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Structural and impedance spectroscopy properties of $Pr_{0.6}Sr_{0.4}Mn_{1-x}Ti_xO_{3\pm\delta}$ perovskites

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ABSTRACT

An exhaustive study of structural, dielectric and impedance analysis on $Pr_{0.6}Sr_{0.4}Mn_{1-x}Ti_xO_{3\pm\delta}$ $(0 \leqslant x \leqslant 0.4)$ perovskites were performed. Polycrystalline samples were prepared using solid state reaction method. The crystallographic structure was studied by X-ray diffraction experiments and Rietveld refinement revealed that all samples crystallize in an orthorhombic structure with *Pnma* space group. The approximate grain size was found from experiments' scanning electron microscopy. The electrical response was studied using the impedance spectroscopy technique over a broad frequency range (0.1 Hz–1 MHz). The values of total conductivity for all samples were well fitted by the Jonscher law $\sigma_{tot}(\omega) = \sigma_{dc} + A\omega^n$. For $0 \leqslant x \leqslant 0.3$ samples, the hopping process occurs through long distance, whereas for $x = 0.4$ compound the hopping occurs between neighboring sites. The $Pr_{0.6}Sr_{0.4}Mn_{0.6}Ti_{0.4}O_{3\pm\delta}$ sample presents the lowest real part Z' and the highest *dc*-conductivity σ_{dc} among these samples. For $x = 0.3$ and 0.4 compounds, the variation of the imaginary part Z'' shows a peak at a relaxation frequency related to the relaxation time (τ) by $\tau = 1/2\pi f_r$. Nyquist plots of impedance show semicircle arcs for samples beyond 20% Ti content and an electrical equivalent circuit has been proposed to explain the impedance results.

1. Introduction

Exploration of properties of inorganic material has been a long-standing goal in the development of functional materials. There exists a close relationship among structure, morphology and physical properties. Extensive studies have been devoted to understanding formation mechanism from both theoretical and experimental views in order to synthesize better functional materials. Dielectric permittivity materials, of about 10^4 and over, have been attracting much attention due to their potential applications in the microelectronic industry [1–4]. There are several works reported for dielectric properties of inorganic materials in recent years such as $CaCu_3Ti_4O_{12}$ [5–12] and Sr_2TiMnO_6 [13] ceramics. Recently alternating current (*ac*) and direct current (*dc*) transport processes have been investigated in hole-doped La-based manganites such as $La_{1-x}Ca_xMnO_3$ [14], $La_{1-x}Sr_xMnO_3$ [15], $La_{1-y}A_yMn_{1-x}Fe_xO_3$ [16,17] and $La_{0.7}Sr_{0.3}Mn_{0.7-x}Ti_xO_3$ [18] where the manganese is in mixed valence state (Mn^{3+}–Mn^{4+}). But their homologous Pr-based manganites are less studied. Recently we have shown interesting magnetic properties, such as magnetic transition near room temperature, canted spin state at low temperature under magnetic field and magnetocaloric effect in $Pr_{0.6}Sr_{0.4}MnO_{3\pm\delta}$ [19]. However, to our knowledge, there is no investigation of the dielectric properties for Pr-based manganites. According to Ulyanov et al. [20] titanium is in tetravalent state (Ti^{4+}) in $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ system. Considering the tetravalent state of titanium $Ti^{4+}(Ar, 3d^0)$ we suggest that the isovalent substitution of Ti^{4+} for Mn^{4+} $(Ar, t_{2g}^3 e_g^0)$ in $Pr_{0.6}Sr_{0.4}MnO_{3\pm\delta}$ improves the dielectric properties of the material due to the overlap of its vacant d_0 orbital with p-orbital of oxygen, which contributes to the higher asymmetry and hence more polarization.

The study of the dielectric properties of such Ti substituted manganites is of a great interest because they are a lead free environmentally friendly material, low cost and easily synthesized in pure form. Complex impedance spectroscopy (CIS) is an important and powerful tool to study dielectric and conduction properties of materials. For a polycrystalline sample, this technique enables us to separate the contributions of grain and grain boundaries very easily [21–23]. In the present paper, *ac*-CIS was used to study the effect of Ti doping for Mn on the structural, dielectric, conductivity and complex impedance analysis properties of Pr-based ceramic bulk perovskites, with developed chemical formula $Pr_{0.6}Sr_{0.4}Mn^{3+}_{0.6}Mn^{4+}_{0.4-x}Ti^{4+}_xO_{3\pm\delta}$ $(0 \leqslant x \leqslant 0.4)$, over the wide range of frequencies at room temperature.

2. Experimental

Perovskite oxides with nominal composition $Pr_{0.6}Sr_{0.4}\ Mn^{3+}_{0.6}Mn^{4+}_{0.4-x}Ti^{4+}_xO_{3\pm\delta}$ $(0 \leqslant x \leqslant 0.4)$ were prepared by the standard solid state reaction using stoichiometric amounts of Pr_6O_{11}, $SrCO_3$, Mn_2O_3 and TiO_2 precursors, all with purity better than

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99.9%. Care was taken to remove moisture before weighing by preheating the precursors at 873 K for 12 h. The mixtures were heated in air at 1073 K for 24 h to achieve decarbonisation. After grinding, they were heated at 1373 K for 48 h and ground again to ensure homogeneity. Intermediate cooling and mechanical grinding steps were repeated in order to get an accurate homogenization and complete reaction. The powders were pressed into pellets and sintered at 1673 K for 48 h in air with several intermediate grinding and repelleting. Microstructure of specimens and their composition analysis were studied by scanning electron microscopy (SEM) using a Philips XL30 microscope with an energy dispersive X-ray spectrometer (EDX). Powder X-ray diffraction (XRD) analyses were carried out with a "PANalytical X'Pert Pro" diffractometer with filtered (Ni filter) Cu radiation. Data for the Rietveld refinement were collected in the 2θ range 10–120° with a step size of 0.017° and a counting time of 18 s per step. Standard Si powder was used to obtain the instrumental resolution function. The structure refinement was carried out by the Rietveld [24] analysis of the powder XRD data with the FULLPROF software. The dielectric properties were examined by an impedance analyzer (Novocontrol Alpha-analyzer) over a broad frequency range (0.1 Hz–1 MHz) at room temperature. In the impedance analyzer, the sintered and polished disk with about 1.5 mm of thickness was placed between two gold parallel electrodes. A circular gold electrode (2 cm in diameter) was sputtered on both surfaces of the sample to ensure good electrical contact with the gold-plated measuring electrodes. The complex dielectric permittivity ε^* and electrical conductivity σ were calculated from the measured complex impedance Z^*, i.e., $Z^* = V^*/I^*$, where V^* and I^* are the applied voltage and the current response, respectively. The relation between ε^*, σ and Z^* are given as follows:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{1}{i\omega C_o Z^*} \tag{1}$$

$$\sigma = \omega\varepsilon_o\varepsilon'' \tag{2}$$

where $\omega = 2\pi f$ is the angular frequency, f is the frequency and $C_0 = \frac{\varepsilon_0 S}{d}$ is the empty cell capacitance with ε_o the permittivity of free space, S the area of the sample top surface and d the sample thickness.

3. Results and discussion

3.1. Microstructure analysis

Fig. 1 shows the SEM micrographs and EDX patterns for $x = 0.2$ and 0.4 Ti contents. SEM images show that the compounds exhibit a well developed grains with a unique chemical contrast corresponding to the perovskite phase. The average grain size increases from 3 to 5 μm as Ti content increases. This increase of grain size may be due to the bigger radius of $Ti^{4+}(r^{4+}_{\text{Mn}} = 0.53$ Å and $r^{4+}_{\text{Ti}} = 0.605$Å [25]). EDX plots show the presence of all chemical species in the $Pr_{0.6}Sr_{0.4}\,Mn^{3+}_{0.6}Mn^{4+}_{0.4-x}Ti^{4+}_{x}O_{3\pm\delta}$ $(0 \leqslant x \leqslant 0.4)$, in particular the increase of Ti content with increasing nominal Ti proportion x. EDX analysis shows that chemical composition of samples is close to the nominal one within the experimental uncertainties.

The XRD patterns for the samples illustrated in Fig. 2 present sharp and intense peaks corresponding to the perovskite phase. In agreement with SEM results, no impurity peaks were detected within the XRD limits. An enlarged scale of the most intense peak (121 Bragg reflection) shows a slightly shift to lower 2θ values indicating that the lattice parameters slightly increase with increasing Ti content. The structure refinement was performed in the orthorhombic setting of *Pnma* space group, with (Pr,Sr) at 4c $(x,0.25,z)$ position, (Mn,Ti) at 4b (0.5,0,0), O_1 at 4c $(x,0.25,z)$ and O_2 at 8d (x,y,z). The inset of Fig. 2 exemplifies the Rietveld refinement for $x = 0.4$ compound showing a good agreement between observed and calculated profiles. Detailed results of the refinement are listed in Table 1, particularly the refined occupancy factor of (Mn/Ti) is close to the nominal one. One can see in this table that the unit cell volume and the average $\langle d_{\text{Mn,Ti–O}}\rangle$ bond length increase monotonically with increasing Ti content. This increase can be directly related to the increase of average ionic radius of B site $\langle r_B\rangle$, due to the substitution of Ti^{4+} for Mn^{4+} ($r^{4+}_{\text{Mn}} = 0.53$ Å and $r^{4+}_{Ti} = 0.605$Å [25]). Whereas the average $\langle\theta_{\text{Mn,Ti–O–Mn,Ti}}\rangle$ bond angle remains almost constant up to $x = 0.3$ and decreases for $x = 0.4$. The decrease of $\langle\theta_{\text{Mn,Ti–O–Mn,Ti}}\rangle$ can be related to the reduction of the Goldschmidt tolerance factor [26]:

$$t_G = \frac{\langle r_A\rangle + r_0}{\sqrt{2}(\langle r_B\rangle + r_0)}, \tag{3}$$

as seen in Table 1, with $\langle r_A\rangle, \langle r_B\rangle$, and r_0 are, respectively, the average ionic radii of A, B and O perovskite sites.

3.2. Dielectric constant and loss tangent (tan δ)

The variations of the real, ε', and imaginary, ε'', parts of dielectric constant with frequency, f, are given in Fig. 3a and b, respectively. It can be seen that for the compositions 0, 0.1 and 0.4, ε' decreases rapidly with increasing frequency in the lower frequency range and appears to attain a plateau for frequencies $>10^2$ Hz. Its magnitude at low frequencies increases as Ti doping increases. Whereas for the compositions 0.2 and 0.3 the ε' is steadily constant in this frequency range and its magnitude is lower for the composition 0.3. It can be also noted that ε'' shows a decrease tendency at low frequency range before exhibiting a dielectric relaxation at frequency corresponding to the decrease of the ε' for each sample except for $x = 0.4$. Variations in the dielectric constant may be attributed to different types of polarizations such as ionic, electronic, dipolar and interfacial or space charge which arise at different stages of materials response to varying frequency of the applied alternating field. Each mechanism involves a short range displacement of charges and contributes to the total polarization and then to the dielectric constant of the material [27]. It is to be noted that the high values of dielectric constant in lower frequency region do not generally correspond to bulk effect. The high values of ε' interestingly observed only at very low frequencies may be attributed to the fact that the free charges buildup at interfaces with in the bulk of the sample (interfacial Maxwell–Wagner (MW) polarization) [28] and at the interface between the sample and the electrodes space-charge polarization [29]. According to Maxwell–Wagner theory of interfacial polarization the observed large values of dielectric constant in the system can be directly associated with the presence of grains and interfaces (grain boundaries) [30]. The greater the polarizability of the molecules, the higher is the dielectric constant of the material. The dispersion occurring in the lower frequency region observed in Fig. 3 was attributed to interfacial polarization since the electronic and atomic polarizations remain unchanged at these frequencies. The electron exchange between Mn^{3+} and Mn^{4+} ($Mn^{3+} \leftrightarrow Mn^{4+}$) in our samples results in local displacement of electrons in the direction of applied field that determines polarization. So with increasing frequency, polarization decreases and exhibits a dielectric relaxation. This is due to the fact that beyond a certain frequency of external field, the electron exchange, $Mn^{3+} \leftrightarrow Mn^{4+}$, will not be able to follow the alternating field, thus the electrons begin to localize leading to a slowdown of the dynamics of this electron exchange, a decrease in dielectric constant and the corresponding peak in dielectric loss. To further elucidate the interfacial polarisation effects, the frequency dependant ac conductivity (σ_{ac}) behavior will be presented in the next section.

The loss factor tangent (tan δ) represents the energy dissipation in a dielectric. It was calculated using the following relation:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{4}$$

The variation of tan δ as a function of frequency at room temperature for all compositions is shown in Fig. 4. We can notice that the loss tangent peak is found to shift towards the lower frequency region with increasing Ti content. The peaking behavior of tan δ is clearly explained in the light of Rezlescu model [31]. According to this model, the peaking behavior appears when the frequency of charge hopping between the two valence states of the same ion (Mn^{3+} and Mn^{4+} in our case) matches with the frequency of the applied field, i.e.:

$$\omega\tau = 1 \tag{5}$$