

# A brief review on the effect of preparation conditions on magnetic properties of some $A_2MMnO_6$ ( $A = La, Eu$ and $Y$ ; $M = Mg, Co, Ni$ ) type perovskites

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**Abstract.** In this article, structural and magnetic properties of a number of  $A_2MMnO_6$  ( $A = La, Eu$  and  $Y$ ;  $M = Mg, Co, Ni$ ) type perovskites prepared under different oxygen partial pressure are compared. The results indicated that both structure and magnetic properties of such materials are sensitive to preparation conditions, which in general is governed by the nature of transition metal ions as well as rare-earth ions. It was also pointed out that even though the deviation in structure is only marginal, they affect appreciably to their magnetic properties.

**Keywords.** Perovskite; crystal structure; magnetic materials; X-ray diffraction.

## 1. Introduction

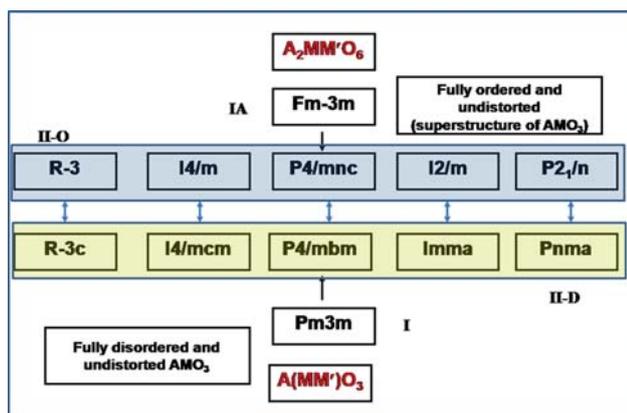
Materials with perovskite type structures truly represent a family of multifunctional materials as they possess diversified physical properties ranging from dielectric, ferroelectric, ferro-/antiferromagnetic as well as electronic/ionic conduction. The origin of the functional properties of perovskites is related to their structure, local distortion, nature and electronic configuration of the ions forming them. In addition, the flexibility of composition and structural arrangement in perovskites render amenability to induce functionality for desired applications. Thus, the perovskite structures are considered as the basis for designing new materials with desired functional properties. For several important functional properties like multiferroic and magnetodielectric properties, the  $AMO_3$  ( $A =$  rare-earth,  $M =$  transition metal ions like Fe, Mn, Cr, etc.) and  $A_2MM'O_6$  ( $R =$  rare-earth or alkaline earth ions;  $M$  and  $M' = 3d$  transition metal ions) type perovskites have drawn significant attention.<sup>1-7</sup> In particular, the  $A_2MM'O_6$  type manganates have been extensively investigated for long time due to their interesting magnetic properties, while the studies got impetus after the discovery of large magnetodielectric

coupling in  $La_2CoMnO_6$  near ambient temperature ( $\sim 280$  K).<sup>5,8-11</sup> These properties are inherently related to the degree of cation ordering, distortion/strain and defects in the structure. Hence they are often found to be sensitive to the methods of preparation. This aspect of the perovskite structure is also useful for tuning their magnetic and/or electrical properties.

In general the cation ordered  $A_2MM'O_6$  type cubic perovskites have aristotype (space group  $Fm\bar{3}m$ ) structure where the undistorted and un-tilted  $MO_6$  and  $M'O_6$  octahedral units are orderly arranged and thus they form super structure of parent  $AMO_3$  type ( $Pm\bar{3}m$ ) perovskite. However, depending on the nature of octahedral units, extent of defects, and external thermodynamic influences like temperature or pressure, they crystallize in various lower symmetric structures.<sup>12-16</sup> But all such structures are closely related to the parent undistorted  $Fm\bar{3}m$  structure. Crystal structure and symmetry of a large number of  $A_2MM'O_6$  type perovskites and their relation with the undistorted cation ordered structures have been reported in the literatures.<sup>15,16</sup>

In the interest of this report, a partial map for the structural relations in perovskite type materials is shown in Figure 1. In brief it can be mentioned here that distortion and tilting of octahedral units can transform the cubic structure to lower symmetric

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**Figure 1.** Partial structure map of perovskite type compounds. The fully disordered octahedral site ions are represented by lower half (I, II-D) rows, and fully cation ordered structures are represented by upper half (IA, II-O) rows. The transitions among these symmetries are order-disorder while transitions within rows are due to tilting and distortion in octahedral units.

structures like monoclinic, orthorhombic, tetragonal, rhombohedral, etc. (II-O of Figure 1), while the addition of disordering of octahedral cations increases the symmetries (II-D of Figure 1). Also the transitions between these lattices are expected by alteration of compositions as well as by the influence of external temperature and/or pressure, and such structural changes are commonly observed in  $A_2MM'O_6$  type perovskites.<sup>13,15,16</sup>

Since the properties of  $A_2MM'O_6$  type materials are dependent on the oxidation states of cations and degree of ordering as well as defects, they become sensitive to the preparation conditions, and that makes a way to tune their functional properties. In the recent years, magnetic and dielectric properties of a number of  $A_2MM'O_6$  (where A = lanthanide ions and M and/or M' = transition metal ion) type materials prepared under different oxygen partial pressures have been investigated, and the sensitivity of these properties to feeble oxygen defects are explained by us.<sup>17–20</sup> Such perovskite type materials have been investigated for long time in the interest of their unusual and tunable magnetic properties.<sup>8,9,21–28</sup> As an example, perovskite type  $\text{LaMnO}_3$  and  $\text{LaNiO}_3$  respectively exhibit anti-ferromagnetic and paramagnetic properties,<sup>27,28</sup> while the cation ordered  $\text{La}_2\text{NiMnO}_6$  shows ferromagnetic properties. The  $\text{Ni}^{2+}\text{-O-Mn}^{4+}$  and  $\text{Ni}^{3+}\text{-O-Mn}^{3+}$  super-exchange interactions have been assigned for the ferromagnetic behavior of  $\text{La}_2\text{NiMnO}_6$ .<sup>5,8,9</sup> Similarly, it is also known that  $\text{LaCoO}_3$  exhibits complex magnetic properties due to the structural transition associated with low spin and high spin  $\text{Co}^{3+}$  ions.<sup>29</sup> However, the combination of  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$

shows a ferromagnetic ordering due to the  $\text{Co}^{2+}\text{-O-Mn}^{4+}$  and  $\text{Co}^{3+}\text{-O-Mn}^{3+}$  super-exchange interactions. Also the coexistences of multiple oxidation states of the transition metal ions are often observed in such compounds.<sup>30–32</sup> Thus the degree of cation ordering and oxidation states of the transition metal ions govern the magnetic and electrical properties of such materials. It may also be noted that the small difference in redox potentials of the transition metal ion pairs causes the coexistence of multiple oxidation state cations and they play crucial role for the properties of  $\text{Ln}_2\text{MM}'\text{O}_6$  perovskites. Hence, the adopted preparation conditions become important for their properties.

In this article we have presented a brief overview on the effect of preparation conditions on the structure and magnetic properties of some  $\text{Ln}_2\text{MM}'\text{O}_6$  type double perovskite type materials. Several rare-earth manganates with  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Y}^{3+}$  as  $\text{Ln}^{3+}$  ion and  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$  as second octahedral (M) ions have been prepared and the role of preparation conditions on their structure and magnetic properties was concluded from the comparative studies. The prepared compounds cover the cases of cation ordered monoclinic and rhombohedral, and disordered orthorhombic perovskites. All the samples were prepared by gel-combustion followed by high temperature reactions. The specific preparation details are reported earlier in the literatures.<sup>17–20</sup> As an example of typical procedure of gel combustion process, the preparation of  $\text{La}_2\text{CoMnO}_6$  is mentioned here. Initially clear nitrate solutions of metal ions were prepared by dissolving  $\text{La}_2\text{O}_3$ ,  $\text{MnCO}_3$  and  $\text{CoCO}_3$  in nitric acid. Desired amount of glycine was added to this solution and then heated on a hot plate to prepare a clear solution. On further heating, the solution transformed to a highly viscous liquids and then auto-ignited to a flame-producing homogenous powder. The powder was calcined at 923 K for 2 h and pelletized. The pellets of calcined powder were heated at 1523 K for 48 h followed by cooling to room temperature at a rate of 1 K/min. The sintered pellets of the samples were then annealed in static air, flowing oxygen and argon atmosphere at 1123 K for 8 h with heating and cooling rate of 1 K/min. The adopted annealing procedure is aimed to prevent the cation diffusion but can introduce minor oxygen defects and/or alternation in oxidations states. All other materials were prepared by closely similar procedures. The structural studies on the prepared materials were carried out by using X-ray diffraction (XRD) method and the magnetic properties were investigated using a squid (superconducting quantum interference device) magnetometer. The effect of defects on the stabilities, structural parameters and

magnetic properties are discussed sequentially in this article.

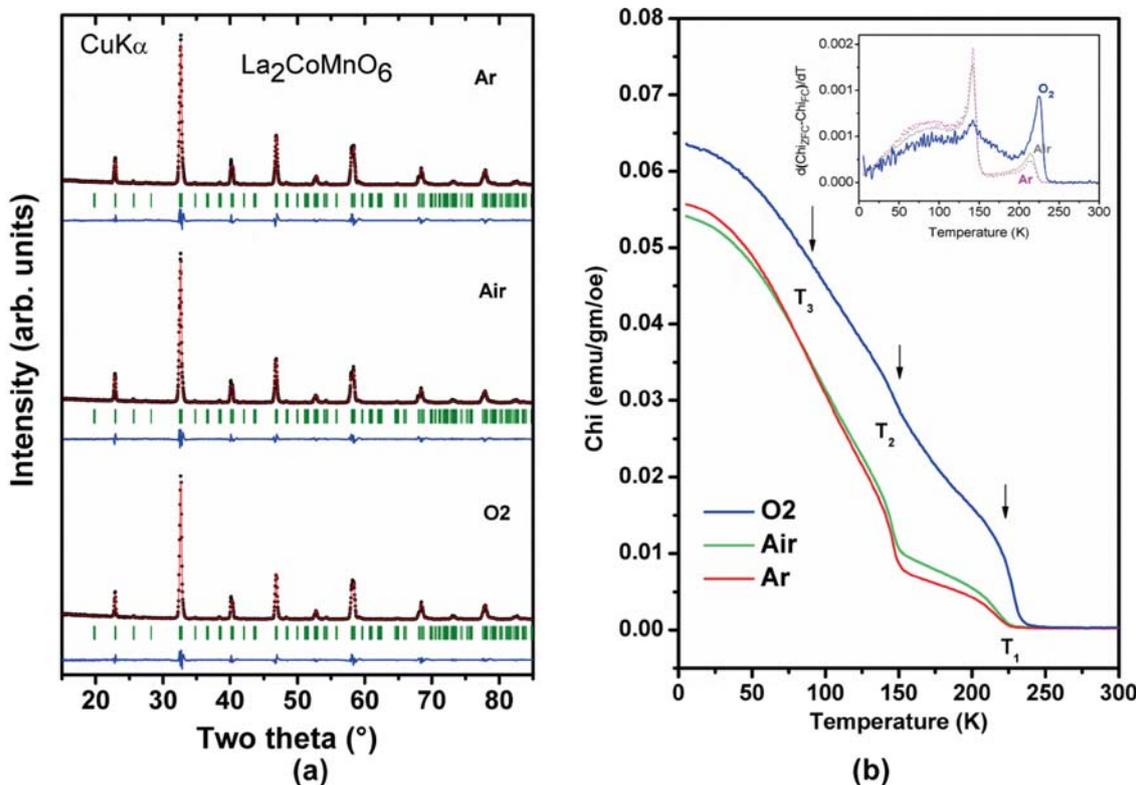
## 2. Results and Discussion

### 2.1 $\text{La}_2\text{CoMnO}_6$

The cation ordered  $\text{La}_2\text{CoMnO}_6$  composition has been one of the most extensively studied perovskite systems due to its near ambient temperature originating from both the  $\text{Co}^{3+}$ -O-Mn<sup>3+</sup> and  $\text{Co}^{2+}$ -O-Mn<sup>4+</sup> super exchange interactions.<sup>8,9,18,22,23</sup> In this section, the role of defects created/annihilated in  $\text{La}_2\text{CoMnO}_6$  during the annealing in environments of different oxygen partial pressure, like pure  $\text{O}_2$ , air or  $\text{N}_2/\text{Ar}$ , is explained. The  $\text{La}_2\text{CoMnO}_6$  samples annealed in air, oxygen or inert atmosphere like  $\text{N}_2$  or Argon did not show appreciable variation in crystal structure to reflect in their XRD patterns.<sup>18</sup> Typical powder XRD patterns of these samples are shown in Figure 2. All the  $\text{La}_2\text{CoMnO}_6$  samples have cation ordered monoclinic ( $P2_1/n$ ) lattices. The Rietveld refinements of the powder XRD data revealed no appreciable variation in the unit cell parameters also. The unit cell parameters (a, b, c,  $\beta$  and V) of the  $\text{La}_2\text{CoMnO}_6$  annealed in the three different

atmospheres are: 5.5139(1) Å, 5.4636(1) Å, 7.7443(2) Å, 89.99(2)°, and 233.30(1) Å<sup>3</sup> (for air annealed); 5.5107(1) Å, 5.4655(2) Å, 7.7459(3) Å, 89.99(2)°, and 233.30(1) Å<sup>3</sup> (for  $\text{O}_2$  annealed); 5.5126(2) Å, 5.4623(2) Å, 7.7452(4) Å, 90.00(1)°, and 233.22(1) Å<sup>3</sup> (for Argon annealed). It can be mentioned here that the monoclinic angle ( $\beta$ ) is almost 90°, but the analyses of profiles of the reflections support for monoclinic lattice over the cation disordered ( $Pnma$ ) lattice. Although there is no significant change in the crystal structures as well as unit cell parameters, the magnetic properties of these materials show noticeable difference, and they are explained below.

The temperature dependent magnetic properties of the studied  $\text{La}_2\text{CoMnO}_6$  samples are shown in Figure 2b. All the samples show ferromagnetic like upward turn in temperature (T) dependent magnetization (M) traces around 225 K, which is in agreement with the reported ferromagnetic transition temperature ( $T_c$ ) in the literature.<sup>24</sup> In addition to this  $T_c$ , some additional deviations in temperature dependent magnetic susceptibility ( $\chi$ , M/H; M = magnetization and H = applied magnetic field) are also observed (marked in Figure 2b). In the differential ZFC and FC (field cooled) magnetic susceptibilities ( $d(\text{ZFC-FC})/dT$ ) vs. T plot shown as an inset in Figure 2b), two distinct transitions around 225 and 150 K are clearly observed in



**Figure 2.** (a) Powder XRD patterns of the  $\text{La}_2\text{CoMnO}_6$  samples prepared in different environment, ( $R_p$ ,  $R_{wp}$ , and  $\chi^2$  for the Rietveld refinement plots are: 10.1%, 13.9%, and 2.40 for sample prepared in  $\text{O}_2$  atmosphere; 9.9%, 13.7%, and 2.68 for sample prepared in air; 10.4%, 14.4%, and 3.96 for sample prepared under inert (argon) atmosphere). (b) The temperature dependent magnetic susceptibility (M/H; M = magnetization and H = applied magnetic field, 100 Oe). Arrows indicate the temperatures at which the changes in slope of magnetization are appeared. Derivative of the difference in ZFC and FC magnetic susceptibility at different temperature is shown as an inset in (b).

these samples. The ZFC (zero field cooled) magnetization (not shown here) shows peak around this temperature and continuous decreasing trend with decreasing temperature.<sup>17</sup> Thus the presence of appreciable antiferromagnetic interactions is evident in these samples. It is expected that the system can have wide varieties of oxidation states, like  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ , and at least a partial intermixing of octahedral cations, and thus a number of possible magnetic interactions can arise in these samples. Among the possible interactions of magnetic ions, only  $\text{Co}^{3+}\text{-O-Mn}^{3+}$ ,  $\text{Co}^{2+}\text{-O-Mn}^{4+}$  and  $\text{Mn}^{3+}\text{-O-Mn}^{3+}$  interactions are only ferromagnetic interactions, while all other interactions are antiferromagnetic interactions.

The distinct magnetic transitions at different temperatures observed in studied  $\text{La}_2\text{CoMnO}_6$  samples suggest the presence of different magnetic domains with different sorts of exchange interactions, like  $\text{Co}^{3+}\text{-O-Mn}^{3+}$  and  $\text{Co}^{2+}\text{-O-Mn}^{4+}$  superexchanges. Dass *et al.*<sup>22</sup> have reported that the  $\text{Co}^{2+}\text{-O-Mn}^{4+}$  superexchanges in fully ordered are responsible for higher ferromagnetic ordering temperature ( $T_c$ , 225 K) in  $\text{La}_2\text{CoMnO}_6$  while Joy *et al.*<sup>33</sup> have attributed  $\text{Co}^{3+}\text{-O-Mn}^{3+}$  superexchange interaction is responsible for the transition temperature. But in later studies it has been confirmed that the  $\text{Co}^{2+}\text{-O-Mn}^{4+}$  superexchange of cation ordered monoclinic  $\text{La}_2\text{CoMnO}_6$  shows high ferromagnetic transition around 225 K.<sup>34,35</sup> The differential ZFC-FC magnetizations (inset in Figure 2b) clearly indicate that the sample annealed in oxygen shows a prominent peak around 225 K while those prepared by annealing in air or inert atmosphere show prominent peak around 150 K. Thus the  $\text{Co}^{2+}\text{-O-Mn}^{4+}$  interaction is suggested for the high temperature transition while  $\text{Co}^{3+}\text{-O-Mn}^{3+}$  interaction leads to the lower transition temperature (150 K). The predominant presence of  $\text{Co}^{2+}$  and  $\text{Mn}^{4+}$  in the sample prepared in  $\text{O}_2$  atmosphere is suggested. This fact is further supported by the EPR (electron paramagnetic resonance spectroscopy) studies.<sup>18</sup> Since the cation diffusion is not expected on annealing at lower temperature than the preparation temperature, only the variations in oxidation states of the transition metal ions occur and they govern the relative proportion of  $\text{Co}^{2+}\text{-O-Mn}^{4+}$  and  $\text{Co}^{3+}\text{-O-Mn}^{3+}$  interactions. Thus the alteration of oxidations states of transition metal ions plays important roles in their magnetic properties. From these observations it can be suggested that the magnetic interactions are sensitive to preparation conditions, in particular to the partial pressure of oxygen in annealing environments. These in fact are related to the creation or annihilation of the  $\text{O}^{2-}$  defects and in turn alter the oxidation states of Co and Mn. Also it could be inferred that the  $\text{Co}^{2+}$  and  $\text{Mn}^{4+}$  are favoured on annealing in oxidizing atmosphere.

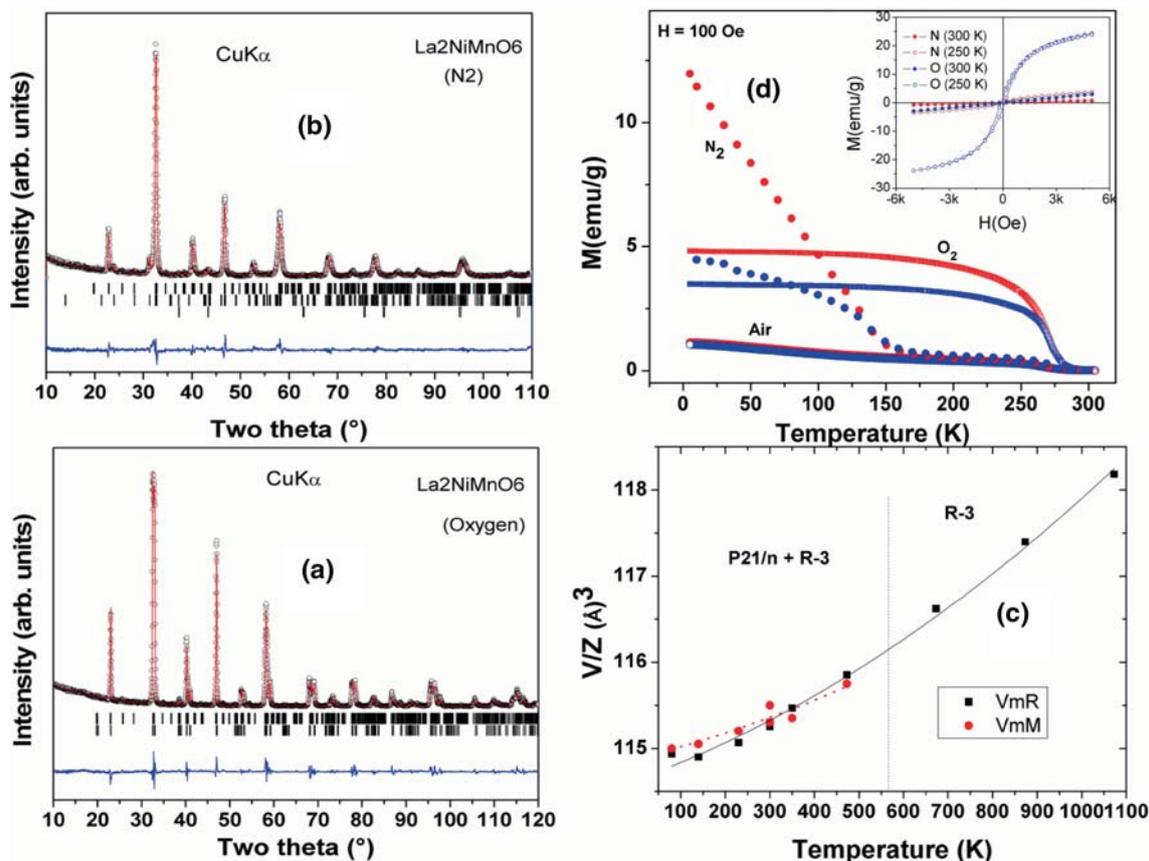
## 2.2 $\text{La}_2\text{NiMnO}_6$

Similar to  $\text{La}_2\text{CoMnO}_6$ , the double perovskite type  $\text{La}_2\text{NiMnO}_6$  has also been of interest for large magnetodielectric

properties.<sup>10,21</sup> Among the rare-earth based double perovskite type manganates,  $\text{La}_2\text{NiMnO}_6$  exhibits the highest ferromagnetic transition temperature ( $T_c = 280$  K). The  $\text{Ni}^{2+}\text{-O-Mn}^{4+}$  superexchange interaction has been attributed to its ferromagnetic properties.<sup>5,21</sup>  $\text{La}_2\text{NiMnO}_6$  has monoclinic ( $P2_1/n$ ) structure at ambient temperature and that transforms to rhombohedral structure at higher temperature (above 648 K<sup>36</sup>). The affect of oxygen partial pressure of preparation environment on the magnetic and dielectric properties of  $\text{La}_2\text{NiMnO}_6$  has also been reported in literature.<sup>17</sup> For such studies, the samples were prepared by a similar gel combustion process followed by high temperature sintering and subsequent annealing in different atmospheres, like air, oxygen and nitrogen.<sup>17</sup> Typical XRD patterns of the samples prepared in air and  $\text{N}_2$  atmosphere are shown in Figure 3. Detailed structural analyses from powder neutron diffraction (ND) studies indicated the coexistence of partially cation disordered monoclinic ( $P2_1/n$ ) and rhombohedral (R-3) phases in them.<sup>17</sup> The unit cell parameters of the monoclinic and rhombohedral phases observed in the  $\text{La}_2\text{NiMnO}_6$  sample prepared in air are:  $a = 5.432(3)$  Å,  $b = 5.485(3)$ ,  $c = 7.739(4)$  Å,  $\beta = 89.71(6)^\circ$ ,  $V = 230.6(2)$  Å<sup>3</sup>, and  $Z = 2$  (for Monoclinic, ( $P2_1/n$ ) phase,  $V/Z = 115.3$  Å<sup>3</sup>, where  $Z =$  number of formula units in the unit cell);  $a = 5.497(1)$  Å,  $c = 13.216(4)$  Å,  $V = 345.9(1)$  Å<sup>3</sup>, and  $Z = 3$  (for Rhombohedral, R-3 phase,  $V/Z = 115.3$  Å<sup>3</sup>).

The quantitative analyses of the rhombohedral and monoclinic phases indicated more of rhombohedral phase compared to the monoclinic phase (rhombohedral (R-3) and monoclinic ( $P2_1/n$ ) in the sample prepared in air (wt. fractions for rhombohedral and monoclinic phases are 67(1) % and 33(1) %, respectively) while almost equal amounts of rhombohedral and monoclinic phases in the samples prepared in oxygen atmosphere (wt. fraction rhombohedral : monoclinic = 49(1) % : 51(1) %). This also indicates that the composition remains closely similar for both phases, but the differences in the degree of disordering and distortions in the lattices reason for the coexistence of these two phases and their inter-conversions. The degree of disordering could be evaluated from the powder neutron diffraction data (disordering in the Ni and Mn sites is about 26% in rhombohedral and 35% in monoclinic phase). The phase evolution with temperature has been investigated from variable temperature neutron and XRD studies where the transformation of monoclinic phase to rhombohedral phase at and above 673 K.<sup>17</sup> The evolution of molar volume ( $V/Z$ ,  $V =$  unit cell volume and  $Z =$  number of formula units in the unit cell) of monoclinic and rhombohedral phases of  $\text{La}_2\text{NiMnO}_6$  with temperature is depicted in Figure 3c. Contrast to the sample prepared in air or oxygen environment, the XRD pattern of sample annealed in  $\text{N}_2$  atmosphere shows additional peaks due to NiO phase (Figure 3b).<sup>17</sup> This suggests that  $\text{La}_2\text{NiMnO}_6$  has also limited stability at high temperature inert environments.

Similar to the structures, the mode of preparation also affects the magnetic and dielectric properties of  $\text{La}_2\text{NiMnO}_6$ .<sup>17</sup>



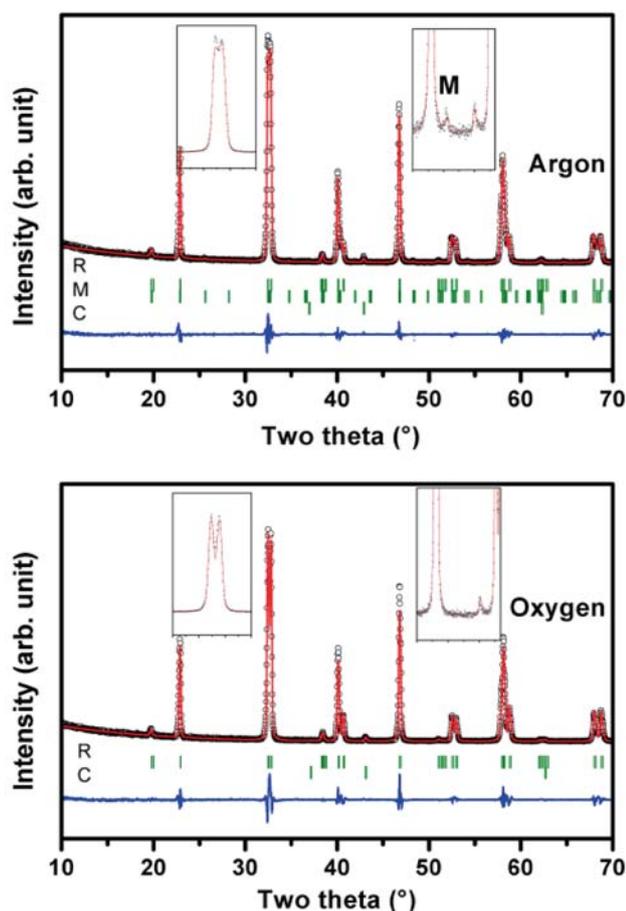
**Figure 3.** (a and b) Powder XRD patterns of the  $\text{La}_2\text{NiMnO}_6$  samples, (a) sample prepared in oxygen atmosphere (Bragg positions: upper row is for rhombohedral phase, and bottom row is for monoclinic phases;  $R_p$ ,  $R_{wp}$  and  $\chi^2$  are: 7.31%, 9.95%, and 2.80, respectively), (b) for sample prepared in  $\text{N}_2$  environment (b) (Bragg positions: upper row is for rhombohedral, middle row is for monoclinic phases and bottom row is for NiO phase;  $R_p$ ,  $R_{wp}$  and  $\chi^2$  are 9.77%, 13.3%, and 2.38, respectively). (c) Evolution of molar volume of monoclinic and rhombohedral  $\text{La}_2\text{NiMnO}_6$  with temperature. (d) The temperature dependent magnetic susceptibilities (FC and ZFC) of the  $\text{La}_2\text{NiMnO}_6$  samples.

In the case of magnetic properties, clear ferromagnetic transition near 280 K is observed only in the samples prepared in oxygen environment (Figure-3d). Thus the  $\text{Ni}^{2+}$ -O- $\text{Mn}^{4+}$  ferromagnetic interaction is observed in this sample only. However, annealing of  $\text{La}_2\text{NiMnO}_6$  in environments with less oxygen partial pressure, like air or inert atmosphere, significantly reduces the ferromagnetic fraction arising from this interaction. But these later two  $\text{La}_2\text{NiMnO}_6$  samples show additional transitions around 100 K. However in any of these samples no saturation of magnetization at lower temperature is observed (Figure 3d). Blasco *et al.*<sup>25,26</sup> have observed such transitions in the cation disordered  $\text{La}_2\text{NiMnO}_6$  phases (i.e.,  $\text{La}(\text{Ni},\text{Mn})\text{O}_3$ ). In the Ni substituted  $\text{LaMnO}_3$ , such transitions are usually appeared below 200 K and the  $T_c$  depends on Ni and Mn stoichiometries. For orthorhombic  $\text{LaNi}_{0.25}\text{Mn}_{0.75}\text{O}_3$ , the ferromagnetic transition occurs around 152 to 156 K.<sup>25</sup> This suggests that the cation composition and deviation of oxidation states of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  are affected by the oxygen partial pressure of annealing atmosphere and they in turn govern their magnetic properties. The influences of these parameters on the dielectric properties have also been reported in the literature.<sup>17</sup> Lower dielectric loss in the sample prepared

under  $\text{O}_2$  atmosphere compared to others is in agreement with the charge ordered state of  $\text{La}_2\text{NiMnO}_6$ .

### 2.3 $\text{La}_2\text{MgMnO}_6$

The  $\text{La}_2\text{MgMnO}_6$  samples prepared in analogous manner as the earlier cases have also been studied for their structural and magnetic properties.<sup>18</sup> Typical XRD patterns of the  $\text{La}_2\text{MgMnO}_6$  prepared by annealing oxygen and inert atmosphere are shown in Figure 4. The XRD patterns of the  $\text{La}_2\text{MgMnO}_6$  sample prepared under  $\text{O}_2$  atmosphere or in air show clear rhombohedral (R-3) structures similar to  $\text{La}_2\text{NiMnO}_6$  while the sample prepared by annealing in inert atmosphere shows a partial conversion of rhombohedral phase to monoclinic phase.<sup>18</sup> The estimation of rhombohedral and monoclinic phase fractions in the sample prepared in inert atmosphere indicates that about 40% of original rhombohedral phase transforms to monoclinic phases. Also peaks due to cubic MgO phase are also noticed in this XRD pattern. This suggests that the structure of  $\text{La}_2\text{MgMnO}_6$  is also sensitive to preparation



**Figure 4.** Powder XRD patterns (X-ray:  $\text{CuK}\alpha$ ) of the  $\text{La}_2\text{MgMnO}_6$  samples prepared in oxygen (Rp = 8.95%, Rwp = 11.8%,  $\chi^2 = 2.73$ ) and argon atmosphere (Rp = 7.37%, Rwp = 10.7%,  $\chi^2 = 2.24$ ). Monoclinic phase is identified from profile shape and weak extra peaks (shown as insets). M and R are monoclinic and rhombohedral phases of  $\text{La}_2\text{MgMnO}_6$  and C is cubic  $\text{MgO}$  impurity phase.

conditions and partially decomposes as in the case of  $\text{La}_2\text{NiMnO}_6$ .

From the comparison of structural details of  $\text{La}_2\text{CoMnO}_6$ ,  $\text{La}_2\text{NiMnO}_6$  and  $\text{La}_2\text{MgMnO}_6$  samples prepared under different conditions it can be suggested that structural stabilities of these perovskites are related to their adaptability for valence fluctuations. Since, the Mg cannot alter the valence, and higher stability of  $\text{Ni}^{2+}$  compared to  $\text{Co}^{2+}$ , the latter two compounds show structural instabilities. As the  $\text{Mg}^{2+}$  ions do not have any contributions to magnetic properties of  $\text{La}_2\text{MgMnO}_6$ , the magnetic properties of these samples are governed by the  $\text{Mn}^{4+}$  sub-lattice. Since the  $\text{Mn}^{4+}$  ions are separated by the  $\text{MgO}_6$  octahedra,  $\text{La}_2\text{MgMnO}_6$  samples mostly show paramagnetic behaviours, and they are less influenced by the annealing conditions.<sup>18</sup> Such paramagnetic nature of  $\text{La}_2\text{MgMnO}_6$  perovskites has been reported in the literatures.<sup>18,23,37</sup> The paramagnetic behaviour of cation ordered  $\text{La}_2\text{MgMnO}_6$  is due to the larger separation of  $\text{Mn}^{4+}$  ions. Thus it could be concluded

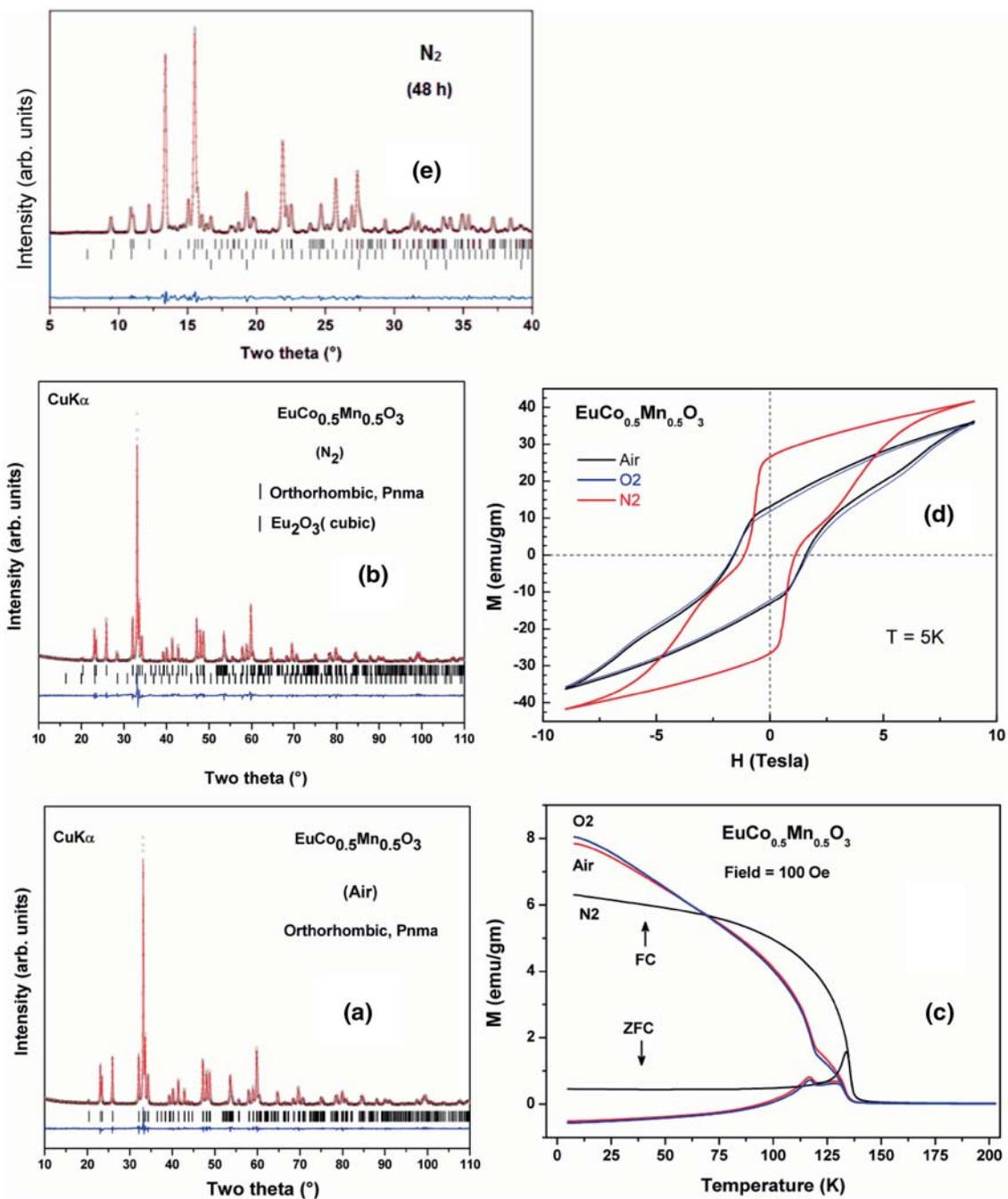
that the higher stabilities of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions, the  $\text{La}_2\text{CoMnO}_6$  shows higher structural stability with respect to oxygen partial pressure of preparation environment. But under long annealing in inert atmosphere such Co and Mn containing perovskites also tend to decompose. Such observations are explained later while discussing the case of  $\text{Eu}_2\text{CoMnO}_6$ .

#### 2.4 $\text{Eu}_2\text{CoMnO}_6$

Among the perovskite type rare-earth manganates,  $\text{Eu}_2\text{CoMnO}_6$  represents an interesting class where distinct structure and properties are observed compared to others explained earlier in this article. Though it has a cation disordered lattice, it exhibits appreciably different properties compared to  $\text{EuCoO}_3$  and  $\text{EuMnO}_3$ .  $\text{EuMnO}_3$  is an orthorhombic perovskite and has A-type antiferromagnetic lattice below 48 K,<sup>38</sup> while  $\text{EuCoO}_3$  is a rhombohedral perovskite and is non-magnetic due to low spin electronic configuration of  $\text{Co}^{3+}$  ions.<sup>39</sup> Partial substitution of  $\text{Mn}^{3+}$  ions of  $\text{EuMnO}_3$  by  $\text{Co}^{3+}$  ion induces ferromagnetism in it, and the  $T_c$  increases with increasing  $\text{Co}^{3+}$  ion concentration in  $\text{EuMn}_{1-x}\text{Co}_x\text{O}_3$ .<sup>19,40,41</sup> The maximum  $T_c$  of 120 K is observed at the composition  $\text{EuMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ .<sup>19,40</sup> The  $\text{Eu}_2\text{CoMnO}_6$  sample prepared in analogous manner as the previous cases show cation disordered orthorhombic ( $Pnma$ ) lattice and thus this composition can be better represented as  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ .<sup>19</sup> Representative XRD patterns of studied  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples are shown in Figure 5.

The samples prepared in air or  $\text{O}_2$  atmosphere are quite similar suggesting that the structure is stable under both the conditions while a partial decomposition is noticed on annealing the sample in inert atmosphere. XANES (X-ray absorption near edge structure) studies on Co and Mn edges of  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples annealed in air and  $\text{O}_2$  suggest that the oxidation state of Co is in between +2 and +3 and Mn is in between +3 and +4. On annealing in  $\text{N}_2$  atmosphere for longer time, viz., 48 h, disproportionation of  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  is confirmed from XRD studies. The decomposed products are identified as  $\text{Eu}_2\text{O}_3$  and cubic  $\text{Co}_{1-x}\text{Mn}_x\text{O}$  solution phases.<sup>19</sup> This indicates the limited stability of  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  in inert atmosphere.<sup>19</sup> Quantitative analysis of phases in this  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  sample (Figure 5e) shows majority of the sample disproportionate while the retained perovskite type phase has only feeble oxygen deficiency. The details of the identified phases in this disproportionated sample are as: Cubic  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}$ , Fm3 m,  $a = 4.3562(2)$  Å, wt. fraction = 21(%); Cubic  $\text{Eu}_2\text{O}_3$ , Ia-3,  $a = 10.8660(2)$  Å, wt. fraction = 47%; and Orthorhombic  $\text{Eu}_{0.973}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{2.983}$ ,  $Pnma$ ,  $a = 5.5712(2)$ ,  $b = 7.5877(3)$ ,  $c = 5.3358(2)$  Å; wt. fraction = 33%. Thus it could be concluded that the excess oxygen defect is not tolerated in the lattice of  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  and hence it decomposes to component oxides.

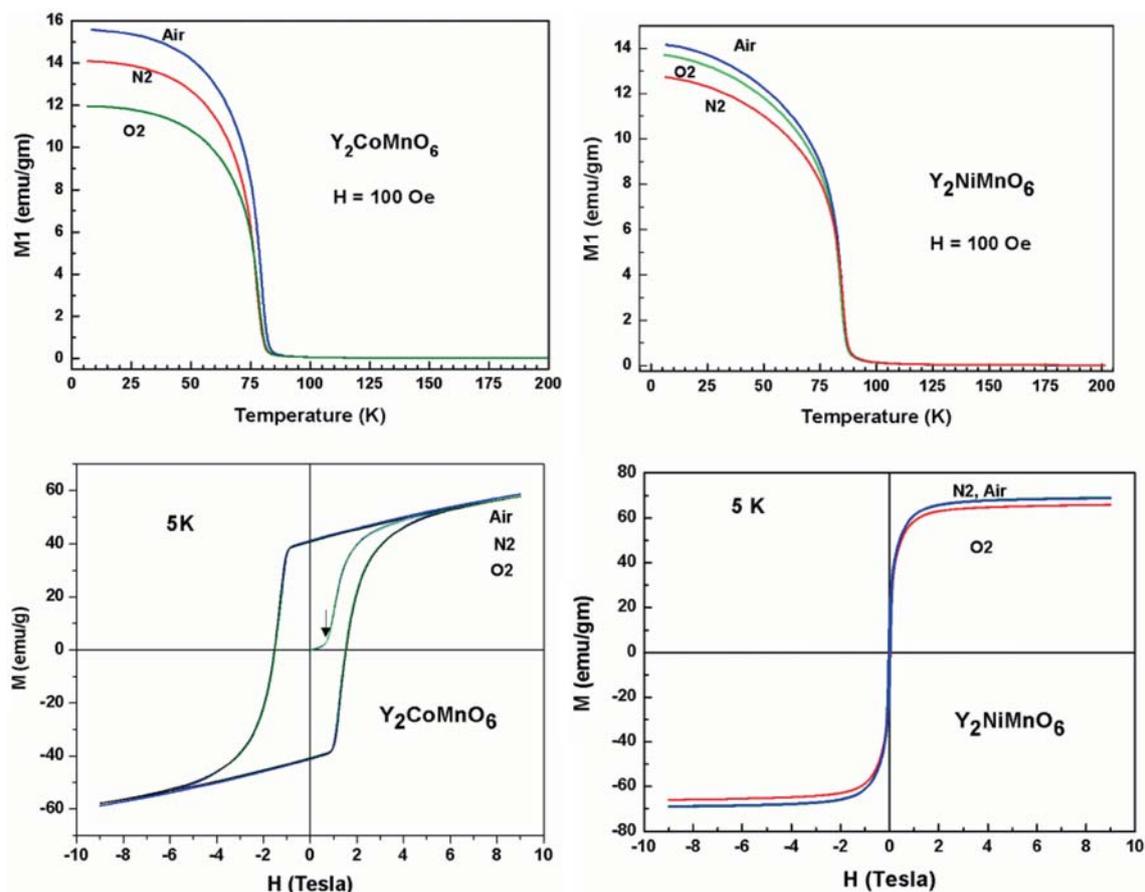
The temperature and field dependent magnetic properties of the studied  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples are shown in



**Figure 5.** (a and b) Powder XRD patterns of the  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples prepared under different conditions, (a) sample prepared in air ( $R_p = 6.65\%$ ,  $R_{wp} = 8.77\%$  and  $\chi^2 = 1.68$ ); (b) sample annealed at  $750^\circ\text{C}$  in  $\text{N}_2$  atmosphere for 10 h ( $R_p = 8.69\%$ ,  $R_{wp} = 10.90\%$ , and  $\chi^2 = 3.27$ ). (c) Variations of FC and ZFC magnetization of  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples with temperature. (d) Field dependent magnetization of  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples prepared in air, oxygen and  $\text{N}_2$  atmosphere. (e) Rietveld refinement plot of the XRD pattern of  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  sample annealed for 48 h in  $\text{N}_2$  atmosphere, X-ray wavelength =  $0.7306 \text{ \AA}$ ; ( $R_p = 4.67\%$ ,  $R_{wp} = 6.45\%$ ,  $\chi^2 = 2.05$ ; Bragg positions are marked as: orthorhombic ( $Pnma$ ) phase (upper row), cubic  $\text{Eu}_2\text{O}_3$  (middle row) and cubic  $\text{Co}_{1-x}\text{Mn}_x\text{O}$  (bottom row)).

Figure 4c and d, respectively. The temperature dependent magnetization studies indicated a ferromagnetic transition at around 132 K in the  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples prepared by annealing in air or  $\text{O}_2$ . The sample prepared by annealing in inert ( $\text{N}_2$ ) atmosphere shows ferromagnetic transition at a little higher  $T_c$  ( $\sim 136 \text{ K}$ ).<sup>19</sup> Additionally, the air or  $\text{O}_2$  annealed  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  sample shows an

extra magnetic transition at around 115 K, which is not observed in the sample annealed in inert atmosphere. The observed effective magnetic moment per formula unit ( $\mu_{\text{eff}}/\text{F.U.}$ ) for the air and oxygen annealed  $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$  samples are 4.94 and 4.96  $\mu\text{B}$ , respectively, while that for sample nitrogen annealed in atmosphere has a larger value (6.63  $\mu\text{B}$ ).



**Figure 6.** Temperature (FC) and field dependent magnetization of  $Y_2CoMnO_6$  and  $Y_2NiMnO_6$  prepared in different conditions. Arrow in the MH loop indicates critical field for metamagnetic transition.

The field dependent magnetizations (MH loops) of all the  $EuCo_{0.5}Mn_{0.5}O_3$  samples indicate metamagnetic like transitions where the antiferromagnetically coupled interactions switched to ferromagnetic type interactions by the magnetic field. Thus the ferrimagnetic interactions of the oppositely aligned spins in  $EuCo_{0.5}Mn_{0.5}O_3$  are switched to ferromagnetic state with field. The MH loops recorded at 5 K for the  $EuCo_{0.5}Mn_{0.5}O_3$  samples show two critical fields  $H_{C1}$  and  $H_{C2}$ , and also indicate that the magnetizations do not tend to saturate even up to 9 T. Also it is observed that the  $H_{C1}$  remains almost unchanged with preparation conditions while the  $H_{C2}$  shifts to lower field on annealing in atmosphere of lower oxygen partial pressure. This can be attributed to the predominant antiferromagnetic interactions present in  $EuCo_{0.5}Mn_{0.5}O_3$  are weakened on annealing in inert atmosphere.

### 2.5 $Y_2NiMnO_6$ and $Y_2CoMnO_6$

The  $LnMnO_3$  type manganates of smaller rare-earth ions, viz.,  $Ln = Ho-Lu, Y, Sc$ , etc., usually crystallize in hexagonal ( $P6_3mc$ ) structures and they exhibit multiferroic (coexisting antiferromagnetic and ferroelectric) behaviour

at lower temperature.<sup>42–44</sup> However substitution of other trivalent ions in the Mn site transforms them to perovskite type structure and beyond certain concentration they also form cation ordered double perovskite type structures. Stability and magnetic properties of typical cases, like  $Y_2NiMnO_6$  and  $Y_2CoMnO_6$  prepared under different conditions are explained here.<sup>20</sup>  $Y_2NiMnO_6$  and  $Y_2CoMnO_6$  prepared by high temperature reactions show cation ordered monoclinic ( $P2_1/n$ ) structures and they remain stable on annealing in air,  $O_2$  and also in inert atmosphere. The monoclinic distortions in the lattices are only feeble, viz.,  $\beta \sim 89.8^\circ$ .<sup>20</sup> However a partial intermixing of octahedral cations (about 24% in case of  $Y_2NiMnO_6$  and  $\sim 10\%$  in  $Y_2CoMnO_6$ ) is observed in these samples. Interestingly, the magnetic properties of these perovskites are least influenced by the oxygen partial pressure of annealing environment.

The temperature and field dependent magnetizations shown in Figure 6 indicate that both the materials show ferromagnetic transition at around 75 K. However, the MH loops recorded at 5 K show two distinct behaviours for them, i.e. the  $Y_2CoMnO_6$  is a ferrimagnet and exhibits switching of ferri- to ferromagnetic states at applied magnetic field of around 2 T while superparamagnetic like nature in  $Y_2NiMnO_6$ . The MH loops of  $Y_2NiMnO_6$  samples

recorded at 5 K show the soft ferromagnetic like nature for  $Y_2NiMnO_6$  where the magnetization increases rapidly and saturates with a field of about 1 to 1.5T. Almost zero coercive-fields further supports for the soft ferromagnetic nature of  $Y_2NiMnO_6$ . Such soft ferromagnetic nature, quite high stability and robust for preparation conditions are the technological relevant characters of  $Y_2NiMnO_6$ . The effective magnetic moments of transition metal ions ( $\mu_{\text{eff}}$ /F.U.) in the  $Y_2CoMnO_6$  and  $Y_2NiMnO_6$  are close to 6.3 and 5.7  $\mu_B$ , respectively. These values are in agreement with the  $Co^{2+}$ -O  $Mn^{4+}$  and  $Ni^{2+}$ -O- $Mn^{4+}$  interactions.

### 3. Summary and conclusions

A systematic comparison of structural and magnetic properties of several  $A_2MMnO_6$  type perovskites suggests both the properties are sensitive to oxygen partial pressure of preparation environments. In general the formation of perovskite type structures is governed by the tolerance factors and hence ionic radii of the cations. According to the tolerance factors, all the trivalent rare-earth cations can form perovskite type structure with transition metal ions, like  $Mn^{3+}$  or  $Mn^{4+}$ . However, their stabilities with respect to oxygen defects are important for their structure and magnetic properties. The sensitivity of the structure and properties are mainly arising from the variation of oxidation state of the transition metal ions and they are also influenced by the nature of the M site cation and rare-earth ions. It is known that in the Co/Ni and Mn containing perovskites,  $Mn^{3+}$ -O- $Mn^{4+}$ ,  $Co^{2+}$ -O- $Co^{3+}$ ,  $Co^{2+}$ -O- $Mn^{4+}$ ,  $Ni^{2+}$ -O- $Mn^{4+}$  and vibronically coupled  $Co^{3+}$ -O- $Mn^{3+}$  superexchange interactions are ferromagnetic while all other interactions are of anti-ferromagnetic natures. The relative proportions of these exchanging couples are dependent on the preparation conditions. Thus diversified magnetic properties are observed in such perovskites. The nature M site cation plays an important role, like balancing the oxygen stoichiometry by fluctuation of its oxidation state. The stability of  $Ln_2MMnO_6$  is lower for  $M = Mg^{2+}$  ions compared to  $Co^{2+}$  and  $Ni^{2+}$  as M site cations. Also it is observed the stability of perovskites and insensitivity to the oxygen partial pressure are more for the smaller trivalent rare-earths like  $Y^{3+}$ , as observed from the studies on  $Y_2NiMnO_6$  and  $Y_2CoMnO_6$ . Although the  $La_2NiMnO_6$  shows close to high (280 K) ferromagnetic transition temperature, its structural stability and magnetic properties are also severely influenced by the relative oxygen partial pressure of preparation conditions.  $Y_2NiMnO_6$  shows extraordinary stability and unperturbed magnetic properties with respect to the preparation conditions.

Despite the lower transition temperature, the soft ferromagnetic nature and high saturation magnetic moment and low saturation magnetic field are noticeable features exhibited by  $Y_2NiMnO_6$ . Further systematic on magnetic properties and other functional properties, like electronic conductivity and dielectric properties are also expected with perovskites gradation of ionic radii. Thus the functional properties of perovskites can be tuned by using combination of  $Ln^{3+}$  ions at A-site and/or tuning the preparation conditions appropriately.

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