Journal of Electron Spectroscopy and Related Phenomena 207 (2016) 19–23

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

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

Signature of covalency and disorder on the dielectric and magnetic properties of $Ba_6Co_6ClO_{16}$

Tanushree Chakraborty[a], Carlo Meneghini[b], Hiroko Yokota[c], Mitsuru Itoh[d], Sugata Ray[a,e,*]

[a] Centre for Advanced Materials, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India
[b] Dipartimento di Scienze, Universitá Roma Tre, Via della Vasca Navale, 84, I-00146 Roma, Italy
[c] Department of Physics, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
[d] Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan
[e] Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form
11 November 2015
Accepted 17 November 2015
Available online 15 December 2015

Keywords:
Transition metal alloys and compounds
EXAFS
NEXAFS
SEXAFS
Dielectric response
Magnetic measurements

ABSTRACT

Hexagonal barium cobalt oxychlorides are an interesting class of materials showing complex interplay between Co–O covalency driven local structural distortions which give rise to strong anomalies in their dielectric and magnetic responses as a function of temperature. The unavoidable presence of oxygen vacancy induces further distortions and frequency dependent fluctuations. Similar instabilities are also found in the title compound $Ba_6Co_6ClO_{16}$. These distortions simultaneously affect dielectric and magnetic structure of the compound which may point toward a new pathway to achieve multiferroicity.

1. Introduction

Recently a joint experimental and theoretical study on a hexagonal barium cobalt oxychloride compound, $Ba_5Co_5ClO_{13}$, revealed [1] that simultaneous existence of tetrahedral and octahedral moieties in an unit cell may give rise to severe rearrangements in charge distribution and consequent structural instabilities. Especially within tetrahedral MO_4 units (M = transition metal atom), the M-O covalency can go significantly higher and the charge density on the metal atom and oxygen can become substantially renormalized with strong hole concentration on oxygen [2–5]. Moreover, aliovalent doping in anionic network in the same compound introduces further modification in the electronic structure of the compound by firstly modifying the charge state of the cation(s) and also by creating local deformations even if the doping is not strictly substitutional. In the above mentioned case of $Ba_5Co_5ClO_{13}$ (BCCO5), the doping is found to be not substitutional but nevertheless the local metal-anion connectivities [6–10] still get modified compared to the parent compound [11,12]. Finally, the above mentioned covalency-driven charge redistribution and the placement of the chloride ion in the neighbourhood give rise to unusual local Coulombic interactions and consequent formation of local dipoles, making clear marks on the corresponding dielectric and magnetic responses of the compound [1].

Here, we report detailed structural (both bulk and local) studies along with magnetic and dielectric data from single and polycrystals of a similar compound, namely $Ba_6Co_6ClO_{16}$ (BCCO6). BCCO6 has one extra face-shared CoO_6 octahedra in the column along z-direction compared to that of BCCO5, which instigates quite different dielectric and magnetic signals even though the local electronic and structural effects remain similar to that of BCCO5.

2. Experimental

The BCCO6 single crystals were grown by flux method, where $BaCl_2$ was used as flux. At first, 5 g mixture of dried $BaCO_3$, Co_3O_4, and $BaCl_2$ was taken with the ratio of 1:1/3:2, respectively, in a morter. Then the mixture was ground thoroughly with ethanol in

* Corresponding author at: Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India. Tel.: +91 33 24734971.
E-mail address: mssr@iacs.res.in (S. Ray).

http://dx.doi.org/10.1016/j.elspec.2015.11.015
0368-2048/

order to get homogeneity. After that the mixture was placed into a covered alumina crucible and then heated at 1000 °C in air for 10 h. The heating was followed by cooling with a rate of 0.5 °C/min to 850 °C and quenching in air to room temperature. Crystals were separated from the flux by brief treatment in a sonic bath with hot water so that the flux $BaCl_2$ gets dissolved and thrown out during filtering. Shiny, black hexagonal crystals were isolated from the solid residue.

BCCO6 polycrystalline powders were prepared by solid state reaction method by taking stoichiometric quantities of dried $BaCO_3$, Co_3O_4, and $BaCl_2$. At first the precursors were homogeneously ground in a mortar with ethanol and calcined at 900 °C for 10 h in air and then the sample was cooled down to room temperature with 5 K/min cooling rate.

The phase purity of the sample was checked by powder XRD in a Bruker AXS: D8 Advanced diffractometer equipped with Cu K_α radiation. Cl *K*-edge (2.8224 keV) X-ray absorption spectra (XAS) were measured at the Elettra (Trieste, Italy) synchrotron radiation facility (XAFS beamline). In order to have a suitable sample, BCCO6 powders were ground, suspended in toluene and deposited on a millipore membrane by filtration. This procedure provides homogenous sample suitable for collecting XAS spectra in transmission geometry. Measurements were carried out at room temperature where up to three spectra were collected and averaged up in order to improve the data statistics. Data treatment, including background subtraction, normalization and extraction of the structural EXAFS (extended X-ray absorption fine structure) signal $\chi(k)$, was carried out using ESTRA program [13]. The quantitative analysis of the EXAFS spectra was performed by fitting the k^2 weighted experimental spectra $k^2\chi(k)$, to theoretical curve calculated using the standard EXAFS formula [14]. FEFF program [15] was used to calculate theoretical amplitude and phase functions from representative atomic clusters as obtained from the BCCO6 crystallographic structure. The dielectric measurements were carried out in a Quantum design PPMS in Tokyo Institute of Technology, Japan. The magnetization measurements were carried out in a Quantum Design SQUID magnetometer in Chiba University, Japan.

3. Results and discussion

Fig. 1(a) shows the reported structure of BCCO6 while panel (b) shows the powder XRD data from the BCCO6 powders along with the standard data. The standards match well with the experimental XRD pattern of the samples, indicating the sample is single phase. There is no impurity observed within the detection level of XRD.

Experimental EXAFS data and the best fit are shown in Fig. 2(a) and 2(b). The refinement of structural parameters was performed

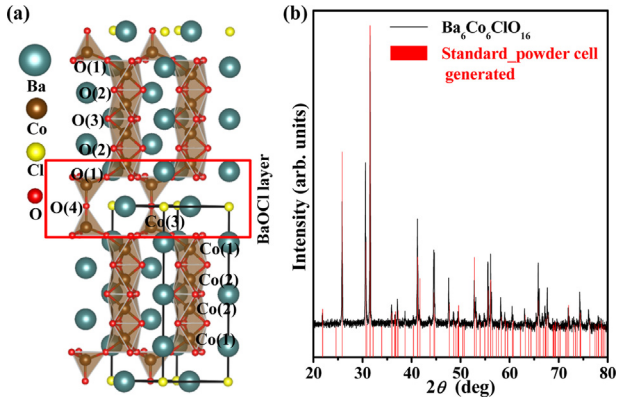

Fig. 1. (a) Crystal structure of BCCO6. (b) Powder XRD from BCCO6 polycrystalline powders along with the standard data.

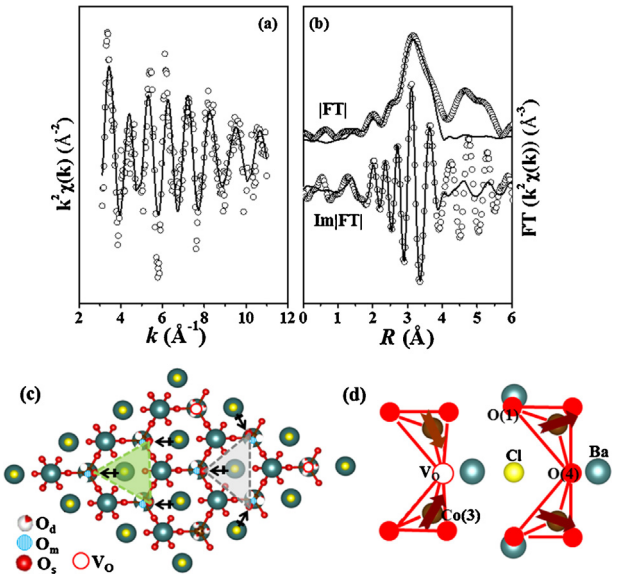

Fig. 2. Experimental (points) and best fit (full line) of (a) k^2 weighted EXAFS data and (b) its Fourier Transform moduli (|FT|) and imaginary part (Im(FT)). (c) Schematics of different defects and their distributions. O_d is the three probable positions of each O(4) atom with 1/3 occupancy according to the crystallographic information [8]. O_m is the mean position of the O(4) atom [1]. O_s is the shifted position of the O(4) atom toward one of the three chlorine atoms surrounding it, each making a closely placed Cl-O(4) pair. V_O denotes the presence of oxygen vacancy at the O(4) site. (d) Co_2O_7 unit with and without a vacancy at the O(4) site. This O(4) vacancy is associated to the distortion of Co(3) atoms: the Co(3) corresponding to the vacancy gets closer to Cl while the others goes away.

Table 1
Results of Cl *K*-edge EXAFS data analysis. The coordination numbers were kept fixed during the refinement.

Shell	*N*	R (Å)	$\sigma^2(\times 10^2$ Å$^2)$
Cl-Ba (apical)	2	2.95 (1)	1.3 (2)
Cl-O(4)$_1$	1	3.00 (5)	1.8 (4)
Cl-O(4)$_2$	2	3.47 (2)	2.3 (2)
Cl-Ba (in plane)	3	3.29 (2)	2.1 (2)
Cl-Co	2	3.44 (2)	1.9 (2)
Cl-Co	4	3.73 (4)	1.9

starting from the Cl local atomic configuration obtained earlier for BCCO5 sample [1]. This structure was obtained from an accurate analysis of polarized Cl *K*-edge XANES spectra collected on a BCCO5 single crystal and confirmed by the analysis of Cl *K*-edge EXAFS spectra on BCCO5 powder sample [1]. In the present case of BCCO6, the coordination numbers were kept fixed during refinement. The best fit structural parameters are summarized in Table 1. The main features of the local atomic structure around Cl in the BCCO6 is definitively similar to the atomic environment found earlier on BCCO5 sample [1]. In particular, the Cl-O distances depict bimodal distribution with a shorter Cl-O (Cl-O(4)$_1$ around 3 Å) and two longer Cl-O (Cl-O(4)$_2$ around 3.5 Å) distances. This creates an isosceles ClO(4)$_3$ triangle in the BaOCl plane (Fig. 2(c)) as has also been observed for the BCCO5 compound [1]. The origin of this local deformation must appear due to the same Co-O(4) covalency effect [1] where large hole concentration on the O(4) atoms makes them effectively positively charged and consequently, each of them moves towards a neighboring Cl^- anion due to pure Coulombic reasons and as a result, a local dipole formation comprising of CoO(4) and Cl (Black arrows in Fig. 2(c)) can be envisaged in the BaOCl plane of BCCO6, just like BCCO5. Interestingly, very similar distribution in Cl-Co distances like in BCCO5 is observed here too (two closer Co atoms (Cl-Co_1 around 3.44 Å) and four further away (Cl-Co_2 around 3.73 Å)), confirming similar local distortions (Fig. 2(d))