

Tunable optical bandgap of chromium doped $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ system

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ABSTRACT

Chromium doped $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system were synthesized by sol-gel method. The X-ray diffraction patterns revealed the formation of single-phase orthorhombic structure (Pnma space group). The crystallite size was observed to vary from 26.12169 nm to 33.19551 nm with Cr doping concentration. The dislocation density was also observed to varied from 0.9074×10^{-3} to $1.4655 \times 10^{-3}\text{nm}^{-2}$ with change in Cr doping concentration. The micro strain was observed to increase from 36.8395×10^{-4} to 46.8197×10^{-4} with change in Cr doping concentration. There was no evidence of characteristic absorbance peaks for all the synthesized samples. The optical energy band gap was calculated using Kubelka-Munk equation based on Tauc's plot and observed in the range 0.52 to 1.12 eV.

Keywords: XRD, Optical energy bandgap, Refractive index, Absorption coefficient, Extinction coefficient, Real and imaginary parts of dielectric constant.

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1. Introduction

Colossal magnetoresistance (CMR) is a property of some materials, generally manganese-based perovskite oxides, that empowers them to vividly change their electrical resistance in the presence of magnetic field. Thus, CMR materials fascinated research community due to their exciting and effective behaviour revealed by them in structural, electrical, transport, optical and magnetic properties and their potential applications [1-3]. The charge-ordered phase in half-doped manganites, with compounds, $\text{RE}_{0.5}\text{A}_{0.5}\text{MnO}_3$ (RE=La, Pr, Sm and Nd; A=Sr and Ca) shown a variation of phenomena such as charge, orbital, and spin ordering, with electric and magnetic field induced transitions [4,5]. Besides, the charge ordered (CO)/orbital ordered (OO) and antiferromagnetic insulating (AFMI) stages can be changed efficiently by adding impurities at Mn site. In detail, Mn site doping with Cr in manganites have attracted boundless consideration as Cr^{3+} ion is iso-electronic with Mn^{4+} ion. Magnetic impurities like Cr and Ru can make both metallicity and ferromagnetism in the insulating antiferromagnetic $\text{Pr}_{0.5}\text{A}_{0.5}\text{MnO}_3$ (A=Ca, Sr) [6,7].

2. Experiment

The samples of Polycrystalline $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) were prepared via the sol-gel method [8] by taking pure materials (99.9 % pure). Mixtures of $(\text{NH}_4)_2\text{CO}_3$, $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$, Pr_2O_3 , SrCO_3 , MnCO_3 , and $\text{CrN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$ precursors in stoichiometric amounts were dissolved in distilled water and nitric acid to get a clear solution. Then citric acid was mixed with this solution as the complexing agent (the molar ratio of cations/citric acid is 1:2). After that, a binding agent ethylene glycol was mixed with the chemical solution and heated under a constant stirring at 353 K for 10 minutes. After

6 h, the obtained gel was dried at 393 K for 24 h and ground the dried gel to a fine black powder. The resulting black powder was finally sintered at 1300 K for 10 h. Based on doping concentration $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system, the samples are designated as $x = 0.0$ - PSMCO-0, $x = 0.1$ - PSMCO-1, $x = 0.2$ - PSMCO-2, $x = 0.3$ - PSMCO-3 and $x = 0.4$ - PSMCO-4 respectively. The Raman spectroscopy measurements were performed using Raman spectrometer (Lab RAM Horiba France) with two grating, using 532nm Nd-YAG laser 100mW. XPS measurements for PSMCO-4 at room temperature were undertaken by XPS spectrometer.

3. Result and Discussion

XRD patterns as shown in Fig.1 for all the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples revealed the formation of single-phase structure without any impurities [9]. The Rietveld refinement technique [9, 10] confirmed the that all the synthesized samples belong to orthorhombic structure (Pnma space group).

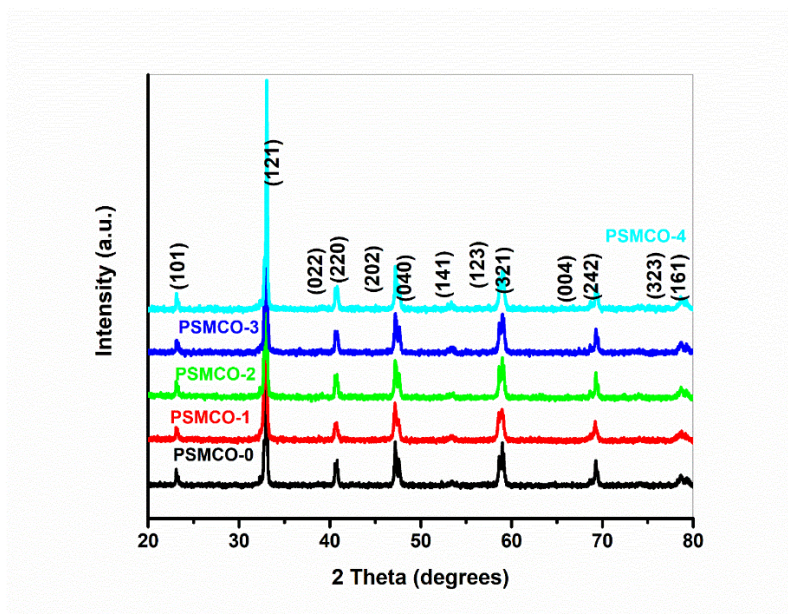


Figure 1: XRD pattern of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system.

It was observed that there is no significant variation in lattice parameters with doping concentrations. This kind of behavior in the lattice parameters may be attributed due to the fact that, there is little difference in the ionic radii between Cr^{3+} and Mn^{3+} ions [11]. The crystallite size was observed to increase for PSMCO-0 to PSMCO-2 with the increase Cr doping concentration and then decreased for PSMCO-3 to PSMCO-4.

The micro strain value can be calculated from equation (1) [12].

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad \text{---(1)}$$

The micro strain value was calculated with increase in Cr doping concentration and found in the range 36.8395×10^{-4} to 46.8197×10^{-4} . Micro strain values were increased from PSMCO-0 to PSMCO-2 samples and decreased from PSMCO-3 to PSMCO-4 samples.

The dislocation density (δ_D) is inversely proportional to the square of crystallite size. The dislocation density increases with the defect occurrence due to several kinds of reason and is calculated using the following relation (2) [12]

$$\delta_D = \frac{1}{D^2} \quad \text{---(2)}$$

The density of dislocation was varied from 0.5755×10^{-3} to $1.048 \times 10^{-3} \text{ nm}^{-2}$ with the doping concentration. It is evident that there is a no systematic effect of Chromium doping on the micro strain and dislocation density of the synthesized samples. The X-ray density for these samples is calculated from the following equation (3) [12, 13].

$$\rho_x = \frac{ZM}{NV} \quad \text{---(3)}$$

The X-ray density was observed to decrease with increasing Cr doping. The X-ray density values decreased from 6383 to 6338 g/cm^3 for PSMCO-0 to PSMCO-3 samples and then increased for PSMCO-4 and its value is 6352 g/cm^3

The UV-visible absorption spectra of all the samples were measured with a spectrophotometer (SYSTRONICS DOUBLE BEAM UV-Vis Spectrometer: 2202) at room temperature in the wave length range 200-800 nm, with a maximum step size of 0.2 nm. The absorbance can be obtained from the instrument and the transmittance can be calculated using the following relation (4).

$$T_s = 10^{-A} \times 100 \quad \text{---(4)}$$

Where, T_s is known as transmittance and A is known as Absorbance. Hence, the absorption coefficient can be calculated using the following relation (5) [14].

$$\alpha = \frac{2.303 \times A}{l} \quad \text{---(5)}$$

Where, α is known as absorption coefficient, A is known as absorbance and l is known as thickness of the specimen. Fig. 2 shows the variation of absorbance and transmittance of all the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples with wavelength in UV-visible range, 200 - 800 nm. In all the synthesized samples we did not observe any characteristic absorbance peak in UV-visible range, probably it would be below 200 nm region.

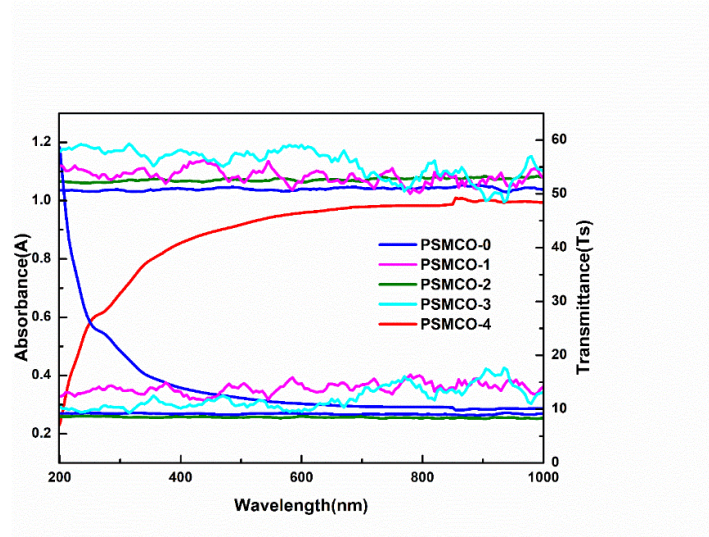


Figure 2: Variation of absorbance and transmittance of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system with wavelength in UV-Visible region.

The refractive index for the samples can be measured with the help of following relation (6).

$$n = \frac{1}{T_s} + \sqrt{\frac{1}{T_s - 1}} \quad \text{---(6)}$$

Where, n is refractive index and T_s is transmittance. Fig. 3 shows the variation of refractive index of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples with wavelength in UV-visible region, 200 - 800 nm. It is observed clearly that, the refractive index remains same for all samples, except for PSMCO-4 which is increased slightly with the frequency without any characteristic absorbance peaks.

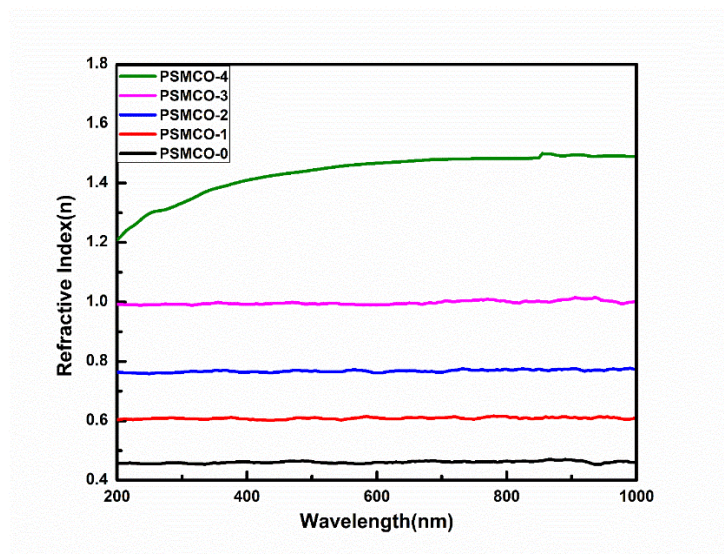


Figure 3: Variation of refractive index of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system with wavelength in UV-Visible region.

Using the following relation (7), extinction coefficient can be calculated [15].

$$k = \frac{\alpha\lambda}{4\pi} \quad \text{---(7)}$$

Where, k is extinction coefficient, λ is wavelength and α is absorption coefficient. Fig. 4 shows the variation of extinction coefficient for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples with wavelength in UV-visible region, 200-800 nm. In case of all the samples, the extinction coefficient was slightly increased with a linear curve.

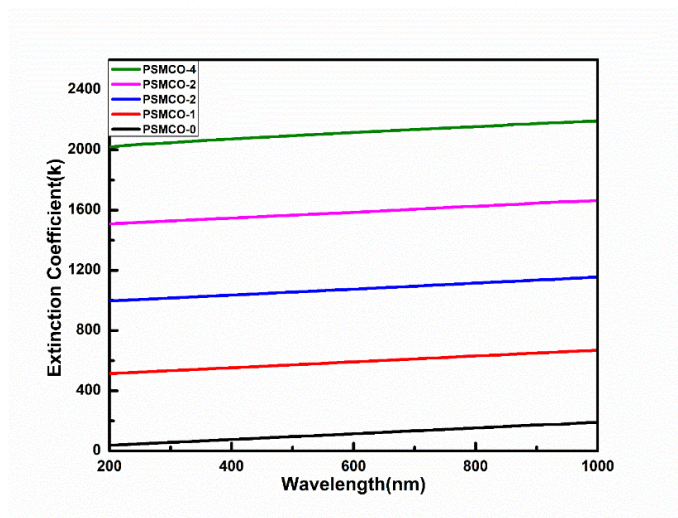


Figure 4: Variation of extinction coefficient of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system with wavelength in UV-Visible region.

The reflectance for all the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples can be calculated with the help of refractive index, as follows (8) [16].

$$R = \frac{(n-1)^2}{(n+1)^2} \quad \text{---(8)}$$

Where, R is reflectance, and n is refractive index. Fig. 5 shows the variation of reflectance for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples with wavelength in UV-visible region, 200-800 nm. PSMCO-0 to PSMCO-3 samples showed no change in the extinction coefficient with frequency, but it is found a linear decrease in the extinction coefficient for PSMCO-4.

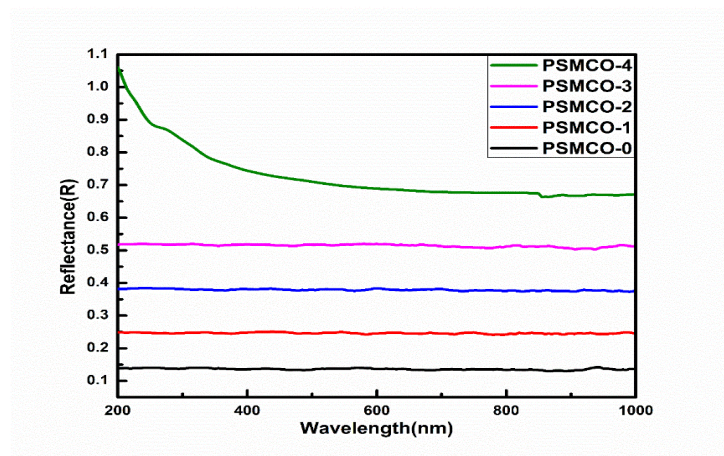


Figure 5: Variation of reflectance of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system with wavelength in UV-Visible region.

Using the refractive index and extinction coefficient, the real and imaginary parts of dielectric constant can be expressed with the following relations (9 and 10) [17, 18].

$$\varepsilon_i = 2nk \quad \text{---(9)}$$

$$\varepsilon_r = n^2 - k^2 \quad \text{---(10)}$$

Fig. 6 shows the variation of real and imaginary parts of dielectric constant for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples with wavelength in UV-Visible region, 200-800 nm. We did not observe any characteristic peak and probably the peak would be below 200 nm region.

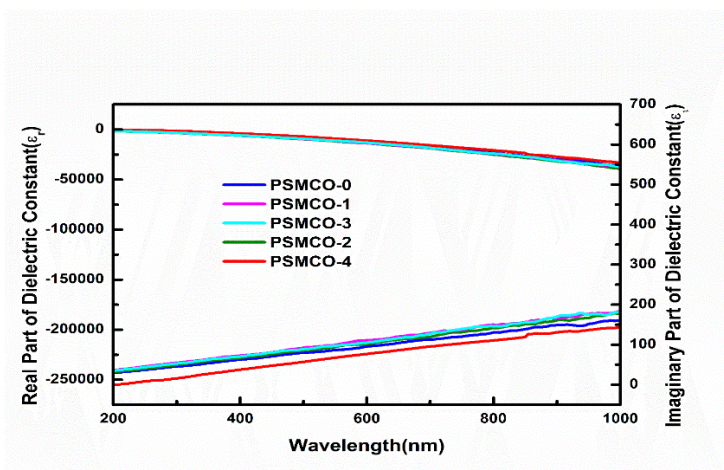


Figure 6: Variation of real and imaginary parts of dielectric constant of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system with wavelength in UV-Visible region.

Optical bandgaps for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples were determined from UV-Vis absorption spectra and corresponding Tauc's plots are plotted as shown in Fig.7 for PSMCO-0, where $h\nu$ is incident light energy and absorption coefficient is denoted by α .

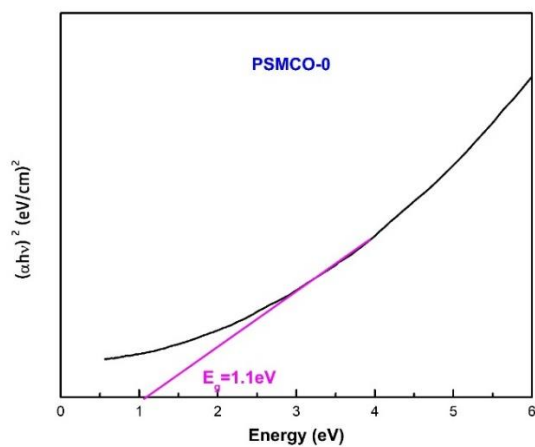


Figure 7: Tauc's plot for PSMCO-0 sample

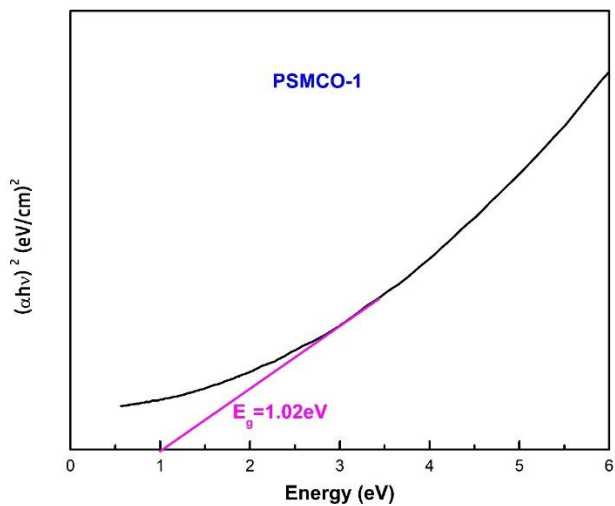


Figure 8: Tauc's plot for PSMCO-1 sample

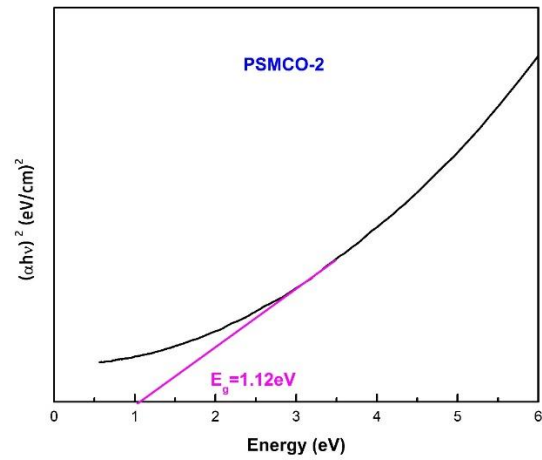


Figure 9: Tauc's plot for PSMCO-2 sample

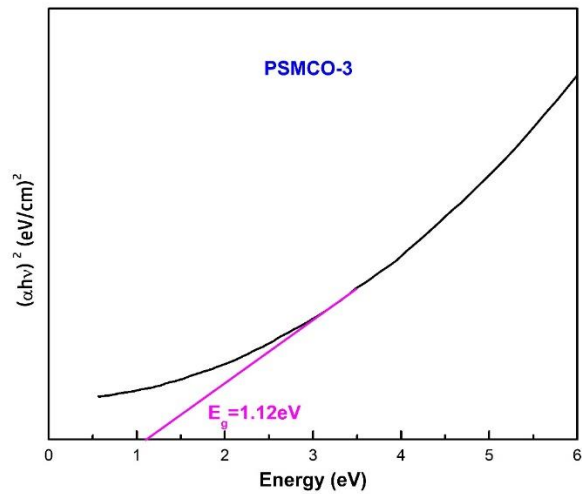


Figure 10: Tauc's plot for PSMCO-3 sample

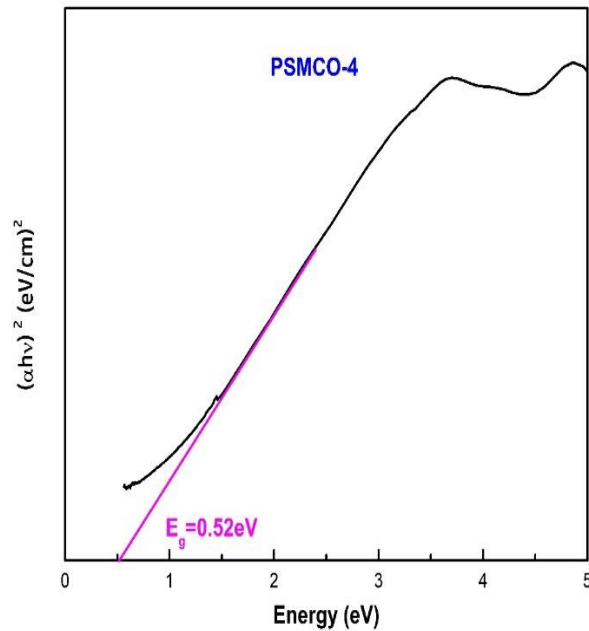


Figure 11: Tauc's plot for PSMCO-4 sample

The optical bandgap plots for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples is shown in Fig's 7 to 11, from which we have seen non-uniform change in energy bandgap values with increase in Cr doping concentration. The absorption coefficient has been determined from the absorption data by using the fundamental relationships (11, 12 and 13) [15, 16].

$$I = I_0 e^{\alpha t} \quad \text{---(11)}$$

$$A = \log \frac{I_0}{I} \quad \text{---(12)}$$

$$\text{and } \alpha = \frac{2.303(A)}{t} \quad \text{---(13)}$$

Where, α is absorption coefficient, A is the absorbance, and t is the thickness of the samples. To calculate the optical absorption for the present ferrite nanoparticles, the following Tauc's relation (14) [15, 16] is used

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad \text{---(14)}$$

Where, α is absorption coefficient, h is plank's constant, ν is frequency, A is absorbance and E_g is optical energy bandgap. $(\alpha h\nu)^{1/n}$ was plotted as a function of the photon energy ($h\nu$) for different n values ($n=1/2, 3/2, 2, 3$). These plots are known as Tauc's plots and are presented in Fig's. 7 to 11. For direct allowed transition $n=1/2$, indirect allowed transition $n=2$, direct forbidden transition $n=3/2$ and forbidden indirect transition $n=3$. To determine the possible transitions, $(\alpha h\nu)^2$ vs $h\nu$ is plotted and corresponding optical energy bandgap were obtained from extrapolating the straight portion of the graph on $h\nu$ axis.

Table-1: Lattice parameters, Bragg's angle, FWHM, crystallite size, density, microstrain and Energy gap of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) system.

Sample code	PSMCO-0	PSMCO-1	PSMCO-2	PSMCO-3	PSMCO-4
Lattice Parameter (a) (Å)	5.4218	5.4228	5.4275	5.4205	5.4268
Volume of Unit Cell (Å ³)	225.9811	226.0074	226.3367	226.0213	226.4728
Bragg's Angle (2θ) (°)	32.93597	32.92538	32.93884	32.9668	32.94974
FWHM (°)	0.31719	0.29186	0.2496	0.25167	0.27568
X-ray Density (ρ _x) (kg/m ³)	6383	6373	6356	6338	6352
Crystallite Size (D) (nm)	26.12169	28.38796	33.19551	32.92485	30.05598
Dislocation Density(δ _D) (nm ⁻²) x10 ⁻³	1.4655	1.2408	0.9074	0.9224	1.1069
Micro strain (ε)x10 ⁻⁴	46.8197	43.0954	36.8395	37.1117	40.6745
Energy Gap (E) (eV)	1.1	1.02	1.12	1.12	0.52

The calculated optical bandgaps were observed in the range 0.52–1.12eV, which are summarized in Table. 1. This optical bandgap range behaves similar to semiconductors (E_g is in the range 0.5–2.5eV). In these samples Mn cations exist a mixed valence of Mn^{3+} and Mn^{4+} , which are surrounded by six O^{2-} anions, forming MnO_6 octahedral structure. The optical bandgaps can be attributed to the electronic transition from up-spin of Mn^{3+} ion and down-spin band of a adjacent Mn^{4+} ion, and the energy difference between two bands is Hund's coupling energy [17].

4. Conclusions

In this article we studied the different properties of sol-gel synthesized $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) samples and its doping effect on the structural and optical properties as follows:

1. The crystallite size was calculated and found in the range 26.12169 nm to 33.19551 nm.
2. The dislocation density was calculated with increase in Cr doping concentration and found in the range 0.5755×10^{-3} to $1.048 \times 10^{-3} \text{ nm}^{-2}$
3. The micro strain was calculated and found in the range 10×10^{-4} to 6.452×10^{-4} with Cr doping concentration.
4. The characteristic absorbance peaks were not observed for any of the synthesized samples and probably it would be below 200 nm region.
5. The optical energy gap was calculated using Kubelka–Munk equation based on Tauc's plot and found in the range 0.52 eV to 1.12 eV, which could be attributed due to electronic transition from up-spin of Mn^{3+} ion and down-spin of an adjacent Mn^{4+} ions.
6. From our results it is evident that the band gaps can be tuned by varying Cr doping concentration.

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