Special Issue of the 8th International Advances in Applied Physics and Materials Science Congress (APMAS 2018)

Examination of Structural and Dielectric Properties of $SrCu_{0.33}Ta_{0.67}O_3$–$Co_{1-x}Mn_xFe_2O_4$ $(0 < x < 1)$ Multiferroics

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Binary $SrCu_{0.33}Ta_{0.67}O_3$–$Co_{1-x}Mn_xFe_2O_4$ (SCTO–(C,M)FO) multilayer composites were investigated by X-ray diffraction, impedance spectroscopy, and DC conductivity measurements. It was established that all synthesized compounds adopted the tetragonal symmetry $P4mm$ and cubic symmetry $Fd\bar{3}m$ for SCTO and mixed (C,M)FO ferrite system, respectively. The numerously electrochemical processes have been isolated from the impedance and electric modulus formalisms as phenomena responsible for a transport of electric charge in various regions of multilayer composite. This result indicates an electrically inhomogeneous SCTO–(C,M)FO materials both morphologically (grain boundary regions) and structurally (interfacial regions). Also, the energy activations E_A of $0.6 \div 0.8$ eV have been found from the Arrhenius plots, whose values are typical for electroceramic materials.

DOI: 10.12693/APhysPolA.135.658

PACS/topics: multiferroics, electroceramics, planar composites, X-ray investigation, magnetostriction

1. Introduction

A progress in electronic technology is related to advanced materials, which are often electroceramic composites. These materials, which are called multifunctional or smart materials, provide a unique possibility to develop new devices whose physical and chemical properties strongly depend on temperature, pressure, electric or magnetic field, etc. In particular, a combination of magnetic and dielectric properties for single materials or composites provides a new subclass of functional materials named magnetoelectrics.

Therefore, many efforts are made for developing the multilayer composites, also with intentionally selected modifiers to enhance the magnetoelectric effect mostly through a generation of mechanical stress at interfacial layers (e.g. adjacent surfaces of magnetic and dielectric regions in planar heterostructure). For this purpose, materials with a high magnetostriction coefficient, e.g. ferrites [1], as well as piezoelectrics with a structure of perovskite-type [2] are mainly focused. In this work, the SCTO–CMFO multilayer composites with ferrite component modified by Mn ($x = 0.2$, 0.5, 0.7) were examined for the structural and dielectric properties.

2. Experimental procedure

In order to fabricate SCTO-(C,M)FO multilayered composites, the initial $SrCu_{1/3}Ta_{2/3}O_3$ and $(Co,Mn)Fe_2O_4$ materials were synthesized by a solid state reaction method. To prepare SCTO and (C,M)FO components, the starting powder oxides CuO, MnO, Ta_2O_5, Co_3O_4, Fe_2O_3, and carbonate $SrCO_3$ were weighted in stoichiometry proportion and then mechanically activated in planetary ball mill (7 h, 300 rpm). The powders of CFO and cobalt ferrite modified by Mn were calcined at 1080 °C for 5 h instead of SCTO, which was calcined three times at 1300 °C (60 h), 1345 °C (30 h) and 1450 °C (2 h), respectively.

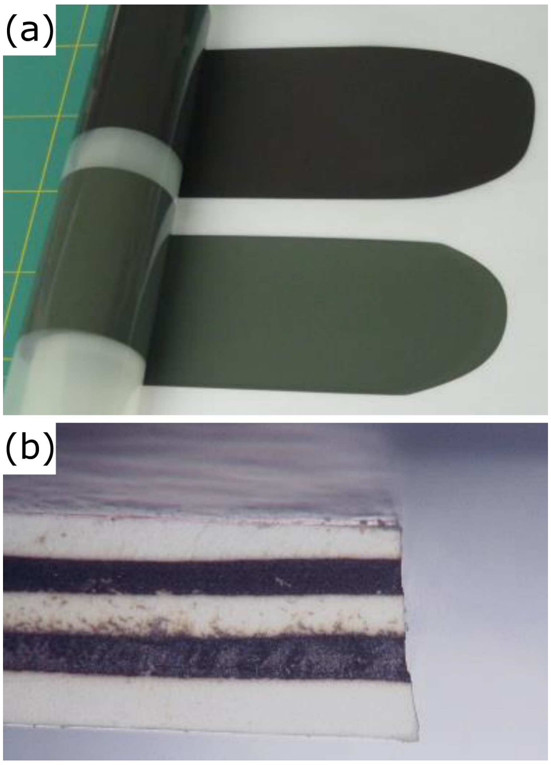

Fig. 1. (a) The "green tapes" of cobalt ferrite (black) and dielectric relaxor (gray) casted onto polyester foil, (b) co-fired SCTO-CFO (L4x:f–m–f–m–f) electroceramic structure optically inspected (120×) near the edge of a multilayer slab.

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After synthesis, the raw materials were milled in planetary ball mill to get the fine powders since the most critical parameter in a solution casting method is homogeneity of ceramic slurries that strongly influences on flexibility of "green tapes" (Fig. 1a) and affects the layer thickness. Therefore, the fine powders of SCTO and (C,M)FO were mixed with organic constituents (solvents, plasticizers, dispersant, and binders) required to fabricate the ceramic tapes. Finally, the electroceramic multilayer structures (Fig. 1b) were prepared by co-firing process at 1050 °C.

3. Results and discussion

X-ray diffraction pattern shows that a pure SCTO (Fig. 2a) crystallizes in tetragonal symmetry $P4mm$ in analogy to isomorphic $SrCu_{0.33}Nb_{0.67}O_3$ compound [3]. The lattice parameters of tetragonal unit cell were estimated to be: $a = 3.947(2)$ Å, $c = 4.135(3)$ Å, $c/a = 1.048$, respectively.

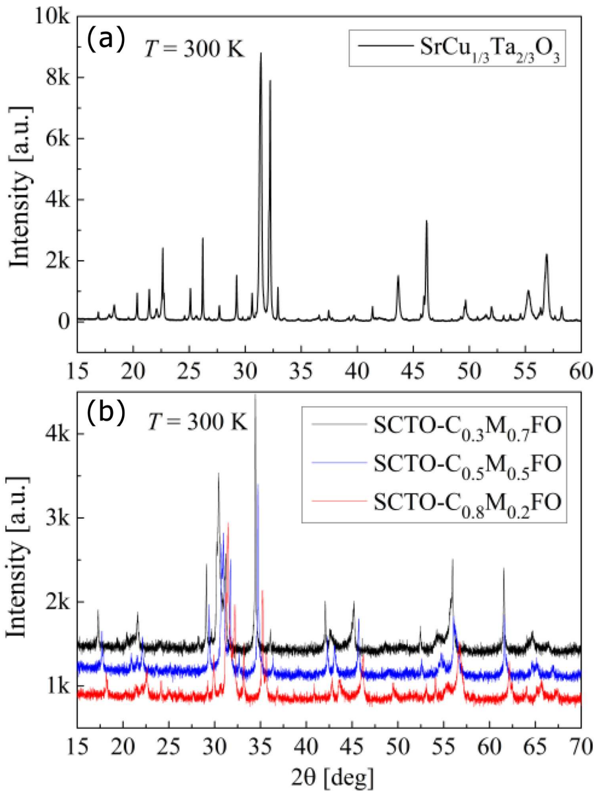

Fig. 2. X-ray diffraction patterns for (a) SCTO piezoelectric, (b) binary SCTO–$C_{1-x}M_x$FO system.

On the other hand, an evolution of SCTO–$C_{1-x}M_x$FO system with Mn content is presented in Fig. 2b. A ferromagnetic component (C,M)FO crystallizes in cubic symmetry $Fd\bar{3}m$ for all x concentration. Figure 2b shows an increase of lattice parameter a with Mn content, as one could expect from a substitution of Co atoms ($r^{\mathrm{ion}} = 0.58$ Å) by Mn atoms ($r^{\mathrm{ion}} = 0.66$ Å) with larger effective ionic radius characteristic for tetrahedral coordination [4]. The extracted lattice parameters for $Fd\bar{3}m$ unit cells based on the Rietveld analysis are as follows: 8.3774 Å, 8.3861 Å, 8.4203 Å, and 8.4217 Å for Mn content $x = 0.0$, 0.2, 0.5, 0.7, respectively. A similar behaviour was previously observed for (C,M)FO spinel ferrite [5].

The electrical conductivity was investigated in a wide range of temperatures [6]. Typical Arrhenius plots characteristic for SCTO-$C_{1-x}M_x$FO system are presented in Fig. 3. Both structural composition of laminates and elemental composition of mixed cobalt ferrite were examined. As an example to clarify, designation as L5x:f–m–f means a laminate with two outer ferroelectric regions and inner core of magnetic component, where each of these regions were formed by five single ceramic layers.

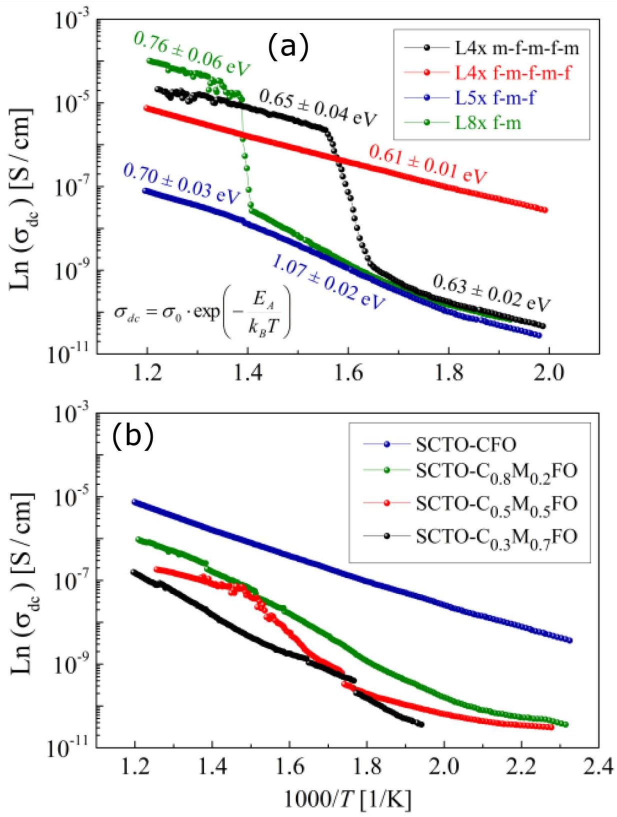

Fig. 3. The Arrhenius plots for (a) SCTO–CFO laminates in function of structural composition, (b) across a binary SCTO–$C_{1-x}M_x$FO system.

One can see a different behaviour of conductivity (Fig. 3a) at low and high temperatures. A larger tendency for changes in character of electrical conductivity manifest composites with balanced contributions of magnetic and ferroelectric regions or with a predominance of magnetic component e.g. L5x:m–f, L4x:m–f–m–f–m. Also, an elemental composition of magnetic (C,M)FO constituent can affect a character of electrical conductivity. The more manganese atoms are there in perovskite-type structure of ferrite spinel, the lower is the electrical conductivity of ceramic laminate (Fig. 3b).

A dielectric response of SCTO–CFO laminate (L4x:f–m–f–m–f) is presented in Fig. 4, where two dielectric relaxations in Z^* formalism and five in complementary M^* formalism were interpreted in terms of the Cole–Cole model [6, 7]. A detailed data analysis allowed to isolate the different relaxation processes related to a transfer of electric charges across the heterostructure of examined composite. The time constants τ_{gb} describe the transfers of electric charges at grain boundary regions, and SCTO component (dominant circle in Fig. 4a) is in much more resistive phase than CFO. Furthermore, the time constants τ^{inter} (Fig. 4b) characterize the transfers of electric charges near the interfaces: homogeneous (adjacent ceramic layers are of the same type) and heterogeneous (in contact are the magnetic and ferroelectric layers). However, the intra-granular processes (τ_{bulk}) were not found in the frequency limit.

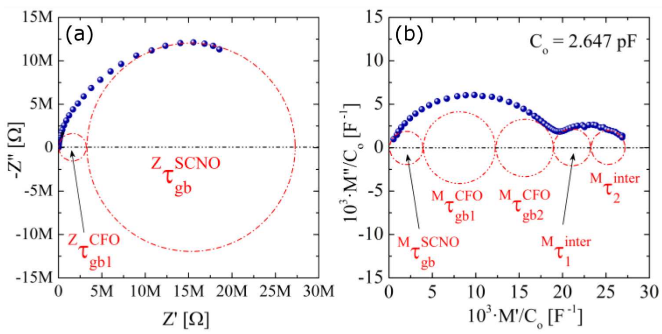

Fig. 4. The isolated relaxation processes of SCTO-CFO (L4x:f–m–f–m–f) laminate shown in two formalisms: (a) impedance Z^*, (b) electric modulus M^*.

4. Conclusion

The electroceramic materials of SCTO–(C,M)FO type have been prepared and investigated for structural and dielectric properties. A multilayer heterostructure of composites allowed to isolate a series of dielectric processes. Moreover, it has been proved that structural configuration and chemical composition of the planar composites can affect the electrical conductivity of SCTO–(C,M)FO material.

Acknowledgments

This work was financed by the National Science Centre Poland under MINIATURA–I project (DEC-201 7/01 /X/ST5 /00547).

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