

Structural and magnetic characterization of manganite-like $\text{Sr}_2\text{FeMnO}_6$ as substrate for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films

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Received 11 October 2004, revised 25 May 2005, accepted 3 June 2005

Published online 29 July 2005

PACS 61.10.Nz, 68.37.Hk, 68.55.-a, 74.72.Bk, 74.78.Bz

We report structural and magnetic studies of $\text{Sr}_2\text{FeMnO}_6$ (SFMO) as possible substrate material for the production of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) superconducting films. X-ray diffraction experiments show that SFMO belongs to the complex cubic perovskite family. Chemical stability and crystallographic coupling between SFMO and YBCO were examined by characterizing SFMO-YBCO (0 to 100 vol%) polycrystalline composites. Morphological and qualitative compositional analyses were performed through scanning electron microscopy and energy dispersive X-ray experiments. Magnetization measurements reveal that the proximity of SFMO does not affect the superconducting transition temperature ($T_c=89.2$ K) of YBCO material. Our results evidenced that the SFMO is an excellent candidate to be substrate for the fabrication of YBCO superconducting thin films.

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1 Introduction

The complex cubic perovskite oxides have been investigated for their use as potential new substrates for the production of cuprate superconducting films [1, 2]. For good quality substrates, the material candidate has to satisfy the following requirements: chemical stability, e.g., absence of chemical reaction at the interface substrate-film; good lattice parameter coupling at the crystallographic plane substrate-film to guarantee the epitaxial growth; the presence of the substrate material must not affect the superconducting properties of the film [3]. The high chemical reactivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) with most of conventional substrate materials at the processing temperature imposes severe restrictions on the availability of substrates for the YBCO superconducting films [4]. Moreover, the divergence of the crystallographic properties at the interface between YBCO and the commonly available substrates, as well as the difficulty to obtain chemical and structural properties compatible with the YBCO superconductor, constitute a great motivation to produce new optimal materials for this application. For example, MgO, the widely utilized substrate for YBCO thin films, produces an interlayer of barium salt at the YBCO-MgO interface, when the processing temperature is above 700 °C [5]. Another extensively used substrate for YBCO, LaAlO_3 , exhibits an excellent lattice coupling but has the disadvantage that it is available only as twinned single-crystal [4]. In this paper, we report the systematical steps followed for the production and characterization of $\text{Sr}_2\text{FeMnO}_6$ (SFMO) as eventual substrate for the fabrication of YBCO high temperature thin films. Pure SFMO and SFMO-YBCO (0 to 100 vol%) were produced and characterized to study the viability to utilize SFMO as substrate to produce YBCO superconducting thin films.

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2 Experimental

SFMO polycrystalline samples have been prepared by a solid-state reaction process. Stoichiometric ratios of the precursor powders SrO (purity 99.5%), Fe_2O_3 (99 %) and MnO (99 %) were finely ground and thoroughly mixed. The precursor powder was pressed into a disc and the material was calcined at 1100 °C for 148 h in ambient atmosphere. With nickel-filtered CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) of a SIEMENS D5000 diffractometer, X-ray diffraction (XRD) spectra were taken of this calcined powder, which showed a multiple-phase structure. The calcined material was again crushed, finely ground and pressed at 6 tons/cm² pressures to form a disc (10 mm diameter, 2 mm thickness). This disc was sintered at 1100 °C for 17 h in vacuum atmosphere and furnace-cooled to room temperature. The XRD pattern of the sintered material showed a single-phase structure. For chemical stability studies, a single-phase YBCO superconductor was prepared by solid-state synthesis. 0 to 100 vol% of SFMO was mixed in YBCO superconductor powder and the mixture was pressed into circular discs (10 mm diameter, 1 mm thickness) at a pressure of 5 tons/cm² and heat treated at 960 °C in oxygen atmosphere for 8 h. After the heat treatment, YBCO-SFMO samples were slowly cooled down to room temperature for proper oxygenation. XRD spectra of these samples were recorded for crystallographic phase characterization, the chemical stability and the crystallographic parameter coupling of the YBCO-SFMO composites. The influence of SFMO on the superconducting properties of YBCO was studied in the composite samples through DC magnetic susceptibility measurements by using a Quantum Design model 2000 MPMS SQUID system. Morphological characterization of samples was systematically effectuated from scanning electron microscopy (SEM), by using Quanta 200 SEI Electron-Optics equipment. Compositional analysis of films was performed by energy dispersive X-ray (EDX) experiments by means of a microprobe coupled to the SEM microscopy.

3 Analysis and results

The Fig. 1(a) XRD pattern consists of strong peaks which are characteristics of a primitive cubic perovskite plus a few weak line reflections arising from the superlattice. No evidence for a distortion from the cubic symmetry is observed in the XRD spectrum. The basic perovskite composition is ABO_3 , where A is a large ion suitable to the 12-coordinated cube-octahedral sites and B is a smaller ion suitable to the 6-coordinated octahedral site. Complex cubic perovskite with mixed species on a site (particularly the B site) may be represented by multiples of this formula unit and a larger unit cell, e.g., $\text{A}_2\text{BB}'\text{O}_6$ [6]. Thus, in the SFMO composition, Sr^{2+} with the largest ionic radius (1.13 Å) occupies position A of the complex cubic perovskite, Fe^{3+} (ionic radius 0.64 Å) and Mn^{5+} (ionic radius 0.52 Å) cations occupy the B and B' positions. Due to the ordering of B and B' on the octahedral site of the ABO_3 unit cell, there is a doubling in the lattice parameter on the basic cubic-perovskite unit-cell. Thus, the whole XRD pattern of SFMO can be indexed in a $\text{A}_2\text{BB}'\text{O}_6$ cubic cell with the cell edge $a=2a_p$, where a_p represents the cell lattice of the cubic perovskite. The XRD spectrum of SFMO is isostructural to $\text{Sr}_2\text{NdSbO}_6$ -type complex cubic perovskite oxide reported in the Joint Committee on Powder Diffraction Standards (JCPDS) files [7], with the number 38-0817, as judged by the similarity in d spacing and intensity ratios. The presence of the superstructure reflection lines (111) and (311) in the XRD spectrum of SFMO is the signature of an ordered complex cubic perovskite structure. In a substitutional solid solution BB' , there is a random arrangement of B and B' on equivalent lattice positions in the crystal structure. It upon stable heat treatment, the random solid solution rearranges into a structure in which B and B' occupy the same set of positions but in a regular way, such a structure is described as superstructure. In the superstructure, the positions occupied by B and B' are no longer equivalent and this feature is exhibited in the XRD spectrum of the material by the presence of superstructure reflection lines [8].

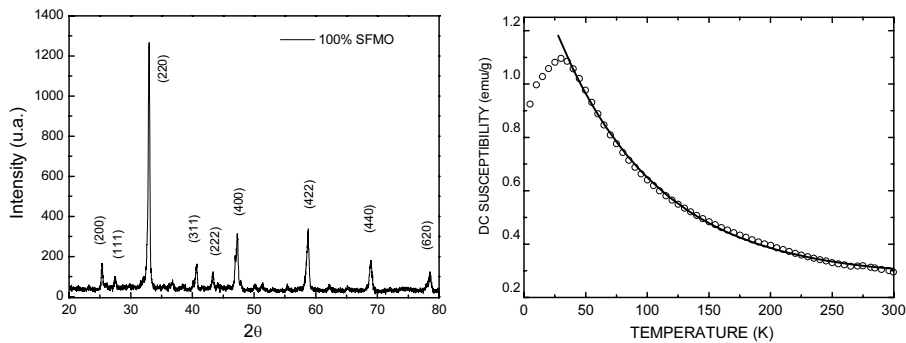


Fig. 1 (a) XRD pattern for the complex cubic perovskite SFMO. (b) DC magnetic susceptibility as a function of temperature for SFMO (data points) and Curie-Weiss fitting of the paramagnetic characteristic (line).

For a double cubic perovskite of the formula $A_2BB'O_6$ the intensity, in particular the (111) superstructure reflection, is proportional to the difference in the scattering power of the B and B' atoms, when all the atoms are situated in the ideal position [8]. A disordered arrangement of B and B' should result in zero intensity. Therefore Fe^{3+} and Mn^{3+} cation ordering in SFMO in B and B' positions is clearly distinguished by the presence of the significant intensity of (111) and (311) superstructural reflection lines. The lattice parameters of SFMO, calculated from the XRD data are $a=7.731(0)$ Å while for the YBCO sample we obtained $a=3.866(1)$ Å, $b=3.874(2)$ Å and $c=11.651(9)$ Å.

Energy dispersive X-ray (EDX) analysis was performed on the single phase SFMO for the quantitative elemental chemistry analysis. The result revealed the expected percentages for the calculated stoichiometric composition, without evidences of impurity traces in the samples.

The magnetic properties of SFMO have been investigated by measuring the DC magnetic susceptibility in the temperature range 5 to 300 K and at an applied magnetic field of 5 kOe. Figure 1(b) shows the temperature dependence of the DC magnetic susceptibility as a function of temperature for SFMO. The magnetic susceptibility data of this picture can be fitted well with the Curie-Weiss law $\chi = \chi_0 + C/(T - \theta_c)$, where $C = N\mu_{eff}^2/3k_B$ is the Curie constant, N is Avogadro's number, μ_{eff} is the effective magnetic moment ($\mu_{eff} = P_{eff}\mu_B$), P_{eff} represents the effective Bohr magneton number, μ_B is the Bohr magneton, k_B is the Boltzmann constant, θ_c is the paramagnetic Curie temperature and χ_0 is the temperature independent susceptibility term.

The value of the temperature independent susceptibility term is $\chi_0 = 1.67 \times 10^{-3}$ emu/mol. The Curie constant, estimated from the fitting in Fig. 2, is $C = 1.01289$ emu K/mol and the Curie temperature is $\theta_p = 1.9995$ K. The effective magnetic moment per Fe ion, calculated from the Curie constant is $\mu_{eff} = 2.84\mu_B$. This value corresponds to 78.5% of the expected $P_{eff} = 3.62$ for an isolated Fe^{3+} calculated by the Hund's rule. This difference may be attributed to the crystal field effects of the trivalent Fe^{3+} cation, which explain the magnetic susceptibility in SFMO.

In order to verify the possibility of using SFMO as a substrate material for thin films of YBCO superconductor, we have studied the chemical reactivity of SFMO with YBCO. Approximate amounts of SFMO (0 to 100 vol%) were mixed with YBCO, as described in Section 2 of this paper. XRD patterns of these composites are shown in Fig. 2(a). As seen from this figure, all the peaks in the XRD could be indexed either for YBCO or for SFMO and no extra XRD peak. Within the accuracy of XRD technique, these results show that YBCO and SFMO remain as two distinct separate phases in the YBCO-SFMO composites and SFMO is chemically stable with YBCO superconductor for all vol% addition of SFMO. Concerning the crystallographic coupling, we notice that there is a matching $\sim 0.02\%$ between the SFMO

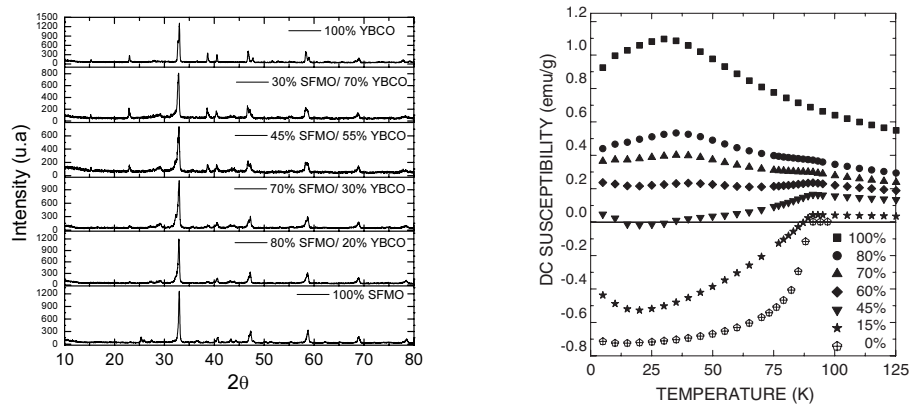


Fig. 2 (a) XRD spectra for 0 to 100 vol% of SFMO in an YBCO matrix. (b) DC magnetic susceptibility for 100, 80, 70, 60, 45, 15 and 0 vol% of SFMO in SFMO-YBCO polycrystalline composites.

lattice parameter $a/2=3.865(5)$ and the YBCO $a=3.866(1)$ Å crystallographic constant. This matching value constituted a record between the lattice constant of possible substrate materials and YBCO ab-plane crystallographic parameter.

The superconductivity in YBCO-SFMO composite samples was studied by measuring the dc magnetic susceptibility with an applied field of 5 kOe and in the temperature range 5 to 300 K. Figure 2(b) shows curves of the dc magnetic susceptibility as a function of temperature for the YBCO-SFMO composites with 0, 15, 45, 60, 70, 80 and 100 vol% of SFMO addition in YBCO superconductor. As seen from this picture, all the YBCO-SFMO composites have the same superconducting transition temperature $T_c = 89.2$ K as that of the pure YBCO superconductor. This shows that even up to 80 vol% of SFMO, an insulating ceramic oxide, addition in YBCO did not have any deteriorating effect on the transition critical temperature of YBCO superconductor. Thus as discussed earlier SFMO is chemically stable with YBCO superconductor and at same time it did not have any deteriorating effect on the superconducting property characterized by the transition temperature T_c .

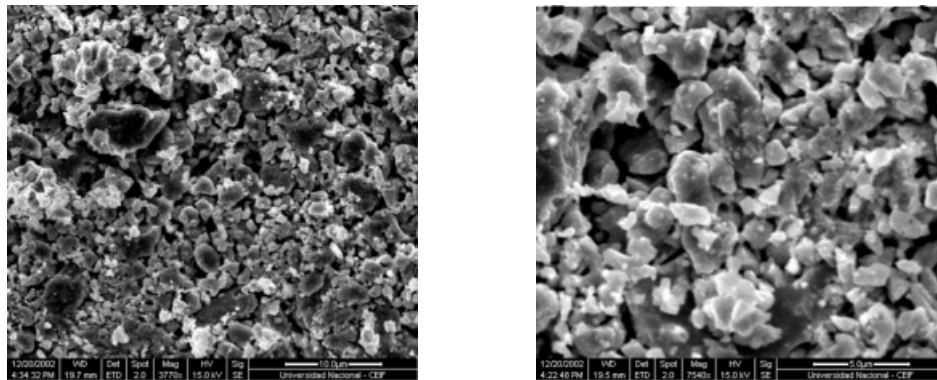


Fig. 3 Scanning electron microscopy for (a) 55 vol% YBCO, 45 vol% SFMO and (b) 20 vol% YBCO, 80 vol% SFMO in SFMO-YBCO composites.

Surface morphology of sintered YBCO-SFMO composites was investigated by scanning electron microscopy (SEM). The results are shown in the micrograph of Fig. 3. These indicate that the surface of the samples present a crystalline character, which is typical of a polycrystalline ceramic material. The SEM micrograph of Fig. 3(a), for 55 vol% YBCO and 45 vol% SFMO, shows homogeneous surface morphol-

ogy and particle size distribution with grain average size estimated to be 1-2 μm for both, YBCO (darkness regions) and SFMO (blank regions) compounds. Figure 3(b) reveals the increase of blank regions when proportion of SFMO is added up to 80 vol%. Notice that there is no detectable interface interaction between SFMO and YBCO grain interfaces and SFMO particles are distinguishably distributed in the YBCO matrix.

4 Conclusion

It is found by the structural characterization that de SFMO has an excellent crystallographic coupling and is chemically non-reacting with YBCO superconducting films even under extreme processing conditions. It is observed that there is no chemical reaction between these compounds into the SFMO-YBCO composites. Morphological characterizations were carrying out to evaluate the chemical reaction between the insulating SFMO and the metallic YBCO materials. In the SFMO-YBCO composites experimental analysis the formation of separate single-phase grains of SFMO and YBCO was observed by SEM images and XRD characterization. Energy dispersive X-ray (EDX) analysis show that there is no evidence of impurity traces in the samples. DC magnetic susceptibility measurements reveal the paramagnetic characteristic of SFMO samples, which follow a Curie-Weiss behavior and permit to report the corresponding magnetic constants. These results show that the presence of SFMO does not affect the superconducting critical temperature of YBCO. This systematical work permitted to corroborate our hypothesis that the SFMO complex cubic perovskite can be utilized as substrate material for the fabrication of YBCO thin films.

Acknowledgements This work was partially supported by the COLCIENCIAS Colombian agency on the project No. 1101-05-13604 and Centro de Excelencia en Nuevos Materiales.

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