Effect of Magnesium Substitution on Dielectric Constant of $Zn_{2-x}Mg_xInV_3O_{11}$ ($x = 0.0, 0.4, 1.6$) Solid Solutions

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The results of magnetic and dielectric measurements of $Zn_{2-x}Mg_xInV_3O_{11}$ phases with $x = 0.0, 0.4$, and 1.6 showed diamagnetic behavior above room temperature and a strong increase in the relative electrical permittivity, ε_r, with an increase in the magnesium content as well as the high loss tangent, $\tan\delta$, above 150 K, irrespective of the magnesium content in the sample. With the increase in the frequency of the electric field both ε_r and $\tan\delta$ strongly decreased. At low temperatures a residual paramagnetism coming from the paramagnetic ions of vanadium was observed. These effects were interpreted within a framework of the vacancy trapping centers acting as the accumulation of electric charges on the one hand and a mixed valence of vanadium ions on the other.

1. Introduction

Vanadates (V) of divalent metals exhibiting the presence of isolated VO_4 tetrahedra in their structure display a good selectivity and high activity as catalysts for the oxidation processes of light hydrocarbons or as cathode materials in high-energy cells. Among phases recently obtained there are some compound which are formed in the systems: $MO-Fe_2O_3/In_2O_3-V_2O_5$, where M = Mg, Zn, Co, Ni, Pb, Ba, Sr [1–6]. The double vanadates of the general formula $M_2^{II}M^{III}V_3O_{11}$, i.e. $M_2FeV_3O_{11}$ (M = Mg, Zn, Co, Ni, Pb) and $M_2InV_3O_{11}$ (M = Mg, Zn, Co, Pb, Ba, Sr) contain isolated VO_4 tetrahedra in their structure [1–6].

Research conducted in the quaternary oxide system $ZnO-MgO-In_2O_3-V_2O_5$ have revealed that a new solid solution of the formula $Zn_{2-x}Mg_xInV_3O_{11}$ is formed in the whole concentration range of $Zn_2InV_3O_{11}-Mg_2InV_3O_{11}$ subsystem [6]. This new phase can be obtained by conventional solid state reaction method. The solid solution crystallized in the triclinic system; its unit cell parameters a and b increased with increase of Mg^{2+} ions incorporation into the crystal lattice of $Zn_2InV_3O_{11}$ while the values of the unit cell parameter c decreased with increase of magnesium content. The solid-state density values obtained experimentally and calculated on the basis of X-ray diffraction (XRD) data decreased as a function of the degree of Mg^{2+} ions incorporation in the crystal lattice of $Zn_2InV_3O_{11}$ [6].

In the present work we have measured magnetic isotherms, electrical permittivity, and loss tangent of $Zn_{2-x}Mg_xInV_3O_{11}$ ceramics.

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2. Experimental details

Magnetization was measured with the use of a Quantum Design MPMS-XL-7AC SQUID magnetometer in the temperature range of 2–300 K and in the magnetic field to 70 kOe.

Broadband dielectric spectroscopy measurements were carried out using pellets, polished, and sputtered with ($\approx$ 80 nm) Ag electrodes in a frequency range from 2×10^2–2×10^6 Hz with the use of a Novocontrol Alpha Impedance Analyzer and in the temperature range 80–400 K. For the electrical measurements, the powder samples were compacted in a disc form (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa and then they were sintered for 2 h at 923 K. The electrical and thermal contacts were made by a silver lacquer mixture (Degussa Leitsilber 200).

3. Results and discussion

The results of magnetization measurements of solid solution of $Zn_{2-x}Mg_xInV_3O_{11}$ ($x = 0.0, 0.4$, and 1.6) composition displayed in Figs. 1–3 showed diamagnetic properties at room temperature and a residual paramagnetism at low temperatures below 30 K visible on the universal function of $M(H/T)$. The deviation from the universal curve of $M(H/T)$ for $x = 0.4$ (Fig. 2) additionally suggests the appearance of a small spin–orbit coupling. It may be the result of defective structure or the appearance of a small amount of vanadium ions at a different degree of oxidation than the fifth (diamagnetic).

The results of the broadband dielectric spectroscopy measurements of $Zn_{2-x}Mg_xInV_3O_{11}$ ($x = 0.0, 0.4$, and 1.6) showed a strong increase in the relative electrical permittivity, ε_r, with an increase in the magnesium content
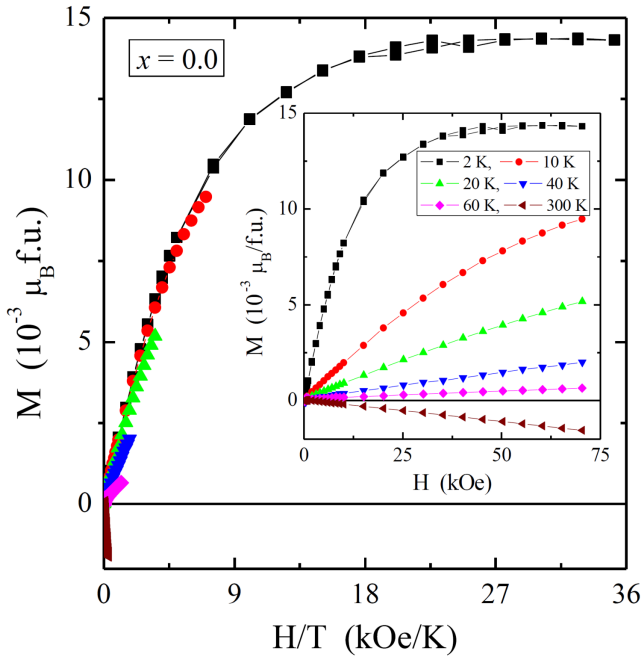
Fig. 1. Magnetization M vs. H/T and H (inset) at 2, 10, 20, 40, 60, and 300 K for $Zn_2InV_3O_{11}$.

Fig. 2. As in Fig. 1, but for $Zn_{1.6}Mg_{0.4}InV_3O_{11}$.

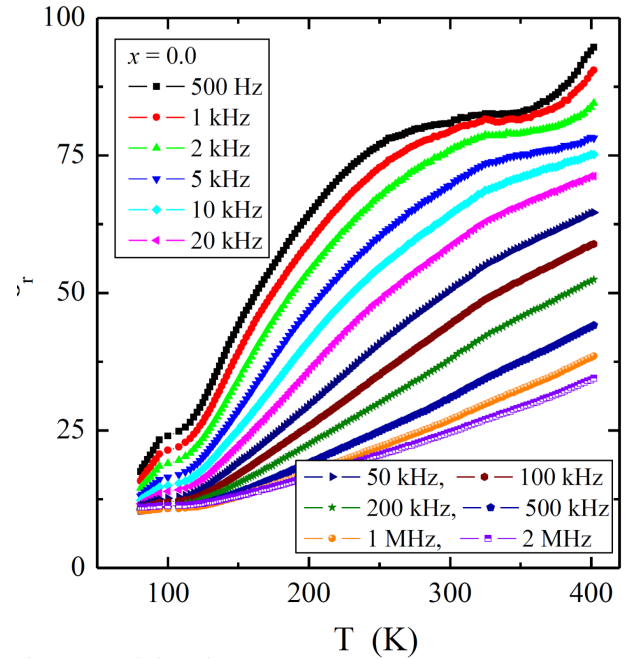
Fig. 3. As in Fig. 1, but for $Zn_{0.4}Mg_{1.6}InV_3O_{11}$.

Fig. 4. Dielectric constant ε_r vs. temperature T for $Zn_2InV_3O_{11}$ in the frequency range 500 Hz to 2 MHz.

(Figs. 4–6) and high loss tangent, $\tan\delta$, above 150 K, irrespective of the magnesium content in the sample (Figs. 7–9). With the increase in the frequency of the electric field both ε_r and $\tan\delta$ strongly decreased.

From Figs. 4–6 one can see that a variation in ε_r strongly depends on the content of magnesium ions, whose presence leads to a greater accumulation of electric charge in the so-called trapping centers [7] with their electronic states located below the bottom of the conduction band. A natural source of these traps can be grain-boundaries with depletion layers of adjacent grains, as it has been observed for ZnO varistors [8], Nb_2VSbO_{10} ceramics [9] and some copper/cobalt and rare-earth metal tungstates [10] as well as reported for $(Co,Mn)Pr_2W_2O_{10}$ [11]. The above-mentioned dielectric properties could be interpreted as related to the relaxation process like with Maxwell–Wagner [12] or Jonscher [13], because the solid-state density of the phases
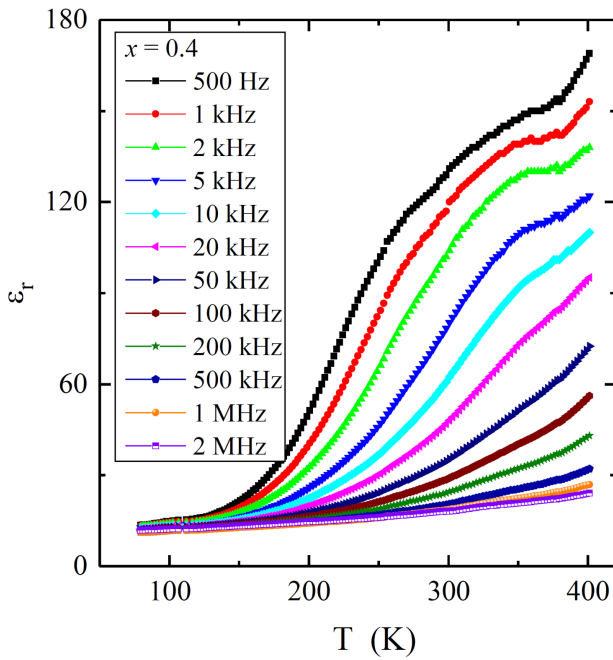
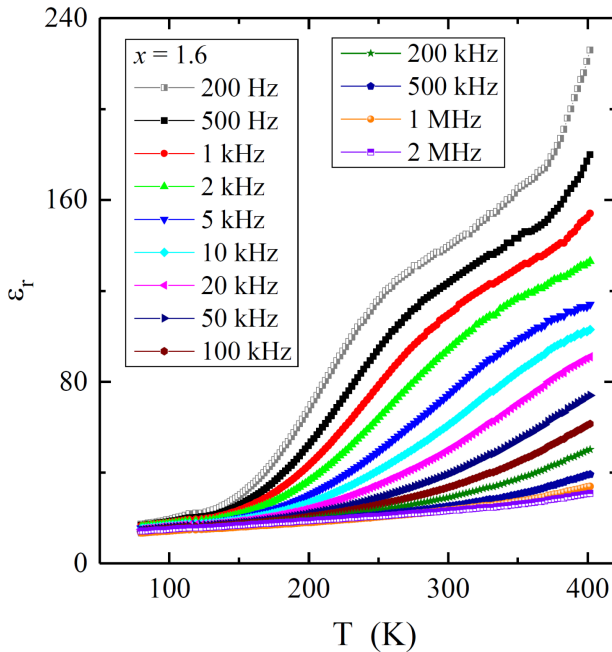Fig. 5. As in Fig. 4, but for $Zn_{1.6}Mg_{0.4}InV_3O_{11}$.

Fig. 7. Loss tangent $\tan\delta$ vs. temperature T of $Zn_2InV_3O_{11}$ in the frequency range 500 Hz to 2 MHz.

Fig. 6. As in Fig. 4, but for $Zn_{0.4}Mg_{1.6}InV_3O_{11}$.

Fig. 8. As in Fig. 7, but for $Zn_{1.6}Mg_{0.4}InV_3O_{11}$.

under study decreased with increasing magnesium content [6]. The reduction in this density was a consequence of the reduction in the number of vanadium ions with mixed valence.

From Figs. 7–9 one can see that a variation in $\tan\delta$ strongly depends on temperature and frequency, and slightly depends on the content of magnesium ions. In particular, high loss is observed at low frequencies, characteristic of the Joule–Lenz type losses.
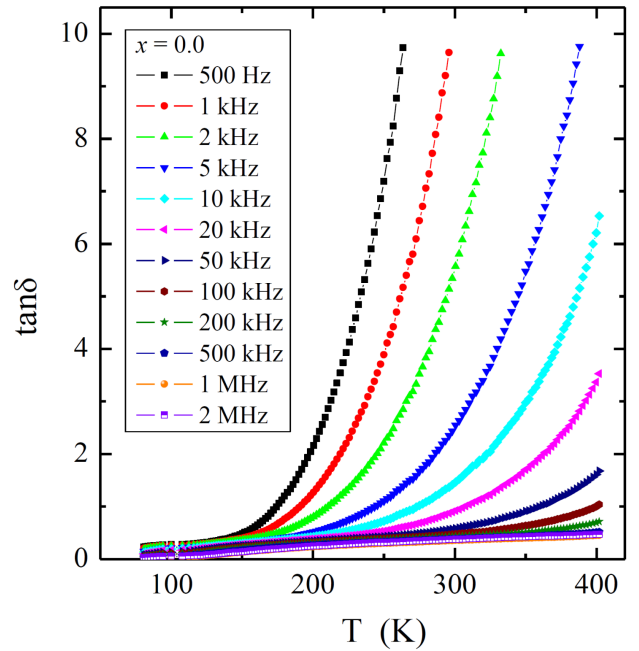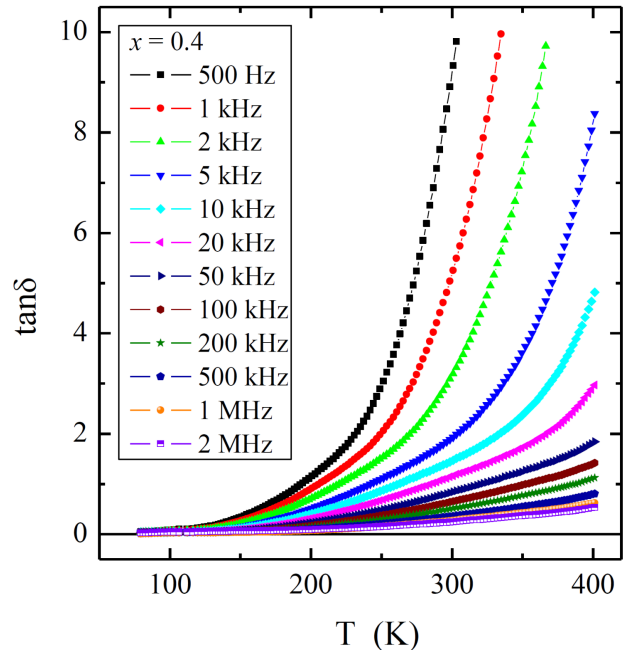
4. Conclusions

In summary, the $Zn_{2-x}Mg_xInV_3O_{11}$ ($x = 0.0$, 0.4, and 1.6) ceramics were characterized by magnetic isotherms and dielectric spectroscopy measurements. They have shown diamagnetic properties and strong dependence on temperature, frequency and magnesium content of relative dielectric constant and loss tangent. These effects were explained within a framework of the vacancy trapping centers and the mixed valence of vanadium ions.

Therefore, diverse and interesting properties of the studied ceramics under study make them much promising for electronic applications.
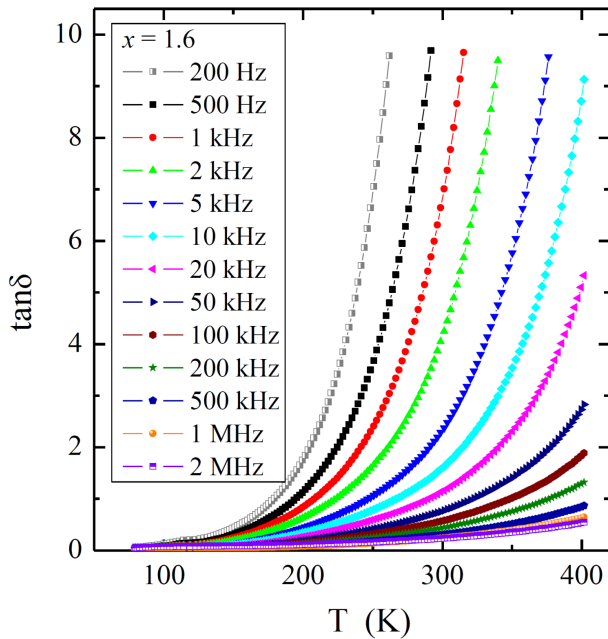
Fig. 9. As in Fig. 7, but for $Zn_{0.4}Mg_{1.6}InV_3O_{11}$.

Acknowledgments

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