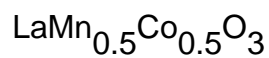


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Unusual charge disproportionation and associated magnetic behaviour in nanocrystalline $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$

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Abstract

Evidence for an unusual double charge disproportionation, $\text{Mn}^{4+} + \text{Co}^{2+} \rightarrow \text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$, is observed in nanocrystalline $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ synthesized by a low-temperature method and annealed in the temperature range 200–1300 °C. The Curie temperature of nanocrystalline $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ is increased from 150 to 230 K when annealed in the temperature range 200–700 °C and is further decreased back to 150 K when annealed in the temperature range 700–1300 °C. This increase and decrease in T_c is found to be associated with the conversion of the spin states of Mn and Co from Mn^{4+} and Co^{2+} to Mn^{3+} and low-spin Co^{3+} , and again back to Mn^{4+} and Co^{2+} as evidenced from x-ray photoelectron spectroscopic studies.

Because of the different structures of LaMnO_3 (orthorhombic) and LaCoO_3 (rhombohedral), two different phases with orthorhombic or rhombohedral structures are possible for $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$. The mixed phase behaviour of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ was first reported by Goodenough *et al* (1961). Two different phases of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$, with different structures (orthorhombic and rhombohedral) and different ferromagnetic transition temperatures, were found to coexist in the samples prepared by the conventional solid state reaction method. From electronic structure calculations of the orthorhombic and rhombohedral forms of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$, Yang *et al* (1999) found that the rhombohedral structure has higher binding energy than the orthorhombic structure. Therefore, it has been concluded that the orthorhombic structure with interlacing doping type, in which each Mn (Co) atom is surrounded by six Co (Mn) neighbours, is the most stable structure for $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$. The ferromagnetic properties of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ have been interpreted earlier by different groups in terms of magnetic superexchange interactions of two different types. Goodenough *et al* (1961) reported that the Co ions are trivalent and in their low-spin diamagnetic states, and therefore $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ superexchange interactions are

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responsible for ferromagnetism. The authors' attempt to make ordered $\text{La}_2\text{Mn}^{4+}\text{Co}^{2+}\text{O}_6$ was not successful and they concluded that the cations favour $\text{La}_2\text{Mn}^{3+}\text{Co}^{3+}\text{O}_6$ where there are no electrostatic forces to induce ordering of the ions on the B sublattice of the double perovskite $\text{A}_2\text{BB}'\text{O}_6$. Later, Blasse (1965) and Jonker (1966) concluded that the transition metal ions are present as Mn^{4+} and Co^{2+} forming an ordered structure and the positive $\text{Mn}^{4+}\text{--O--Co}^{2+}$ superexchange interactions are responsible for ferromagnetism in $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$.

Recently, we have been able to synthesize two different phases of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$, in single-phase forms, by following a low-temperature method of synthesis (Joy *et al* 2000a). It was found that conventional solid state reaction method of synthesis of the oxide always gives a mixed phase because one of the phases, which is stable only at low temperatures, is slowly converted into the other phase at high temperatures. A high- T_c phase ($T_c \approx 230$ K) in single phase form was obtained at 700 °C and a low- T_c phase ($T_c \approx 150$ K) was obtained when heated to 1300 °C. From high temperature magnetic susceptibility (Joy *et al* 2000b) and x-ray photoelectron spectroscopic (Joly *et al* 2001) studies, it was found that the spin states of Mn and Co are Mn^{3+} and low-spin Co^{3+} in the high- T_c phase and Mn^{4+} and Co^{2+} in the low- T_c phase of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$. Mixed phase behaviour was observed for the low-temperature synthesized samples when heated between 700 and 1300 °C or the sample prepared by the conventional solid state reaction method.

In this paper, we report an unusual behaviour of the nanoparticles of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$, processed at very low temperatures. The Curie temperature and electron spectroscopic characteristics of the nanocrystalline material obtained at 200 °C are comparable to that of the low- T_c phase of the compound obtained after heating at 1300 °C, indicating identical spin states of Mn and Co in these two samples as Mn^{4+} and Co^{2+} . This nanocrystalline material obtained at low temperatures is slowly converted to the high- T_c phase of the compound, with spin states of Mn and Co as Mn^{3+} and Co^{3+} , when annealed in the temperature range 200–700 °C. This indicates a double charge disproportionation of the type $\text{Mn}^{4+} + \text{Co}^{2+} \rightarrow \text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$, in $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ annealed in air in the temperature range 200–1300 °C.

The powder sample obtained at ~ 200 °C, following the procedure reported in the literature (Chick *et al* 1990), was annealed in air in the temperature range 200–700 °C at intervals of 100 °C for 12 hours each and furnace cooled to room temperature. The samples annealed at 200, 300, 400, 500, 600, and 700 °C are labelled as LMC200, LMC300, LMC400, LMC500, LMC600 and LMC700, respectively, and the phase obtained after annealing at 1300 °C is labelled as LMC1300. The samples were characterized by powder x-ray diffraction (XRD) using Cu $K\alpha$ radiation, zero field cooled (ZFC) magnetization measurements and x-ray photoelectron spectroscopic (XPS) studies, as reported previously in detail (Joy *et al* 2000a, 2000b, Joly *et al* 2001).

Powder XRD patterns of LMC200, LMC400 and LMC600 are compared with those of the two different single phases of the compound reported earlier, LMC700 and LMC1300 (obtained after heating at 700 and 1300 °C), in figure 1. A perovskite phase is obtained after heating at 200 °C, with a pseudocubic lattice parameter $a \approx 3.90$ Å. All the reflections of LMC200 are weak and extremely broad due to the fine particle nature of the low-temperature synthesized sample. The average particle size is obtained as ~ 15 nm from x-ray line broadening, calculated using the Scherrer formula (Cullity 1978), $t = 0.9\lambda/\beta \cos \theta$. The particle size is found to be independent of annealing temperature below 700 °C. An additional broad reflection is observed at ~ 3.0 Å, in the XRD patterns of samples heated below 500 °C. Additional weak reflections are also observed in the XRD pattern of the sample heated at 1300 °C (LMC1300).

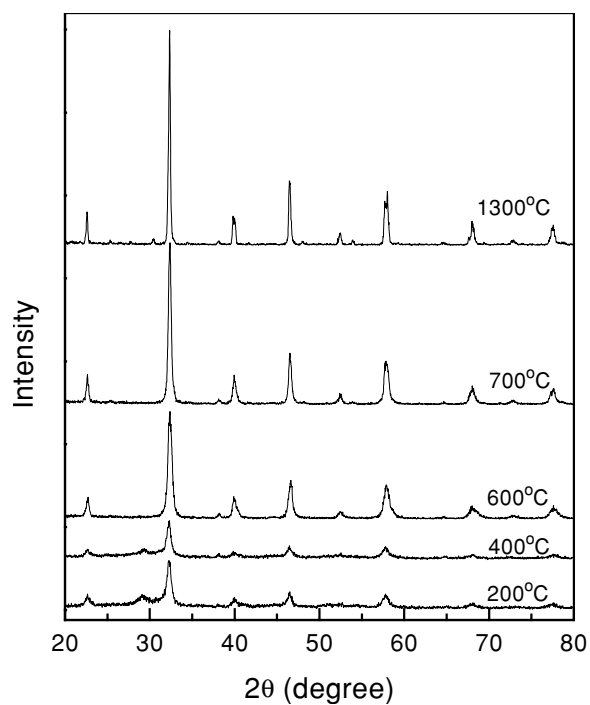


Figure 1. Powder x-ray diffraction patterns of the $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ samples annealed at different temperatures.

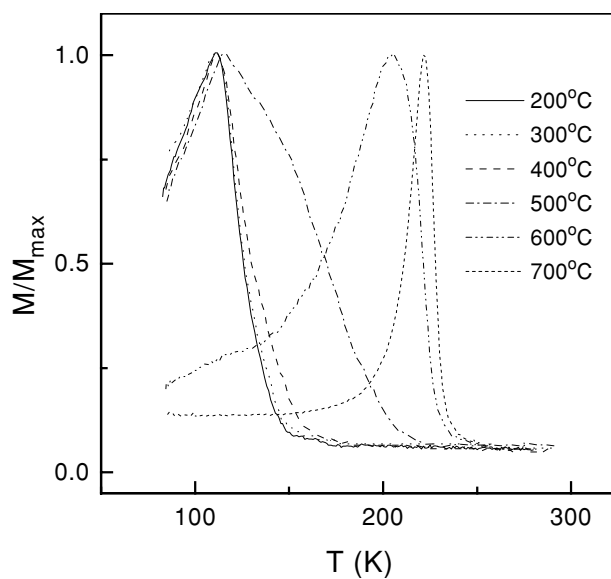


Figure 2. ZFC magnetization curves ($H = 50$ Oe) of the $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ samples annealed in the temperature range 200–700 °C.

The temperature variation of the ZFC magnetization of the samples heated between 200 and 700 °C is compared in figure 2. Identical features are obtained for LMC200 and LMC300;

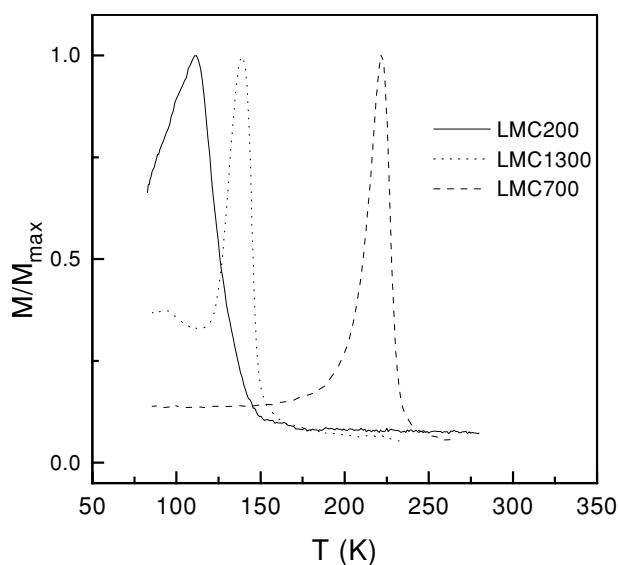


Figure 3. Comparison of the ZFC magnetization curves ($H = 50$ Oe) of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ sample annealed at 200°C (LMC200), 700°C (LMC700; high- T_c phase) and 1300°C (LMC1300; low- T_c phase).

onset of a magnetic transition is observed at ~ 150 K. Though the features of the M_{ZFC} curve of LMC400 are almost identical to that of LMC300, a further broadening of the magnetic transition with a slight increase in the onset of the magnetic transition is observed for this sample. A maximum T_c is obtained as 230 K after heating at 700°C forming the high- T_c phase of the compound as reported previously (Joy *et al* 2000b). The increase in T_c , with increasing annealing temperature between 200 and 700°C , is not due to any particle size effect, as the average particle size was found to be almost constant for samples heated in the temperature range 200 – 700°C . Moreover, the magnetic transition is expected to become sharper, instead of becoming broad, if there is a real effect of increasing particle size. The broadness of the magnetic transition and increase in the magnetic transition temperature may be due to mixed phase behaviour, as observed for samples heated in the temperature range 700 – 1300°C (Joy *et al* 2000a).

The ZFC magnetization curve of LMC200 is compared in figure 3 with those of the two different phases of the compound, LMC700 ($T_c \approx 230$ K) and LMC1300 ($T_c \approx 150$ K), obtained after heating at 700 and 1300°C (Joy *et al* 2000b). LMC200 shows a broad magnetic transition with an initial increase in magnetization from the base line below $T_c \approx 150$ K and a peak in M_{ZFC} at $T_p = 110$ K. Broadness of the magnetic transition and the large difference between T_c and T_p of LMC200 may be ascribed to the superparamagnetic nature of the 15 nm sized particles. Interestingly, the temperature at which the initial increase in magnetization is observed for LMC200 is at the Curie temperature of LMC1300 which is the low- T_c phase of the compound. Earlier high-temperature magnetic susceptibility studies (Joy *et al* 2000b) have indicated that the spin states of Mn and Co are different in the two different phases of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$. A higher $T_c \approx 230$ K is observed for the phase containing Mn^{3+} and low-spin Co^{3+} ions (LMC700, high- T_c phase) and a lower $T_c \approx 150$ K is observed for the phase containing Mn^{4+} and Co^{2+} ions (LMC1300, low- T_c phase). This was further confirmed by core-level XPS studies (Joly *et al* 2001). The identical Curie temperatures

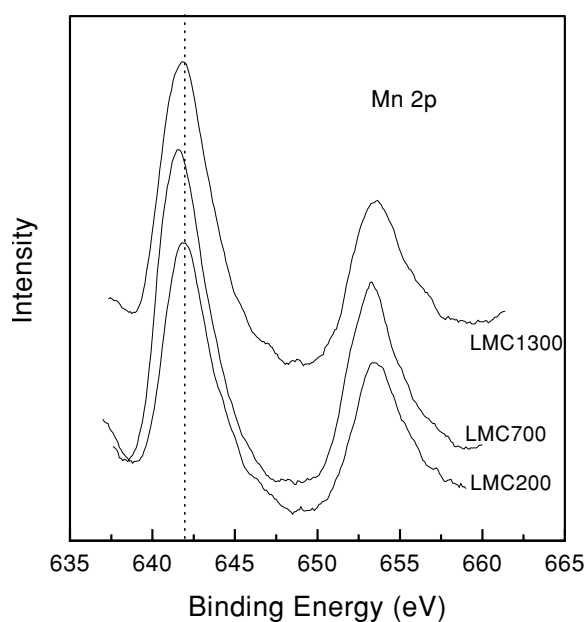


Figure 4. Mn 2p XPS of LMC200, LMC700 and LMC1300.

of LMC200 and LMC1300 are then an indication for the formation of the low- T_c phase of the compound at low temperatures, containing Mn^{4+} and Co^{2+} ions. If this phase is formed initially at low temperatures, then it is converted to the high- T_c phase after heating to 700 °C because of a possible charge disproportionation $\text{Mn}^{4+} + \text{Co}^{2+} \rightarrow \text{Mn}^{3+} + \text{Co}^{3+}$. If this charge disproportionation is completed only after heating at 700 °C, the samples annealed between 300 and 700 °C may contain the two different spin states of Mn and Co and this can explain the broad magnetic transitions of these samples.

Evidence for the identical spin states of Mn and Co in LMC200 and LMC1300 is obtained from core-level XPS studies. The 2p core-level XPS of Mn and Co in $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ are compared in figures 4 and 5 respectively, for LMC200, LMC700 and LMC1300. The Mn and Co $2p_{3/2}$ peaks are observed at 641.9 and 780.1 eV respectively, for both LMC200 and LMC1300 whereas these peaks are observed at lower binding energies for LMC700. As reported previously in detail (Joly *et al* 2001) the Mn and Co $2p_{3/2}$ binding energies were found to be different for the two different phases of the compound obtained after heating at 700 °C (LMC700) and 1300 °C (LMC1300). The Mn $2p_{3/2}$ peaks were observed at 641.6 and 641.9 eV respectively, in the high- T_c and low- T_c phases of the compound, indicating different spin states of Mn. Similarly, the Co $2p_{3/2}$ peaks were observed at 779.6 and 780.1 eV respectively, indicating different spin states of Co in the high- T_c and low- T_c phases of the compound. Results from both XPS and high-temperature susceptibility studies gave evidence for the spin states of Mn and Co as Mn^{3+} and low-spin Co^{3+} in LMC700 ($T_c \approx 230$ K) and as Mn^{4+} and Co^{2+} in LMC1300 ($T_c \approx 150$ K). The identical XPS binding energies of LMC200 and LMC1300 then indicate that the spin states of Mn and Co are identical in the samples processed at very low temperatures (200 °C) and at very high temperatures (1300 °C). This then explains why the magnetic transition temperatures are almost identical for LMC200 and LMC1300, ignoring the relatively broader magnetic transition of LMC200 which is due to the superparamagnetic behaviour of the sample.

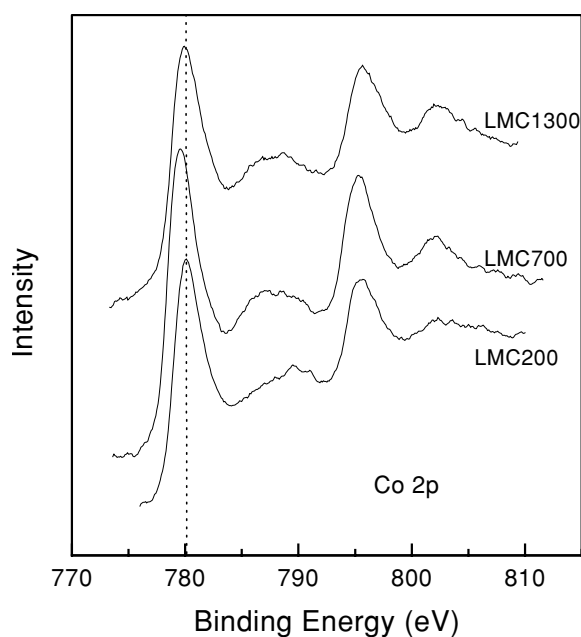


Figure 5. Co 2p XPS of LMC200, LMC700 and LMC1300.

It is not possible to identify the exact crystal symmetry of LMC200 because of the broadness of the powder XRD peaks of the samples heated at low temperatures. However, the sample heated to 1300 °C (LMC1300) has the orthorhombic structure (Joy *et al* 2000a). Since the magnetic transition temperatures, and the XPS binding energies are identical for LMC200 and LMC1300, it is possible that both LMC200 and LMC1300 may have identical structures. If this is true, it can be assumed that the orthorhombic structure of the compound is more stable than the rhombohedral structure, as concluded by Yang *et al* (1999) from electronic structure calculations. If LMC200 contains Mn^{4+} and Co^{2+} , then there is a possible charge disproportionation of the type $\text{Mn}^{4+} + \text{Co}^{2+} \rightarrow \text{Mn}^{3+} + \text{Co}^{3+}$, which gives rise to the formation of the high- T_c phase after heating at 700 °C, and again another charge disproportionation which is exactly the reverse of the first one, $\text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$, giving rise to the formation of the low- T_c phase after heating at 1300 °C. The weak additional reflections observed in the powder XRD patterns of LMC200 and LMC1300 may be due to superlattice reflections, as reported for $\text{La}_2\text{MnFeO}_6$ (Ueda *et al* 2001) because of the ordering of Mn^{4+} and Co^{2+} in the lattice due to their differing charges and ionic sizes. This weak reflection disappears after heating the sample above 400 °C which may be due to the disruption in the ordering due to the onset of charge disproportionation $\text{Mn}^{4+} + \text{Co}^{2+} \rightarrow \text{Mn}^{3+} + \text{Co}^{3+}$ above this temperature. The increase in the magnetic ordering temperature as the sample is heated above 400 °C may be an evidence for this charge disproportionation because higher T_c is obtained for the phase having $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ superexchange interactions.

The driving force for the double charge disproportionation $\text{Mn}^{4+} + \text{Co}^{2+} \rightarrow \text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$ forming a high- T_c phase from a low- T_c phase and then again the low- T_c phase from the high- T_c phase, when heated in the temperature range 200–1300 °C, is not clear at present. Mixed phase behaviour is observed for samples heated between 300–700 °C and 700–1300 °C, indicating that complete charge disproportionation is achieved after heating

at 700 and 1300 °C. It was found that the low- T_c phase of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$, obtained after annealing at 1300 °C (LMC1300), is not susceptible to any phase change when the sample is further annealed at 700 °C. This indicates that the charge disproportionation $\text{Mn}^{4+} + \text{Co}^{2+} \rightarrow \text{Mn}^{3+} + \text{Co}^{3+}$ is not a thermally activated phenomenon taking place at 700 °C when annealed in air and the orthorhombic phase of the compound obtained at 1300 °C, containing Mn^{4+} and Co^{2+} , is a stable phase. The initial charge disproportionation from $\text{Mn}^{4+} + \text{Co}^{2+}$ to $\text{Mn}^{3+} + \text{Co}^{3+}$, when heated between 200–700 °C, may therefore, be due to the nanoparticle nature of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ obtained at low temperatures and this needs further detailed investigations.

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