

Phase Optimization of Oxygen Deficient and Oxygen Excessive Ruddlesden-Popper type Perovskite Oxides

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Abstract— Defects in materials are found to be the frontage of research in material science. Defects can be vacancies (an atom is missing from its position in the lattice) or interstitials (filling of voids). Each type of defect has a certain influence on the chemical formula which describes the compound under observation. For example interstitials of atoms of one type will induce excess of the content of atoms of that type in the chemical formula, vacancies of atoms of one type will decrease the content of atoms of that type in the chemical formula and in a similar way the effect of other type of defects can be estimated. Ruddlesden-Popper (RP) oxides are highly flexible in terms of content of oxygen. Therefore the loss or gain of oxygen is highly usual in this RP phase system. Loss of oxygen or gain of oxygen results in vacancy or interstitial filling. Oxygen excessive $\text{La}_4\text{Co}_3\text{O}_{10+}$ and oxygen deficient SrFeO_3 are the compounds of my interest. The oxygen deficient and oxygen excessive compounds have been prepared by adopting simple thermal decomposition and co-precipitation method, respectively. The phase optimization of the synthesized samples has been carried out by X-ray diffraction and vibrating sample magnetometer measurements. The results will be discussed.

Keywords- ruddlesden-popper; oxygen vacancy; oxygen excess; x-ray diffraction; vibrating sample magnetometer

I. INTRODUCTION

The family of perovskites is large with compounds having crystal structure related to the mineral perovskite CaTiO_3 . Of the several perovskite related phases, Ruddlesden-popper phase oxides have a wide range of oxygen non-stoichiometry. The physical property of the Ruddlesden-popper oxide materials change with respect to the content of oxygen. Hence the study of oxygen excessive or deficient Ruddlesden-popper materials exhibiting different properties relating to the content of oxygen is interesting. Ruddlesden-popper oxides have a general formula of $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ or $\text{AO}(\text{ABO}_3)_n$ (where A is rare earth/alkaline earth ion, B is a transition metal ion). Oxygen excessive or deficient compounds of Ruddlesden-popper oxides are created either by heterovalent or homovalent doping. The oxygen deficient Sr-Fe-O and oxygen excessive La-Co-O systems are belonging to homologous series.

A. Oxygen Deficient SrFeO_3 compound

The compound SrFeO_3 has been receiving intense attention due to their unique and technologically useful structural, magnetic and electrical properties. The unusual valency of Fe^{4+} in SrFeO_3 making it an oxygen deficient system as a result of homovalent doping is the reason for their interesting physical properties. Stoichiometric SrFeO_3 has cubic structure with metal-like conductivity [1]. Depending on the deviation from their stoichiometry, corresponding to the oxygen vacancy, it takes tetragonal ($\delta=0.13$), orthorhombic ($\delta=0.27$) and brownmillerite ($\delta=0.5$) phases [2, 3]. Any intermediate composition results in a mixture of two neighbouring phases [4]. The compound in its defect state is so sensitive that even 1% oxygen vacancy affects the metallic behaviour and leads to semiconducting nature [5]. It is quite rare to observe the properties of a compound getting enhanced with defects. This compound SrFeO_3 exhibit enhanced electrical and structural behaviour corresponding to various defects which makes the study of this compound more interesting.

B. Oxygen Excessive $\text{La}_4\text{Co}_3\text{O}_{10+}$ Compound

Oxygen deficient compounds have been widely studied whereas the oxygen excessive compounds are studied comparatively lesser. The La-Co-O family that belongs to oxygen excessive system has a general formula $\text{La}_{n+1}\text{Co}_n\text{O}_{3n+1}$ or $(\text{LaO}(\text{LaCoO}_3)_n)$. The members of La-Co-O family are La_2CoO_4 ($n=1$), $\text{La}_3\text{Co}_2\text{O}_7$ ($n=2$), $\text{La}_4\text{Co}_3\text{O}_{10}$ ($n=3$) and LaCoO_3 ($n=$) [6]. Of these members $\text{La}_4\text{Co}_3\text{O}_{10+}$ compound has a wide range of homogeneity for oxygen content of $0.00 < \delta < 0.30$ [7]. This compound shows similar property to that of a high

temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. This system can be ideally described by stacking of 'n' two dimensional perovskite type layers with CoO_6 corner sharing octahedral along the crystallographic *c*-direction into layers with intermediate NaCl-type LaO layers. Within these NaCl-type LaO layers there are tetrahedral voids which can incorporate oxygen atoms in their voids [8]. The system undergoes structural transition from monoclinic to tetragonal with intermediate orthorhombic phase around 840 K. No compositional change is seen during structural transformation whereas in high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7-x$ structural transition is accompanied with loss or randomization of oxygen. Long range anti-ferromagnetic ordering is seen below $T_N \sim 13$ K. Above 20 K, there are three temperature regimes with nearly Curie–Weiss paramagnetic behaviour for the magnetic susceptibility. This indicates a temperature induced change from lower via intermediate, to a higher spin state configuration for Co(III) [9].

It is therefore of great interest to optimize oxygen deficient SrFeO_3 and oxygen excessive $\text{La}_4\text{Co}_3\text{O}_{10}$ phases. In this present work, I have tried to optimize single phase SrFeO_3 and $\text{La}_4\text{Co}_3\text{O}_{10+x}$ compounds using XRD and VSM analysis.

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation of SrFeO_3 .

Analytical grade $\text{Sr}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were weighed to 1:1 stoichiometric ratio and dissolved in ethylene glycol with continuous stirring. After complete dissolution, the solution was heated with stirring until a desired gel form is attained. This was further heated to form flakes, powdered and subjected to sintering at 1000 °C for 2 hr, 4 hr and 8 hr in an ambient atmosphere.

B. Sample Preparation of $\text{La}_4\text{Co}_3\text{O}_{10+x}$

The stoichiometric quantity of analytical grade $\text{Co}(\text{NO}_3)_3$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were taken as precursors and the sample was prepared by Co-Precipitation method. The precursors are taken in 1:1 weight percentage ratio and NH_3OH is added in drops until it forms precipitate while it is continuously stirred. The precipitate is then heated at 573 K, 873 K and 1173 K for 12 hour in oxygen atmosphere for optimization of $\text{La}_4\text{Co}_3\text{O}_{10+x}$ phase.

III. RESULTS AND DISCUSSION

A. Optimisation of single phase SrFeO_3 .

XRD Analysis

Figure 1 shows the X-ray diffractogram ($\lambda = 1.5406 \text{ \AA}$) of prepared samples sintered at 1000 °C for 2 hr, 4 hr and 8 hr. All the observed peaks were indexed to cubic perovskite structure (JCPDS NO: 40-0905). The 2 hr and 4 hr sintered samples show an additional peak of Fe_2O_3 but the sample sintered for 8 hr has no additional peak, indicating single phase nature. Its lattice parameter values are determined to be $a = b = c = 3.857(1) \text{ \AA}$.

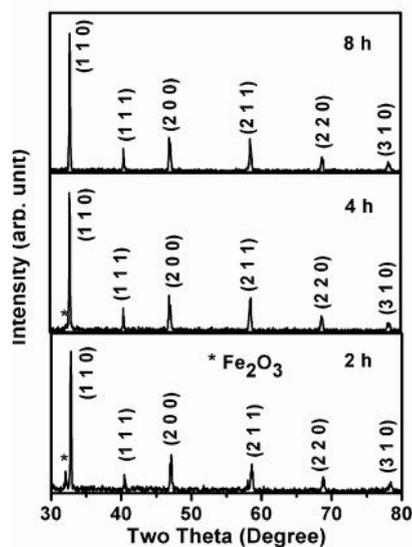


Figure 1. XRD pattern of SrFeO_3 samples heated for 2 hr, 4 hr, and 8 hr at 1000 °C (* indicates secondary peak belongs to Fe_2O_3).

Magnetiz

The room temperature M-H curve of 1000 °C for 8 hr sintered sample shows paramagnetic behaviour whereas 2 hr and 4 hr sintered samples show the presence of high coercive ferromagnetic behaviour which is due to the presence of small amount of impurity phase (Fe₂O₃) and is clearly seen in figure 2. This is also a clear evidence of single phase nature of 1000 °C for 8 hr sintered sample, because the anti-ferromagnetic to paramagnetic transition (i.e., Neel transition) of SrFeO₃ is occurred at 134 K.

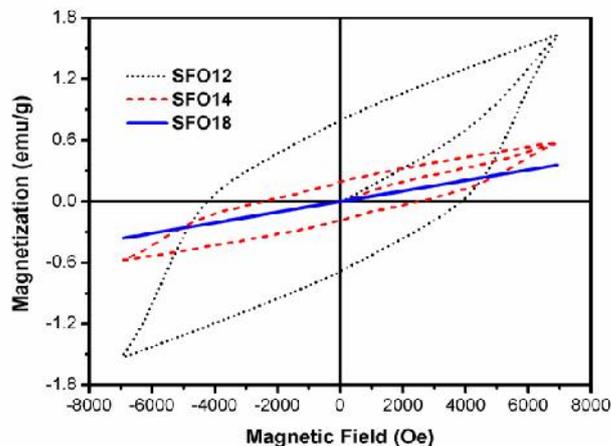


Figure 2. VSM of SrFeO₃ samples heated for 2 hr, 4 hr, and 8 hr at 1000 °C.

B. Optimisation of single phase La₄Co₃O₁₀₊

XRD Analysis

Figure 3 shows the X-ray diffractogram (with a scan rate of 0.02 steps per second) of the prepared sample heat treated at 573 K and 873 K for 12 hour at oxygen atmosphere. The XRD pattern of the sample heat treated at 573 K shows multiphase nature i.e., LaCoO₃ with minor La₂CoO₄. Further the sample heat treated at 873 K indicates the formation of La₂CoO₄ phase and minor La₄Co₃O₁₀ phase. Figure 4 shows XRD of the sample heat treated at 1173 K for 12 hour in oxygen atmosphere. This XRD pattern confirms the formation of La₄Co₃O₁₀₊ compound. A secondary peak is seen indicating the presence of La₄Co₃O₉ formation in small amounts. The formation of secondary phase (La₄Co₃O₉) can be rectified by heating the sample at higher temperatures in higher oxygen pressures.

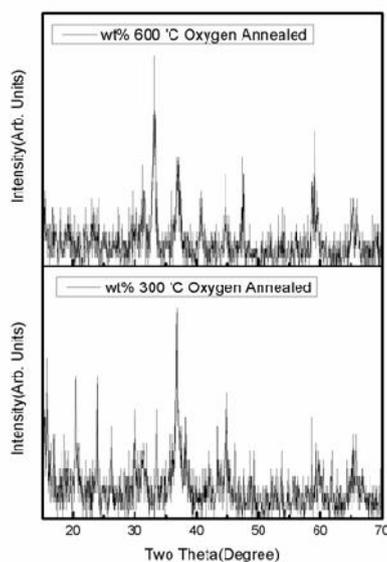


Figure 3. XRD pattern of La₄Co₃O₁₀₊ samples heated at 573 K and 873 K for 12 hr in oxygen atmosphere.

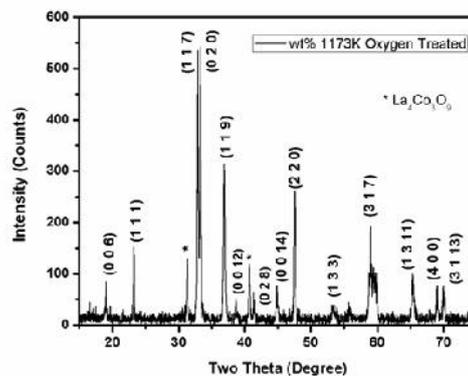


Figure 4. XRD pattern of La₄Co₃O₁₀₊ sample heated at 1173 K for 12 hr in oxygen atmosphere.

IV. CONCLUSIONS

SrFeO₃ was successfully optimized through thermal decomposition method using XRD and VSM results. La₄Co₃O₁₀₊ phase was prepared by co-precipitation method and sintered at 1173 K for 12 hour in oxygen atmosphere showing an additional peak belonging to La₄Co₃O₉. La₄Co₃O₁₀₊ phase can be successfully optimized by heating the sample at higher temperatures in oxygen atmosphere.

After optimization, the role of defects affecting the physical properties of the materials will be analyzed using different characterization techniques.

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