcination temperature is presented on fig.1 from the figure it is obvious that ε_r at T=20°C strongly depends on the ceramic composition and at x=0.15 mol it has maximum value. However, over the given the value for "x" the dielectric permittivity decreases monotonously and it is explained by the increasing of $MgZrO_3$ concentration having considerably lower ε_r. The composition $0.65Ba_{07}Sr_{0.3}TiO_3.035MgZrO_3$ has times lower ε_r=1050 in comparison with $Ba_{07}Sr_{0.3}TiO_3$ (ε_r=3450 according the data by Parvanova 2002). On the figure it is seen that the dielectric permittivity slightly depends on the temperature of calcination. It has maximum value at 1400°C ε_r=3400. T_{cal}=1300°Cis insufficient for the formation of isomorphous structure of the ceramic (ε_r=2100).

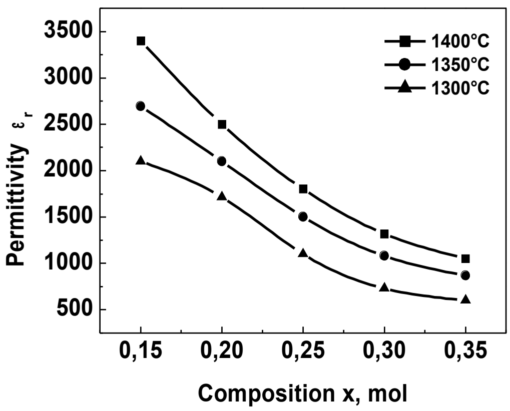

Fig. 1. Dependence of the dielectric permittivity ε_r of the materials on the concentration of $MgZrO_3$ and calcination temperature

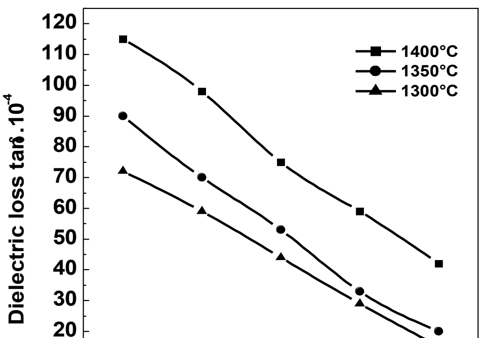

Fig. 2. Dependence of the dielectric losses tan δ of the materials on the concentration of $MgZrO_3$ and calcination temperature

The graphical dependence between the dielectric losses of the system composition and calcination temperature is given on fig.2. It is seen on it that the losses follow the pattern of the dielectric permittivity.It is known that $MgZrO_3$ has low dielectric losses. That is why the system $(1\text{-}x)Ba_{0.7}Sr_{0.3}TiO_3.x\ MgZrO_3$ would have decreasingly losses having increased the $MgZrO_3$ concentration. The increased dielectric losses having increased the temperature of calcination probably due to the structure defects caused by the high temperature calcination (T_{cal}=1400°C). Similar dependence is discussed by Jlin and Wu, 1990. The increasing of the ceramic conductivity is also confirmed by fig.3. It shows the dependence between the specific volume resistivity at the temperature of calcination and the system composition (x). It is seen on the figure that ρ_v depends at the same extent on T_{cal} and on the composition of the studied system. Having compared fig. 2 and 3 it is seen that the dielectric losses are mostly losses of conductivity. The temperature dependence between the relative dielectric permittivity and the system composition at T_{cal}=1400°C is presented on fig. 4. It follows form the figure that increasing the "x" value the maximum of the Curie temperature gradually decreases and it seems that the depressor character of $MgZrO_3$ is observed. It leads to improving the temperature stability of the capacitors.

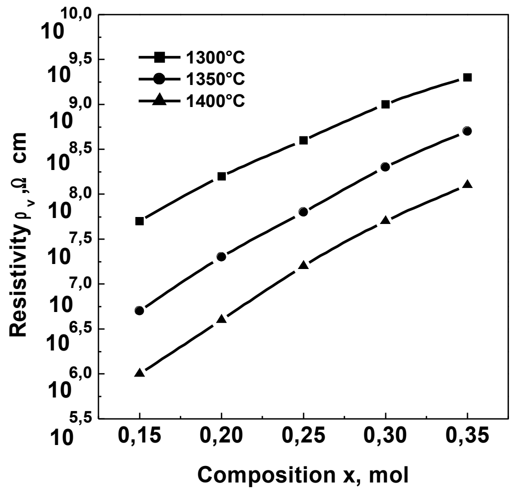

Fig. 3. Dependence of the resistivity ρ_v of materials on the concentration of $MgZrO_3$ and calcination temperature

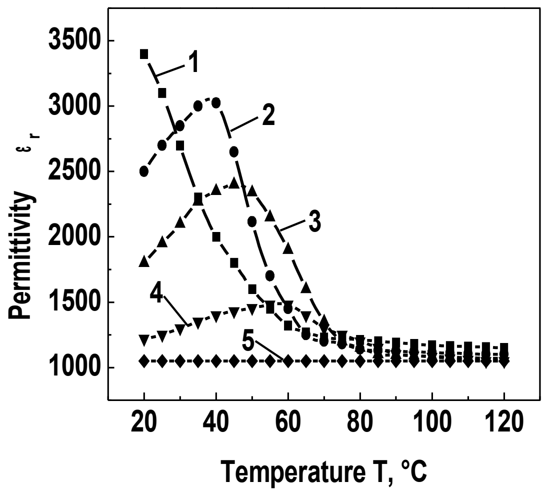

Fig. 4. Dependence of the dielectric permittivity ε_r on the concentration of the $MgZrO_3$ calcinated at a temperature of 1400°C; 1) x=0.15 mol; 2) x=0.20 mol; 3) x=0.25 mol; 4) x=0.30 mol; 5) x=0.35 mol

The substitution of $BaTiO_3$ with $SrTiO_3$ lead to the Curie temperature to the lower values. Similar dependence is discussed by Parvanova 2003. For x=0.35 mol the relative dielectric permittivity is constant with the temperature change i.e. temperature coefficient of dielectric permittivity $TK\varepsilon_r \rightarrow 0$. The composition x=0.30 mol in the range of 20-80°C has $TK\varepsilon_r = 5200.10^{-6}$°$C^{-1}$.

The system $0.65Ba_{0.7}Sr_{0.3}TiO_3.0.35MgZrO_3$ obtained at T_{cal}=1400°C is suitable for the production of thermal stability capacitors with low dielectric losses. The system in the temperature range 20-120°C has ε_r=1050, $TK\varepsilon_r \rightarrow 0$ and very good dielectric losses $\tan\delta = 42.10^{-4}$.

Conclusion

The system $(1\text{-}x)Ba_{0.7}Sr_{0.3}TiO_3.x\ MgZrO_3$ where x=0.15; 0.20; 0.25; 0.30; 0.35 mol at calcination temperature T=1300; 1350; 1400°C for 4 hours was synthesized.

The most important electric characteristics relative dielectric permittivity (ε_r), dielectric losses (tan δ) and specific volume resistivity (ρ_v) were studied.

The system $0.7Ba_{07}Sr_{0.3}TiO_3.035MgZrO_3$ has ε_r=1050, low dielectric losses $\tan\delta = 42.10^{-4}$, in the temperature range 20-120°C $TK\varepsilon_r \rightarrow 0$, and $\rho_v = 10^8\ \Omega$ cm. Those values make it suitable for production of thermal stability capacitors as well as capacitors with low dielectric losses working at high frequencies.

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