

Probing Oxygen Vacancies Using Raman and Fourier Transform Infrared Investigations on “B-Site” Chromium-Doped Strontium Titanate

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(Received October 09, 2017)

Abstract: Pure and “B-site” doped strontium titanate ($\text{SrCr}_x\text{Ti}_{1-x}\text{O}_3$; $x = 0.0 - 0.2$) were prepared by solid-state ceramic route. The phase and crystallinity of the synthesized powders were studied using X-ray diffraction. These studies revealed that the prepared samples were single phase and possessed cubic structure. The chromium doping at “B-site” has been investigated using spectroscopic techniques such as Raman and Fourier transform infrared techniques. The effect of the doping on the oxygen vacancies has been investigated using these spectroscopic techniques. Additionally, the enhanced room temperature electrical conductivity has been discussed in support of the influence of doping generated defects on the charge carrier concentration.

Keywords: Strontium Titanate, XRD, FTIR, Raman, Oxygen Vacancies, Conductivity.

1. Introduction

Strontium Titanate (ST) is a ceramic material used for many applications such as SOFCs (solid oxide fuel cells), gas sensing and photo-catalysis^{1,2}. Its low cost and stable nature even at elevated temperatures, make it more reliable to work for many applications¹. Different dopants may help in the tuning of its properties for various applications. Strontium Titanate is a cubic perovskite at room temperature. Titanium occupies body center position in TiO_6 octahedral. Chromium ions generally acquire either 3+ or 6+ oxidation state while titanium in pure and defect-free strontium titanate

acquires a 4+ oxidation state. Therefore, B-site doping of chromium may generate point defects like oxygen vacancies in the sample. These materials may have found applications in switchable memory devices and photocatalysis³.

Wang et al. in 2006 reported the work on Cr^{3+} ions doping at both "A" as well as "B-site" of strontium titanate to increase the absorption of visible light for the polycrystalline powdered sample⁴. T. Hara et al. prepared Cr doped ST for oxygen sensing purpose⁵. W. Wei et al. also studied the effect of Cr doping at both of its sites theoretically by Density Functional Theory⁶. Till now, no research has been reported on the correlation effect of B-site chromium doping and correspondingly generated oxygen vacancies to the best of our knowledge.

2. Experimental

Pure and Chromium (Cr) doped strontium titanate ($\text{SrTi}_{(1-x)}\text{Cr}_{(x)}\text{O}_3$; named as SrCrTx ; where $x = 0.0, 0.1, 0.2$) were prepared by mixing high purity Strontium Carbonate (Aldrich Chemical, 99.9% purity), titanium oxide (Merck, > 99% purity) and chromium oxide (Sentury, 99.9% purity) in a high energy planetary ball mill for 120 minutes in their stoichiometric proportion². IPA (Iso-propanol) was used as a mixing medium. The obtained suspension was then dried at 100°C for 8 hrs. After Drying, the mixture was ground for an hour by hand using mortar pestle followed by calcination at a constant temperature of 1100 °C for 4 hr⁷. The heating rate was also kept constant at 200 °C/hr and then the samples were allowed to cool naturally to RT. The calcined material was mixed with PVA (Poly-Vinyl-Alcohol) as a binder (2% by weight) to press pellets. A pressure of 120 MPa was applied for 5 minutes and then released under a uniaxial pellet pressing machine in a cylindrical die of 10 mm diameter. These pellets were sintered at 1300 °C⁸ and then lapped on a very fine sand paper followed by silver coating at both of its flat surfaces for conductivity measurement.

Room temperature powder X-ray diffraction (XRD) was carried out to analyze its phase formation. This was done by Discover D-8 X-Ray Diffractometer using $\text{Cu-K}\alpha$ radiation (0.15418 nm) at a scanning rate of 2 °/min. Raman spectroscopy was done on powder samples using RenishawinVia Raman Microscope. This was done under a green laser of wavelength 514 nm. Fourier Transformation Infrared (FTIR) spectra were studied on FTIR-Spectrum RX I Perkin-Elmer spectrometer using kBr method. The room temperature conductivity of the samples was measured from the linear portion of IV curves obtained by Keithley 2400 Source meter.

3. Results and Discussion

The XRD patterns of pure and Cr-doped ST are shown in Fig. 1. It confirms the formation of single phase crystalline perovskite material, which can be matched with the Joint Committee on Powder Diffraction Standards (JCPDS) card # 86-0177¹. The non-split peak around 45° of 2θ value (plane (200)) confirmed cubic nature of the material. Some minor extra peaks were also seen in the XRD patterns as the higher doping was achieved (Represented by Astrick in Fig. 1).

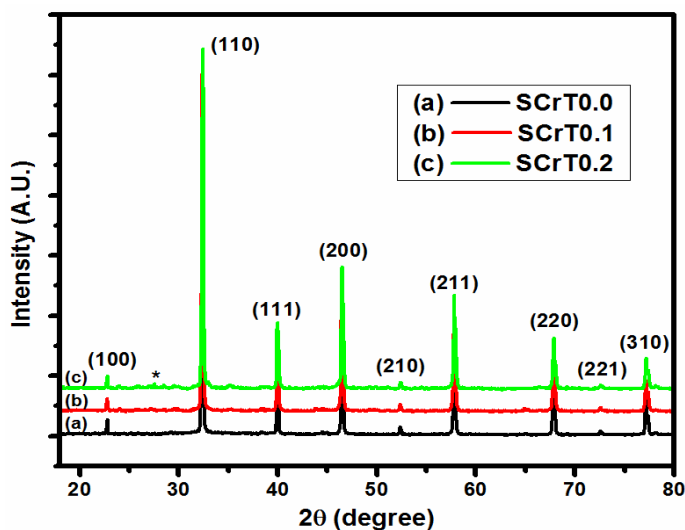


Figure 1: XRD patterns of $(\text{Sr Ti}_{(1-x)} \text{Cr}_x)\text{O}_3$; (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$

Infrared transmittance spectroscopy has been extensively used to reveal the structural details of the material through the appearance of various fundamental vibrational modes of different bonding groups present in it. These spectra show Ti-O and Cr-O stretching modes at $\sim 600 \text{ cm}^{-1}$ and 800 cm^{-1} respectively. FTIR transmission spectra of pure and chromium doped samples are shown in figure 2. The band appearing at about 650 cm^{-1} shows the stretching mode of Ti-O bond in a perovskite (TiO_6) structure^{8,9}. No extra band was visible after 2000 cm^{-1} confirmed the formation of pure strontium titanate as no organic impurity was left out after synthesis. The ionic radius of Cr ion (55 pm) is smaller than that of Ti ion (60.5 pm). Cr doping at Ti site can effectively alter the nature of Ti-O bond structure and its surrounding. As the dopant concentration was increased the width of Ti-O band decreased and two new peaks emerged close to 848 cm^{-1} and 906 cm^{-1} . The extra transmission bands appeared in these spectra are due to newly formed Cr-O bonds in place of Ti-O bonds¹⁰.

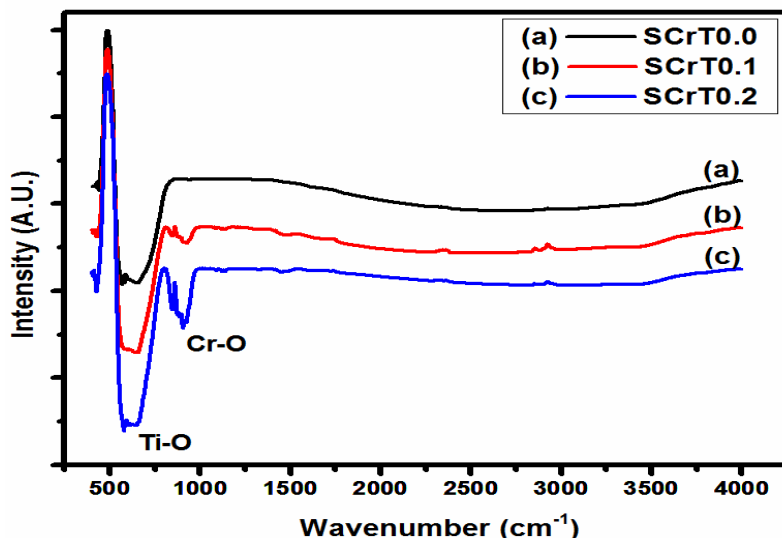


Figure 2: FTIR spectra of (a) SCrT0.0, (b) SCrT0.1 and SCrT0.2

Chromium exhibits different ionization states than titanium. It also shows multiple oxidation states such as Cr^{3+} and Cr^{6+} . It has been stated that Chromium ion in Cr^{6+} state acts as a donor and leaves at least one oxygen vacancy in its vicinity¹¹. The effect of oxygen vacancies on the lattice dynamics of ST was investigated by Raman spectroscopy in 100 - 2000 cm^{-1} region. These spectra (Fig. 3) exhibit the broad absorption phonon peak superimposed by fine component peaks in 100 - 500 cm^{-1} , 550 - 900 cm^{-1} and broad weak hump $\sim 1050 \text{ cm}^{-1}$. The peaks at 248, 364, 646 and 1023 cm^{-1} are due to second order Raman mode. By comparing the Raman spectra with the reported data three first order phonon modes were identified at approximately 176 cm^{-1} , 615 cm^{-1} and 789 cm^{-1} (Fig. 3)¹². Un-doped Strontium Titanate exhibits prominent second-order phonon modes. The first-order Raman scattering is symmetry forbidden in cubic perovskite-like Strontium Titanate. The first order phonon modes become prominent when the bond structure of ST is altered by doping or any other treatment. D. A. Tenne et. al. annealed the ST in oxygen deficient environment and observed a dedicated peak for oxygen vacancies in their Raman analysis. This peak disappeared on re-oxidation¹³. Therefore, on doping chromium ions in ST, the introduction of oxygen vacancies leads to the appearance of the symmetry-forbidden first-order Raman peaks with a maximum at 760 cm^{-1} . The change in the crystalline field effect from the neighboring atoms, lattice strain and oxygen vacancy cause activation of these modes to vibrate at different frequencies as compared to un-doped ST.

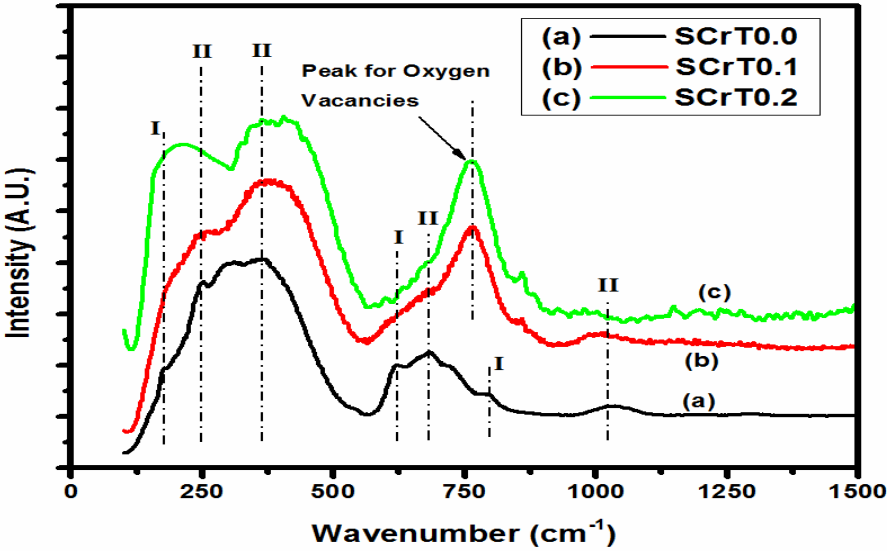


Figure 3: Raman spectra of $(\text{Sr Ti}_{1-x}\text{Cr}_x)\text{O}_3$; (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$

The conductivity of these samples was found to be increasing with increasing doping concentration (Fig. 4). The formation of oxygen vacancies as a result of doping leads to the generation of free charge carriers. Each oxygen vacancy leaves two free electrons that in turn contribute in the conductivity of the material. The increase in the charge carrier concentration can be validated by the increase in conductivity of the doped samples¹³.

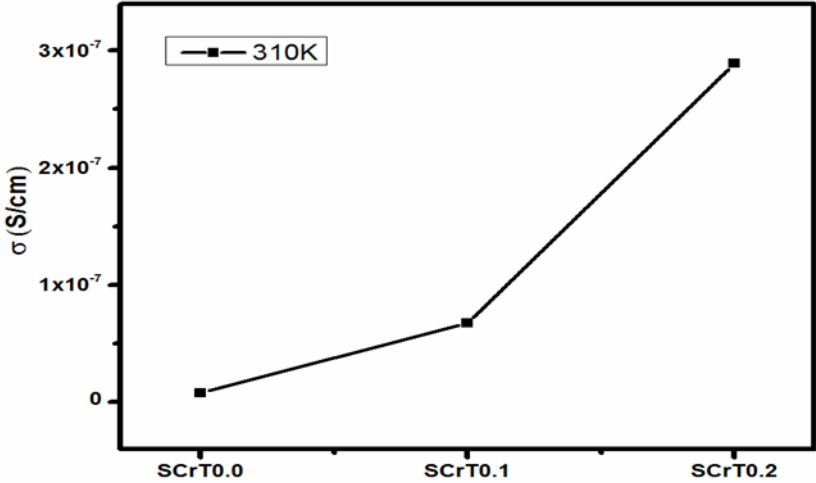


Figure 4: The conductivity of the pure and chromium doped strontium titanate

4. Conclusion

Pure and Cr-doped ST was prepared by solid-state method. Phase formation was confirmed by XRD pattern. The doping of smaller Cr ion at Ti-site altered the Ti-O bond structure in oxygen octahedral. Subsequently, this was confirmed by FTIR transmission spectra of pure and doped samples. Moreover, Cr doping at titanium site generates oxygen vacancies. This was substantiated by the additional peak observed in Raman spectra. The increase in sample conductivity with Cr-doping also supported the formation of oxygen vacancies and its corresponding phenomenon of the release of charge carriers.

Acknowledgement

Authors are thankful to Star College Grant (Department of Biotechnology), Gargi College-wide SAN/No.102/IFD/DBT/SAN/1911/2008-09; which partly supported this research work. We are thankful to Principal, Gargi College and pay our gratitude towards USIC, University of Delhi for providing various facilities. One of the authors, Sachin Kumar is also thankful to UGC (University Grant Commission) for providing JRF (Junior Research Fellowship) scholarship.

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