# Effect of Ce substitution on magnetic and dielectric properties of BiMn<sub>2</sub>O<sub>5</sub>

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Polycrystalline  $BiMn_2O_5$  and  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  have been prepared by a solid-state reaction. A crystalline structure study shows that all x-ray diffraction patterns can be indexed successfully in an orthorhombic phase. Substitution of Ce for Bi ions induced in the unit cell a slight distortion and enlargement. Magnetic and dielectric measurements all reveal that Ce substitution induces great effects:  $BiMn_2O_5$  is in the antiferromagnetic (AFM) phase with a Néel transition temperature at about 42 K, whereas  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  is in the ferromagnetic (FM) phase with a Curie temperature at about 46 K. The permittivity of  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  is much higher than that of  $BiMn_2O_5$ , and two dielectric relaxation peaks have been observed in the former, instead of one dielectric loss peak as observed in  $BiMn_2O_5$ . The valent state of Ce ions has been analyzed mainly as tetravalent by the core-level spectrum of Ce 3*d* from x-ray photoemission spectroscopy. The possible mechanisms of the magnetic transition from AFM to FM and the peculiar dielectric relaxation peaks induced by Ce substitution have been discussed in detail. © 2006 American Institute of Physics. [DOI: 10.1063/1.2190716]

# INTRODUCTION

A multiferroic material is a compound that simultaneously displays two or more properties of ferroelectricity, (anti-) ferromagnetism, and ferroelasticity. This fascinating behavior originates from the coupling of two or three ferroic order parameters in the material. The mutual coupling between magnetic and electric degrees of freedom leads to linear and quadratic magnetoelectric effects, in which magnetization as the linear or quadratic function of the electric field strength is induced by an applied electric field and an electric polarization can be induced by an applied magnetic field. This material is interesting in both fundamental and applied investigations for the understanding of the fundamental physics mechanism and due to its potential application on information technology, such as spintronics, data storage, and sensor and magneto-optical devices based on the mutual control of magnetic and electric fields. However, the number of candidate materials is limited, and the coupling effect is often too small to be useful in applications. The exploring of materials and fundamental studies of multiferroics thus has become one of the most important subjects in the investigation of condensed matter physics recently.<sup>1-14</sup>  $RMn_2O_5$  series oxides,<sup>9-11</sup> where *R* denotes rare-earth

 $RMn_2O_5$  series oxides,<sup>9–11</sup> where *R* denotes rare-earth metals, or Y and Bi, are among the few oxides showing significant magnetoelectric or megnetodielectric effects. BiMn\_2O\_5 is one member of the  $RMn_2O_5$  family, and its structure and magnetic properties have been studied extensively.<sup>15–19</sup> It crystallizes in the orthorhombic structure with the space group *Pbam*, (*z*=4) and contains two crystallographic sites for Mn atoms, with different oxygen coordination and oxidation states. The Mn<sup>3+</sup> ions occupy the 4*h* site

and form a distorted tetragonal Mn<sup>3+</sup>O<sub>5</sub> pyramid, whereas the  $Mn^{4+}$  ions occupy the 4*f* site and are located at the center of the Mn<sup>4+</sup>O<sub>6</sub> octahedral. The Mn<sup>4+</sup>O<sub>6</sub> octahedral shares edges to form infinite chains along the c axis, which are linked together by Mn<sup>3+</sup>O<sub>5</sub> pyramids and BiO<sub>8</sub> unites. BiMn<sub>2</sub>O<sub>5</sub>, at low temperatures, is antiferromagnetic (AFM) with Néel temperatures  $T_N$  of 39–42 K. The magnetic ordering structure is commensurable with the chemical cell, with a propagation vector  $\mathbf{k} = (1/2, 0, 1/2)$ , which is different from the former reported  $RMn_2O_5$  series compounds (R=Tb and Dy).<sup>9-11</sup> On the other hand, BiMn<sub>2</sub>O<sub>5</sub> shows the dielectric, pyroelectric, and ferroelectric orders below 290 K, which was due to the presence of highly polarizable Bi<sup>3+</sup> ions with an unshared electron pair.<sup>18</sup> Golovenchits et al.<sup>19</sup> simply studied the magnetic and structural correlations of BiMn<sub>2</sub>O<sub>5</sub> in the paramagnetic temperature range, which just act as a comparison of the EuMn<sub>2</sub>O<sub>5</sub> compound, and pointed out that there are correlations between the magnetic and dielectric properties.

Aiming to change magnetic interactions between Mn ions in RMn<sub>2</sub>O<sub>5</sub>, we chose the Ce atoms as dopants and BiMn<sub>2</sub>O<sub>5</sub> as a parent compound. If Ce ions exist in a tetravalent state, the ratio of Mn<sup>3+</sup> and Mn<sup>4+</sup> may be changed accordingly; thus the double exchange (DE) interaction will be changed and will affect the final magnetic properties of Cedoped materials. According to our experiments, the maximum solid solubility of Ce in BiMn<sub>2</sub>O<sub>5</sub> was found to be about 10 at. %. In this article, we report the magnetic and dielectric properties of polycrystalline BiMn<sub>2</sub>O<sub>5</sub> and Cedoped BiMn<sub>2</sub>O<sub>5</sub> (Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub>) materials prepared by a solid-state reaction. Experimental results show that BiMn<sub>2</sub>O<sub>5</sub> and Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> have the same crystal structure but different magnetic and dielectric behaviors. The x-ray photoemission spectroscopy (XPS) of the Ce 3d and Mn 2p core levels was used to analyze the valence of Ce ions and the

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FIG. 1. X-ray diffraction pattern for Bi0.9Ce0.1Mn2O5

changing of the Mn ions, and these results give some fundamental basis for understanding the variation of the magnetic and dielectric properties of the materials.

## **EXPERIMENTS**

Polycrystalline ceramic samples were prepared by a solid-state reaction. Stoichiometric mixtures of Bi<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, and CeO<sub>2</sub> were mixed, grounded, and precalcinated at about 973 K and then at 1073 K. The final sintering condition of BiMn<sub>2</sub>O<sub>5</sub> and Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> is at 1123 and 1223 K for about 24 h in air, respectively. X-ray diffraction (XRD) data were collected using a Rigaku D/Max-2400V powder diffractometer. Magnetization and magnetic hysteresis loop measurements were carried out on a commercial superconducting quantum interference device (SQUID) magnetometer. The dc susceptibility measurements were performed in a 5 kOe magnetic field ranging from 5 to 300 K under a zero-field-cooling condition. Dielectric measurements were carried on an Agilent 4294A precision impedance analyzer. The thickness of the samples was about 0.3 mm, and Ag was used as electrodes for the dielectric measurements.

An x-ray photoelectron spectroscopy study of BiMn<sub>2</sub>O<sub>5</sub> and Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> was carried out using a VG electronic spectrometer equipped with a twin anode (Mg and Al). Mn 2*p* core-level spectra for the two samples were collected using Al  $K\alpha$  as the x-ray source, whereas the Ce 3*d* core-level spectrum was collected using Mg  $K\alpha$  to avoid the effect of Auger lines L3M23M45 of Mn. The surfaces of all samples were cleaned by Ar<sup>+</sup> ion bombardment before they were measured, and all the spectra were referenced to the adventitious C1*s* peak at 285.0 eV. In addition, in order to analyze and compare the collected experimental data, the backgrounds that came from the second electrons have been subtracted.

#### **RESULTS AND DISCUSSION**

The XRD patterns of  $BiMn_2O_5$  and  $Bi_{0.9}Ce_{0.1}Mn_2O_5$ were collected. The pattern for  $BiMn_2O_5$  showed a clean single-phase pattern similar to that in Ref. 20, while the pattern for  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  is shown in Fig. 1. All the diffraction lines of the two materials can be indexed successfully in



FIG. 2. Temperature dependence of magnetic susceptibility of  $BiMn_2O_5$  (curve 1) and  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  (curve 2) under a 5 kOe magnetic field in zero-field cooling (ZFC). The inset shows an enlargement of the magnetic susceptibility vs the temperature for  $BiMn_2O_5$ .

the orthorhombic structure. The lattice parameters of BiMn<sub>2</sub>O<sub>5</sub> are a=7.5554(6) Å, b=8.5250(7) Å, and c=5.7551(6) Å, and for Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> the lattice parameters are a=7.5494(5) Å, b=8.5397(5) Å, and c=5.7572(4) Å. These results show that the Ce substitution for Bi ions induces the unit cell to distort and enlarge slightly, for the ionic radius of Ce<sup>4+</sup> (0.98 Å) is larger than that of Bi<sup>3+</sup> (0.96 Å). It is worth noting that 10 at. % of Ce is well incorporated into the lattice of the BiMn<sub>2</sub>O<sub>5</sub>.

The temperature dependence of the magnetic susceptibility of the materials is shown in Fig. 2. It clearly shows that BiMn<sub>2</sub>O<sub>5</sub> is in the AFM phase at low temperatures and the Néel temperature is about 42 K, while Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> is in the FM phase with a Curie temperature of 46 K. The magnetic transition temperature is defined as the temperature corresponding to the differential maximum of the  $\chi$ -T curve. As the temperature is higher than 130 K,<sup>19</sup> the susceptibility of BiMn<sub>2</sub>O<sub>5</sub> follows Curie-Weiss behavior characterized by a paramagnetic temperature  $\theta p = -287$  K, with an effective magnetic moment of  $6.24 \mu_B$  that is very close to the theoretical estimated value of  $6.29 \mu_B$  calculated from the expression  $P_{\text{eff}} = \sqrt{P_{\text{eff}}^2(\text{Mn}^{3+}) + P_{\text{eff}}^2(\text{Mn}^{4+})}$ . Above 140 K, the susceptibility of Bi0.9Ce0.1Mn2O5 also follows a Curie-Weiss behavior and can be characterized by a paramagnetic temperature  $\theta p = -291$  K. The effective paramagnetic moment for  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  is  $6.50\mu_B$ , which is also close to the theoretical value of  $6.42\mu_B$  calculated from  $P_{\text{eff}} = \sqrt{[1.1 \times P_{\text{eff}}(\text{Mn}^{3+})]^2 + [0.9 \times P_{\text{eff}}(\text{Mn}^{4+})]^2}$ . Here, two hypothesis are made: firstly, we suppose that there is no coupling among the ions on Mn sites, the effective magnetic moment is  $4.90\mu_B$  for Mn<sup>3+</sup> and  $3.87\mu_B$  for Mn<sup>4+</sup>; secondly, we suppose that in Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> the doped Ce atoms, presumably shown as Ce<sup>4+</sup> ions, replace the A-site Bi<sup>3+</sup> ions, which simultaneously leads to a change from Mn<sup>3+</sup> to Mn<sup>4+</sup>. This can be simply described as follows:

$$Ce^{4+} \to Bi^{3+} + e, \tag{1}$$

$$\mathrm{Mn}^{4+} + e \to \mathrm{Mn}^{3+}.$$
 (2)

Figure 3 displays a hysteresis loop observed at 5 K for the  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  material. There are two special phenom-



FIG. 3. Magnetic hysteresis of  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  at 5 K. The inset shows the dependence of magnetization on the magnetic field of  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  at 5 K.

ena we should note. For one thing, the hysteresis loop shows that Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> demonstrates a FM order, which confirms the observation made in the susceptibility measurements. The remnant magnetization is about 492 emu/mol, and the coercive force is about 0.29 T. Second, the magnetic moment of Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> is unsaturated even at an applied field of 5 T, as shown by the inset in Fig. 3. And such magnetization curve may consist of two components: one is a saturation component, and another is in proportion to the applied magnetic field. The linear portion of the magnetization curve can be interpreted by coexisting AFM and FM orders in the material. Presumably, the moments of the AFM order have been canted or flipped under the action of the applied magnetic field. An analysis of Arrott plots ( $M^2$ -H/M) shows that there is no positive intercept on the  $M^2$ axis, which indicates the absence of a long-range FM order. The hysteresis then may be caused by a short-range FM ordering. Such short-range FM order may be due to the substitution of Ce4+ for Bi3+ ions. In the parent compound BiMn<sub>2</sub>O<sub>5</sub>, Mn<sup>4+</sup> ions are distributed in  $z=1-z_0$ ,  $z=z_0$ , and  $z=-z_0$  lattice planes ( $z_0=0.261$ ). The Mn<sup>4+</sup>O<sub>6</sub> octahedral forms infinite chains along c axis, which are intercalated either by a  $Bi^{3+}$  or a  $Mn^{3+}$  plane.<sup>17</sup> For the  $Bi^{3+}$  plane, the adjacent  $Mn^{4+}-O-Mn^{4+}$  interaction is AFM; and for the Mn<sup>3+</sup> plane, an admixture of a direct interaction between the Mn<sup>4+</sup> planes (Mn<sup>4+</sup>-O-Mn<sup>4+</sup>) and an indirect interaction among the  $Mn^{3+}$  ions  $(Mn^{4+}-O-Mn^{3+}-O-Mn^{4+})$  lead to a final coupling between Mn<sup>4+</sup> ions showing a FM behavior. So the Mn<sup>4+</sup> magnetic moments are alternatively FM and AFM arrangements in  $BiMn_2O_5$  along the *c* axis. Whereas, when Ce was doped, Ce<sup>4+</sup> occupies a portion of the Bi<sup>3+</sup> sites. The excess electrons make some Mn ions from  $t_{2g}^{3}e_{g}^{0}$ Mn<sup>4+</sup> changed into a  $t_{2g}^{3}e_{g}^{1}$  Mn<sup>3+</sup> electronic state, as mentioned in Eq. (1), and induce a partially filled electron band, which leads to the weakness of the direct superexchange interaction of Mn<sup>4+</sup>-O-Mn<sup>4+</sup> bridges and the AFM coupling between Mn<sup>4+</sup> ions. And the double exchange interaction of the bridge  $Mn^{3+}-O-Mn^4$  could be activated. Thus, it may make Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> showing a local FM order and a ferromagnetic characteristic.

The temperature dependence of permittivity at a fre-



FIG. 4. Temperature dependence of the permittivity at 30 kHz for  $BiMn_2O_5$  and  $Bi_{0.9}Ce_{0.1}Mn_2O_5$ 

quency of 30 kHz for BiMn<sub>2</sub>O<sub>5</sub> and Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> is shown in Fig. 4, which demonstrates the permittivity increasing with temperature and having a nonlinear temperature behavior. Moreover, the Ce substitution for Bi in BiMn<sub>2</sub>O<sub>5</sub> induces the permittivity increase in the measured temperature interval. In addition to the dramatic increase of the permittivity, the permittivity versus temperature in Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> shows two stages, noted as  $R_1$  and  $R_2$ , which demonstrate that there are two relaxation processes. Only one,  $R_1$ , is observed for BiMn<sub>2</sub>O<sub>5</sub>.

Such kinds of peculiar dielectric behaviors were also observed by the temperature dependence of the dielectric loss at different frequencies in the temperature interval of 80-300 K for  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  and  $Bi_{0.9}Ce_{0.1}Mn_2O_5$ , which are shown in Figs. 5(a) and 5(b), respectively. Comparing these two, we can also find that there are two dielectric relaxation progresses in  $Bi_{0.9}Ce_{0.1}Mn_2O_5$ , whereas only one in its parent compound,  $Bi_{0.9}Ce_{0.1}Mn_2O_5$ . The relaxation phenomena can be described by the Arrhenius equation

$$\tau = \tau_0 \exp(E/kT_p),\tag{3}$$

$$\omega\tau = 1, \tag{4}$$

where  $T_p$  is the peak temperature,  $\tau_0$  the relaxation time, k the Boltzmann constant, and E the activation energy. As  $\omega = 2\pi f$ , then we can get

$$\ln f = -\ln(2\pi\tau_0) - E/kT_p.$$
 (5)

Arrhenius plots for the relaxation peaks are shown in Fig. 6 for  $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{Mn}_2\text{O}_5$  and in the inset for  $\text{Bi}\text{Mn}_2\text{O}_5$ . Each line corresponds to one relaxation process. The activation energy E and the relaxation time  $\tau_0$  of peak  $R_1$  in  $\text{Bi}\text{Mn}_2\text{O}_5$  are obtained as 0.37 eV and  $4.5 \times 10^{-14}$  s respectively. The similar activated parameters are obtained for peak  $R_1$  in  $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{Mn}_2\text{O}_5$  as E=0.32 eV and  $\tau_{01}=6.7 \times 10^{-14}$  s. The relaxation peak  $R_2$  existing only in Ce-doped  $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{Mn}_2\text{O}_5$  has  $E_2=0.12$  eV and  $\tau_{02}=1.1 \times 10^{-10}$  s, which are similar to the values for the peak located near 130 K reported by Golovenchits *et al.*<sup>19</sup>

From the above results, we can see that the dopant Ce induced fundamental changes in the magnetic and dielectric properties. So how the doped Ce ions exist in  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  is now the most important question for us. We turn to the XPS to analyze the valence of the doped Ce



FIG. 5. Temperature dependence of the dielectric loss for  $BiMn_2O_5$  (a) and  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  (b) at different frequencies.  $R_1$  and  $R_2$  denote relaxation processes.

ions. The core-level spectra of Ce 3d and Mn 2p in  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  and that of Mn 2p in BiMn<sub>2</sub>O<sub>5</sub> are shown in Figs. 7(a)-7(c). There are four peak structures shown in Fig. 7(a) with binding energies (BEs) of about 884.1, 900.8, 905.4, and 916.6 eV, which are very close to the experimental value of CeO<sub>2</sub> (Refs. 18 and 19) and are attributed to the electron configuration of  $3d^94f^0$  and  $3d^94f^1$  or the splitting of  $3d_{3/2}$  and  $3d_{5/2}$  levels. And the highest existing binding energy (BE) peak (916.6 eV), which only exists in  $CeO_2$ (Refs. 21 and 22) and is absent in Ce<sub>2</sub>O<sub>3</sub> (Ref. 23) also show that the Ce ions in  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  exist in a tetravalent state. However, the full peak width at half maximum (FWHM) at the 884.1 eV peak is about 3 eV, which means that there are other contributions that come from unknown electronic states, such as the Ce<sup>3+</sup> state. So the Ce ions in the compound could be a mixed valence state, but the dominant part is the tetravalent state. From Figs. 7(b) and 7(c), pronounced differences can be seen by the Mn 2p core-level spectra between BiMn<sub>2</sub>O<sub>5</sub> and Ce-doped Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub>. The low BE peak in the two spectra is 642.0 eV, which lies Mn<sup>3+</sup>(641.9 eV) between in the interval and Mn<sup>4+</sup>(642.2 eV).<sup>24</sup> Along with the asymmetrical peak, we



FIG. 6. Graph of  $\ln f$  vs 1000/T for  $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{Mn}_2\text{O}_5$ . The inset shows the result for  $\text{Bi}\text{Mn}_2\text{O}_5$ .  $R_1$  and  $R_2$  denote the different relaxation progresses in accordance with the same peaks shown in Figs. 5(a) and 5(b).

conclude that Mn ions showed two valence states,  $Mn^{3+}$  and  $Mn^{4+}$ . Comparing Figs. 7(b) and 7(c), the ratio of  $Mn^{3+}/Mn^{4+}$  is increased with Ce doping. According to the results of the Gaussian fit, shown in Figs. 7(b) and 7(c), the ratio of the areas for  $Mn^{3+}/Mn^{4+}$  is about 1:1 in Bi $Mn_2O_5$ , while in Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> this ratio changed to about 11:9, which is consistent with the 10 at. % Ce-doped amount, just as Eqs. (1) and (2) show.

Now, we know that there are Ce ions that really exist in the tetravalent state in the doped material Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub>, and when Ce<sup>4+</sup> replaces part of Bi<sup>3+</sup> in BiMn<sub>2</sub>O<sub>5</sub>, the magnetic and dielectric properties are changed accordingly. For the dielectric relaxation peak  $R_1$ , the two compounds are both in the paramagnetic phase, and we think the magnetic properties at low temperatures cannot produce an effect on this relaxation progress. But due to Ce<sup>4+</sup> replacing part of Bi<sup>3+</sup>, the ratio of Mn<sup>3+</sup>/Mn<sup>4+</sup> increased accordingly. The different surroundings of  $Mn^{3+}(Mn^{3+}O_5)$  and  $Mn^{4+}(Mn^{4+}O_6)$ lead to some released oxygen ions, which might make the conductance of Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> larger than that of undoped BiMn<sub>2</sub>O<sub>5</sub>. The larger conductance might be the cause of the weak  $R_1$  peak in Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub>. Moreover, this peak ( $R_1$ ) found in BiMn<sub>2</sub>O<sub>5</sub> is also observed, which was not reported by Golovenchits et al.<sup>19</sup> perhaps due to the quality of their used single crystal. In their experimental result, the dielectric loss tangent had higher values than what we got here. For the Arrhenius parameters of  $R_1$ ,  $\tau_0$  (10<sup>-14</sup> s) is less than the phononic relaxation time scale  $(10^{-12} \text{ s})$  and larger than free-electronic one  $(10^{-16} \text{ s})$ . This may be attributed to a polaroniclike relaxation, which originates from the interaction between a free charge and a lattice, and the interaction leads to the forming of local dipoles.<sup>25</sup> Taking the value of the active energy into consideration, peak  $R_1$  could be associated to the oxygen vacancies.<sup>26</sup>

As to the second relaxation peak in  $Bi_{0.9}Ce_{0.1}Mn_2O_5$ , its Arrhenius parameters are similar to those of  $EuMn_2O_5$ .<sup>19</sup> The relative lower relaxation time of  $10^{-10}$  s, compared to the Debye time of  $10^{-14}$  s, might indicate a collective characteristic of the relaxation process. We recall the magnetic prop-



FIG. 7. Ce 3*d* core-level spectrum of Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> (a):  $\bullet$ , experimental points;  $\star$ , Gaussian function fit. Mn 2*p* core-level spectrum of BiMn<sub>2</sub>O<sub>5</sub> (b) and Bi<sub>0.9</sub>Ce<sub>0.1</sub>Mn<sub>2</sub>O<sub>5</sub> (c):  $\bullet$ , experimental points; line, Gaussian function fit;  $\star$ , Gaussian function fit for Mn<sup>3+</sup>;  $\blacktriangle$  Gaussian function fit for Mn<sup>4+</sup>.

erties described in the earlier paragraphs stating that the correlated magnetic-order domains can be preserved in the temperature range of  $T > T_N$ . When Ce was doped in BiMn<sub>2</sub>O<sub>5</sub>, magnetic properties changed from antiferromagnetic to ferromagnetic accordingly; this might also affect the dielectric properties just as we observed. Just as we depicted in the magnetic parts, the doping of Ce<sup>4+</sup> can change not only the ratio of Mn<sup>3+</sup>/Mn<sup>4+</sup> in the lattice but also the distribution of Mn<sup>3+</sup> ions in the different positions in the unit cell. Con-

sequently, the exchange coupling between Mn<sup>3+</sup> and Mn<sup>4+</sup> ions is modulated, a relevant spin fluctuation with correlation lengths comparable to the size of the unit cell might exist. At an applied electric field, the motion of such collective spins could lead to lower a relaxation time. In other words, peak  $R_2$  implies another polaronic relaxation with local lattice distortion and spin flipping induced by the Ce<sup>4+</sup> substitution of Bi<sup>3+</sup> ions.

## CONCLUSIONS

In summary we have elaborated the single phase of  $BiMn_2O_5$  and  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  materials by the solid-state reaction technique. And the substitution of Ce atoms for the Bi atoms in  $BiMn_2O_5$  leads to a dramatic modulation of the magnetic behavior. At low temperatures,  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  shows ferromagnetism, while its parent material  $BiMn_2O_5$  is antiferromagnetic. Moreover, doping of Ce has induced a peculiar dielectric behavior in  $Bi_{0.9}Ce_{0.1}Mn_2O_5$ , that of having two relaxation progresses taking place in the materials. The peak existing in  $BiMn_2O_5$  may be interpreted by the motion of oxygen vacancies, and another peak observed in  $Bi_{0.9}Ce_{0.1}Mn_2O_5$  may imply the spin fluctuations induced by Ce on the distribution of the exchange coupling between  $Mn^{3+}$  and  $Mn^{4+}$  and on local lattice distortion.

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