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Effect of Sr concentration on microstructure and magnetic properties of $(Ba_{1-x}Sr_x)(Ti_{0.3}Fe_{0.7})O_3$ ceramics

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ABSTRACT

Fe-doped $(Ba_{1-x}Sr_x)TiO_3$ ceramics were prepared by solid-state reaction, and ferromagnetism was realized at room temperature. The microstructure and magnetism were modified by the Sr concentration control ($0 \le x \le 75$ at%) at a fixed Fe concentration, and the relevant magnetic exchange mechanism was discussed. All the samples are shown to have a single perovskite structure. When increasing the Sr concentration, the phase structure is transformed from a hexagonal perovskite into a cubic perovskite, with a monotonic decrease in lattice parameters induced by ionic size effect. The room-temperature ferromagnetism is expected to originate from the super-exchange interactions between Fe^{3+} on pentahedral and octahedral Ti sites mediated by the O^{2-} ions. The increase in Sr addition modifies two main influencing factors in magnetic properties: the ratio of pentahedral to octahedral Fe^{3+} and the concentration of oxygen vacancies, leading to a gradually enhanced saturation magnetization. The highest value, obtained for Fe-doped $(Ba_{0.25}Sr_{0.75})TiO_3$, is an order of magnitude higher than that of the Fe-doped $BaTiO_3$ system with similar Fe concentration and preparation conditions, which may indicate $(Ba_{1-x}Sr_x)TiO_3$ as a more suitable matrix material for multiferroic research.

1. Introduction

The materials of barium strontium titanate, $(Ba_{1-x}Sr_x)TiO_3$ (BST), have received continuous attention due to their desirable ferroelectric and dielectric properties. They have been identified as a potential alternative to the current silicon oxide and nitride dielectrics in the next generation dynamic random access memories (DRAM) [1,2] because of their high dielectric response, especially in the vicinity of the ferroelectric Curie temperature T_C [3]. The voltage-tunable dielectric constants with low dielectric loss show great promise for applications in microwave devices such as phase shifters, tunable filters, tunable resonators, varactors and switches [4–7]. In addition, high pyroelectric coefficients make BST a promising candidate for infrared (IR) detectors [8], most particularly, as the active sensing elements of focal plane arrays in thermal imaging systems. These applications rely on the ferroelectric and dielectric properties of BST materials which can be controlled by a proper selection of the Ba/Sr ratio [9–12]. Especially, T_C can be tuned for the required application temperature and the optimal values of permittivity can be obtained through the composition modification.

In the semiconductor industry there is an uninterrupted evolution towards higher and higher integration which results in capability increase of the devices and dimension reduction of their elements. Therefore numerous researches on multifunctional materials, e.g. diluted magnetic semiconductors (DMS) [13–15] and multiferroic materials [16–18], have been motivated both in technological as well as in scientific fields. For multiferroic research, ferromagnetic ordering has been achieved in barium titanate ($BaTiO_3$, BTO) [19–22] and strontium titanate ($SrTiO_3$, STO) [21]. However, almost no relevant studies have been reported on BST. $(Ba_{1-x}Sr_x)TiO_3$ is a continuous solid solution of $BaTiO_3$ and $SrTiO_3$ over the entire range of concentration. Compared with the latter two, BST exhibits more excellent properties (such as higher peak values of dielectric constant at T_C than pure BTO), and high tunability (i.e., the degree of variation in the dielectric constant as a function of the applied electric field) [23]. Meanwhile, the ability of perovskite BST compounds to accommodate a wide variety of cations on both the A and B sites offers the potential of possessing a very high degree of flexibility on composition, structure and properties. Consequently, ferromagnetism can be expected to obtain through the doping of BST by 3d transition metals, which will facilitate exploring new multiferroic materials and sufficiently broaden the application fields of BST.

Considering the situation above and on the basis of our previous work [24–26] on magnetism of transition-metal-doped $BaTiO_3$, room-temperature ferromagnetism will be realized for $(Ba_{1-x}Sr_x)TiO_3$ in this paper by partial substitution of Fe for Ti. Due to the remarkable influence of the Ba/Sr ratio on ferroelectric

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and dielectric properties, several common Ba/Sr ratios were selected to investigate the corresponding microstructure, magnetic properties and exchange mechanism at a fixed Fe content.

2. Experimental

The polycrystalline system with nominal composition $(Ba_{1-x}Sr_x)(Ti_{0.3}Fe_{0.7})O_3$ (x=0, 20, 50 and 75 at%) was synthesized by the conventional ceramic method. AR grade (99.9% purity) chemicals $BaCO_3$, $SrCO_3$, TiO_2 and Fe_2O_3 were used for processing. Stoichiometric amounts of the chemicals were thoroughly mixed by grinding with an agate mortar and pestle for 40 min, and calcined in alumina crucibles at 1000 °C for 36 h. The powders were added with polyvinyl alcohol (PVA) solution and compacted to form discs. The discs were then heat treated at 550 °C for 2.5 h to remove PVA, followed by sintering at 1300 °C for 24 h. Subsequently, the products were annealed in vacuum at 1000 °C for 3 h.

Crystal structure was analyzed by X-ray diffraction (XRD) using a Rigaku D/max 2550 V diffractometer with CuKα radiation in a range of $15^\circ \leq 2\theta \leq 85^\circ$ at a scanning rate of 2°/min. ^{57}Fe Mössbauer spectra were recorded in transmission mode on a constant acceleration spectrometer with a ^{57}Co(Pd) source. The velocity scale is calibrated periodically relative to α-Fe foil. Physically realistic fitting to the spectra was provided in terms of the sample structure and the ranges of isomer shifts (IS) and quadrupole splittings (QS) reported for different Fe valences and occupational sites. Magnetic properties were measured using an HH-15 vibrating sample magnetometer (VSM). All the measurements were performed at room temperature.

3. Results and discussion

3.1. Effect of Sr concentration on crystal structure

Phase purity of $(Ba_{1-x}Sr_x)(Ti_{0.3}Fe_{0.7})O_3$ samples is determined from the XRD patterns as shown in Fig. 1. Only the reflections of 6H–$BaTiO_3$ are observed for 0 at% Sr, indicating a hexagonal perovskite structure. The Fe ions seem to have been dissolved into the matrix, and secondary phases (such as Fe_2O_3 and Fe_3O_4) are absent.

After the addition of 20 at% Sr, the phase composition maintains a single phase of 6H–$BaTiO_3$-type hexagonal perovskite. Besides, almost all the diffraction peaks are of a symmetric shape, suggesting no phase separation (barium- and strontium-rich phases). The third strongest peak is presented in the inset of Fig. 1 to be more closely examined, since the first and second strongest peaks are located too closely.

For the samples with 50 and 75 at% Sr, however, all the peaks can be assigned to a C–$SrTiO_3$-type cubic perovskite structure. The absence of multiple sets of diffraction patterns, as seen by other authors [27], indicates that all the samples are not phase separated. In fact, the peaks for 0 and 20 at% Sr can be indexed to the hexagonal lattice (space group $P6_3/mmc$) of $BaTiO_3$. The lattice constants calculated from the XRD patterns are a=5.777, 5.644 Å and c=13.992, 13.831 Å, respectively, values compatible with the literature results of a=5.724 Å and c=13.96 Å (JCPDS No. 34-0129). Similarly, the peaks for 50 and 75 at% Sr are consistent with the cubic lattice (space group Pm3m) of $SrTiO_3$ with the lattice constants of a=3.967, 3.938 Å, respectively, which are in turn slightly higher than the literature value of a=3.904 Å (JCPDS No. 79-0176). That is to say, the hexagonal structure undergoes a phase transition into a cubic phase in the Sr concentration range from 0 to 75 at%, also indicated clearly by the gradual disappearance of several peaks corresponding to 6H–$BaTiO_3$ such as (1 0 3) and (2 0 3) peaks. Secondly, the diffraction peaks shift towards higher angles with the increasing Sr concentration, suggesting a progressive reduction in lattice parameters, which can be ascribed to the substitution of the smaller Sr^{2+} ions for the larger Ba^{2+} ions. This also confirms that the Sr^{2+} ions have occupied the site of Ba^{2+} instead of Ti^{4+} whose ionic radius (0.61 Å) is much smaller as compared with Sr^{2+} (1.44 Å) and Ba^{2+} (1.61 Å) [28]. Finally, it is observed that the full-width at half-maximum (FWHM) of peaks decreases at first and then increases gradually with the increasing Sr addition. Since the BST crystal sizes were reported to increase with the Sr concentration [29], the broadening may be primarily related to the increase of defects in the samples.

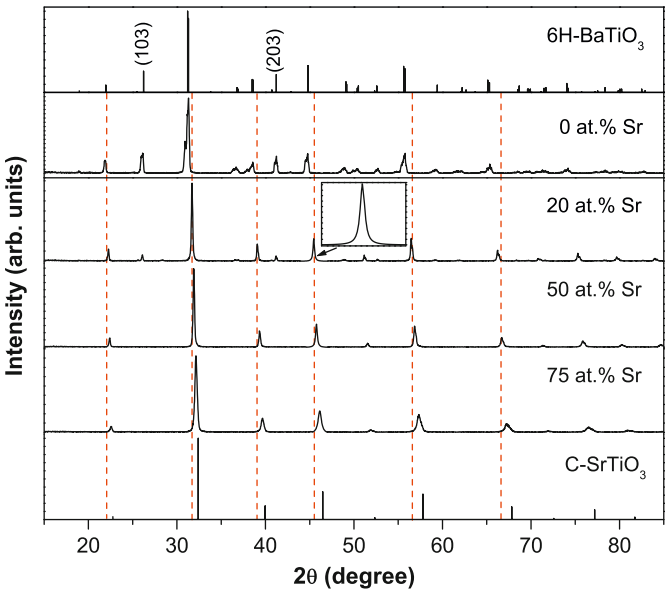

Fig. 1. XRD patterns of $(Ba_{1-x}Sr_x)(Ti_{0.3}Fe_{0.7})O_3$ ceramics with the indicated Sr concentrations. The dashed line is a guide for eyes.

For a closer observation, Fig. 2 exhibits the (1 1 0) peaks for all the ceramics. At the Sr concentrations of 0, 20, 50 and 75 at%, the peak position is 30.92°, 31.71°, 31.91° and 32.15°, respectively, and the corresponding FWHM values are 0.17°, 0.16°, 0.18° and 0.30°, both showing a consistent trend as mentioned above. It is seen obviously in $Ba(Ti_{0.3}Fe_{0.7})O_3$ that there exist two peaks (1 1 0) and (1 0 4) at 2θ values between 30.5° and 33.0°. For the 20 at% Sr sample, a slight asymmetry of peak can be explained by its 6H–$BaTiO_3$-type hexagonal perovskite structure. This peak is actually the superposition of two peaks with a 0.08° interval, located at 31.68° and 31.76°, respectively, corresponding to the (1 1 0) and (1 0 4) peaks of 6H–$BaTiO_3$ with a 0.09° interval (JCPDS No. 34-0129). With the increase of Sr concentration, the peaks become symmetric due to the C–$SrTiO_3$-type cubic perovskite structure where there exists only an (1 1 0) peak nearby.

3.2. Effect of Sr concentration on Fe valence and occupational site

The Fe configuration was characterized by Mössbauer spectroscopy which is highly sensitive to the Fe-atom surroundings. The Mössbauer spectra are presented in Fig. 3, and the hyperfine parameters are listed in Table 1. One can see that all the spectra are composed of two overlapping doublets whatever the Sr concentration is. Based on the isomer shift (IS) [30–32], a parameter sensitive to the Fe valence and the geometry of the coordinating anions, the presence of Fe^{2+} and Fe^{4+} is ruled out. The Fe ions are shown to take the form of Fe^{3+} in the 0 at% Sr