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Influence of cation substitution on dielectric and electric properties of bismuth stannates Bi$_2$Sn$_{1.9}$Me$_{0.1}$O$_7$ (Me=Cr, Mn)

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Abstract. The article studies effect of nonstoichiometric substitution of the tin ions by chromium and manganese ions on the dielectric and electrical properties of bismuth pyrostannate. The research performs measurements of the current-voltage characteristics, capacitance and tangent of the dielectric loss angle in the temperature range from 300 to 800 K; it finds a qualitative difference in the temperature behavior of the permittivity of bismuth pyrostannate with chromium and manganese ions. A change in the type of conductivity from hopping to tunneling emission is established. The change in the activation energy as a function of the ion radius is found.

1. Introduction

Bismuth pyrostannate attracts attention both from the fundamental point of view as multiferroics, spin ice [1] and as optical devices [2] and sensors [3] use it. Substitution of the tin ions in Bi$_2$Sn$_2$O$_7$ by 3d magnetoactive ions will lead to a magnetic order that can be controlled by an electric field as a result of the displacement of the oxygen ion. Variation of ferroelectric properties by a magnetic field is due to magnetoelastic interaction. Ferroelectric properties may be enhanced by non-stoichiometric substitution which gives an additional electron contribution to the polarization.

The aim of this study is to establish the role of non-stoichiometric substitution of tin ions by chromium ions as compared to manganese ions on the dielectric and electrical properties of bismuth pyrostannate.

2. Experimental

Samples of Bi$_2$ (Sn$_{0.9}$Me$_{0.1}$)$_2$O$_7$(Me = Cr,Mn) were synthesized using the solid-state reaction technique. The powder X-ray diffraction pattern of samples was obtained at room temperature using a Bruker D8 ADVANCE diffractometer, a VANTEC linear detector, and the CuK$_\alpha$ - radiation. All peaks, except several weak impurity peaks of an unknown phase corresponded, to the monoclinic *Pc* cell in the α-phase of Bi$_2$Sn$_2$O$_7$ [4]. The crystal structure contains 32 Bi^{3+} ions, 32 Sn^{4+} ions and 112 O^{2-}ions in the independent part of the cell. Fig.1 shows the crystal structure of Bi$_2$(Sn$_{0.9}$Mn$_{0.1}$)$_2$O$_7$. All Bi^{3+} ions are surrounded by eight O^{2-} ions and form a distorted cubeand Sn^{4+} is located in the oxygen octahedron, which are connected by vertices.
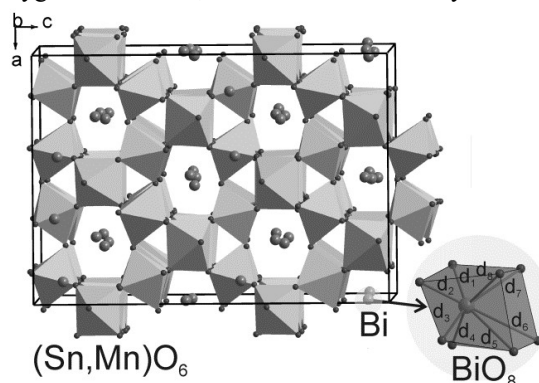
**Figure 1.**Crystal structure of Bi$_2$(Sn$_{0.9}$Mn$_{0.1}$)$_2$O$_7$. The inset shows one of 32 independent polyhedrons BiO$_8$ that form the unit cell. The d_{1-4} bond lengths takes values 2.2–2.5 Å, and the d_{5-8} bond lengths takes values 2.5–3.2 Å

The decrease in the cell volume $Bi_2 (Sn_{0.9}Me_{0.1})_2O_7$ (Me = Cr, Mn) correlates with the ionic radius IR (Cr^{3+}) = 0.615 Å, IR (Mn^{4+}) = 0.53 Å, they are smaller than the tin ion radius IR (Sn^{4+}) = 0.69 Å [5].

The electrical properties of $Bi_2 (Sn_{0.9}Me_{0.1})_2O_7$ (Me = Cr, Mn) are investigated by a four-probe technique on a 6517 V electrometer in the temperature range of 350–700 K. Capacitance, and loss-angle tangent are measured on an AM-3028 component analyzer in the frequency range of 0.1–1000 kHz at temperatures of 300–750 K. The current-voltage characteristics are obtained on an electrometer Keithley 6517b in an electric field from -800 to 800 V/cm.

3. ResultsandDiscussion

Permittivity. Figure 2 shows the real and imaginary parts of the $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$ permittivity versus temperature for several frequencies. The temperature dependencies of ε(T) reveal inflection points in the real part (Fig. 2a) and wide maxima of the dielectric losses (Fig. 2b) at the same temperature, increasing from T_m = 370 K to 560 K according to the logarithmic law from frequency. The relaxation time is described by the exponential law$\tau = \tau_0 epx(\Delta E/kT)$ with an activation energy ΔE = 0.4 eV. The dielectric susceptibility increases sharply at approaching to the $\beta \rightarrow \gamma$ phase transition temperature.
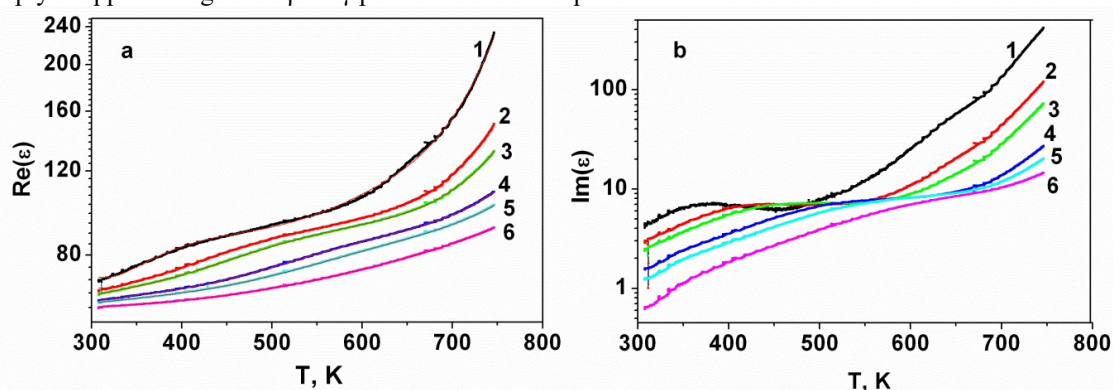
Figure 2. Temperature dependence of the permittivity of $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$ at different frequencies: (a) real part and (b) imaginary part. Curve 1 corresponds to 1 kHz, 2 - 5 kHz, 3 - 10 kHz, 4 - 50 kHz, 5 - 100 kHz, 6 - 300 kHz

The permittivity in the range of $5 \cdot 10^4 - 10^6$Hz frequencies and in the range of 300-500 K temperatures is well described in term of the Debye model:

$$Re(\varepsilon) = \varepsilon_0 + \chi_0/(1+(\omega\tau)^2), \tag{1}$$
$$Im(\varepsilon) = \chi_0\omega\tau /(1+(\omega\tau)^2), \tag{2}$$

where ε_0 is the temperature-independent contribution to the permittivity, χ_0 is the static susceptibility of the dipoles, ω is the frequency, and τ is the relaxation time of $1.5 \cdot 10^{-5}$sec. At temperatures above 550 K the permittivity is described by a power function $\varepsilon = A/\omega^n$with n <1. The exponent increases at the heating.

The real and imaginary parts of the permittivity are well described by the exponential law $\ln\varepsilon = A + \Delta E/T$ with the activation energy ΔE = 0.3 eV for the real part and ΔE=0.6 eV for the imaginary part of the permittivity. The activation process is due to the diffusion of current carriers in the domain and the accumulation of charge on the surface of the domain.

The real part of the permittivity $Bi_2(Sn_{0.9}Mn_{0.1})_2O_7$(Fig. 3a) has a small minimum in the vicinity of $\alpha \rightarrow \beta$ phase transition. At farther heating the permittivity sharply increases. The anomalytemperature isagreement with the temperature of small maximum on the differential-scanning calorimetry curve at T = 420 K [6]. The real and imaginary parts of the permittivity reveal a wide maximum at T>500 K, that is absent on the DSC curve. A similar temperature dependence of the permittivity above T = 550 K is observed in $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$.

The behavior of the permittivity at high temperatures occurs due to a change in the electronic structure as a result of the large electronic polarization of the Bi-O bond. Oxygen ions are known to possess a significant polarization; it increases at the presence of covalence and anisotropy. The polarization of bismuth ions arises from $6s^2$ lone pair electrons. The effect of the lone pair causes a large mobility of oxygen ion in the Bi_4O' sublattice and strong displacements of them from the sites of the ideal lattice of the pyrochlore structure. The absence of significant structural changes in $Bi_2Sn_2O_7$ in the temperature range of 500-600 K; it allows to make the assumption that the observed singularities in the behavior of the dielectric susceptibility due to processes of charge transfer and a sharp change in the ions polarization. A similar behavior of the dielectric constant is

observed in α-Bi$_2$O$_3$ [7]. The substitution of Sn ions by Cr and Mn ions will lead to deformation of the oxygen - bismuth bond and to an increase in the dipole moment, since their ionic radii are different. The heterovalent substitution of tin by chromium leads to an electronic contribution to the permittivity and an increase in Re (ε) compared to the manganese ions giving the ionic contribution.
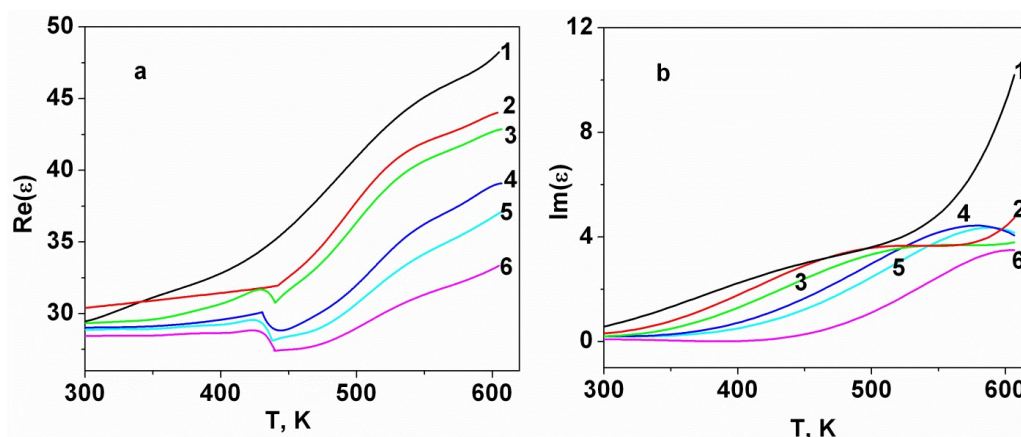
Figure 3. Temperature dependence of the permittivity of Bi$_2$(Sn$_{0.9}$Mn$_{0.1}$)$_2$O$_7$ at different frequencies: (a) real part and (b) imaginary part. Curve 1 corresponds to 1 kHz, 2 - 5 kHz, 3 - 10 kHz, 4 - 50 kHz, 5 - 100 kHz, 6 - 300 kHz

Electrical properties. The electrical resistance determined from the current-voltage characteristic shows a typical semiconductor conductivity for two samples of Bi$_2$(Sn$_{0.9}$Me$_{0.1}$)$_2$O$_7$(Me=Mn, Cr). The electrical resistance for Bi$_2$(Sn$_{0.9}$Cr$_{0.1}$)$_2$O$_7$ is independent on temperature at T=500-550 K, that agrees with the anomalies in the dielectric susceptibility. The change from the Mott conductivity mechanism to the Poole-Frenkel conduction mechanism occurs also in this temperature range. The values of activation energies ΔE, calculated from the temperature dependence of lg(ρ) on the reciprocal temperature (Fig.4) are described by the linear function $ln\rho=ln\rho_0+\Delta E/(k_BT)$) in the temperature range 300-500 and are equal to 1.58 and 1.17 eVfor Bi$_2$(Sn$_{0.9}$Mn$_{0.1}$)$_2$O$_7$ and for Bi$_2$(Sn$_{0.9}$Cr$_{0.1}$)$_2$O$_7$.
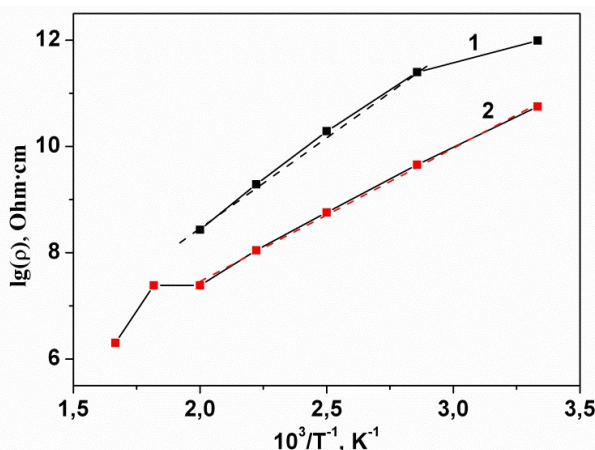
Figure 4. Temperature dependence of logarithm of the resistivity of Bi$_2$(Sn$_{0.9}$Mn$_{0.1}$)$_2$O$_7$ and Bi$_2$(Sn$_{0.9}$Cr$_{0.1}$)$_2$O$_7$. Curve 1– Bi$_2$(Sn$_{0.9}$Mn$_{0.1}$)$_2$O$_7$, 2 – Bi$_2$(Sn$_{0.9}$Cr$_{0.1}$)$_2$O$_7$

The conduction mechanism and the existence of inhomogeneous electronic states are determined from the current-voltage characteristics. The shape of the curve I (U) varies with increasing temperature. In the temperature range where charge ordering is observed, the conductivity is described in a model of currents limited by the space charge and is described by the quadratic Mott law [8] for both Bi$_2$(Sn$_{0.9}$Mn$_{0.1}$)$_2$O$_7$ and Bi$_2$(Sn$_{0.9}$Cr$_{0.1}$)$_2$O$_7$:

$$j = \frac{9}{8}\tau_\mu\sigma_0\mu\frac{U^2}{L^3},$$

(3)

where j – the current density, τ_μ– the Maxwell relaxation time, σ_0 – the electrical conductivity in the bulk of the material in the absence of charge carrier injection, μ – the mobility of the charge carriers, U – the applied voltage, and L – the thickness of the sample. In Fig. 5a, the experimental data of the I-V characteristic in logarithmic coordinates are well described by the relation (3) for $Bi_2(Sn_{0.9}Mn_{0.1})_2O_7$ to T = 400 K, and for $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$ to T=500 K. The Pool- Frenkel conduction mechanism prevails in the range of high temperatures at T>450 K for the $Bi_2(Sn_{0.9}Mn_{0.1})_2O_7$ and at T >550 K for $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$ (Fig. 5b), according to which the strong electric field applied to the sample changes the form of the potential barriers for charge carriers. In this case, the current depends exponentially on the applied voltage and the exponent contains the square root of voltage:

$$I = e\mu n_0 \frac{U}{L} \exp \frac{\beta U^{1/2}}{kTL^{1/2}}, \qquad (4)$$

where, e – the charge of the electron,μ – the mobility of the charge carriers, n_0- the electron concentration in the conduction band in the absence of the field, U – the applied voltage, L – the thickness of the sample, k – the

Boltzmann constant,β – the Pool-Frenkel constant, $\beta = \left(\dfrac{e^3}{\pi\varepsilon\varepsilon_0}\right)^{1/2}$, ε is the permittivity of a semiconductorε_0 –

the dielectric constant. The linearity plots in the ln(I/U) the dependence from $U^{1/2}$in the Pool-Frenkel coordinates indicates that the transport of charge carriers is carried out mainly by as hopping conduction mechanism and due to the tunneling electron emission [9].
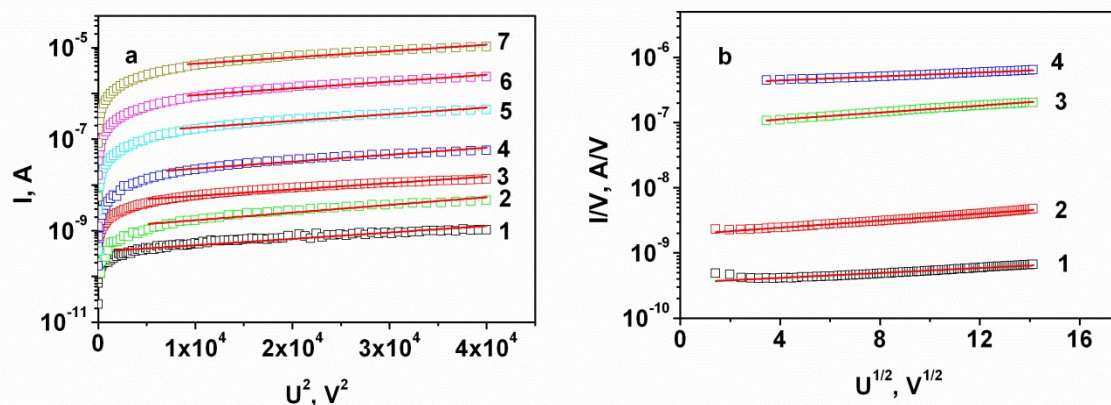
Figure 5.I–V characteristics of $Bi_2(Sn_{0.9}Mn_{0.1})_2O_7$ and $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$, positive voltage. (a) Dependence of the current on the squared applied voltage. Curve 1,3 corresponds to $Bi_2(Sn_{0.9}Mn_{0.1})_2O_7$ at T = 350 and 400 K, 2,4,6,7 - $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$, T = 300, 350, 400 450 and 500 K accordingly. (b) Pool–Frenkel I–V characteristic measured. Curves 1,2 - $Bi_2(Sn_{0.9}Mn_{0.1})_2O_7$ at T = 450 and 500 K; 3,4 - $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$, T = 550 and 600 K

4.   Conclusion

The maximums in the temperature behavior of the dielectric loss at $Bi_2(Sn_{0.9}Cr_{0.1})_2O_7$ hole doping for α – phase are found. The jump in the temperature dependence of permittivity and an electronic transition are detected in the case of isovalent substitution for $Bi_2(Sn_{0.9}Mn_{0.1})_2O_7$. The electronic transition with the variation in the conductivity type from hopping to Pool–Frenkel emission is established. The research also determines a decrease in the activation energy at hole substitution as compared to the isovalent substitution tin ions by manganese.

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