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The effect of Fe content on dielectric and relaxation characteristics in $TbFe_xMn_{1-x}O_3$

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ABSTRACT

Various ceramic composites of $TbFe_xMn_{1-x}O_3$ (x = 0, 0.25, 0.5, 0.75) were prepared by conventional solid-state reaction. The electrical properties such as dielectric constant, loss and resistivity have been studied as a function of the temperature from 77 to 400 K and the frequency from 0.1 to 1000 kHz. The XRD and SEM for these four types of materials show similar patterns with the increasing of the Fe concentration. Instead, the dielectric constant and loss for them will change dramatically in properties. The figures of all samples display two distinct semicircular arcs in the Nyquist plots at 300 K and all figures located at high frequency region are independent of the applied ac biases. By analyzing the values of the activation energy, it is found that the origin of the relaxation in dielectric loss is related to the changing of octahedral structure.

1. Introduction

$TbMnO_3$ has been used widely as a typical ferromagnetic and ferroelectric materials in multifunctional devices [1–7] to enhance the dielectric constant and weaken the dielectric loss by doping. Doping in Tb site has been reported and made plenty of achievements in electrics and magnetics [8–14]. However, quite a few reports involve in doping in Mn site as blending with different radii of Mn and doping element might lead to destruction of the perovskite structure.

It is worth noting that Mn^{3+} and Fe^{3+} have the nearly same radii which are in the high-spin state [15–21], so $TbFe_xMn_{1-x}O_3$ provides a good solubility due to Fe doping in Mn site [22–24]. However, the Mn^{3+}—O and Fe^{3+}—O octahedral distances might be different linear structures depending on distortion. Moreover, Mn^{3+} is the Jahn-Teller ion and Fe^{3+} is the non-Jahn-Teller ion, so the samples may demonstrate interesting properties when two different types of ions are mixed with each other. Some reports show that doping in Mn site could not necessarily destroy the perovskite structures, but also exhibits some unique electrical properties [25–28]. Wang [25] et al. found that, with the increasing Fe content in $TbFe_xMn_{1-x}O_3$, the crystal unit cell shrunk in the *ab*-plane and extended along *c*-axis. The change of the Mn—*O*—Mn(Fe) bond angle could be related to the dielectric response. Cuartero [26] et al. found when doping Co in Mn site, the low and high doped samples were distorted orthorhombic single phase, but the intermediate samples possessed a double perovskite structure. Thus, the $TbMn_{0.5}Co_{0.5}O_3$ showed interesting magnetic response because of the smaller magnetic clusters. Li [27] et al. showed the ferromagnetic component will enhance with the Cr doping in Mn site, which may drive the spin configuration to partially change from the *E*-AFM order in o-YMO to the spiral spin order in doped $YMnO_3$.

We mainly focus on the electrical properties for the samples of $TbFe_xMn_{1-x}O_3$ (x = 0, 0.25, 0.5, 0.75) prepared by the conventional solid-state reaction. The position of relaxation peaks could be confirmed to be strongly impacted by the Fe concentration, which may originate from the changing of octahedral structure. Meanwhile, activation energy should be further investigated to explain this phenomenon.

2. Experimental

Polycrystalline samples of $TbFe_xMn_{1-x}O_3$ (x = 0, 0.25, 0.5, 0.75) were prepared by conventional solid-state reaction. The high-purity raw powders (not less than 99.99%) of Tb_4O_7, MnO_2 and Fe_2O_3 were thoroughly mixed and grounded in an agate mortar and then sintered at 1250 °C in air for 12 h, repeatedly. Then the reactants were reground, pressed into pellets with 8 mm in diameter and about 1.5 mm in thickness. After sintered at 1300 °C in air for another 12 h, the four samples had been prepared. X-ray diffraction (XRD) was examined using CuKα as the X-ray source. Scanning electron microscopy (SEM), the model is S-4800, was used for microstructural analyses. The

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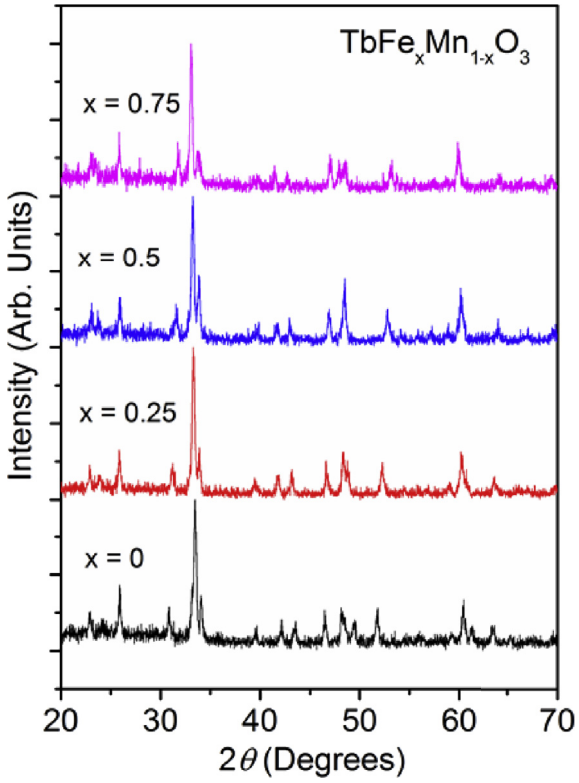

Fig. 1. The XRD patterns for $TbFe_xMn_{1-x}O_3$ (x = 0, 0.25, 0.5, 0.75).

temperature-dependent electrical properties were measured using a QuadTech ZM2353 LCR Digibridge under a cooling rate of 2.5 K/min in a frequency range from 40 Hz to 200 kHz, and the frequency-dependent electrical properties were measured using a Precision Impedance Analyzer 6500B in a frequency range from 100 Hz to 1 MHz. The dc resistivity was measured by Keithley 2400 with the two probe method and 1.0 V dc voltages were given to the samples. Silver paste was used on both sides of all samples for the electrodes.

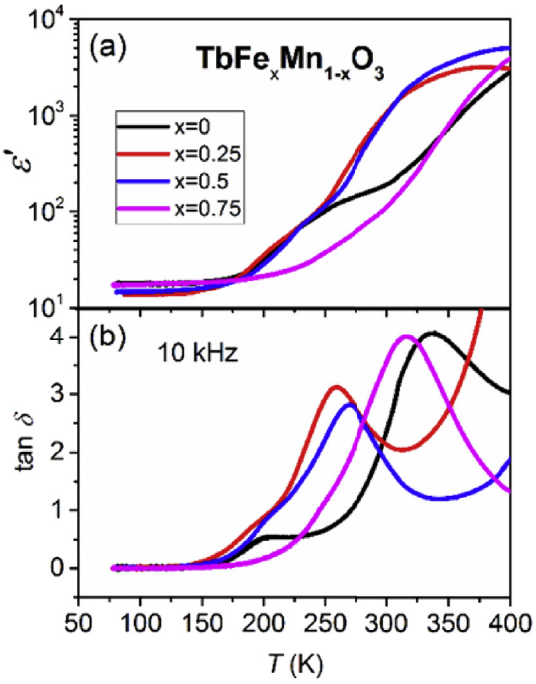

Fig. 3. The temperature dependence of (a) the dielectric constant (ε') and (b) the dielectric loss ($\tan\delta$) of four composites at 10 kHz.

3. Results and discussion

The XRD spectra of $TbFe_xMn_{1-x}O_3$ (x = 0, 0.25, 0.5, 0.75) are shown in Fig. 1. The patterns of Fe-doped samples are similar to the XRD pattern of pure $TbMnO_3$ powders, demonstrating that the different doping samples are single phase with the monophasic perovskite-type structure. However, for the Fe-doped samples, the set of reflections shift noticeably to lower 2θ scales at 49° and 61°, which are even distinguished with the peaks at 48° and 60°, respectively.

Fig. 2 shows the surface SEM micrograph of the four sintered ceramics. The Fe-doped samples are porous and have the same size of the pure $TbMnO_3$. Therefore, it is known that the Fe doped with Mn ions can ensure that the samples are still a typical perovskite structure

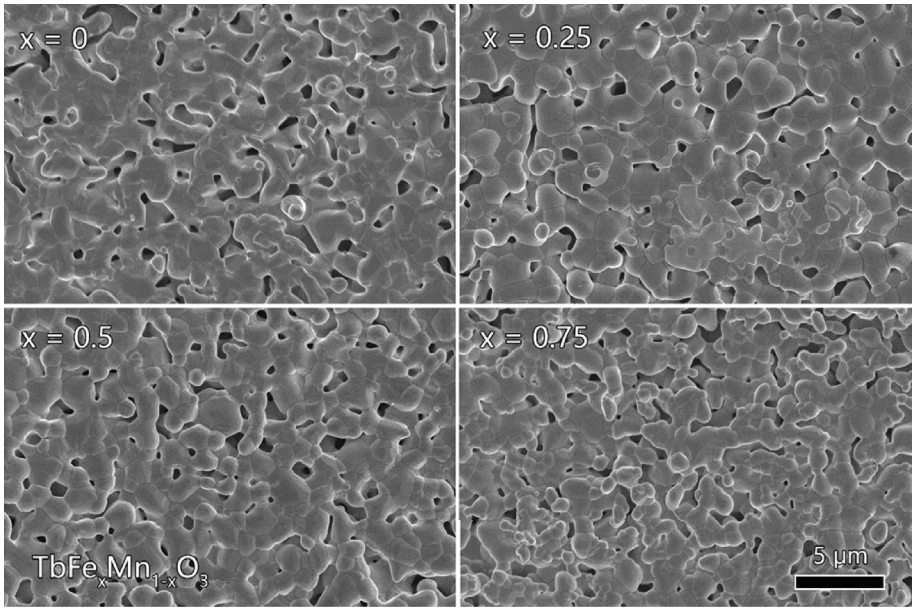

Fig. 2. The typical SEM of the polycrystalline $TbFe_xMn_{1-x}O_3$ (x = 0, 0.25, 0.5, 0.75).