Ceramics International 42 (2016) 13834–13840

Contents lists available at ScienceDirect

Ceramics International

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

Raman and dielectric spectroscopic analysis of magnetic phase transition in $Y(Fe_{0.5}Cr_{0.5})O_3$ multiferroic ceramics

Tirupathi Patri [a,*], Justin Ponnaiah [b], Prabahar Kutty [c], Avijit Ghosh [d,*]

[a] Department of Physics, Rajiv Gandhi Universities of Knowledge Technologies, RK Valley 516330, India
[b] Department of Chemistry, Rajiv Gandhi Universities of Knowledge Technologies, RK Valley 516330, India
[c] Advanced Magnetic Group, Defense Metallurgical Research Laboratory, Hyderabad 500058, India
[d] Centre for Applied Physics, Central University of Jharkhand, Ranchi, Jharkhand 835205, India

ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form
28 May 2016
Accepted 28 May 2016
Available online 1 June 2016

Keywords:
Raman spectroscopy
Dielectric spectroscopy
Multiferroics
Magnetic phase transition

ABSTRACT

Here, we report the Raman and dielectric spectroscopic studies as a function of temperature of orthorhombically distorted $Y(Fe_{0.5}Cr_{0.5})O_3$ (YFC) ceramics, measured from 80 to 300 K. The dc-magnetization measurements under field cooled (FC)-zero field cooled (ZFC) protocol indicate a small onset of magnetic ordering at T_N~270 K. The field dependent magnetization plot recorded at 50 K, 150 K and 200 K show a clear opening in hysteresis loops. The linear dependence of magnetization plot at high field without any saturation of magnetization indicates the coexistence of weak ferromagnetic (WFM) component within the canting antiferromagnetic (CAFM) matrix. Temperature evolution of Raman line-shape parameter of $B_{2g}(4)$ phonon mode clearly exhibits an anomalous behavior of phonon shift near T_N~270 K, indicating the spin-phonon coupling in the ceramics. From the temperature dependent dielectric permittivity ($\varepsilon(T)$) study, two dielectric relaxation peaks are detected below 200 K and above 250 K. The appearance of former relaxation peak is responsible for polaronic conduction mechanism, while the later one is associated with magnetic phase transition which might be relevant to the presence of magnetoelectric coupling in YFC ceramics. The observed P-E hysteresis loops at room temperature indicate weak ferroelectric nature of the ceramics.

1. Introduction

The giant magnetoelectric (ME) coupling coefficient in multiferroic systems involving with controllability of magnetization by the applied electric field (E) or vice versa are become the subject of great interest for multifunctional device applications [1–3]. Considering the magneto-electric and magneto-dielectric device applications in operation at room temperature (RT) using single phase multiferroic system are more important rather than that at lower temperature. Most of the single phase multiferroic system with large value of ME coupling coefficient are very much limited. As a fact, the large value of ME coupling coefficient in multiferroic systems obtained at low temperatures are not useful for ME applications. Hence, there is large timely search for new single phase multiferroic system which can exhibit large value of ME coupling coefficient at RT. Nevertheless, the large value of ME coupling coefficient can also be achieved through developing ferroic orderings towards RT. Recent reports dealing with single phase magnetic multiferroic systems such as rare-earth orthomanganite ($RMnO_3$), orthochromite ($RCrO_3$) and orthoferrite ($RFeO_3$) ceramics with special spin arrangement can produce ferroelectricity owing to an incommensurate lattice modulation at low temperatures. As a consequence of it, a large value of ME coupling coefficient is observed [4–10]. Most of these systems exhibit a magnetic ordering at low temperature and ferroelectric ordering relatively at high temperature regime. Therefore, to get magnetic ordering towards RT, doping of magnetic ions (Fe or Mn) is an effective strategy, which is already detected in $YFe_{1-x}Mn_xO_3$ system [11,12].

From the literature survey it was known that, Kadomtseva et al. studied for the first time a series of $Y(Fe_{1-x}Cr_x)O_3$ system and asserted that the concentration near $x=0.5$ is most complicated region for unusual magnetic behavior [13]. Later, Dahmani et al., also studied the magnetic behavior in $Y(Fe_{1-x}Cr_x)O_3$ ($0.0 \le x \le 0.5$) system and noted a signature of spin-glass behavior for the concentration at $x=0.5$ [14]. Recently, a rich variety of intriguing magnetic properties, such as field induced magnetization exchange bias effect [15] and spin reorientation transition to the ME effect was also observed in $Y(Fe_{0.5}Cr_{0.5})O_3$ [15–17]. However, the correlation between magnetic behavior with dielectric and Raman spectroscopic investigation in $Y(Fe_{0.5}Cr_{0.5})O_3$ (YFC) system at low temperature seems to be absent. Therefore, in order to get better

* Corresponding authors.
E-mail addresses: ptirupathi36@gmail.com (T. Patri), avijitphy@gmail.com (A. Ghosh).

http://dx.doi.org/10.1016/j.ceramint.2016.05.188
0272-8842/

understanding the underlying mechanism of magnetic phase transition in YFC system, we have carried out a detailed magnetic, dielectric and Raman spectroscopic investigation at low temperature. The present work brings out another interesting investigation of magnetic, dielectric behaviors at low temperature and its correlation with lattice dynamics. Thus, one can design single phase multiferroics at RT, which can be useful for multifunctional device applications.

2. Experimental

The YFC ceramics was prepared by conventional solid state route. Prior to conventional solid state route, initially all precursors were milled through high energy ball milling technique. AR-grade: Y_2O_3, Fe_2O_3, and Cr_2O_3 were used as raw materials. All the required precursors were milled for 24 h in a high energy planetary ball mill set up using methanol as a mixing media. To get the desired stoichiometry, the required amount of powders were weighed, mixed thoroughly using acetone and then the mixed powders were calcined at 1150 °C in an ambient condition for 12 h. Furthermore, the calcination was carried out at 1200 °C for 12 h and phase purity was checked by using X-ray diffractometer (PHILIPS-PW3373 XPERT-PRO) with Cu K_α radiation (λ=1.5405 Å) in the range of $10° \leq 2\theta \leq 70°$ at RT. The pellets were sintered in an ambient condition at 1300 °C for 10 h to ensure densification and complete phase formation. The grain growth and size distribution was estimated using the micrographs collected on a scanning electron microscope (model: Carl Zeiss Supra SEM 40). The core level spectra of atoms were collected on the PHI 5000VERSA Probe II, (ϕ ULVAC-PHI Inc.) X-ray photoelectron spectroscopy (XPS) set up. The phonon modes at low temperature were obtained with the excitation wavelength of 488 nm by using Renishaw Raman System: RM-1000B coupled with LEICA microscope DMLM. The dielectric data at low temperature was collected using an impedance analyzer (model no.: HP 4192A) in the frequency range from 100 Hz to 3 MHz, while keeping the electrode pellets in sandwich geometry. The magnetic data (M-H and M-T) was obtained using quantum design SQUID-VSM (USA) within the temperature range of 5–400 K. The polarization (P-E) loops of the sample were obtained by using (M/S Radiant Technology Inc., USA) P-E loop tracer at RT.

3. Results and Discussion

Fig. 1 shows the Rietveld refined X-ray diffraction pattern of YFC ceramics at RT. The X-ray diffraction pattern is well refined in orthorhombically distorted crystal system with *Pnma* space group using Fullprof software. The observed low values of R factors: R_p=5.3%, R_{wp}=8.23% and χ^2=4.21, indicate best fitting between the observed and calculated diffraction patterns. The calculated lattice parameters and volume of the unit cell are a=5.2640 Å, b=5.5532 Å, c=7.5690 Å and V=221.27 Å^3, respectively. The calculated values are well agreed with recent reported values [15–17]. Furthermore, the calculation of bond valence in YFC ceramics is carried out using Rietveld refined crystallographic information file (CIF). The orthorhombic crystal unit cell of YFC is drawn from the DIAMOND software package (trial version 3.2) using the refined cell parameters as shown in Fig. 2. In orthorhombic crystal structure of YFC, each Fe/Cr atom forms an octahedron with six neighboring oxygen atoms. All FeO_6/CrO_6 octahedra are connected in three dimensional networks through corner sharing oxygen atom as depicted in Fig. 2. The estimated bond angles of Fe/Cr–O_1–Fe/Cr and Fe/Cr–O_2–Fe/Cr are 139.88° and 142.15°, respectively are represented in Fig. 2. The tilt angle θ_T is determined to be 20.06° from the relationship of $\theta_T=(180-\theta)/2$, where θ is bond angle of

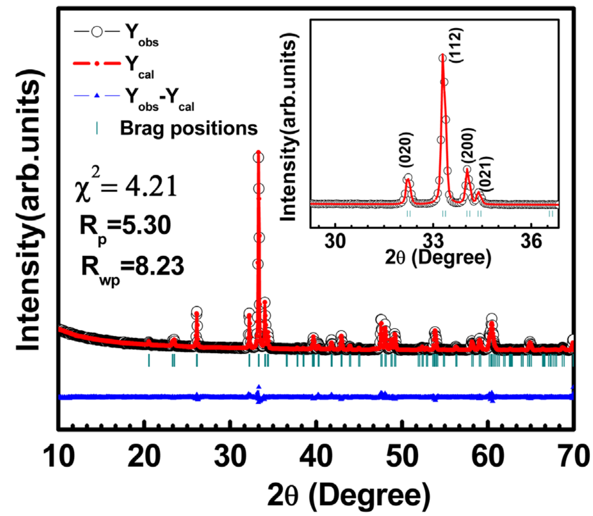

Fig. 1. Rietveld refined X-ray diffraction (XRD) pattern of $Y(Fe_{0.5}Cr_{0.5})O_3$ (YFC) ceramics. Inset shows the magnified view in the region of $29° \leq 2\theta \leq 37°$.

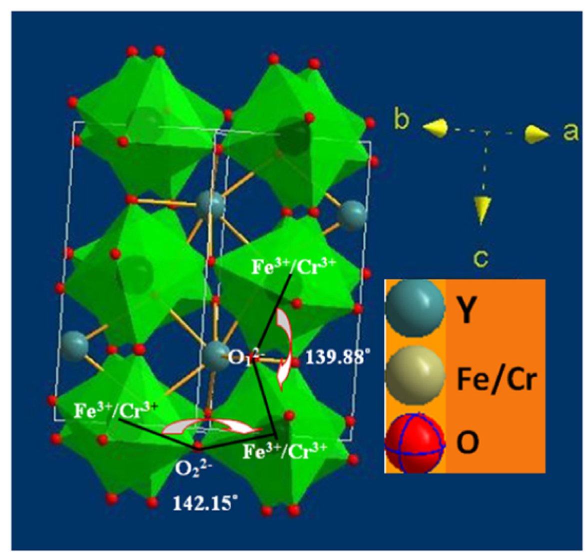

Fig. 2. Model for orthorhombic unit cell with *Pnma* space group of YFC multiferroic ceramics. The corner sharing oxygen octahedra in FeO_6/CrO_6 and estimated Fe/Cr–O_1–Fe/Cr and Fe/Cr–O_2–Fe/Cr bond angles are depicted here also.

Fe/Cr–O_1–Fe/Cr along c-axis. The rotation angle Θ_R is also evaluated to be −26.075° from relationship of $\Theta_R=(90-\Phi)/2$, where Φ is the angle among three oxygen ions in a, b plane. These calculated values of tilt angle and rotation angle are well agreed with recent reports [18,19].

Fig. 3(a) displays the Field emission scanning electron microscope (FESEM) micrograph from sintered pellet of YFC ceramics. The grain growth mechanism is well established during sintering process, which is also seen in the inset of Fig. 3(a). The micrograph reveals that the polycrystalline grains of different in size but spherical in shape with a minimum number of holes or cracks. The observed average grain size is in the order of 1–1.5 μm, which is estimated by counting number of grains with grain size (Fig. 3(b)). The nominal composition and phase purity of the ceramics are also investigated through Energy Dispersive X-ray Spectroscopic (EDS) analysis as shown in Fig. 3(c–d). This particular spectroscopic study confirms the compositional homogeneity of this ceramics.

The oxidation states of constituting elements in the ceramics are investigated through X-ray photo electron spectroscopic (XPS)