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Magnetocaloric effect in composite structures based on ferromagnetic–ferroelectric $Pr_{0.6}Sr_{0.4}MnO_3/BaTiO_3$ perovskites

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ABSTRACT

We have prepared composite materials composed of ferromagnetic and ferroelectric compounds having the general formula $(1-x)(Pr_{0.6}Sr_{0.4}MnO_3)/x(BaTiO_3)$, with x is the molar ratio ($x = 0.0$, 0.03, 0.05, 0.10 and 0.30) using conventional ceramic double sintering process. We report the structural, magnetic and magnetocaloric properties of all samples. The presence of the two phases of $Pr_{0.6}Sr_{0.4}MnO_3$ (PSMO) and $BaTiO_3$ (BTO) was confirmed by X-ray diffraction (XRD) technique and the structural analysis. Magnetic measurements of magnetization versus temperature and magnetic applied field were performed. The temperature dependence of magnetization reveals that the composite samples show paramagnetic to ferromagnetic phase transition (PM–FM) when the temperature decreases. These samples have the same Curie temperature as the parent PSMO compound ($T_c \approx 273$ K). The magnetic entropy change $|\Delta S_M|$ was deduced from the $M(H)$ data by the Maxwell relation. Close to T_c, a large change in magnetic entropy has been observed in all samples. The maximum value of the magnetic entropy $|\Delta S_M^{max}|$ decreases from 2.88 J kg^{-1} K^{-1} for $x = 0$–1.86 J kg^{-1} K^{-1} for $x = 0.3$ for an applied magnetic field of 2 T. At this value of magnetic field the relative cooling power (RCP) decreases equally from 63 J kg^{-1} for the parent sample to 38.3 J kg^{-1} for $x = 0.3$. The temperature dependence of the Landau coefficients has been deduced using the Landau expansion of the magnetic free energy, indicating the second order nature of the magnetic transition.

1. Introduction

The mixed valence manganites with the general formula $Ln_{1-x}A_xMnO_3$ (Ln is a trivalent rare earth element and A is a divalent alkali-earth one) have renewed extensive interests thanks to their colossal magnetoresistance (CMR) effect and also to their potential applications in magnetoresistive transducers, magnetic sensors and magnetic refrigeration [1–4]. A big interest is being paid to multiferroic materials with coupled electric and magnetic properties because they can exhibit both electrical polarization induced by a magnetic field and magnetization induced by an electric field [5–9]. If these materials are to be used in practical applications, it is necessary to make a composite of magnetic and electric compounds with an improved magnetoelectric effect. Various such composites have been studied mainly showing enhancement of the CMR phenomena mostly observed near T_c and caused by the double exchange (DE) mechanism proposed by Zener in 1951 [10].

The extrinsic CMR is related to natural and artificial grain boundaries. Spin polarized tunneling or spin dependent scattering of the charge carriers at the grain boundaries seems to be responsible for this kind of CMR effects [11]. This extrinsic effect may enhance MR in a wide temperature range and can be more useful to satisfy practical applications in magnetic and switching of recording devices. Previous studies on magnetoelectric composites were focused on bulk samples composed of LCMO/BTO [12–14], LSMO/BTO [15,16], PCMO/BST [17,18] LCMO/PZT [19], etc. showing enhancement in MR and magnetoelectric couplings.

The aim of this article is to study the effect of the coexistence of both the ferroelectric $BaTiO_3$ with the ferromagnetic $Pr_{0.6}Sr_{0.4}MnO_3$ in many proportions on the structural, magnetic and magnetocaloric properties of these composites. In this paper we present especially the influence of the ferroelectric phase on the magnetic properties of ferromagnetic PSMO phase.

2. Experimental

The samples were prepared in three steps. At first, the PSMO phase was prepared through normal solid-state reaction route taking Pr_6O_{11}, $SrCO_3$ and MnO_2 in stoichiometric proportions. The mixed powders were presintered at 1000 °C for 24 h. The resulting powder was pressed into pellets, and then sintered at 1350 °C

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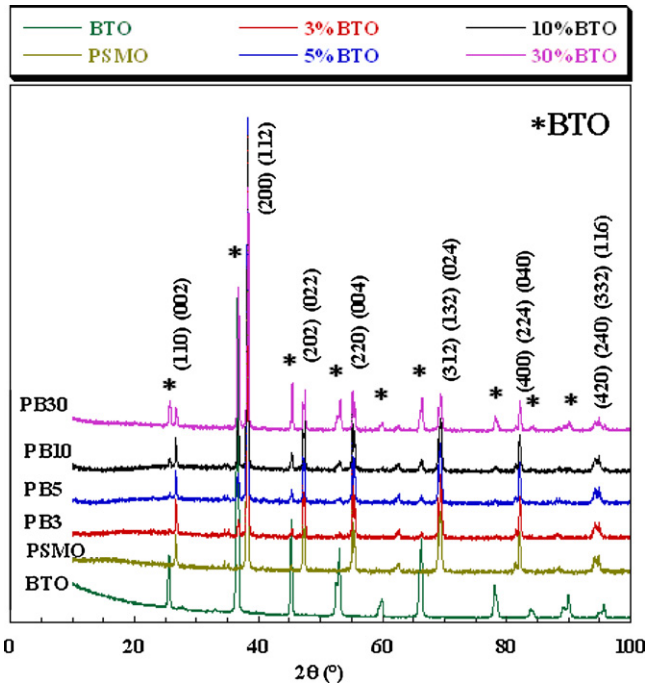

Fig. 1. XRD patterns of PSMO/BTO composites with varying compositions (asterisks are noted for BTO phase and *h k l* for PSMO phase).

for 24 h with intermediate regrinding and re-pelletizing. These pellets were rapidly quenched to room temperature in air in order to freeze the structure at the annealed temperature. Secondly, the ferroelectric phase, BTO was prepared by the same method as PSMO using $BaCO_3$ and TiO_2 in molar ratios as starting materials. BTO phase was presintered at 850 °C for 24 h and then pressed into pellets and sintered at 1000 °C for 24 h with intermediate regrinding and re-pelletizing. Finally, the composites were prepared by thoroughly mixing 3, 5, 10 and 30% of ferroelectric phase (BTO) with 97, 95, 90 and 70% of ferromagnetic phase (PSMO) respectively, and then were pelletized and sintered at 900 °C for 24 h. The obtained samples will be referred as, PB3, PB5, PB10 and PB30 respectively and PSMO for the parent compound ($x = 0$). The samples were characterized by X-ray powder diffraction at room temperature using Mo radiation and the structure refinement was carried out by the Rietveld analysis of the X-ray powder diffraction data. Magnetization measurements were carried out using a Foner magnetometer equipped with a super-conducting coil in different magnetic fields.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the powder X-ray diffraction patterns at room temperature for the parent PSMO and BTO samples and equally all synthesized composites. Rietveld refinement was performed for all the samples, we show in Fig. 2 the refinement for PB3 sample as an example. The analysis shows that the parent compounds are single phase with orthorhombic Pbnm space group for PSMO for which the lattice parameters are estimated as $a = 0.5481$ nm, $b = 0.5441$ nm and $c = 0.7673$ nm, and tetragonal P4mm space group for BTO with the lattice parameters $a = b = 0.3994$ nm and $c = 0.4027$ nm. As we can see in the composites, with the increase of BTO content, the peak intensity corresponding to BTO phase increases and also the peaks positions related to PSMO have no shift due to the addition of BTO, which indicates that the PSMO and BTO phases exist independently and form a solid mixture without any chemical reaction between the parent compounds during the heat treatment. For these samples, the estimated lattice parameters of the PSMO and BTO phases remained almost unchanged.

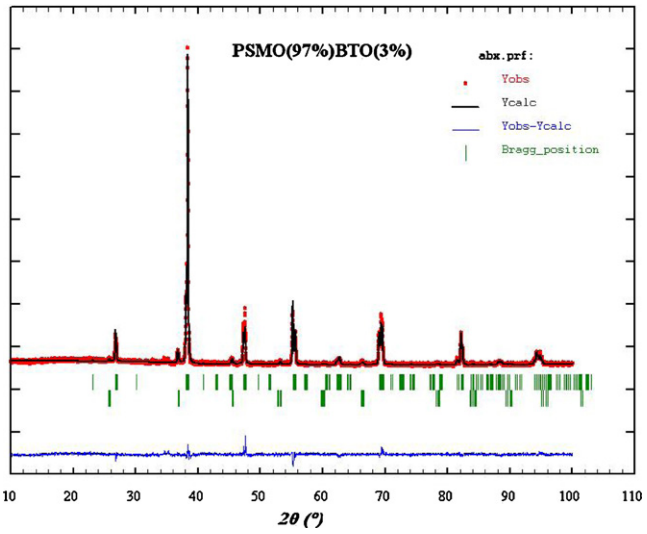

Fig. 2. XRD patterns of 0.97PSMO/0.03BTO composite. Squares indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.

3.2. Magnetic properties

Fig. 3 shows the temperature dependence of magnetization (M) measured at an applied magnetic field of 0.05 T. All composites show a paramagnetic–ferromagnetic transition when the temperature decreases. These composites have the same Curie temperature as the parent compound PSMO ($T_c \approx 273$ K) obtained from the peak in dM/dT versus temperature (T) plot and also by the temperature dependence of the inverse of magnetic susceptibility plot shown inset of Fig. 3 for the PSMO compound. The Curie temperature is not affected by the increase of BTO content. This is due to the fact that the PM–FM phase transition is an intrinsic and intragrain property. The observed constancy of T_c also indicates that stoichiometry of PSMO phase within the grains remains essentially unchanged as BTO is not accommodated within the perovskite structure and its

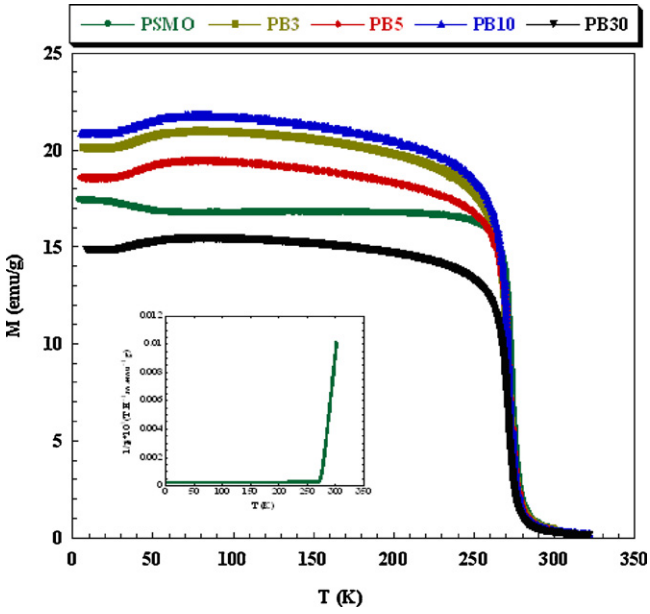

Fig. 3. Temperature dependence of magnetization for PSMO/BTO composites. The inset presents the temperature dependence of the inverse of the magnetic susceptibility for PSMO compound.