Effect of cobalt doping in Nd$_{1-x}$Sr$_x$Mn$_{1-y}$Co$_y$O$_3$

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Abstract. We investigate the effects of Co substitutions associated with magnetic phase changes and the orthorhombic lattice distortions in Nd$_{0.6}$Sr$_{0.4}$Mn$_{1-x}$Co$_x$O$_3$. The effect of Co substitutions on the magnetic state and the orthorhombic lattice distortions has been studied. The orthorhombic distortion is found to be maximum ($7.377 \times 10^{-3}$) for the pure manganite phase and decreases almost linearly with Co doping, reaching its minimum value $1.044 \times 10^{-3}$ for the pure cobaltites. Similar behavior has been found for unit cell volume. Since Co may have several oxidation states, it may also affect the (Mn$^{4+}$/Mn$^{3+}$) ratio, the double magnetic exchange interaction, the magnetic state and metal insulator transition.

1. Introduction

Manganite are perovskite materials that lend itself to several interesting practical applications [1-3]. The rich magnetic phase diagram arising from the interplay between the spin, orbital, charge, and lattice degrees of freedom results in considerable changes in their physical properties, such as magnetoresistance (MR) and magnetocaloric effect (MCE) [4].

Perovskite manganite compounds are represented as R$_{1-x}$M$_x$MnO$_3$, where R is trivalent rare-earth elements (Nd, La, …etc), and M is divalent alkaline earth metal like Sr, Ca, and Ba [5]. Upon cooling below its transition temperature, manganites commonly undergoes two kinds of transitions: electric; metal-insulating, and magnetic transition (FM or AFM) to paramagnetic states depending on the substituted elements and level. Variations of these transitions with substitution is a key idea in exploring their rich phase diagram. Our interest in Nd$_{1-x}$Sr$_x$MnO$_3$ system is mainly due to its possible use in near room temperature magnetic refrigeration [6]. Cobaltites on the other hand, have additional spin and lattice degrees of freedom; namely Co ion may exist in more than one oxidation state with multiple spin state in which Hund’s coupling energy is comparable to the crystal field splitting energy. Hence, it is interesting to study a material that contains manganite and cobaltites, and investigate the transition from one system to the other [7-9]. In this paper, we investigate changes in magnetic states of Nd$_{0.6}$Sr$_{0.4}$MnO$_3$ upon Co substituting at the Mn sites.

2. Experimental Details

One set of Nd$_{0.6}$Sr$_{0.4}$Mn$_{1-x}$Co$_x$O$_3$ ($x= 0, 0.3, 0.7$, and $1$) was prepared using co-precipitation method (see ref. [10] for details) and another set was prepared by standard solid-state reaction. High purity ($4N$ to $5N$) powder of Nd$_2$O$_3$, SrCO$_3$, MnO$_2$, and CoO were used. Stoichiometric ratios of the elements were mixed, grind and pressed into pellets and calcinated in air for 10 hours at 1000 $^\circ$C. Samples were grinded,
pressed and re-annealed at 1000 °C and 1300 °C for another 10 hours at each temperature. The samples were furnace cooled to room temperature.

A homemade ac-susceptometer was fitted in closed cycle refrigerator (Model SHI-4T). Real and imaginary parts of the susceptibility were measured using SR850 Lock-in-amplifier. The temperature was monitored using Lake Shore 336 temperature controller along with LABVIEW software to control all measuring systems. The X-ray powder diffraction patterns were obtain using Rigaku XRD (MiniFlex-600).

3. Results and discussions

3.1. X-ray analyses

XRD-diffraction patterns for Nd_{0.6}Sr_{0.4}Mn_{1-x}Co_{x}O_{3} are presented in figure 1. XRD-patterns were analyzed using Fullprof and Maud software, the goodness of fit \( x \) was in the range 5–6. The crystalline structure of Nd_{0.6}Sr_{0.4}Mn_{1-x}Co_{x}O_{3} is orthorhombic with Pnma-space group (No 62). Traces of non-reacted Nd_{2}O_{3} are found near 30 degrees for samples prepared by solid state reaction. Samples prepared using chemical rout and annealed at lower temperatures (850 °C) did not show traces of non-reacted Nd_{2}O_{3} and were in all subsequent XRD- analyses. All calculated lattice parameters and the unit cell volume are listed in table 1. Data belongs to samples prepared by solid state reaction are marked as (a) in the table 1. The observed variations in the lattice parameters reflects the sensitivity of the lattice parameters to the annealing temperatures and cooling process. The orthorhombic lattice distortion (d) is an important parameter that is correlated with electrical and magnetic properties. The unit cell volume and the \( D \)-values are given in table 1 and plotted in figure 1(b). The lattice distortion and the volume of the unite cell are maximum for the pure manganite sample Nd_{0.6}Sr_{0.4}MnO_{3} and decrease with increasing Co-substitution, reaching their minimum values in the pure cobaltites sample Nd_{0.6}Sr_{0.4}CoO_{3}.

![Figure 1](image1.png)

**Figure 1.** (a) Room temperature XRD-pattern for Nd_{0.6}Sr_{0.4}MnO_{3}. (b) Variations of unit cell volume and the orthorhombic distortion with Co-concentrations.

3.2. AC-susceptibility

The variations of real part of the ac-susceptibility with temperature is presented in figure 2. The figure shows that he pure manganite sample Nd_{0.6}Sr_{0.4}MnO_{3} is ferromagnetic with a wide maximum centered around 180 K, followed by a sharp transition to the paramagnetic state near 260 K. The figure also reveals the presence of another maximum near 45 K, in agreement with previously published data and was attributed to the charge ordered state. The cobaltite Nd_{0.6}Sr_{0.4}CoO_{3} susceptibility reveals a sharp
peak at 190 K. This is reminiscent of the sharp peak often observed in spin glass material and has been confirmed by ZFC and FC susceptibility shown in figure 2(b) [10-12]. The transition temperatures $T_c$ are presented in table 1.

Table 1. Lattice parameters for samples with different Co concentration.

| $x$ | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ ($Å^3$) | $D$ ($×10^{-3}$) | $T_c$ (K) |
|-----|---------|---------|---------|---------|-------------|---------|
| 1.0 | 5.3632(5) | 7.5499(10) | 5.3266(7) | 215.68(5) | 1.044 | 190 |
| 0.7 | 5.4524(5) | 7.6682(6) | 5.4094(6) | 226.17(4) | 2.98 | 147 |
| 0.3 | 5.4605(4) | 7.6944(6) | 5.4035(4) | 227.03(3) | 3.839 | 119 |
| 0.0 | 5.4646(7) | 7.6519(13) | 5.4107(10) | 226.74(6) | 7.377 | 180 |
| 0.0 (a) | 5.4787(5) | 7.6859(8) | 5.4439(7) | 229.24(2) | - | - |

Goodness of fit $\chi = 5 – 6$

4. Conclusion
Cobalt substitutions in Nd$_{0.6}$Sr$_{0.4}$Mn$_{1-x}$Co$_x$O$_3$ dramatically affects its magnetic state and structural properties. The unsubstituted Nd$_{0.6}$Sr$_{0.4}$MnO$_3$ material showed wide superparamagnetic peck near 175 K and sharp drop to paramagnetic phase near 250 K, while the cobaltites Nd$_{0.6}$Sr$_{0.4}$CoO$_3$ showed sharp antiferromagnetic peck near 180 K. Moreover, the orthorhombic distortion is found to decreases almost linearly with Co substitutions, reaching its minimum value the pure cobaltites.

5. Acknowledgments
We would like to acknowledge the help and support provided by King Fahd University of Petroleum and Minerals (FUPM) through funding the project number IN121002.

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