

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

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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  $\text{Tb}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  solid solution, for the first time, using neutron powder diffraction technique. The sample  $\text{Tb}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  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  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ , 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  $R_{1-x}A_x\text{CoO}_3$  ( $R$  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  $\text{La}^{3+}$  sites with trivalent rare earth ions ( $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Gd}^{3+}$  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  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  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  $\text{Tb}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  using neutron powder diffraction technique from 300 to 12 K. We replace  $\text{Tb}^{3+}$  ( $\langle r_R \rangle = 1.14 \text{ \AA}$ ) ion for  $\text{La}^{3+}$  ( $\langle r_R \rangle = 1.25 \text{ \AA}$ ) 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  $\text{Tb}_4\text{O}_7$ ,  $\text{SrCO}_3$  and  $\text{Co}_3\text{O}_4$  were mixed in stoichiometric ratio and the mixture was heated at  $1000^\circ\text{C}$  for 56 h. The final sintering of the powder was done at  $1150^\circ\text{C}$  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  $\text{Tb}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  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  $\text{Tb}_4\text{O}_7$  (4.7%) and CoO (3.2%) as impurities. The CoO impurity is understood to form, due to reduction of the  $\text{Co}^{4+}$  cation, when the solid reaction, in presence of air, takes place, while the observed  $\text{Tb}_4\text{O}_7$  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  $168^\circ$ . It should be noted that the departure of Co–O2–Co bond angle from  $180^\circ$  is indicative of the departure from ideal cubic structure for perovskites. This fact is confirmed from our calculation of tolerance factor  $t = d_{\text{Tb-O}}/\sqrt{2}d_{\text{Co-O}}$ . 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

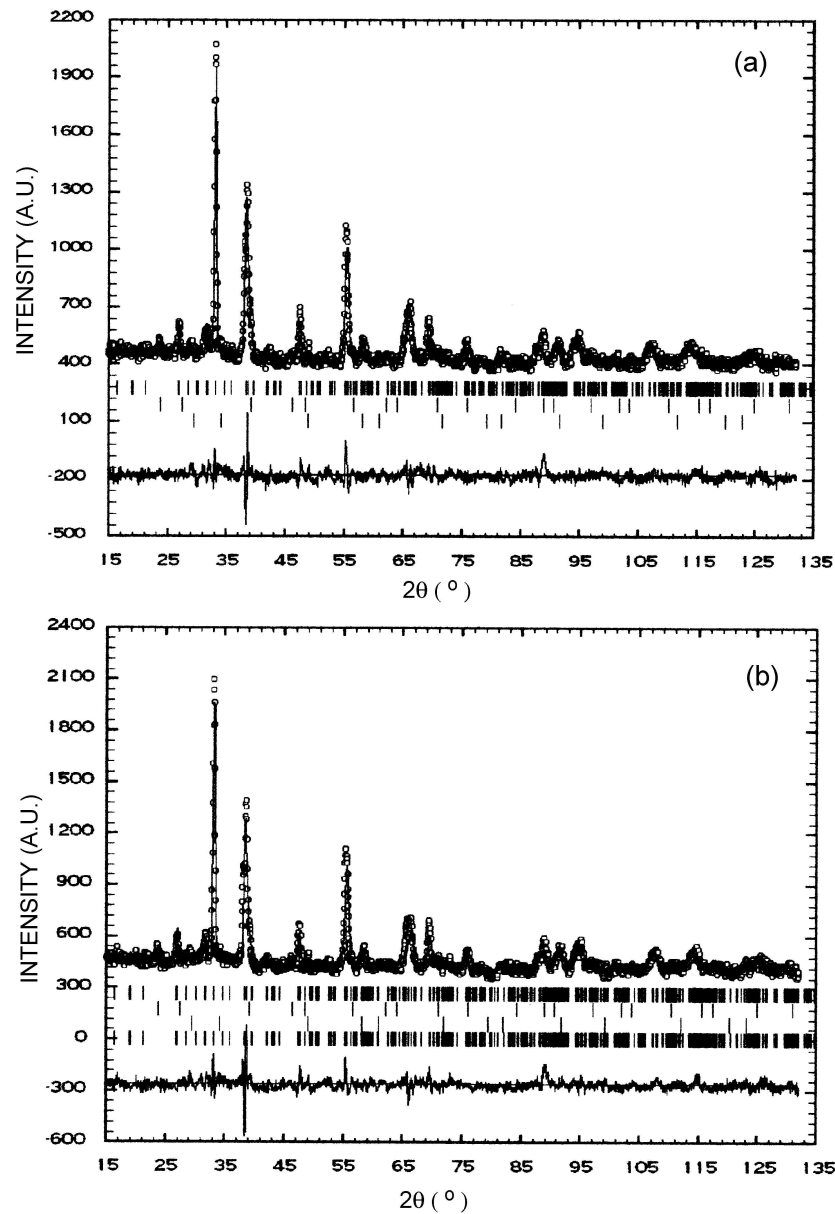


Figure 1. (a) Rietveld refinement of neutron diffraction data at 300 K with minor impurities of  $Tb_4O_7$  and  $CoO$  respectively. (b) Rietveld magnetic refinement of neutron diffraction data at 12 K.

considerably different from that for  $La_{0.5}Sr_{0.5}CoO_3$  with Co–O–Co bond angle of  $171.12^\circ$  and  $t$  value of 0.996 in rhombohedral (R-3c) symmetry [6]. The lowering of symmetry along with considerable changes in bond lengths and  $t$  can be attributed

**Table 1.** Structural and magnetic parameters obtained from Rietveld refinement of  $\text{Tb}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ . The compound occurs in Pbnm space group. The Tb/Sr atoms occupy  $(x, y, 1/4)$  positions, Co occupy  $(1/2, 0, 0)$  positions, O1 occupy  $(x, y, 1/4)$  positions and O2 occupy  $(x, y, z)$  positions respectively. The last column in the table gives the parameters of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  [6] with (R-3c) symmetry for comparison.

Parameters	$T = 300$ K	$T = 12$ K	$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$
$a$ (Å)	5.388(2)	5.375(3)	5.427
$b$ (Å)	5.399(3)	5.381(3)	5.427
$c$ (Å)	7.550(2)	7.536(2)	13.254
$V$ (Å <sup>3</sup> )	219.6(1)	218.0(2)	338.15
Tb/Sr			
$x$	0.001(3)	0.001(4)	–
$y$	–0.005(1)	0.010(3)	–
O1			
$x$	0.929(4)	0.930(2)	0.4776
$y$	0.467(3)	0.512(6)	–
O2			
$x$	0.268(3)	0.267(5)	–
$y$	0.730(2)	0.728(2)	–
$z$	0.015(1)	0.017(1)	–
$B_{\text{Tb/Sr}}$ (Å <sup>2</sup> )	0.21(4)	0.11(6)	0.259
$B_{\text{Co}}$ (Å <sup>2</sup> )	0.13(5)	0.03(1)	0.5
$B_{\text{O1}}$ (Å <sup>2</sup> )	0.68(3)	0.57(1)	0.715
$B_{\text{O2}}$ (Å <sup>2</sup> )	0.96(4)	0.65(6)	–
$\chi^2$	1.49	1.88	–
$N_{\text{Tb/Sr}}$	0.49(1)	0.49(1)	
$N_{\text{Co}}$	1.01(3)	1.00(2)	
$N_{\text{O1}}$	0.94(3)	0.94(2)	
$N_{\text{O2}}$	2.05(3)	2.04(2)	
Co–O (Å)	1.93(9)	1.92(8)	1.9226
Co–O–Co (°)	168.11(3)	168.41(1)	171.12
W (meV)	0.989	0.996	–
$\mu$ ( $\mu_{\text{B}}/\text{Co}$ )	–	1.7(5)	–
$R_{\text{p}}$ (%)	4.39	4.68	8.2
$R_{\text{exp}}$ (%)	4.66	4.59	9.84
$R_{\text{WP}}$ (%)	5.75	6.15	10.5
$R_{\text{mag}}$ (%)	–	27.3	–

to the strong ionic effects arising due to substitution of Tb for La in the compound  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ . We calculated the one-electron  $e_g$  bandwidth from the structural parameters defined as  $W \propto \cos \frac{1}{2}(\pi - \langle \Theta \rangle) / d^{3.5}$ , where  $\langle \Theta \rangle$  is the average Co–O bond angle and  $d$  is the Co–O bond length [7]. The low value of the one-electron  $e_g$  bandwidth is related to  $J_{\text{ex}}$ , the exchange integral. Since  $J_{\text{ex}} \propto T_{\text{c}}$ , which is found to be  $\sim 120$  K [8], we expect a low value for  $W$ .

### 3.2 Magnetic structure

The Rietveld magnetic refinement for the 12 K data was carried out to obtain the ordered magnetic moments. All magnetic reflections can be indexed with the same unit cell as nuclear one. However, CoO is AFM with  $T_N \sim 283$  K, but the weight percentage being only 3.2% does not contribute significantly towards AFM magnetic Bragg peak [9]. It is to be noted that these effects show up collectively at low temperatures as reflected by the high value for  $R_{mag}$ . A significant amount of magnetic intensity enhancement was observed for overlapped (020+200) and (112) peaks. The best fit was obtained taking into account the magnetic moments of  $1.75(2) \mu_B/Co$  ion at 12 K. The obtained value for magnetic moments is also consistent with our magnetization measurements that turns out to be  $1.73 \mu_B/Co$  ion. Magnetization measurements show that the sample undergoes a paramagnetic to a ferromagnetic transition at  $T_c$  around 120 K [8]. However the moment does not saturate even at 12 K over an applied field of 50 kOe. Since  $T_c \propto J$ , the magnetic exchange integral, the reduction in  $T_c$  is suggestive of reduction in  $J$ . Due to this the electron transfer probability  $t_0$  reduces and also the  $e_g$  bandwidth compared to  $La_{0.5}Sr_{0.5}CoO_3$  with  $T_c = 240$  K [5]. Thus, it is evident that the ground state properties are altered considerably in terms of Co–O–Co bond angle, Co–O bond lengths,  $T_c$ ,  $J$  the magnetic exchange integral and  $e_g$  bandwidths leading to a ferromagnetic insulating state on substitution of Tb for La in  $La_{0.5}Sr_{0.5}CoO_3$ .

## 4. Conclusions

We have studied, for the first time, the solid solution  $Tb_{0.5}Sr_{0.5}CoO_3$ , using neutron powder diffraction technique. The sample is found to crystallize in orthorhombic (Pbnm) symmetry. The unit cell volume, Co–O bond length and Co–O–Co bond angles are reduced compared to the parent compound  $La_{0.5}Sr_{0.5}CoO_3$ . Low temperature neutron diffraction profiles exhibit magnetic contribution to the fundamental Bragg peaks indicating a ferromagnetic ordering. The reduction in  $T_c$  compared to the parent compound as found in our magnetization measurements can be attributed to substitution of smaller  $Tb^{3+}$  ion at  $La^{3+}$  site. With the reduction in  $\langle r_R \rangle$ , the Co–O–Co bond angles and  $e_g$  electron transfer probability  $t_0$  reduce leading to a ferromagnetic insulating ground state on substitution of Tb for La in metallic  $La_{0.5}Sr_{0.5}CoO_3$ .

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