Structural and FTIR Analysis of SrCoO₃ Perovskite Ceramics

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Abstract:
Solid-state reaction route method was adopted and analytically grade reagents were used for the perovskite SrCoO₃ sample preparation. The structural phase was determined by X-ray diffractometer. The average particle size was found to be 25.7 nm. The infrared spectra of the material were recorded and analysed by FTIR spectroscopy which indicated the presence of fingerprint region of perovskite ABO₃ type structure. Multiphase of the polycrystalline ceramic were found.
Key Word*: Perovskite; Ceramics; Strontium Cobaltates; Microstructures; X-ray diffractometer; FTIR Spectroscopy.*


I. Introduction

The cobaltates exhibit a class of material due to the coupling encompassed by charge, spin, and orbital degrees of freedom and the delicacy of the spin-state. This makes strong correlation with the materials and have basic and prospective implementations [1–5]. The perovskite SrCoO₃ ceramic has higher value of oxygen evaluation rate (OER) [6] and also shows vastly active catalytic gesture [7] which signifies that oxygen vacancies can efficiently be fabricated inside the materials. The fabrication of oxygen vacancies in the ABO₃ type perovskite ceramics improves the conductivity of the materials in supercapacitor implementations [8]. The reason behind it, the geometric and chemical properties of the transition metal oxide (TMO) get change due the creation of oxygen vacancies in the materials [8]. Because of the presence of the mixed Co valence states (Co^{3+}, Co^{4+}) and their complex interaction, exchange bias properties, $SrCoO_{3-\delta}$ reveals the divergent magnetic spin order serving as ferro, antiferro and ferro [9].

Expressly in this study, we have recited the microstructure of the perovskite SrCoO₃ ceramic by X-ray diffractometer and FTIR spectroscopy.

II. Material and Methods

The perovskite SrCoO₃ (SCO) was prepared by using solid-state reaction route method. The starting materials were prepared by mixing the AR grade powders of $SrCO_3$ (extrapure, SRL) and Co_3O_4 (pure, SRL) in stoichiometric proportion. The mixture was calcined in air for 12 hours at 1050^0C in muffle furnace and quenched to room temperature. The calcined powder was ground and compressed into a pellet at 8 MPa using hydraulic press machine. Thereafter, pellets were sintered at 1200^0C in oxygen stream for 24 hours in the furnace. The possible solid-state reaction of the preparation of perovskite SrCoO₃ (SCO) follows:

$$3SrCO_3 + Co_3O_4 + O_2 \xrightarrow{Solid-State\ Reaction} 3SrCoO_3 + 3CO_2$$
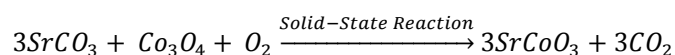
Characterizations:

X-ray Diffractometer: The sample perovskite SrCoO₃ (SCO) was analyzed their phase structure using X-ray diffractometer (Rigaku X-ray diffractometer with Cu Kα radiation) at the physics department, NIT Patna. The XRD patterns were recorded in the range of Bragg's angle 2θ from 20 to 80^0 with step size of 0.020 followed by the scanning rate of 2^0 per min at 40 kV and 30 mA set up of the machine.

FTIR Spectroscopy:

The Fourier Transform Infrared (FTIR) Spectroscopy is one of the techniques used to identify and analyses materials like organic, polymeric and also the inorganic substances. This method wields infrared radiation of 10000 to 100 cm⁻¹ for the scanning of test samples to analyses the chemical properties. Some radiation absorbed and some passed through sample. The radiation absorbed by the sample is converted into rotational and/or

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vibrational energy. Detector detect the resulting signal and shows a spectrum, in the range from 4000 cm⁻¹ to 400 cm⁻¹. which represents a molecular fingerprint of the test sample. This technique is wielded to identify and characterize the unknown materials such as solids, powders, films, or liquids and also identify the contamination on or a material like powders, particles, fibers, or liquids. This also signifies the oxidation, decomposition, or uncured monomers in case of failure analysis investigations [10]. The Fourier Transform Infrared (FTIR) spectra were recorded using Alpha Bruker FT-IR Spectrometer. It has beauty of convenience to measure powdered sample without making pellets by mixing preheated KBr powder or dried at overnight in microwave oven.

III. Result

Analysis of XRD pattern:

Figure 1 shows the XRD pattern of perovskite $SrCoO_3$ (SCO) samples. In this pattern, it can be observed that the diffraction peaks of perovskite $SrCoO_3$ (SCO) at Bragg's angle 2θ =29.45, 32.33, 32.70, 40.40, 44.46, 47.03, 57.43, 58.41, 67.66 and 68.58 and 78.12 corresponded to the (310), (110), (102), (112), (004), (004), (212), (114), (220), (204) and (302) planes of $SrCoO_3$ respectively. The phase of the samples found to be the tetragonal phase from the analysis of the XRD pattern. Average particle size of the sample was calculated from XRD data and found to be 25.7 nm.
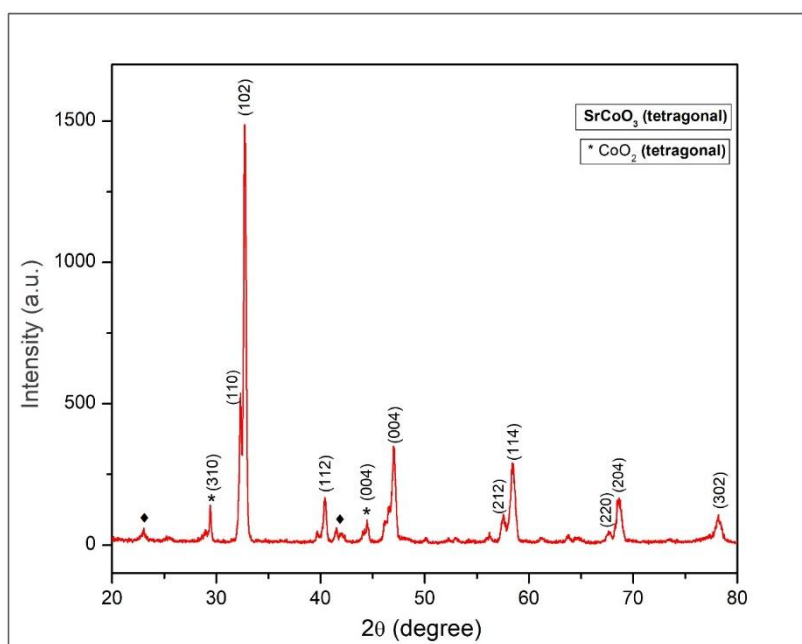

Figure 1:XRD pattern of SrCoO₃ (SCO) Perovskite

The tolerance factor of perovskite $SrCoO_3$ predict as:

$$t_{IR} = \frac{(R_{Sr} + R_O)}{\sqrt{2}(R_{Co} + R_O)}$$

where, R_{Sr}, R_{Co} and R_O are the ionic radii of Sr^{2+}, Co^{3+} and O^{2-} respectively. Values of crystal ionic radii $R_{Sr^{2+}} = 132\ pm$, $R_{Co^{3+}} = 79\ pm\ (for\ low\ spin); 88.5\ pm\ (for\ high\ spin)\ and\ R_{O^{2-}} = 126\ pm$. The value of tolerance factor $t_{IR} = 0.89$ (for low spin) or 0.85 (for high spin) was estimated using $CN = 6$ for Sr, Co and O ions. The crystallite size of the sample was obtained by using the Scherrer' formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

The crystallite size of the sample $SrCoO_3$ corresponds to $2\theta = 32.70$ with respect to (102) peak has been calculated by using the Scherrer' formula and is found to be 32.8 nm. Table no 1 Shows the values of Bragg's angle (2θ), d-spacing, crystallite size, FWHM, corresponding crystal planes of perovskite $SrCoO_3$ (SCO) samples.

Table no 1: Peaks information of perovskite SrCoO₃ (SCO) samples

2 theta (deg.)	d (ang.)	Pick height (counts)	FWHM (deg)	Size (ang.)	Relative Intensity I (a.u.)	Relative height (a.u.)	Plane
29.45	3.030	65	0.25	345	10.16	6.22	310
32.33	2.766	331	0.271	319	32.22	31.51	110
32.70	2.735	1050	0.264	328	100	100	102
40.40	2.230	104	0.32	281	14.61	9.9	112
44.46	2.035	51	0.27	331	7.79	4.9	004
47.03	1.930	245	0.34	269	46.35	23.29	004
57.43	1.603	57	0.50	188	9.92	5.41	212
58.41	1.578	184	0.51	186	32.62	17.53	114
67.66	1.383	24	0.52	193	4.44	2.31	220
68.58	1.367	104	0.539	186	19.85	9.88	204
78.12	1.222	54	0.53	201	12.38	5.17	302

The perovskite sample has mainly double-phase structures. One has SrCoO₃ of tetragonal phase of the space group P4/mmm [123] which was matched with the materials project database (materials id: mp-1273854). Second phase has hexagonal structure. While other also has CoO_2 of tetragonal phase of the space group I4₁/amd [141] which was matched with materials project database (materials id: mp-1282586). On the other hand, XRD patterns analyses and it showed some impurities peaks indicated by diamond (♦) symbol.

Analysis of FTIR spectra:
Figure 2 Shows the FTIR spectroscopic spectra of SrCoO₃ perovskite samples recorded at room temperature. The infrared spectrum of the SrCoO₃ perovskite has intense bands at 1548.08 cm⁻¹, 1507.34 cm⁻¹, 1456.90 cm⁻¹ and 1386.63 cm⁻¹ in medium frequency regions and has also in the higher frequency regions at 2943.52 cm⁻¹ and 2861.06 cm⁻¹. The absorbance peaks were found at 2361.06 cm⁻¹ and 2327.08 cm⁻¹.
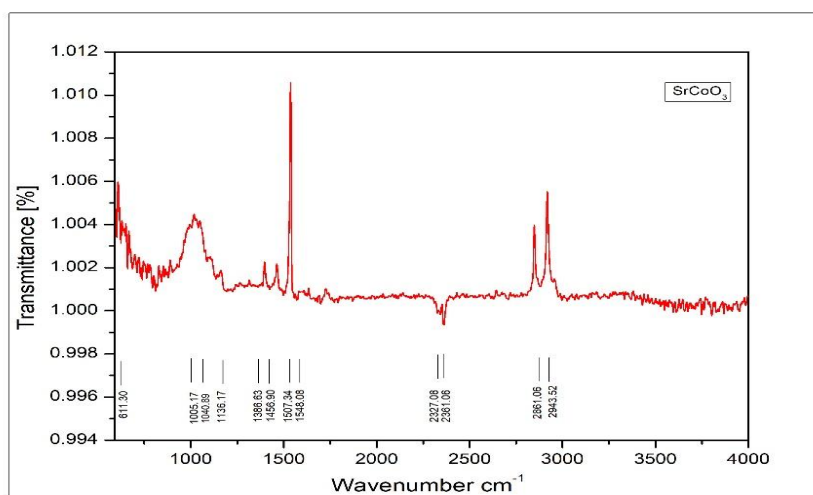

Figure 2: Infrared spectra for SrCoO₃ (SCO)

IV. Discussion
On analyzing the XRD patterns, it had been observed that SrCoO₃ perovskite sample was prepared the polycrystalline sample and multiphase structure of SrCoO₃ tetragonal phase (P4/mmm) along with tetragonal CoO_2 (I4₁/amd) and of unidentified impurities (indicated as diamond ♦ symbol in the XRD pattern). The high intensity peak was found at Bragg's an angle of 32.70⁰ showing tetragonal phase. The diffraction peaks at Bragg's angle 2θ =32.33, 32.70, 40.40, 47.03, 57.43, 58.41, 67.66, 68.58 and 78.12 corresponded to the (110), (102), (112), (004), (212), (114), (220), (204) and (302) planes had been observed as tetragonal phase SrCoO₃. While tetragonal CoO_2 phase peaks had been observed at 2θ =29.45 and 44.46 corresponded to the (310) and (004) planes. The unidentified impurities detected at 2θ = 23.02 and 41.41.

It is important to studies about the vibrational frequencies lying in the infrared regions for the manipulation of properties and advancement of materials and their processes. The metal-oxide M-O (M= Sr, Co, V) bands revealed in different modes of vibration. The Co-O reveals vibrational modes which depend upon their different valence Co^{2+}, Co^{3+}, and Co^{4+}. The Octahedral coordinated valence Co^{3+} and tetrahedral coordinated

valence Co^{2+} have asymmetric stretching vibrational mode and are attributed absorption bands at 580 cm^{-1} and 670 cm^{-1} respectively [11]. The M-O groups (M = Co, Sr and V) also make possible asymmetric stretching bands at 421 cm^{-1} and 512 cm^{-1} in the lower frequency regions [11, 12]. It has been reported that the intense bands occurred between 1000 cm^{-1} and 1800 cm^{-1} (at 997 cm^{-1}, 1159 cm^{-1}, 1389 cm^{-1} and 1560 cm^{-1}) due to the stretching of V-O and V-O-V type vibrational mode [9, 13]. In our case study, the SrCoO$_3$ perovskite exhibits intense bands around 1500 cm^{-1} (at 1548.08 cm^{-1}, 1507.34 cm^{-1}, 1456.90 cm^{-1} and 1386.63 cm^{-1}) and also between 3000 cm^{-1} and 2500 cm^{-1} (at 2943.52 cm^{-1} and 2861.06 cm^{-1}) due to the M-O and M-O-M type stretching vibrational mode. The absorbance peak of the perovskite SrCoO$_3$ obtained in higher frequency regions between 2500 cm^{-1} and 2000 cm^{-1} (at 2361.06 cm^{-1} and 2327.08 cm^{-1}). while other peaks found at medium frequency regions such as 1136.17 cm^{-1}, 1040.89 cm^{-1} and 1005.17 cm^{-1}. The metal-oxygen (M-O) bond in the perovskite structure is corresponded at the absorption bands of 607 cm^{-1} and 746 cm^{-1} respectively [14-16], while in the present study, it is assigned at 611.30 cm^{-1}. The assigned absorbance bands at 858 cm^{-1} and 1450 cm^{-1} shown the existence of the carbonate in the specimen and correspond to the twisting and stretching vibration of CO_3^{2-} respectively [15-16], while in case of our study, stretching vibration of CO_3^{2-} band was found at 1456.90 cm^{-1}. The absorbance peaks at 1118 cm^{-1} are corresponded to the stretching vibrations of C-O and CO_3^{2-} anions in the spectrum of Co_3O_4 [17], while we have attributed the peak band at 1136.17 cm^{-1}. The assigned absorbance peak at 1386 cm^{-1} was correspond to the C-O-C type stretching vibrational mode [18], while in this study we have assigned the peak at 1386.63 cm^{-1}.

V. Conclusion

A multiphase SrCoO$_3$ perovskite ceramic sample was synthesized by solid-state route method. XRD pattern analysis discloses the perovskite crystal of tetragonal phase with 19-35 nm of average crystallite size. FTIR spectroscopic measurements reveal the intense bands. This polycrystalline SrCoO$_3$ perovskite offers an interesting alternative further experimental investigation.

Acknowledgements

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