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# Effect of pH value on ionic state of iron in double perovskite Sr<sub>2</sub>FeCoO<sub>6</sub> synthesised by gel-combustion method

M. Siddique<sup>a</sup>, S. K. Durrani<sup>b</sup> and E. Ahmed<sup>a</sup>

<sup>a</sup>Physics Division PINSTECH, P.O. Nilore Islamabad, Pakistan <sup>b</sup>Materials Division PINSTECH, P.O. Nilore Islamabad, Pakistan

The double perovskite  $Sr_2FeCoO_6$  oxide powder has been prepared by nitrate-citrate gel-combustion process for different ratios of citric acid and metals under various pH values and calcined at 700 °C for the complete decomposition of the carbonaceous residues. The effect of pH on crystal development and ionic state of iron has been determined by X-ray diffraction and Mössbauer spectroscopic studies. The analysis revealed that calcinated powder is a single phase cubic perveoskite structure  $SrFe_{0.5}Co_{0.5}O_3$  with space group Pm3m and lattice parameter 3.867 Å. Mössbauer spectroscopic results indicate that as-synthesized and calcined samples have mixed ionic states like  $Fe^{3+}$ ,  $Fe^{3.5+}$  and  $Fe^{4+}$  in the tetrahedral framework of  $SrFe_{0.5}Co_{0.5}O_3$ .

Key words: Gel-combustion, Perovskite oxide, X-ray diffraction, Mössbauer spectroscopy.

## Introduction

After the discovery of colossal magnetoresistance in the manganites the interest of solid-state chemists and physicists has been increased to prepare new compounds that could have the properties due to this effect is of technological interest. These materials exhibit a large magnetoresistance (MR) ratio at room temperature, thus promising technological applications [1]. The family of magnetic oxides with an ordered double perovskite structure is complex materials with high technological potential in the area of spin electronics. The double perovskites have general formula A<sub>2</sub>BB'O<sub>6</sub>, where A can be an alkali metal such as Sr, Ca or Ba, or a lanthanide, and B and B' are transition metals. Each transition metal site is surrounded by an oxygen octahedron and A atoms are located in holes produced by eight adjacent oxygen octahedra [2]. The transition metal perovskites, SrFe<sub>1-</sub>  $_{x}Co_{x}O_{3}$  ( $0 \le x \le 1$ ) are of great significance because of their interesting magnetic properties and also the high oxidation states of the transition metal (Fe<sup>4+</sup>, Co<sup>4+</sup>) can be stabilized [3]. Oxygen permeable membranes made of mixed oxygen ionic and electronic conductors are being successfully used in the separation of oxygen from air and partial oxidation of light hydrocarbons. Among the most widely investigated materials the strontium-cobalt-iron oxide are of particular interests.

In general co-precipitation, sol-gel, micro-emulsion, solvothermal and hydrothermal methods are being used

to synthesize these oxides. Recently a simple and versatile gel-combustion method has emerged as an important technique for synthesis and processing of advanced ceramics, catalysts, composites, alloys and nano-sized materials. Combustion synthesis having fast heating rate and short reaction time makes it an attractive method for manufacturing the technologically useful materials at very low cost as compared to conventional ceramic method [4]. The interest in this method is growing in the sense that it provides a direct method to prepare the homogeneous, very fine, crystalline and unagglomerated powders with good sintering behaviour. It is generally very fast and self sustaining chemical reaction between the desired metal salts like nitrates, chlorides and sulfates and a suitable organic fuel such as urea which is ignited at a temperature much lower than actual phase formation temperature [5].

Mössbauer spectroscopy is a very suitable, very sensitive and well established technique which can provide valuable information in many fields of natural sciences. It is based upon the resonant absorption and recoilless emission of  $\gamma$ -rays by the nuclei in solids. A Mössbauer spectrum described by the number, position, shape and relative intensity of the absorption lines is governed by the nature of the hyperfine interactions like isomer shift ( $\delta$ ), quadrupole splitting ( $\Delta$ ) and the magnetic hyperfine field ( $H_{\text{eff}}$ ). These parameters give valuable information regarding the symmetry of the bonding environment, ionic state and local structure around the Fe atoms.

The present work is carried out to synthesize  $Sr_2FeCoO_6$  double perovskite by citrate-nitrate gelcombustion, a very simple low cost method, for different pH values. X-ray diffraction (XRD) and

<sup>\*</sup>Corresponding author:

Tel : +92 51 2207224

Fax: +92 51 9248808

E-mail: siddique56@hotmail.com

Mössbauer spectroscopy techniques have been used to characterize the material, especially Mössbauer spectroscopy for the determination of ionic states of iron at different pH values.

## **Experimental**

Sr<sub>2</sub>FeCoO<sub>6</sub> powders were synthesized using citratenitrate gel-combustion process. All chemicals used were of analytical reagent grade, metal nitrate salts, citric acid and sodium hydroxide from Fluka. Known concentration of nitrate solutions was prepared by dissolving strontium, iron and cobalt nitrates in double de-ionized water (DDW). These solutions were then mixed by volume at the required proportions and appropriate amount of citric acid was finally added in the mixed solution. The pH of the solution was adjusted in the range 6.0-10.75 and the mixture was evaporated at 70 °C with constant stirring until a viscous mixture was obtained. This mixture was transferred into a bowel and was heated on a hot plate at  $\sim 250$  °C. The gel was then subjected to a sudden raising of the temperature up to 250-300 °C which brought about the boiling and swelling of the gel with evolution of a large amount of nontoxic gases i.e. CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. The flameless combustion started in the hottest zones of the bowel and propagated from the bottom to the top like the eruption of volcano. A rapid and auto-combustion reaction was completed within a few minutes. The resultant powder was calcined at 700 °C for various time durations for the completion of reaction to get the required product i.e. Sr<sub>2</sub>FeCoO<sub>6</sub>. The combustion process is shown in Figure 1. The crystal structure and phases were determined by X-ray diffraction (XRD), using Rigaku Geiger flux instrument with  $CuK_{\alpha}$ radiation ( $\lambda = 1.54056$  Å). The XRD data were collected in the 20 range from 15  $^{\rm o}$  to 80  $^{\rm o}$  by step-scanning 0.05  $^{\rm o}$ increment and scanning rate of 5 °/min. Mössbauer measurements were performed at room temperature (RT) using a <sup>57</sup>Co source with the conventional constant acceleration-type Mössbauer spectrometer, calibrated with  $\alpha$ -Fe foil. The data analysis was performed using a computer programme Mos-90, assuming that the peaks are Lorentzian in shape [6].



**Fig. 1.** Gel-combustion process for strontium iron cobalt based (SrFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub>) perovskite oxide powder. (a) Combustion at 250  $^{\circ}$ C (b) Black brown powder collected after combustion.

## **Results and Discussion**

Figure 2 shows the XRD patterns of as-synthesized and heat-treated samples for different pH values. For assynthesized samples SrCO<sub>3</sub>, SrCoO<sub>2.5</sub> and Sr<sub>2</sub>CoFeO<sub>6</sub> phases are detected which matched well with the JCPDS card # 05-0418, 48-0875 and 46-0335 respectively. All the peaks are broad showing that the powder is not fully crystalline yet. But when the powders are heat-treated at 700 °C they become very sharp and there are no diffraction trace peaks of SrCO<sub>3</sub> and SrCoO<sub>2.5</sub> in XRD pattern. The sharp peaks indicate that the heat treatment at 700 °C transformed the partially crystalline samples to very refined crystalline shape. The analysis further revealed that calcinated powder is a single phase cubic perveoskite structure Sr<sub>2</sub>FeCoO<sub>6</sub> with space group Pm3m and lattice parameter 3.867 Å matching very well with the JCPDS card # 46-0335.

Mössbauer spectra of as-synthesized and heat-treated samples for different pH values are shown in Figure 3. As-prepared sample for pH = 6.0 is a broad irregular singlet like structure (single-line spectrum) showing that it consists of more than one subspectra. Therefore, it is fitted with a quadrupole doublet (two-line spectrum) and a singlet. The two paramagnetic components represent the two different cation environments around the probe atom Fe. The quadrupole doublet originating from the electric field gradient of the surrounding environment shows the deviation of the system from the cubic symmetry and its contribution is 43%. In perfect cubic symmetry arrangement of the oxygen ions in FeO<sub>6</sub> octahedra is regular and value of quadrupole splitting (D) should be nearly zero. The presence of non-zero quadrupole splitting can be referred as the existence of oxygen vacancy in the neighbourhood of Fe atom [7]. The quadrupole doublet having D = 0.56 mm/s and isomer shift  $\delta = 0.16$  mm/s is due to the Fe<sup>3.5+</sup> [8] at octahedral site and singlet (i.e.  $\Delta = 0.00 \text{ mm/s}$ ) is due



**Fig. 2.** XRD patterns of  $Sr_2FeCoO_6$  before (a, c, e) and after (b, d. f) heat-treatment for 6.0, 8.3 and 10.75 pH values respectively.



**Fig. 3.** Mössbauer spectra of  $Sr_2FeCoO_6$  before and after heat-treatment for different pH values.

Table 1. Mössbauer parameters of  $Sr_2FeCoO_6$  perovskite for different pH values.

Sample	Spectrum	Δ (mm/s)	δ (mm/s)	Ionic State of Iron (+)	Relative Area (%)
As-synthesized	Doublet	0.56	0.16	3.5	43
(pH = 6.0)	Singlet	0.00	0.11	4	57
Heat-treated	Doublet	0.75	0.29	3	26
	Singlet	0.00	0.09	4	74
As-synthesized $(pH = 8.3)$	Doublet	0.66	0.30	3	94
	Singlet	0.00	0.20	3.5	6
Heat-treated	Doublet	0.42	0.19	3.5	64
	Singlet	0.00	0.07	4	36
As-synthesized $(pH = 10.75)$	Doublet1	0.51	0.31	3	75
	Doublet2	0.98	0.31	3	25
Heat-treated	Doublet Singlet	0.63 0.00	0.22 0.10	3.5 4	44 56

to  $Fe^{4+}$  [9] at tetrahedral site, having cubic symmetry because singlet is generally observed for an ideal cubic

environment [10]. It seems that Fe has mix type of ionic state in this material. When this sample is heattreated at 700 °C still constituted a doublet and a singlet however, Mössbauer parameters of doublet correspond to  $Fe^{3+}$  state [11, 12]. The relative area of quadrupole doublet decreased and area of singlet increased accordingly (74%). The Mössbauer spectrum of sample for pH = 8.3 is somewhaat different from the previous two spectra. It looks like a quadrupole doublet with a small imbalance in the two peaks. This is due to a small contribution of the singlet in one peak. Most of iron is present in the form of Fe<sup>3+</sup> state while calcined sample is a mixture of  $Fe^{3.5+}$  and  $Fe^{4+}$  states. For pH = 10.75 only  $Fe^{3+}$  state is present in the sample while in calcined sample the mixture of Fe<sup>3.5+</sup> and Fe<sup>4+</sup> states are observed. The presence of doublet/singlet in the as-synthesized and heat-treated samples indicates that the system is completely paramagnetic in nature. Mössbauer parameters are summarized in Table 1.

## Conclusions

X-ray diffraction results indicate the presence of SrCo<sub>3</sub>, SrCoO<sub>2.5</sub> and Sr2FeCoO<sub>6</sub> in as-synthesized samples while heat-treated samples are single phase cubic perovskites structure Sr<sub>2</sub>FeCoO<sub>6</sub> with space group Pm3m. Mössbauer spectroscopic results reveal that as-synthesized and heat-treated samples are paramagnetic and constituted mixed states of iron like Fe<sup>3+</sup>, Fe<sup>3.5+</sup> and Fe<sup>4+</sup> in the tetrahedral framework of SrFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub>.

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