ELECTRIC CONDUCTIVITY AND DIELECTRIC PROPERTIES OF POLYCRYSTALLINE SOLID SOLUTIONS MgTiO$_3$–CaTiO$_3$

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Abstract. The temperature dependence of dielectric constant ε_r, the loss factor D, the alternating-current conductivity $\sigma_\sim$ and the direct-current conductivity $\sigma_=$ of four compositions of the polycrystalline system Mg$_x$TiO$_3$-Ca$_{1-x}$TiO$_3$ was investigated in the 293–473 K temperature range. The materials exhibit good temperature stability of ε_r and low dielectric losses ($\tan \delta \approx 10^{-4}$–$10^{-2}$ at room temperature) due to the determining role of the electronic and ionic polarization. The activation energies of the materials have been determined and they show the impurity character of the dc conductivity.

The X-ray-phase analysis has shown the presence of three additional phases in the materials determined as MgTi$_2$O$_5$, MgO and TiO$_2$.

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1. Introduction

The solid solutions MgTiO$_3$–CaTiO$_3$ have applications in the microwave technique as materials for producing resonators and high-frequency condensers [1, 2]. The parameters needed for these elements: low dielectric losses, a constant value and high temperature stability of the relative dielectric constant ε_r depend mainly on the materials production technology.

In the present work the temperature dependences of ε_r, the loss factor D as well as dc ($\sigma_=$) and ac ($\sigma_\sim$) conductivities of four compositions of the polycrystalline system Mg$_x$TiO$_3$.Ca$_{1-x}$TiO$_3$ were studied. The materials were produced by the peroxidate method [3, 4]. In this way a better homogeneity and smaller sizes of the grains formed

by the initial dusts were obtained. Moreover, the materials are more purity as the grinding being duty in usual ceramic technologies [2] was avoided.

2. Sample Preparation and Measurements

The following compositions are used as raw materials for preparing of the magnesium and calcium titanate: $TiCl_4$: $Mg(CH_3COO)_2.4H_2O$: $(CaCl_2.6H_2O)$: H_2O_2 in mol ratio 1:1:10 at the temperature $T = 10-12\,°C$ and pH for $MgTiO_3$ is equal to 10–11 (for $CaTiO_3$ — pH = 8–9.5) by adding of NH_3. The synthesized product has the following composition:

$$Mg_2[Ti_2(O_2)_4(OH)_4].4H_2O, \qquad \text{resp.} \qquad Ca_2[Ti_2(O_2)_4(OH)_4].4H_2O.$$
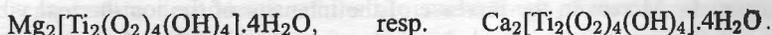
These peroxititanium compounds were calcinated at $T = 650\,°C$ for 4 h whereat they being decomposed to $MgTiO_3$, resp. to $CaTiO_3$. The obtained titanates studied by roentgenography show good crystallinity. The sizes of the particles are below 1 mm because of that a grinding is not needed. Thus obtained dusts were pressed with $P = 0.5$ tons/cm^2. 10 % solution of polyvinyl alcohol where it was used as plastifier. The prepared disks were 9 mm in diameter and 2 mm thick. They were calcinated at $T = 1400\,°C$ 2 h as at $360\,°C$ they were retaining for 0.5 h with the purpose of plastifier evaporating. The disks were metallized using silver paste.

The temperature dependence of the capacity C, the loss factor D and ac conductivity $\sigma_\sim$ were studied by means of digital LCR meter type E7 at a frequency of 1 MHz.

The direct-current conductivity $\sigma_=$ was measured by Teraohmmeter TR-2201. The temperature range was 293–473 K with a sweep rate of 2 K/min. The roentgenophase analysis was made with the apparatus TUR-U-62.

3. Results and Discussion

Figure 1 shows the temperature dependence of the relative dielectric constant ε_r of the studied compositions. For the composition *1* the dielectric constant ε_r slightly depends on the temperature (it almost does not change) and for the composition *4* its increase is about 8 %.
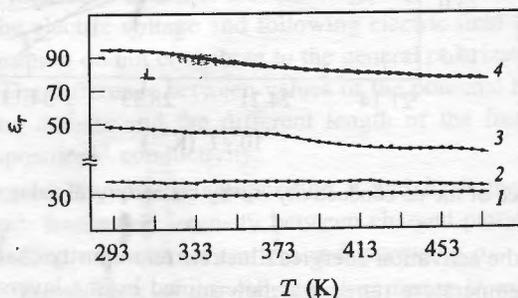

Fig. 1. Temperature dependence of relative dielectric constant ε_r of the following compositions (*1*) $MgTiO_3$; (*2*) $Mg_{0.9}Ca_{0.1}TiO_3$; (*3*) $Mg_{0.7}Ca_{0.3}TiO_3$; (*4*) $Mg_{0.5}Ca_{0.5}TiO_3$

The good temperature stability of the dielectric constant of the compositions shows that it is determined by the fast type polarizations: the electronic elastic and the ionic elastic, and on increasing the temperature both the electronic and the ionic polarization caused by thermal diffusion of the electrons and ions, have a contribution.

On increasing the concentration of $CaTiO_3$, the dielectric constant increases and the temperature stability decreases slight. The increase of ε_r is due to the higher dielectric constant of $CaTiO_3$ as to the increase of the concentration of the structure defects which increase the polarizability of the materials.

The slight decrease of ε_r at the higher temperature is due to the decrease of the electronic polarization as on increasing the temperature we have a decrease of the density of materials. Moreover, the increase of the intensity of the ion thermal vibrations together with the temperature impedes to the arrangements of the relaxing grains in the electric field and decreases their contribution to the general polarization.

The dc conductivity $\sigma_=$ of three compositions as a function of reciprocal temperature is shown in Fig. 2. On all curves there are two ranges with linear dependence of dc conductivity on $1/T$, corresponding to two different activation energies. The activation energies for the composition 1 and composition 2 in the temperature range of 20–90 °C are respectively 0.16 eV and 0.24 eV and in the high temperature range they are respectively 1.04 eV and 0.8 eV. For the composition 4 the activation energy in the range of 20–140 °C is 0.68 eV, and in the range of 140–200 °C it is equal to 2.4 eV.
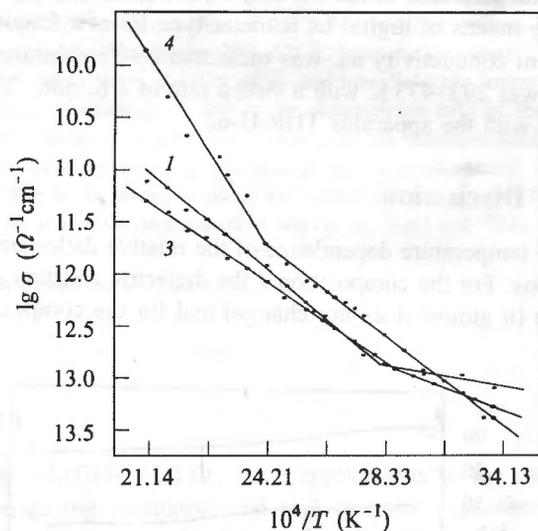

Fig. 2. Dependence of the dc conductivity $\sigma_=$ by the reciprocal value of the temperature

These values of the activation energies illustrate an impurity character of the conductivity. In the low-temperature range it is determined by the layers between the grains (crystals). On decreasing the temperature, additional phases participate in conductivity; those phases were identified by X-ray-phase analysis as: $MgTi_2O_5$, MgO and TiO_2

[5]. In the range of the highest temperature the conductivity is due mainly to the own effects in $MgTiO_3$ and $CaTiO_3$; among them the oxygen vacancies formed in the process of high-temperature sintering of the materials [6]. The electric compensation of these defects goes through decreasing the valence of the cations arranged nearest to the vacancies, i. e., to the appearing electrons having slight linkages with the neighbour ions.

The higher conductivity of composition *4* shows that it has the highest concentration of the structural defects. Moreover, because of the increased content of $CaTiO_3$, formation of new impurity levels in the prohibited area is possible, which increases the conductivity of this composition additionally.

The temperature dependence of the ac conductivity of the compositions (Fig. 3) shows that $\sigma_\sim$ is much higher than the dc conductivity $\sigma_=$ respectively.
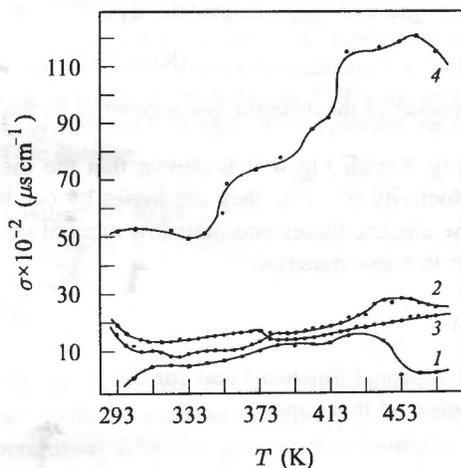

Fig. 3. Temperature dependence of ac conductivity $\sigma_\sim$

At comparatively high frequency of the measuring electric voltage a part of the current carriers has been localized earlier by potential barriers, structural defects and borders between crystals and does not succeed to go back in its equilibrium state in a quarter period of the electric voltage and following electric field change, increase $\sigma_\sim$. In such state their motion do not contribute to the general polarization and influence on the amount of ε_r. The difference between values of the potential barriers, the different concentration of the defects and the different length of the free run of the current carriers in the compositions' conductivity.

The higher polarizability of the composition *4* and its higher dielectric constant reduces the Coulomb interaction intensity between charged particles and increase the probability of generating new current carriers and increasing $\sigma_\sim$.

The temperature dependence of the dielectric loss factor $D = \varepsilon_r \tan \delta$ of the compositions is shown in Fig. 4. The 1st composition has minimum losses and the 4th composition has maximum losses.
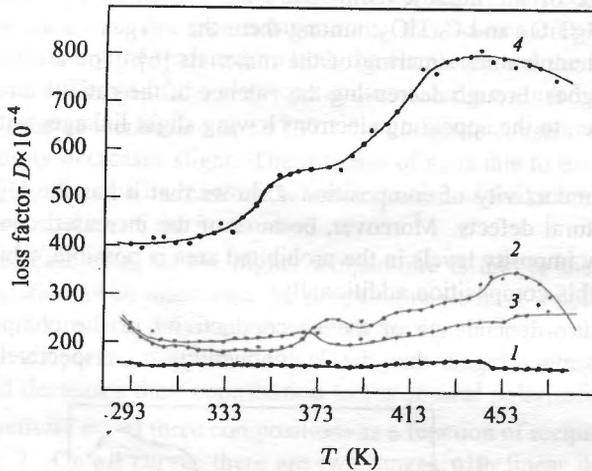
Fig. 4. Dependence of the dielectric losses factor D by the temperature

By comparison of Fig. 3 with Fig. 4 it is shown that the dielectric losses lead the changes of the ac conductivity $\sigma_\sim$, i. e. they are losses by conductivity.

This behaviour of the electric losses and their low amount confirms the leading role of the type polarization in these materials.

Acknowledgement

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