Structure and magnetic properties of colossal magnetoresistance compound Tb$_{0.5}$Sr$_{0.5}$CoO$_3$

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Abstract. The structure and the magnetic properties of the doped rare earth cobaltite systems are of recent interest owing to the CMR phenomenon that occur in them. In this paper, we investigate the structure and magnetic properties of Tb$_{0.5}$Sr$_{0.5}$CoO$_3$ solid solution, for the first time, using neutron powder diffraction technique. The sample Tb$_{0.5}$Sr$_{0.5}$CoO$_3$ is found to crystallize in orthorhombic (Pbnm) symmetry. The unit cell volume and Co-O bond length reduce with temperature. The calculated $e_g$ bandwidth obtained from structural parameters turns out to be 0.989 eV. Low temperature neutron diffraction profiles exhibit a magnetic contribution to the fundamental Bragg peaks indicating a ferromagnetic ordering below $T_c$. The results are compared with Co-O-Co bond angles and Co-O bond length of La$_{0.5}$Sr$_{0.5}$CoO$_3$, highlighting the ionic size effects on substitution of Tb ion for La in the compound.

Keywords. Perovskite; ferromagnetism; neutron diffraction.

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1. Introduction

The structural and magnetic properties of $R_{1-x}A_xCoO_3$ ($R$ is rare earth and $A$ is alkaline earth metal) perovskite compounds are of recent interest owing to the phenomenon of colossal magnetoresistance (CMR) that occur in these compounds. The structural and magnetic properties of these compounds are found to be sensitive to the ionic radius of the $R$ ion [1,2]. Substitution of La$^{3+}$ sites with trivalent rare earth ions (Pr$^{3+}$, Nd$^{3+}$, Tb$^{3+}$, Gd$^{3+}$ etc.) is supposed to bring about strong lattice effects and disorder, ultimately influencing the magnetic and transport properties of these compounds. The lattice distortion due to the La-site substitution by $R$ ions influence the FM coupling by changing the Co–O–Co bond angle and Co–O bond length. The competition between the FM double exchange (DE) interactions and AFM superexchange (SE) interactions determines the magnetic ground state of the compound [3,4]. These changes can be understood phenomenologically in terms of tolerance factor $t$ for the perovskite structure explained in terms of the average ionic size $\langle r_R \rangle$ at La site. Due to La site substitution, a decrease in $\langle r_R \rangle$ reduces the transition temperature $T_c$. Within the framework of DE interactions, the effective $e_g$ electron transfer between Co$^{3+}$ and Co$^{4+}$ ions is given by $t_0 \cos(\theta/2)$ where $t_0$ is...
the $e_g$ electron transfer probability when the localized $t_{2g}$ spins are parallel and $\theta$ represents the angle between two neighboring $t_{2g}$ spins. With the reduction in $\langle r_R \rangle$, the Co–O–Co bond angles and $e_g$ electron transfer probability $t_0$ reduce. Thus, La-site substitution is supposed to influence indirectly the magnetic couplings between the Co ions.

However, a detailed study of these features is not available in literature, especially the compounds containing Tb, Gd or Nd ion. In this paper, we report, for the first time, the structure and magnetic behavior of the compound Tb$_{0.5}$Sr$_{0.5}$CoO$_3$ using neutron powder diffraction technique from 300 to 12 K. We replace Tb$^{3+}$ ($\langle r_R \rangle = 1.14$ Å) ion for La$^{3+}$ ($\langle r_R \rangle = 1.25$ Å) ion in the compound to study in detail the $R$-site ionic size effects in the cobaltites.

2. Experimental

Polycrystalline samples were prepared by the standard solid state reaction method. The powders Tb$_4$O$_7$, SrCO$_3$ and Co$_3$O$_4$ were mixed in stoichiometric ratio and the mixture was heated at 1000°C for 56 h. The final sintering of the powder was done at 1150°C for 30 h. The neutron measurements were carried out on the powder diffractometer (T1013) at the Dhruva reactor. The profile analysis for all temperatures was performed using the Rietveld fitting in the Winplotr suite [5].

3. Results and discussion

3.1 Chemical structure

Figures 1a and 1b show the Rietveld refined plots for Tb$_{0.5}$Sr$_{0.5}$CoO$_3$ sample at 300 and 12 K respectively. The sample is found to crystallize in the orthorhombic (Pbnm) symmetry, using the powder neutron diffraction data obtained at room temperature. The Tb/Sr atoms occupy $(x, y, 1/4)$ positions, Co the $(1/2, 0, 0)$ positions, O1 the $(x, y, 1/4)$ positions and O2 the $(x, y, z)$ positions respectively. The diffraction profiles show weak extra lines corresponding to a small amount of Tb$_4$O$_7$ (4.7%) and CoO (3.2%) as impurities. The CoO impurity is understood to form, due to reduction of the Co$^{4+}$ cation, when the solid reaction, in presence of air, takes place, while the observed Tb$_4$O$_7$ impurity is the unreacted component of the starting compound in the reaction. For all the temperatures, these impurity phases were included in the refinements.

The results of the refinement are illustrated in table 1. The unit cell volume is found to reduce at low temperatures. The Co–O1 bond length is also found to decrease at 12 K. This feature is in agreement with the reduction in the lattice strain field that reduces with temperature. The Co–O2–Co bond angle is found to be 168°. It should be noted that the departure of Co–O2–Co bond angle from 180° is indicative of the departure from ideal cubic structure for perovskites. This fact is confirmed from our calculation of tolerance factor $t = d_{\text{Tb-O}} / \sqrt{2d_{\text{Co-O}}}$. We obtain $t = 0.987$ in accordance with values of $t$ for other orthorhombic perovskites [2]. The values obtained for bond lengths and tolerance factor are found to be