Journal of Magnetism and Magnetic Materials 345 (2013) 106–110

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Enhancement of magnetic and ferroelectric behaviour in (Ca, Co) co-doped $HoMnO_3$ multiferroics

P.P. Rout, S.K. Pradhan, S.K. Das, S. Samantaray, B.K. Roul *

Institute of Materials Science, Planetarium Building, Bhubaneswar 751013, India

ARTICLE INFO

Article history:
Received 2 May 2013
Available online 24 June 2013

Keywords:
Multiferroic
Dielectric
Ferroelectric
Ferromagnetic

ABSTRACT

The effect of sintering temperature on structural, electrical and magnetic behaviours of polycrystalline samples of $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ prepared by the solid state reaction route sintered at three different temperature 1250 °C, 1350 °C, 1450 °C for 10 h are investigated. XRD, SEM, magnetization, dielectric and ferroelectric measurements were carried out. Experimental results showed the nucleation of orthorhombic phase as the sintering temperature increases from 1250 °C to 1450 °C. Ferroelectric (T_c) and antiferromagnetic transition temperature (T_N) increases with increase in sintering temperature. Strong bifurcation of FC and ZFC curve in sample sintered at 1450 °C showed a clear onset of ferromagnetic state around 165 °K, which is confirmed from M to H graph at 165 °K. All the sample showed ferroelectric behaviour at room temperature which are leaky in nature. Sintering temperature along with Ca and Co doping in $HoMnO_3$ ceramics plays an important role in phase transformation along with enhancement in multiferroic properties.

1. Introduction

The observation of spontaneous electric polarization and magnetic control of ferroelectricity in rare earth manganite [1,2] has developed enormous interest for searching new magnetoelectric multiferroic materials due to their great technological and fundamental importance [3–5].

In the type-I ferroelectric materials, the polarization arises either due to off center shifts of the transition metal ion making covalent bond with oxygen atom (e.g., $BaTiO_3$) [6], or ordering of $6s^2$ lone pair electron that breaks the inversion symmetry (e.g., $BiMnO_3$, $BiFeO_3$) [7,8]. Even if magnetic ions are present in these materials, the spins order at much lower temperature than the electric dipoles and the coupling of magnetic and ferroelectric subsystem is weak. In contrast, the new family of magnetoelectric multiferroics (type-II) exhibits applied magnetic field dependant electric polarization reversal [9,10] which indicates the electric polarization is induced by the magnetic order. The onset of ferroelectricity correlates with the transition to the spiral spin order. The intimate link between these two order parameters marks the prominent and intriguing feature of the new class of multiferroics. Most technologically important ferroelectrics are perovskite structure oxides, but there is increasing interest in the class of ferroelectric hexagonal and orthorhombic rare earth manganites as non-volatile memory materials [11], as gate ferroelectrics in field-effect transistors [12] and because of their coupled magnetic and ferroelectric behaviour [13].

Among all multiferroic system $HoMnO_3$ (HMO) is special class of promising magnetoelectric material showing magnetic field dependant polarization and vice versa. Depending on synthesis procedure HMO system crystalizes in two structure i.e. hexagonal (h) and orthorhombic (o). The major difference between h-HMO to that of o-HMO is the mode of origin of ferroelectricity in both the system. In h-HMO, the structural distortion arising from an asymmetric coordination of oxygen around Ho leads to a net polarization but in o-HMO ferroelectricity is attributed to a complex spiral spin order that break the inversion symmetry [14]. However, both the structure has magnetic transition temperature far below room temperature, making potential application more difficult to realize. In order to address this issue Ca and Co ions are substituted at Ho and Mn site, respectively, with high temperature sintering for enhancement of the ferroelectric and magnetic property as well as development of orthorhombic phase.

In this study we partially substitute Ho ions by larger Ca ion and Mn ion by Co ion and single phase $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ compound are successfully prepared by solid state reaction route with three different sintering temperature 1250 °C, 1350 °C & 1450 °C for 10 h. The Ca and Co doping can cause structural distortion which can suppress the formation of hexagonal structure. Since HMO compounds in either the orthorhombic or hexagonal structure are mutiferroic and exhibiting both antiferromagnetic and ferroelectric order below AFM transition temperature, the (Ca, Co) doped HMO

* Corresponding author. +91 674 2587649; fax: +91 674 2300142.
E-mail address: ims@iopb.res.in (B.K. Roul).

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.06.035

samples become interesting due to formation of ferromagnetism of Mn moments and structural distortion in the lattice, which can induces dipole ordering well above room temperature. The main effects of the various substitutions are to vary the number of electrons in the 3d band and to alter the interatomic distances and bond angles [15]. These co-doped HMO samples could be the potential candidate for multiferroic application exhibiting both ferroelectrics and ferromagnetism in its orthorhombic phase.

2. Experimental details

Pure $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ bulk ceramic was synthesized by solid state reaction route. High pure (99.999%) Ho_2O_3, Mn_2O_3, Co_3O_4, $CaCO_3$ powders were taken with appropriate composition in agate mortar and heated at 500 °C for 6 h which were subsequently quenched to room temperature for immediate grinding. This procedure was repeated five times in order to achieve homogeneous mixture with smaller particle size. Calcined powders are palletized using freshly prepared Poly Vinyl Alcohol (PVA) as binder. Cylindrical pellets having dimension 10 mm diameter and 2 mm thickness were prepared by hydraulic press with a pressure of 8 t/cm^2 for electrical measurements. Pressed pellets were slowly heated (50 °C/h) to 200 °C and kept for 4 h to release PVA binder from pellets using high temperature programmable (Eurotherm controller, Model: 2204) vacuum furnace. Sintering schedule of pellets were carried out @50 °C/h heating rate with a constant soaking periods of 4 h at 600 °C. This soaking period is required to remove any volatile impurities/organic materials (binder) from pellets. Finally samples are sintered at three different temperature i.e. 1250 °C, 1350 °C, 1450 °C, for 10 h by slow step sintering schedule. All sintered samples were characterized through XRD, SEM, magnetization, dielectric, ferroelectric measurement. X-ray diffraction pattern of the samples were carried out in the 2θ range (20°–70°) using Cu$K\alpha$ (λ=1.54059 Å) radiation by a Bruker D-8-advance fitted with Lithium filter and operated at 40 kV and 40 mA. Microstructural analysis was carried out by a scanning electron microscope (SEM) HITACHI (S3400). Silver paste was applied on both surfaces of all the samples for electrical measurements. Dielectric measurement of the sample carried out by an LCR meter bridge (Quadtech 7600 precision). The ferroelectric (electric polarization as a function of electric field) measurements of sintered pellets were carried out using a ferroelectric hysteresis loop tracer precession premier II (Radiant make, USA) and magnetic properties measurements were carried out using VSM (Lakeshore, model 7410) over a wide temperature range between 10 and 350 K in fields up to 5 T.

3. Results and discussion

Fig. 1(a)–(c) showed XRD pattern of $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sintered at 1250 °C, 1350 °C, 1450 °C. It is observed from XRD that sample sintered at 1250 °C and 1350 °C are present in mixed phase. For sintering temperature 1250 °C all peaks are assigned to hexagonal phase except (1 1 2) & (2 0 0) which are indexed to be the onset of orthorhombic phase. Splitting of peaks at 33.2° clearly signifies the structural phase transformation from hexagonal to orthorhombic. As sintering temperature increases to 1350 °C, the hexagonal peaks observed at 1250 °C sintered sample were supressed except (1 1 0) and (1 1 2) with nucleation of new peaks which are indexed to be orthorhombic phase and the most intense peak starts to merge into one peak. Finally at 1450 °C the XRD pattern showed orthorhombic phase with *Pbnm* space group [16]. All the peaks are indexed using search test programme [17] and details of the refined value of lattice parameter are listed in

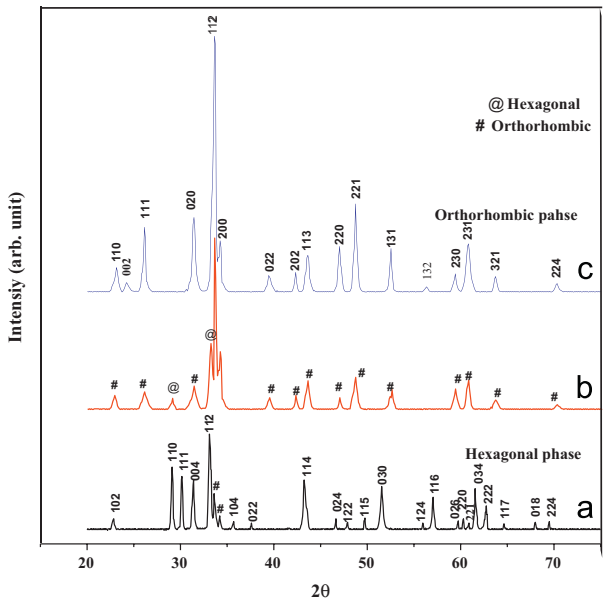

Fig. 1. XRD pattern of $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sintered at 1250 °C, 1350 °C, 1450 °C for 10 h.

Table 1
Lattice parameters and unit cell volume of $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sintered at 1250 °C, 1350 °C and 1450 °C for 10 h.

Sintering temperature of $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ ceramics	a(Å)	b(Å)	c(Å)	Volume (Å^3)
1250 °C (Hexagonal)	6.139	6.139	11.401	372.107
1350 °C (Orthorhombic)	5.275	5.836	7.358	226.538
1450 °C (Orthorhombic)	5.276	5.838	7.345	226.235

Table 1. In addition, with increase in sintering temperature, there is gradual increase in intensity and narrowing of diffraction peaks, indicative of better crystallization and grain growth. Atomic radii of Ca (1.80 Å) is slightly more than that of Ho (1.75 Å) and Co (1.35 Å) is lower than that of Mn (1.40 Å), which may be one of the reason for contraction of unit cell volume (Table 1) along with lattice parameter '*c*' and dilation of '*a*' and '*b*', resulting origin of chemical pressure in the lattice. The effect of chemical pressure increase further for higher sintering temperature leads to distortion in structure and supports stabilization of orthorhombic perovskite structure.

SEM microstructure of $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sintered at 1250 °C, 1350 °C, 1450 °C for 10 h are shown in Fig. 2(a)–(c). At lower sintering temperature (1250 °C), irregular grain growth develops with no sharp grain boundaries. Pores of different dimension are visible in the micrograph. It is interesting to note that with increase in sintering temperature mass flow among the grains occurs leaving minimum room for any kind of pore development. Finally, at 1450 °C complete grain growth occur with sharp grain boundary and uniform surface texture. Pores present at lower sintering temperature are completely absent making highly dense ceramics. Microstructure, i.e. grain size, morphology, orientation and texture, as well as presence of secondary phase plays an important role on functional properties of multiferroic ceramics [18]. The estimated average crystallite size of $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sintered at 1450 °C is about 900 nm.

M–T curves for zero field cooled (ZFC) and field cooled (FC) at 100 kOe in the temperature range of 10–350 K for $Ho_{0.9}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sample sintered at 1250 °C, 1350 °C, 1450 °C for 10 h are shown in Fig. 3(a)–(c). In the temperature range 85–165 K, there is