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**Synthesis and Characterization of  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{M}_{0.5}\text{O}_{4-\delta}$  (M=Fe, Mn)****H. El Shinawi<sup>1</sup>, J. F. Marco<sup>3</sup>, F. J. Berry<sup>1,2</sup> and C. Greaves<sup>1</sup>**<sup>1</sup> *School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK*<sup>2</sup> *Department of Chemistry, The Open University, Milton Keynes MK7 6AA, UK*<sup>3</sup> *Instituto de Quimica-Fisica "Rocasolano", Consejo Superior de Investigaciones Cientificas, Serrano 119, 28006 Madrid, Spain*

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## Abstract

The  $M^{4+}$ -containing  $K_2NiF_4$ -type phases  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  have been synthesized by a sol-gel procedure and characterized by X-ray powder diffraction, thermal analysis, neutron powder diffraction and Mössbauer spectroscopy. Oxide ion vacancies are created in these materials via reduction of  $M^{4+}$  to  $M^{3+}$  and of  $Co^{3+}$  to  $Co^{2+}$ . The vacancies are confined to the equatorial planes of the  $K_2NiF_4$ -type structure. A partial reduction of  $Mn^{3+}$  to  $Mn^{2+}$  also occurs to achieve the oxygen stoichiometry in  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.6}$ .  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$  contains  $Co^{2+}$  and  $Fe^{3+}$  ions which interact antiferromagnetically and result in noncollinear magnetic order consistent with the tetragonal symmetry. Competing ferromagnetic and antiferromagnetic interactions in  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$ ,  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.6}$  induce spin glass properties in these phases.

**Keywords:** Ruddlesden-Popper, oxygen-deficient, neutron powder diffraction, Mossbauer spectroscopy, magnetic order.

## Introduction

The recent interest in oxides with a  $K_2NiF_4$ -type structure is, in part, associated with their importance as models for understanding physical properties such as superconductivity and magnetoresistance. Additionally,  $K_2NiF_4$ -type phases such as  $La_2NiO_{4+\delta}$  have recently attracted considerable interest as alternative materials for solid oxide fuel cells due to their interesting transport properties [1,2]. As  $n=1$  members of the Ruddlesden-Popper phases, the  $K_2NiF_4$ -type oxides have shown an enhanced stability under reducing conditions due to their ability to accommodate a wide range of coordination environments and oxidation states. Ruddlesden-Popper phases such as  $Sr_3Fe_2O_{7-\delta}$  [3] and  $Sr_{3-x}La_xFe_{2-y}Co_yO_{7-\delta}$  [4] have shown a high degree of structural stability in reducing environments at elevated temperature and reasonably good transport properties making them possible candidates for oxygen separation membranes and solid oxide fuel cells. We have previously shown that  $LaSrCo_{0.5}Fe_{0.5}O_4$  is able to withstand reducing condition (10%  $H_2/N_2$ ) up to 1000°C via reduction of  $Co^{3+}$  into  $Co^{2+}$  and formation of  $LaSrCo_{0.5}Fe_{0.5}O_{3.75}$  [5]. The oxide ion vacancies were disordered and distributed within the equatorial planes of the structure. In an attempt to characterize  $M^{4+}$ -containing phases, we have now synthesized the materials  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  as precursors to phases with higher degrees of oxygen deficiency and structural stability under reducing conditions. In particular, we show here that  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  is able to sustain an oxygen content as low as  $O_{3.6}$  with retention of crystal symmetry when heated in 10%  $H_2/N_2$  at 1000°C. We present in this work the synthesis and characterization of  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  and of their reduced forms  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.6}$ .

## Experimental

The materials  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$  and  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  were synthesized by a sol-gel procedure. Stoichiometric amounts of  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Fe}(\text{CH}_3\text{COO})_2/\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  were dissolved in acetic acid and boiled under reflux for 3h. Small amounts of hydrogen peroxide and water were added and the mixture was further refluxed overnight to obtain a clear solution. This solution was evaporated to a dark red gel in the case of  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$  and a dark violet gel in the case of  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$ . The gel was dried and decomposed in air at  $400^\circ\text{C}$  and the resulting powder pressed into pellets and calcined in flowing oxygen at  $1350^\circ\text{C}$  for 18h. The oxygen deficient materials ( $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$  and  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$ ) were obtained by reducing the as-prepared materials in flowing 10%  $\text{H}_2/\text{N}_2$  for 12 h at 700 and  $1000^\circ\text{C}$ , respectively.

X-ray powder diffraction (XRD) data were collected using a Siemens D5000 diffractometer in transmission mode, employing  $\text{CuK}\alpha_1$  radiation from a germanium monochromator. Thermogravimetric analysis was performed using a Rheometric Scientific STA 1500 thermal analyzer where samples (~30 mg) were reduced at  $10^\circ\text{C}/\text{min}$  in 10%  $\text{H}_2/\text{N}_2$ . Neutron powder diffraction (NPD) data were collected at room temperature and 1.5 K on the HRPT diffractometer at SINQ, PSI using wavelengths of 1.8852 Å and 1.4942 Å. Rietveld refinements were performed on the powder diffraction data using the GSAS suite of programs [6] employing a pseudo-Voigt profile function. A correction for preferred orientation along the [001] direction was allowed in the refinement. Magnetic data were collected using a Quantum Design MPMS SQUID magnetometer in the temperature range 5–300 K. Zero-field-cooled (ZFC) and field-cooled (FC) data were collected on warming using an applied field of 0.5 T. The ac susceptibility was measured by varying the frequency from 30 Hz to 1 kHz with the field amplitude of 3 Oe.  $^{57}\text{Fe}$  Mössbauer spectra were recorded at 298 and 16K in constant acceleration mode using a ca.25 mCi  $^{57}\text{Co}/\text{Rh}$  source and a helium closed-cycle cryorefrigerator. All the spectra were computer fitted and the chemical isomer shift data are quoted relative to metallic iron at room temperature.

## Results

**Structural Characterization:** XRD patterns showed the as-prepared and the reduced materials to be single-phase with no evidence of starting materials or product impurities. The patterns were indexed on a body-centred tetragonal unit cell related to a  $K_2NiF_4$ -type structure (Figure 1). Structural refinements of the XRD data were performed employing the ideal tetragonal  $I4/mmm$  space group; however, as expected for X-ray diffraction data from materials of this type, the refinements were insensitive to oxide ion site occupancy. Oxide ion sites were therefore fixed at full occupancy in all samples and the refined unit cell parameters are given in Table 1.

The reduction behaviour of the as-prepared materials was followed by thermogravimetric measurements in which the materials were heated ( $10^\circ\text{C}/\text{min}$ ) in flowing 10%  $H_2/N_2$  (Figure 2). The measurements suggest that, assuming the as-prepared materials are stoichiometric in oxygen, the reduced materials at  $700^\circ\text{C}$  have very similar oxygen contents:  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.65}$ .  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$  undergoes slight decomposition due to separation of  $La_2O_3$  (as indicated by XRD) at  $T > 800^\circ\text{C}$ ; however,  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  undergoes further reduction as the temperature increases and reaches the stoichiometry  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.6}$  at  $1000^\circ\text{C}$ .

NPD data were collected from the reduced materials ( $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$  reduced at  $700^\circ\text{C}$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  reduced at  $1000^\circ\text{C}$ ) at room temperature to confirm oxygen stoichiometries suggested by TG analysis and to determine the oxide ion vacancy distribution in these materials. Rietveld profile refinements of the NPD data were performed adopting the  $I4/mmm$  space group. Profile fits and difference patterns are shown in Figure 3; structural data and some selected bond lengths are given in Table 2 and Table 3 respectively.

The NPD data were in good agreement with the TG results showing the overall stoichiometries of the reduced materials as  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.67}$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.60}$ . The results are therefore consistent with the view that the as-prepared materials are stoichiometric in oxygen, and the oxygen-deficient materials are, within experimental error,  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.6}$ .

Refinements showed no evidence of symmetry lowering due to cation or vacancy order. The scattering length contrast in Co/Mn and Co/Fe is such that ordering would have been easily detected [7]. The oxide ion vacancies created in these materials are confined to the equatorial planes of the  $K_2NiF_4$  -type structure. Attempts to refine a model in which oxide ion vacancies were distributed between axial and equatorial positions in a manner similar to  $NdSrCuO_{3.56}$  [8] proved unstable. A displacement of equatorial oxygens (O1) in the  $xy$  plane was also observed, which transforms the oxide ion at  $(0.5,0,0)$  to the split position  $(0.5,y,0)$ . The retention of the tetragonal

symmetry under reduction with an equatorial distribution of oxide ion vacancies has been observed in related  $K_2NiF_4$ -type phases such as  $LaSrCoO_{3.5+x}$  [9] and  $La_{1+x}Sr_{1-x}Co_{0.5}Fe_{0.5}O_{4-\delta}$  [5].

**Mössbauer spectroscopy:** The  $^{57}Fe$  Mössbauer spectra recorded from  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$  are shown in Figure 4-a. The  $^{57}Fe$  Mössbauer parameters are collected in Table 4. The spectrum recorded at 298 K was best fitted to two quadrupole split absorptions. The doublet with chemical isomer shift  $\delta=0.30$  mm s $^{-1}$  is characteristic of  $Fe^{3+}$ . The magnitude of the quadrupole splitting,  $\Delta=0.83$  mm s $^{-1}$ , would indicate a distortion of the octahedral array of oxygen ions around iron. The chemical isomer shift of the other doublet,  $\delta=0.28$  mm s $^{-1}$ , is intermediate between that characteristic of  $Fe^{3+}$  and  $Fe^{4+}$  and, given the oxygen stoichiometry, we associate this with charge sharing between neighbouring  $Fe^{3+}$  and  $Fe^{4+}$  ions with a timescale smaller than  $10^{-8}$ s.

The spectrum recorded at 16K was characterised by a complex broad lined magnetic hyperfine pattern which was best fitted to two discrete sextets ( $H=45.4$  and  $41.1$ T) and a distribution of magnetic hyperfine fields ( $H=33.9$ T). The large quadrupole interactions associated with the discrete sextets are indicative of a distorted octahedral array of oxygen around iron and is consistent with the large quadrupole splitting observed at 298K for the  $Fe^{3+}$  component. We would associate the overall complexity of the spectrum with the occurrence of complex magnetic interactions between  $Fe^{3+}$ ,  $Fe^{4+}$ ,  $Co^{3+}$  and  $Co^{4+}$ .

The  $^{57}Fe$  Mössbauer spectra recorded from  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$  are shown in Figure 4-b. The spectrum recorded at 298K was composed of a single doublet with chemical isomer shift  $\delta=0.31$  mms $^{-1}$  characteristic of  $Fe^{3+}$ . The large quadrupole splitting ( $\Delta=1.43$  mms $^{-1}$ ) is indicative of the  $Fe^{3+}$  ion being located in less than six-fold coordination. The spectrum recorded at 16K showed a single magnetic hyperfine pattern with parameters (Table 4) compatible with this situation.

**Magnetic Characterization:** The variation of magnetic susceptibility with temperature for the different samples is shown in Figure 5. The as-prepared materials generally showed higher magnetization than the reduced ones, with a paramagnetic enhancement of susceptibility at low temperatures. A distinct divergence between ZFC and FC susceptibilities is indicative of spin glass behaviour. As shown in the inset of Figure 5-a, the susceptibility of  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$  shows a well defined maximum at 195°C, indicating antiferromagnetic (AFM) ordering in this material. NPD data collected from this material at 1.5 K were used to confirm magnetic order at this temperature. A series of additional Bragg reflections, compared with the data sets collected at room temperature, were clearly observed in the low temperature data (see Figure 6). The low temperature diffraction data showed no evidence of symmetry lowering from tetragonal to orthorhombic, and the magnetic reflections were indexed on a primitive tetragonal cell with lattice parameters  $a'=\sqrt{2}a$

and  $c'=c$ . A strong magnetic peak at  $2\theta\sim 20^\circ$  (see Figure 6), which corresponds to the (100) reflection of the magnetic supercell, indicates the ferromagnetic component of the moments to be perpendicular to the  $\langle 100 \rangle$  directions, and is therefore consistent with noncollinear magnetic order [9,10] previously reported, for example, for  $\text{La}_{1+x}\text{Sr}_{1-x}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{4-\delta}$  [5] (Figure 7). The profile fit and structural results of the Rietveld analysis of the low temperature NPD data are shown in Figure 6 and Table 5 respectively. No evidence of long-range AFM ordering was observed in the low temperature data recorded from  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$ . The low temperature NPD data confirmed the absence of long-range magnetic order in the manganese-containing samples.

Plots of inverse susceptibility against temperature for the materials studied are shown in Figure 8. For  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$ , the limited temperature range above  $T_N$  precluded any fitting of the data; however, for  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$ , the behaviour is close to Curie-Weiss in nature with  $\theta = -24$  K and  $\mu_{\text{eff}}=3.06 \mu_B$ . For  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$ , the  $1/\chi$  versus T plot shows an increased gradient at low temperature which is consistent with magnetic frustration [11]. The application of the Curie-Weiss law for  $T > 200$  K gives an effective moment of  $5.06 \mu_B$  and  $\theta = -174$  K, consistent with predominantly AFM interactions. Data for  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  with  $T > 200$  K imply  $\mu_{\text{eff}}=4.79 \mu_B$  and  $\theta=81$  K, suggesting mainly ferromagnetic (FM) interactions.



## Discussion

The overall stoichiometries of the materials were determined by NPD and TG analyses as  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$ ,  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  and  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$ ,  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$  for as-prepared and reduced materials, respectively. Mössbauer spectroscopy confirmed that iron exists in  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$  as  $\text{Fe}^{3+}$  which suggests the divalent state of cobalt ( $\text{Co}^{2+}$ ) in this material. This material shows long-range AFM magnetic ordering below 195K which can be readily explained by the presence of  $\text{Co}^{2+}$  ( $t_{eg}^5 e_g^2$ ) and  $\text{Fe}^{3+}$  ( $t_{eg}^3 e_g^2$ ), for which AFM exchange is expected for all  $180^\circ$  superexchange interactions. The magnetic order has been investigated by low temperature NPD and the ordering scheme shown in Figure 7 used to account for coupling between  $\text{Fe}^{3+}/\text{Co}^{2+}$  spins. The model suggests a refined moment of 3.33(5)  $\mu_B$  for  $\text{Fe}^{3+}/\text{Co}^{2+}$ , where an average form factor of  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  was used. The moment is lower than the expected moments for a mixture of high spin  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  due to covalence, the low dimensionality of the magnetic order and quantum mechanical effects. Similar effects have been observed previously in  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{4-\delta}$  [5].

$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$ , on the other hand, exhibits near Curie-Weiss behaviour with a negative  $\theta$  value which indicates AFM interactions. The material contains a mixture of  $\text{M}^{3+}$  and  $\text{M}^{4+}$  ions; the oxygen stoichiometry suggests the presence of, ca. 20%  $\text{M}^{4+}$  which is not inconsistent with Mössbauer data which implies the presence of some  $\text{Co}^{4+}$  in this material.  $\text{Co}^{3+}$ - $\text{Fe}^{3+}$  magnetic interactions have been shown in related materials [5] to be ferromagnetic with  $\text{Co}^{3+}$  in the low-spin state. The relatively low moment calculated from the Curie-Weiss law (3.06  $\mu_B$ ) also suggests a low-spin state of  $\text{Co}^{3+}$  in  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$ . The complexity of the Mössbauer data of this material at 16 K is consistent with a spin glass state at this temperature (see Figure 5) and is indicative of complex magnetic interactions between  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Fe}^{4+}$  and  $\text{Co}^{4+}$ .

The oxygen stoichiometry in  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  suggests a combination of oxidation states ( $\text{Co}^{3+}/\text{Mn}^{3+}+\text{M}^{4+}$ ) or ( $\text{Co}^{2+}/\text{Mn}^{4+}+\text{Co}^{3+}$ ), although the latter is chemically unlikely. However, in the three-dimensional perovskite  $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  [12], an ordered  $\text{Co}^{2+}/\text{Mn}^{4+}$  state is reported. No cation order is observed in  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  and the oxidation state combination ( $\text{Co}^{3+}/\text{Mn}^{3+}+\text{M}^{4+}$ ) is preferred, with 20% of the ions being  $\text{M}^{4+}$  as suggested by the oxygen stoichiometry. The reduction behaviour of this material (see Figure 2) suggests reduction of  $\text{M}^{4+}$  to  $\text{M}^{3+}$  followed by reduction of  $\text{Co}^{3+}$  into  $\text{Co}^{2+}$  to reach the stoichiometry  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.65}$  at  $700^\circ\text{C}$ . Karen et al [13] have suggested that the  $\text{Co}^{2+}/\text{Mn}^{3+}$  state is more electrochemically favoured than the  $\text{Co}^{3+}/\text{Mn}^{2+}$  state, which supports the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  rather than reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$ . This behaviour is also consistent with the behaviour of cobalt in iron-containing systems [5]. Further slow reduction as temperature increases suggests partial reduction of  $\text{Mn}^{3+}$  into

$\text{Mn}^{2+}$  in  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$ ; the oxygen stoichiometry suggests that 20% of  $\text{Mn}^{3+}$  is reduced to  $\text{Mn}^{2+}$ .  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$  is a spin glass antiferromagnet. This behaviour can be attributed to competing FM and AFM interactions between high-spin  $\text{Co}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$ . The effective moment observed at  $T > 200\text{K}$  ( $5.06 \mu_{\text{B}}$ ) is in good agreement with the theoretical spin-only value corresponding to high-spin  $\text{Co}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ( $5.01 \mu_{\text{B}}$ ). It is likely that competing FM and AFM interactions account for the spin glass state observed in case of  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  which may correspond to competing AFM and FM interactions between  $\text{Co}^{3+}$ ,  $\text{Mn}^{3+}$  and  $\text{M}^{4+}$  ions. The uncertain nature of the cation oxidation states makes it difficult to interpret the observed effective magnetic moment of  $4.79 \mu_{\text{B}}$ .

The spin glass behaviour has been confirmed by ac magnetic susceptibility measurements. The frequency dependence of the ac magnetic susceptibility of  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$ , for example, is shown in Figure 9. The data clearly show that the location of the cusp at the freezing temperature is dependent of the frequency of the ac susceptibility measurement which is a characteristic feature of spin glasses.

TG and NPD data indicate that  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  withstands reducing conditions (10%  $\text{H}_2/\text{N}_2$ ) up to  $1000^\circ\text{C}$  with retention of structural stability and crystal symmetry. Large oxygen nonstoichiometry along with the structural stability at high temperature in reducing environments suggests a possible use for this material in applications such as oxygen separation membranes.

The reduced materials are formed via deintercalation of oxygen from the equatorial sites of the  $\text{K}_2\text{NiF}_4$ -type structure. Oxygen stoichiometries in these materials suggest the formation of unusual  $\text{MO}_x$  coordination polyhedra with  $x < 6$ . All polyhedra exhibit elongation parallel to the  $c$  axis ( $\text{M-O}_2/\text{M-O}_1 = 1.14$  for both samples). These results are consistent with the large quadrupole splitting ( $\Delta = 1.43 \text{ mms}^{-1}$ ) observed in the Mössbauer spectrum recorded from  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$ . It might be worth mentioning that formation of oxygen-deficient compounds have been commonly observed in Co-containing perovskite-type materials with layered structure [5,9,14-16], and a variety of unusual geometries with coordination number less than six have been assigned to B-site ions in these systems.

Under reduction, an expansion in  $c$  occurs as a result of  $\text{MO}_x$  expansion due to reduction of low-spin  $\text{Co}^{3+}$  to high-spin  $\text{Co}^{2+}$ . However,  $\text{MO}_x$  expansion in the  $xy$  plane is inhibited by a contraction in the La/Sr coordination sphere due to lowering of the coordination number ( $< 9$ ), this usually results in freezing or contraction in  $a$  [5,9] (see Table 1). This effect explains the observed displacement of equatorial oxygen O1 in the  $xy$  plane in order to maintain M-O1 bond lengths. The displacement moves oxygen atoms from the ideal sites (0.5,0,0) to (0.5,y,0) sites, with  $y$  being dependent on the degree of oxygen deficiency. This is clearly observed here, where the  $y$  value is

0.061(1) and 0.0543(8) for  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$  and  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$  as compared with 0.0333(7) and 0.0509(6) for  $\text{La}_{1.2}\text{Sr}_{0.8}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.85}$  and  $\text{LaSrCo}_{0.5}\text{Fe}_{0.5}\text{O}_{3.75}$  [5].

Accepted manuscript

## Conclusions

The  $M^{4+}$ -containing  $K_2NiF_4$ -type phases  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_4$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_4$  have been synthesized by a sol-gel technique. The materials are stoichiometric in oxygen and exhibit spin glass behaviour at low temperature due to competing FM and AFM interactions. Under reduction, the oxidation states  $Co^{2+}/Fe^{3+}$  and  $Co^{2+}/Mn^{3+}(Mn^{2+})$  were produced in  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$  and  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.6}$  respectively. Oxide ion vacancies are distributed within the equatorial planes of the structure with an associated twisting of  $MO_x$  polyhedra around the  $z$  axis.  $Co^{2+}$  and  $Fe^{3+}$  ions couple antiferromagnetically in  $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$  with a tetragonal noncollinear order of magnetic moments. A ferromagnetic component of interaction due to the presence of  $Mn^{3+}$  in  $La_{0.8}Sr_{1.2}Co_{0.5}Mn_{0.5}O_{3.6}$  results in a spin glass state in this material.

## Acknowledgements

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## References

- [1] S. J. Skinner, J. A. Kilner, *Solid State Ionics* **135** (2000) 709–712.
- [2] V. V. Vashook, H. Ullman, O. P. Olshevskaya, V. P. Kulik, V. E. Lukashevich, L. V. Kokhanovskii, *Solid State Ionics* **138** (2000) 99–104.
- [3] S. E. Dann, M. T. Weller, D. B. Currie, *J. Solid State Chem.* **97** (1992) 179–185.
- [4] F. Prado, T. Armstrong, A. Caneiro, A. Manthiram, *J. Electrochem. Soc.* **148** (2001) J7–J14.
- [5] H. El Shinawi, C. Greaves, *J. Solid State Chem.* **181** (2008) 2705–2712.
- [6] A. C. Larson and R.B. Von Dreele, General Structural Analysis System, Los Alamos National Laboratory, Los Alamos, NM, 1994.
- [7] V. K. Sears, *Neutron News* **3** (1992) 29.
- [8] P. H. Labbe, M. Ledesert, V. Caignaert, B. Raveau, *J. Solid State Chem.* **91** (1991) 362–369.
- [9] M. A. Hayward, M. J. Rosseinsky, *Chem. Mater.* **12** (2000) 2182–2195.
- [10] A. L. Hector, C.S. Knee, A.I. MacDonald, D.J. Price, M.T. Weller, *J. Mater. Chem.* **15** (2005) 3093–3103.
- [11] K. V. Rao, M. Fahnle, E. Figueroa, O. Beckman, L. Hedman, *Phys. Rev. B* **27** (1983) 3104–3107.
- [12] C. L. Bull, D. Gleeson, K. S. Knight, *J. Phys.: Condens. Matter* **15** (2003) 4927–4936.
- [13] P. Karen, E. Suard, F. Fauth, P. M. Woodward, *Solid State Sciences* **6** (2004) 1195–1204.
- [14] J. M. Hill, B. Dabrowski, J. F. Mitchell, J. D. Jorgensen, *Phys. Rev. B* **74** (2006) 174417.
- [15] Y. Bréard, C. Michel, M. Hervieu, F. Studer, A. Maignan, B. B. Raveau, *Chem. Mater.* **14** (2002) 3128–3135.
- [16] A. Bowman, M. Allix, D. Pelloquin, M. J. Rosseinsky, *J. Am. Chem. Soc.* **128** (2006) 12606–12607.

Table 1 XRD refined parameters for different samples

Material	$a$ (Å)	$c$ (Å)
$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$	3.82509(4)	12.5598(2)
$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$	3.77148(9)	12.9725(4)
$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$	3.83073(7)	12.5124(3)
$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$	3.77928(3)	12.9802(1)

Table 2 Structural results for the refinement of the NPD data collected from reduced samples at room temperature.

Atom	$x$	$y$	$z$	100×Uiso (Å <sup>2</sup> )	Occupancy	Site Symmetry
<b><math>\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}</math>, Space Group <math>I4/mmm</math></b>						
Co/Fe	0	0	0	0.81(7)	0.5/0.5	2a
La/Sr	0	0	0.3551(1)	0.95(5)	0.4/0.6	4e
O1	0.5	0.061(1)	0	1.19(1)	0.417(3)	8j
O2	0	0	0.1675(2)	2.14(6)	1	4e
$a = 3.7981(1)$ Å; $c = 13.0515(5)$ Å $wRp = 0.059$ ; $Rp = 0.0467$ ; $\chi^2 = 1.4$						
<b><math>\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}</math>, Space Group <math>I4/mmm</math></b>						
Co/Fe	0	0	0	0.5(3)	0.5/0.5	2a
La/Sr	0	0	0.35634(9)	1.68(3)	0.4/0.6	4e
O1	0.5	0.0543(8)	0	1.46(8)	0.400(3)	8j
O2	0	0	0.1674(1)	2.97(5)	1	4e
$a = 3.79614(6)$ Å; $c = 13.0116(3)$ Å $wRp = 0.052$ ; $Rp = 0.0412$ ; $\chi^2 = 1.39$						

Table 3 Selected bond lengths (Å) for the refined phases.

Bond	$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$	$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$
Co/M–O1*	1.9132(5)	1.9092(3)
Co/M–O2	2.187(2)	2.178(2)
La/Sr–O1*	2.520(3)	2.521(2)
	2.849(3)	2.815(2)
La/Sr–O2	2.448(3)	2.459(2)
	2.7019(3)	2.7019(2)

\*Splitting of O1 sites gives twice the number of bonds compared with the ideal site.

Table 4  $^{57}\text{Fe}$  Mossbauer parameters

Material	Temperature of measurement	$\delta \pm 0.04$ (mms $^{-1}$ )	$\Delta$ or $e^2Q_q/2 \pm 0.04$ (mms $^{-1}$ )	$H \pm 0.05$ (T)	Area $\pm 3\%$
$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$	298	0.30	0.83		45
		0.28	0.38		55
	16	0.42	-0.32	45.4	22
		0.44	-0.26	41.1	28
		0.41	-0.14	33.9	50
$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$	298	0.31	1.43		100
	16	0.44	-0.64	50.1	100

Table 5 Structural results for the refinement of the NPD data collected from  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$  at 1.5K

Atom	x	y	z	100 x Uiso ( $\text{\AA}^2$ )	Occupancy	Site Symmetry	Bond	Bond Length ( $\text{\AA}$ )
$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$ : Space Groups $I4/mmm$ (Nuclear) and $P4_2/mn'm$ (Magnetic)								
Co/Fe	0	0	0	0.85(9)	0.5	2a	Co/Mn-O1*	1.9108(5)
La/Sr	0	0	0.3556(1)	0.89(7)	0.6	4e	Co/Mn-O2	2.171(2)
O1	0.5	0.064(1)	0	1.02(1)	0.415(4)	8j	La/Sr-O1*	2.503(3)
O2	0	0	0.1668(2)	1.87(7)	1	4e		2.847(3)
			$a = 3.79067(5) \text{\AA}$ ; $c = 13.0133(2) \text{\AA}$				La/Sr-O2	2.456(3)
								2.6962(3)
Atom	x	y	z	$M_x/\mu_B$	$M_y/\mu_B$	$M_z/\mu_B$	$ M /\mu_B$	
Co/Fe	0	0	0	2.35(4)	2.35(4)	0	3.33(5)	
wRp = 0.0366; Rp = 0.0289; $\chi^2 = 1.715$								

\*Splitting of O1 sites gives twice the number of bonds compared with the ideal site.

## Figure Captions

**Figure 1.** Crystal structure of  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{M}_{0.5}\text{O}_{4(-\delta)}$ .

**Figure 2.** TG data for the reduction of as-prepared materials using 10%  $\text{H}_2$  in  $\text{N}_2$

**Figure 3.** Observed, calculated and difference plots for the Rietveld profile refinement of NPD data collected from the reduced samples at room temperature.

**Figure 4.**  $^{57}\text{Fe}$  Mössbauer spectra recorded from  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$  and  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$  at 298 and 16 K.

**Figure 5.** Variation of magnetic susceptibility (ZFC and FC) with temperature.

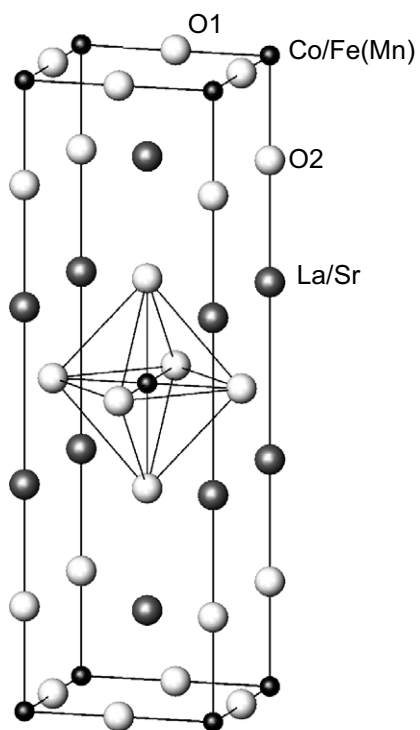
**Figure 6.** Observed, calculated and difference NPD profiles collected at 1.5 K from  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$  showing nuclear (lower tick marks) and magnetic (upper tick marks) reflections.

**Figure 7.** Magnetic structure of  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$ . Only Co/Fe atoms are shown. The arrows indicate the direction of Co/Fe magnetic moments.

**Figure 8.** Variation of the inverse magnetic susceptibilities (ZFC) with temperature.

**Figure 9.** Plot of real component ( $\chi'$ ) of ac susceptibility versus temperature for  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$ .



**Fig. 1**

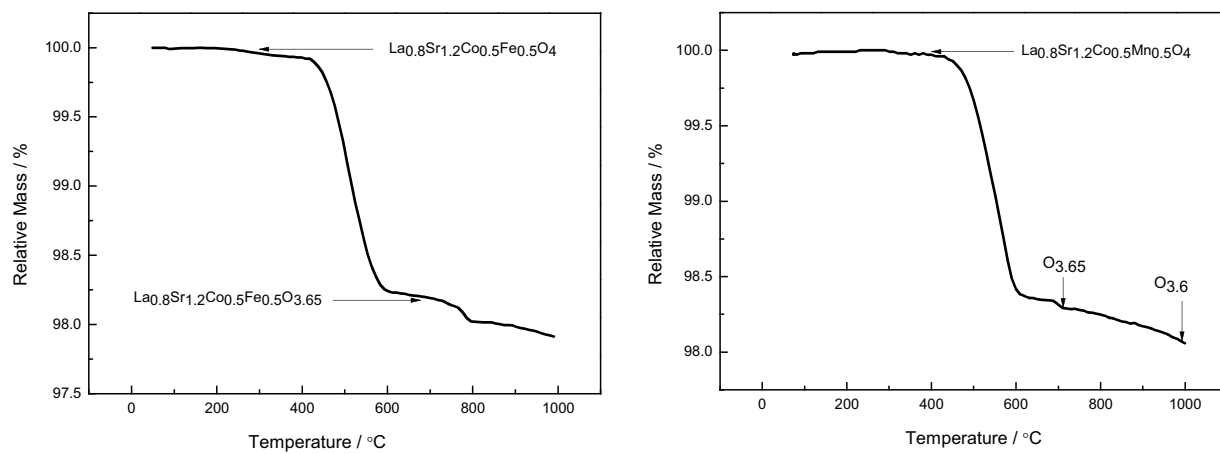


Fig. 2

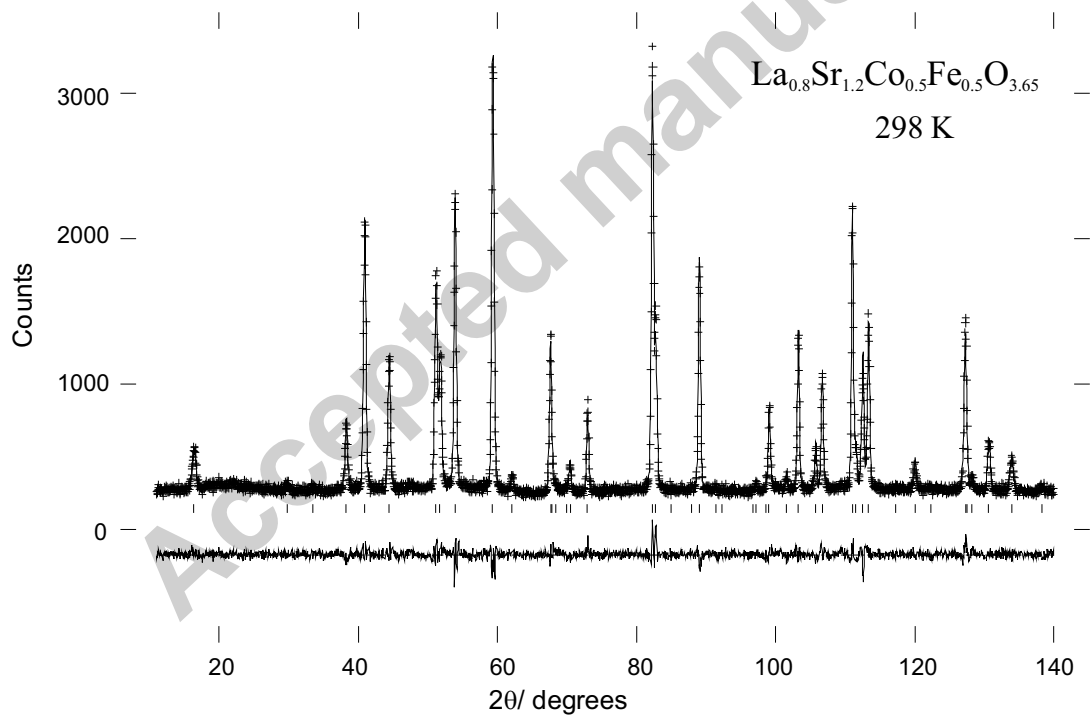


Fig. 3-a

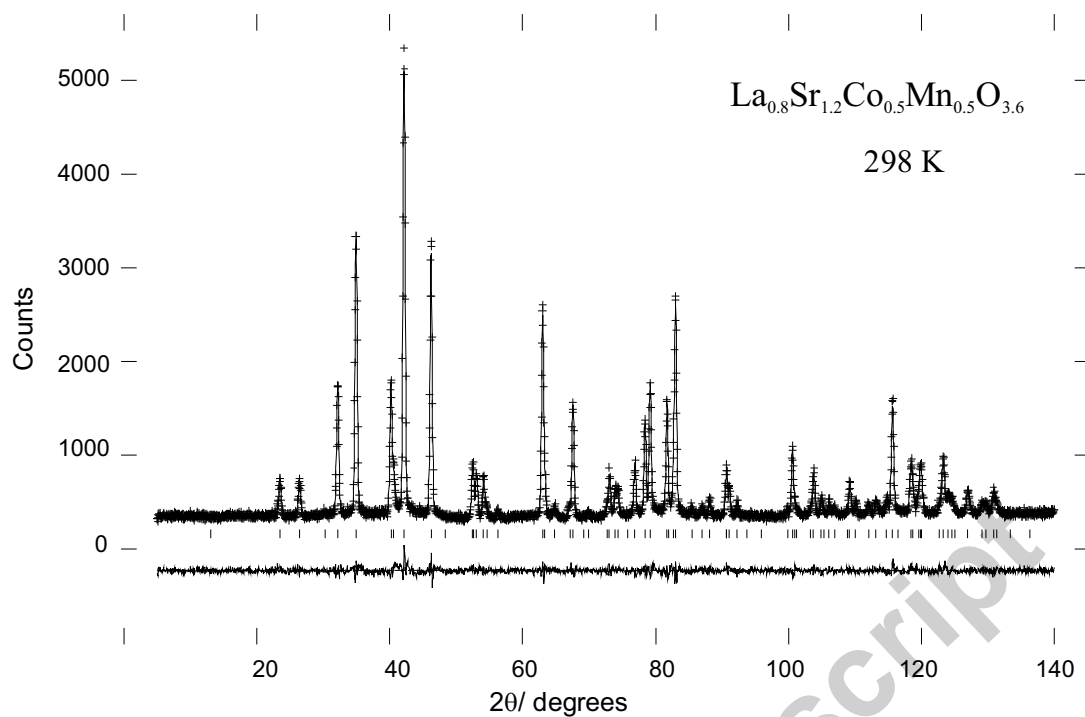


Fig. 3-b

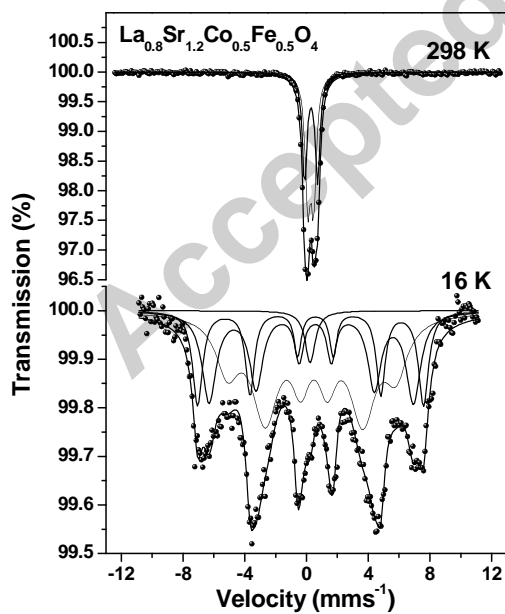


Fig. 4-a

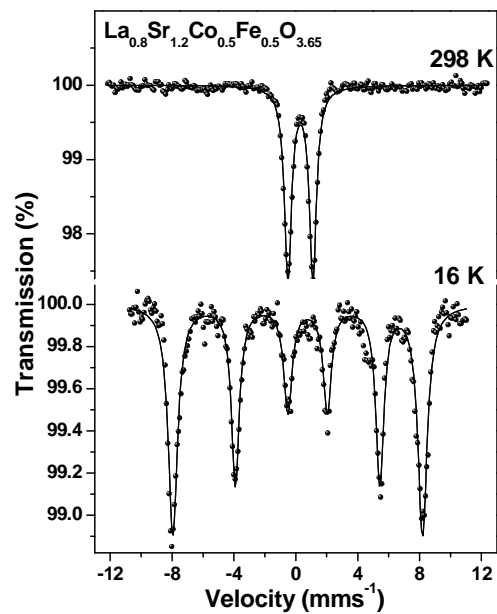


Fig. 4-b

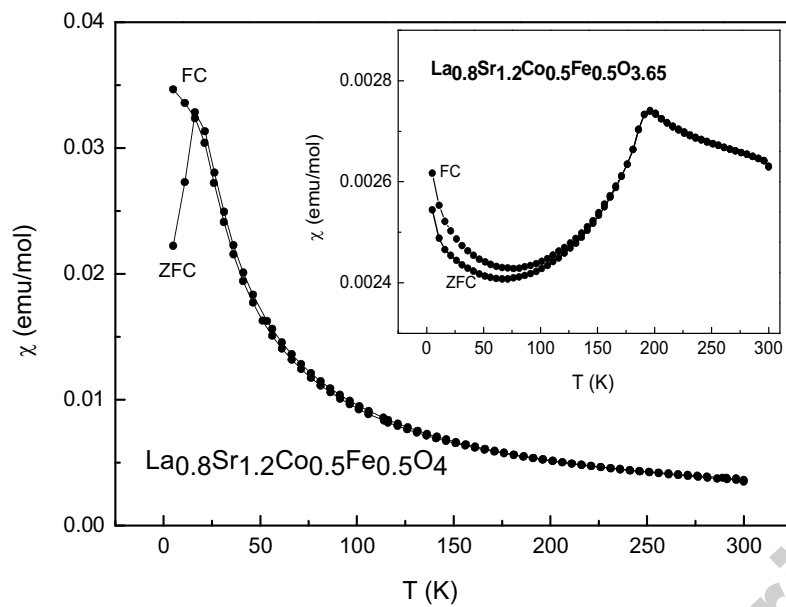


Fig. 5-a

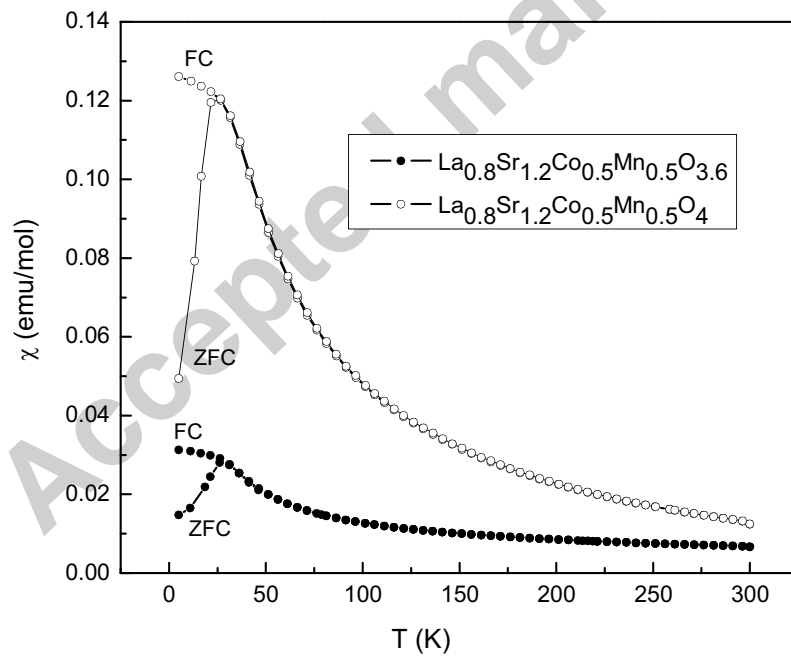


Fig. 5-b

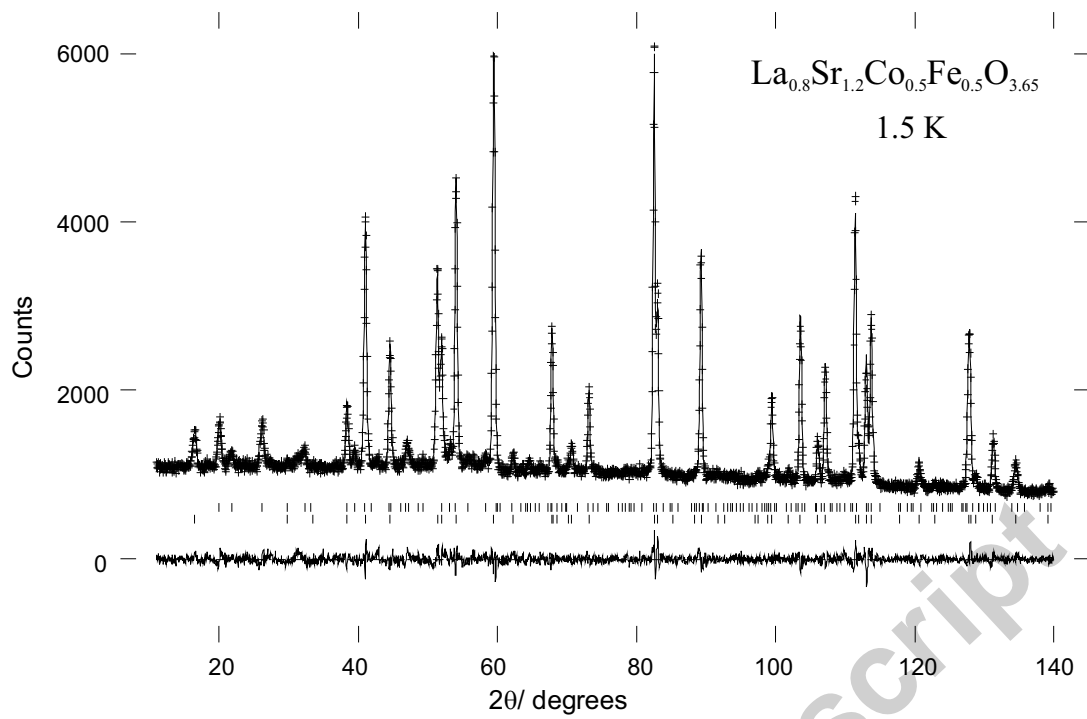


Fig. 6

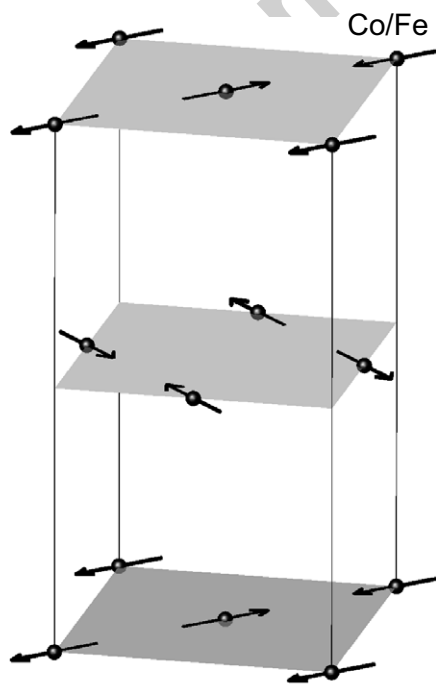


Fig. 7

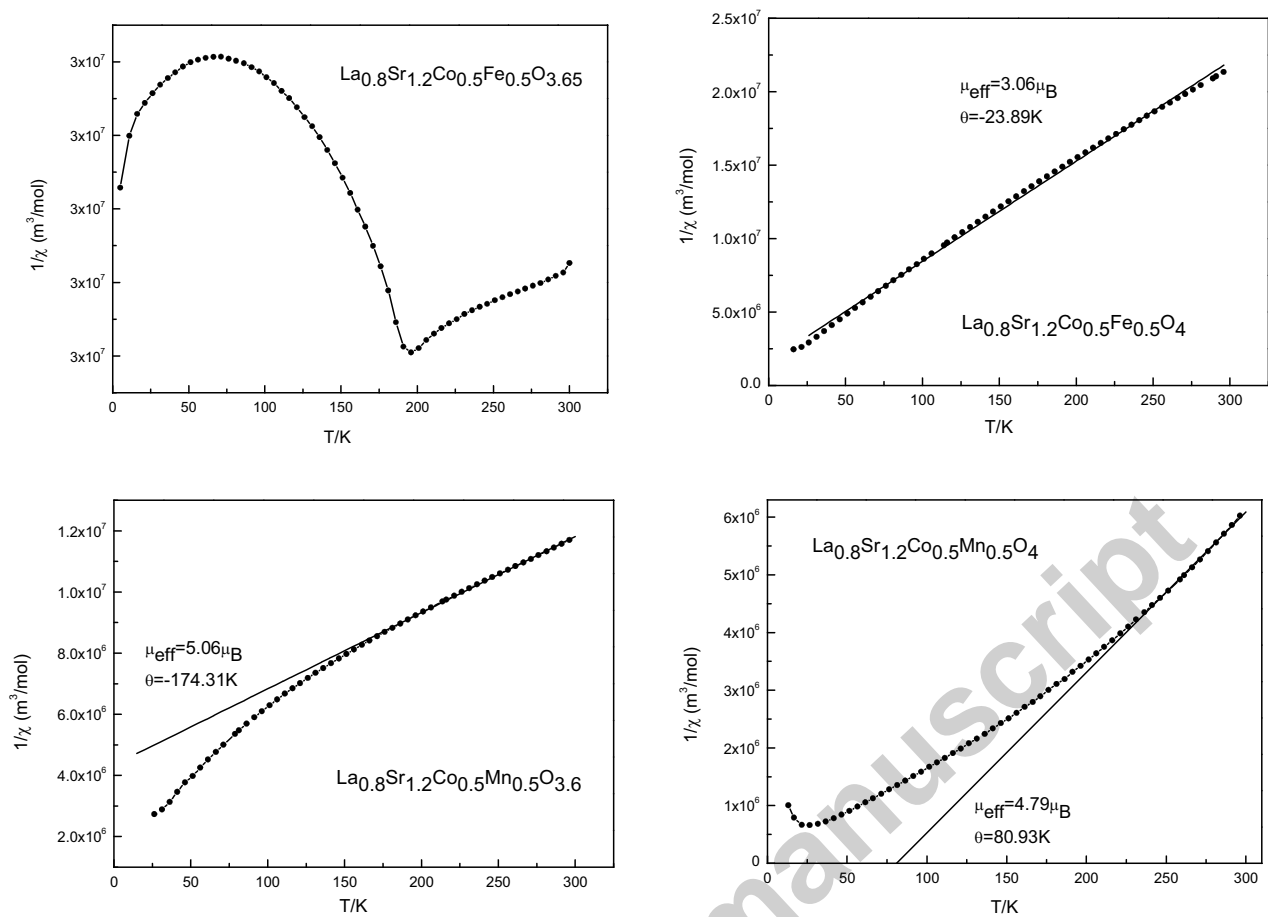


Fig. 8

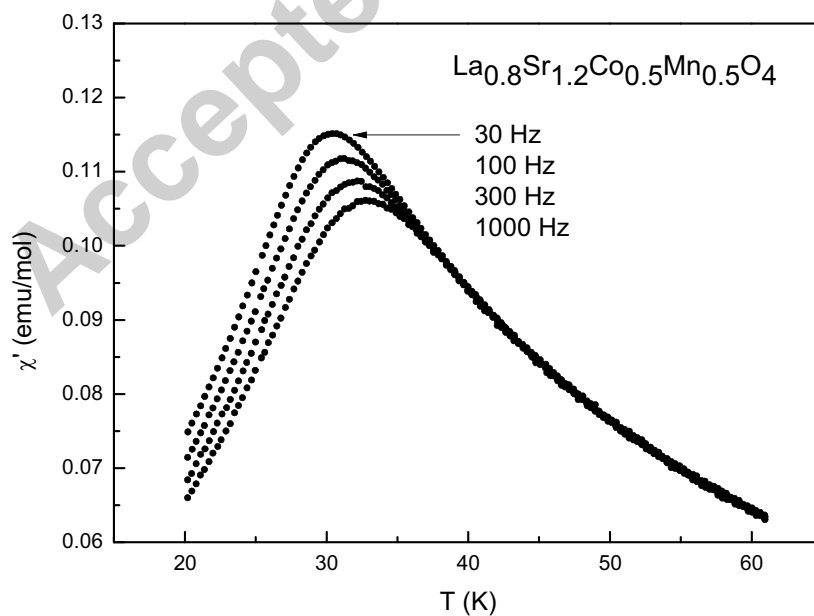


Fig. 9

## Graphical Abstract

### Synthesis and Characterization of $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{M}_{0.5}\text{O}_{4-\delta}$ (M=Fe, Mn)

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$\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$  and  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  have been synthesized by a sol-gel procedure and characterized by diffraction techniques, thermal analysis, and Mössbauer spectroscopy. Oxide ion vacancies, created via reduction are located in the equatorial planes of the  $\text{K}_2\text{NiF}_4$ -type structure.  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.65}$  shows antiferromagnetic, noncollinear magnetic order, whereas competing ferromagnetic and antiferromagnetic interactions in  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_4$ ,  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_4$  and  $\text{La}_{0.8}\text{Sr}_{1.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3.6}$  induce spin glass behaviour.

