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## On the structural, morphological and dielectric properties of Cr-doped SrTiO<sub>3</sub> nanoparticles

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### Abstract

Undoped and chromium (Cr) doped SrTiO<sub>3</sub> (STO) nanoparticles were synthesized by coprecipitation method. The cubic structure and perovskite phase were confirmed by X-ray diffraction (XRD). The crystallite size of STO is 45 nm and when Cr ion concentration is increased, the crystallite sizes also increased. The nanoparticles are observed from SEM analysis and the purity of the undoped and doped samples are confirmed by EDS spectrum. The dielectric constants are increased at low frequencies when increase the Cr ions in the STO matrix.

**Keywords:** SrTiO<sub>3</sub>, Nanoparticles and Dielectric constant.

### 1 Introduction

Due to the extensive works on perovskite (ABO<sub>3</sub>) materials for its outstanding potential application in ferroelectrics, superconductor, random access memories, photovoltaics or photocatalysis and thermoelectric devices [1,2]. Due to the technological applications in the field of capacitors, transducers and nonvolatile random access memory devices, the alkaline earth titanates ATiO<sub>3</sub> (A = Ca, Mg, Ba and Sr) have much interest to investigated intensively for fast few years. In the various ATiO<sub>3</sub> materials, Strontium titanate (SrTiO<sub>3</sub>) is one of the most investigated material due to their peculiar quantum paraelectric nature, semi-conducting behaviour, in addition with it has been widely used in the field of pyroelectric detectors, electro optical modulators, thin film capacitors and optical memories [1]. STO is wide band gap semiconductor materials (3.2 eV) like TiO<sub>2</sub> and the optical band gap is easily tuned by doping of suitable transition metal ions at Sr or Ti site. Also, STO have higher relative dielectric constant ( $\epsilon_r$ ) and this materials is the most promising dielectric materials for high-voltage capacitor applications [3]. Transition metal doped STO has often considered as a way to induce a long range magnetic ordering in dielectric materials. STO is an incipient ferroelectric material, i.e. it possesses polar soft modes but does not exhibit any ferroelectric phase transition down to 0 K. It is known that the dielectric response and other related properties of STO can be modified by controlling the Sr/Ti ratio and oxygen vacancy concentration, by oxygen isotope exchange and by doping/substituting Sr

and/or Ti ions [4]. The radius of Cr cations in octahedral coordination is close to that of Ti<sup>4+</sup> and there are several works in which a Cr<sup>3+</sup> dopant was reported to occupy Ti sites in STO. These works observed conductivity, magneto-resistance and ferromagnetic properties for the application of nonvolatile random-access memories. Shen et al [3] reported a high dielectric constant for rare earth doped SrTiO<sub>3</sub> ceramics and Tkach et al [4] observed high dielectric constant for Cr doped SrTiO<sub>3</sub>. Only very few reports available for dielectric and ferroelectric behaviour in Cr doped STO ceramics. Since, an attempt is made to synthesize Cr doped STO nanoparticles by co-precipitation method and studied the structural, morphological, optical and dielectric properties.

### 2 Experimental

Undoped and Cr doped strontium titanate nanoparticles were prepared by coprecipitation method. Strontium nitrate Sr(NO<sub>3</sub>)<sub>2</sub>, Titanium (IV) iso-propoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>) and oxalic acid [(COOH)<sub>2</sub>·2H<sub>2</sub>O] were used as a starting precursor. Typically, 0.1 M of strontium nitrate was dissolved in 150 ml of distilled water and magnetically stir for 10 min and 0.1 M of titanium (IV) isopropoxide was dissolved in 150 ml of distilled water and magnetically stirred for 10 min, separately. Then these solutions were mixed with the above solution slowly. After that 0.2 M of oxalic acid was dissolved in 200 ml of distilled water then it was added to the above stock solution. White oxalate precipitates were formed and then stirring is continued for another 2 hours. After that the white precipitate were kept as for 2 hours for aging. Then these precipitates were centrifuged and washed with distilled water for several times, for removing unreacted impurities. Then the wet precipitate was further dried at 80 °C for overnight. Cr doping is done made by adding appropriate amount of 0.1 M CrCl<sub>3</sub> in titanium iso-propoxide. The undoped sample showed white color, while Cr doping leads to a light green coloration of the powder, indicating successful incorporation of Cr<sup>3+</sup> into the SrTiO<sub>3</sub>

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lattice. Undoped and Cr doped SrTiO<sub>3</sub> nanoparticles were obtained by calcinations of dried samples at 1000 °C for 3 hours. These SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> samples are designated as STCRX, where X is the dopant concentration in at. %.

The crystalline nature and phase purity of the SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> nanoparticles were characterized by using X-ray diffractometer (XRD) (PANalytical X'Pert Pro (with Cu-K $\alpha$  radiation)). The morphology of the samples was examined by scanning electron microscopy (SEM) (Tescan VEGA 3). The elemental analysis was carried out by energy dispersive spectroscopy (EDS) (Oxford Instruments, Model No. 7582). The UV-Vis absorption spectrum was recorded at room temperature using UV-Vis absorption spectrometer (Shimadzu 4100). FT-IR spectrum of synthesized sample was recorded by FT-IR (Shiraz) spectrometer in the range of 4000-400 cm<sup>-1</sup>. The impedance studies were carried out with an input signal level of 1.3 V in the room temperature using a computer-controlled impedance analyzer (HIOKI LCR Hi TESTER, Model: 3532-50) in the frequency range of 100 Hz to 1 MHz.

### 3 Results and Discussion

#### 3.1. XRD Analysis

X-ray diffraction pattern of undoped and Cr-doped SrTiO<sub>3</sub> nanoparticles is shown in Fig.1. All the peaks agrees with the reported JCPDS data (Card No. 89-4934) of the cubic phase. Sharp single peaks, which are almost similar to that of SrTiO<sub>3</sub> with a change in peak intensity, confirm the formation of single-phase polycrystalline compounds. A shift in XRD peak positions compared to that of SrTiO<sub>3</sub> on Cr-doping confirms substitution of Cr at Ti site. The crystallite size and lattice parameter ('a' for cubic) of the undoped and doped samples are estimated using the Scherrer's formula, and the calculated values are given in Table 1. When Cr is introduced, the crystallite size increase, due to the ionic radius of Cr<sup>3+</sup> (0.62 Å) is slightly higher to the radius of the Ti<sup>4+</sup> ion (0.61 Å). The increase in doping concentration increases the crystallinity of STO and its average crystallite size. No other secondary phase or impurity peaks like CrO or Cr<sub>2</sub>O<sub>3</sub> were detected in these samples. High temperature (1000 °C) annealing in the presence of O<sub>2</sub> decreases the structural defects or oxygen vacancies.

#### 3.2. SEM and EDX Analysis

Fig. 2 shows the SEM images of SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> nanoparticles. Fig. 2 (a-b) shows a different magnification of undoped STO nanoparticles and it shows spherical morphology in which the particles arranged in flower like appearance. The size of the different cubes is in the range of 60-260 nm, which is larger than the crystallite size estimated from XRD. This is due to the agglomeration of particles. Similarly, Fig. 2 (c-d) shows spherical particles of 1 at. % and Fig. 2 (e-f) shows 5 at. % of Cr ions doped STO nanoparticles. The size of the particles range is 60-280 nm and 70-280 for 1 % and 5% of Cr doped STO, respectively. The chemical composition and purity of the samples were examined using EDS and also whenever a material is doped, it is necessary to see whether the dopant has

entered the host system completely or not which can be seen from the EDS spectrum. Fig. 3 shows the EDS spectra of undoped and Cr doped STO nanoparticles. The EDS spectra confirm the presence of Sr, Ti, O, and Cr ions only in the prepared samples without any other impurities.

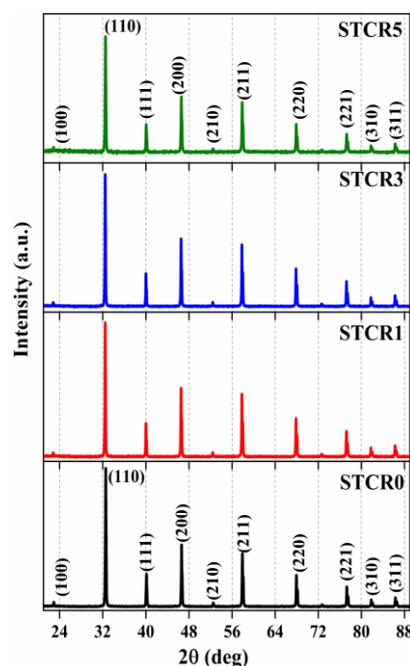


Fig. 1. XRD pattern of SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> nanoparticles

Table 1: Parameters calculated from XRD pattern of undoped and Cr doped SrTiO<sub>3</sub> nanoparticles

Materials	Crystalline Size (nm)	Dislocation Density $\rho \times 10^{15}$ (lines/m <sup>2</sup> )	Strain ( $\eta \times 10^{-3}$ )	Lattice Constant (Å)
STCR0	45	4.87	3.07	3.881
STCR1	45	4.85	3.07	3.893
STCR3	46	4.75	3.04	3.902
STCR5	47	4.65	3.02	3.905

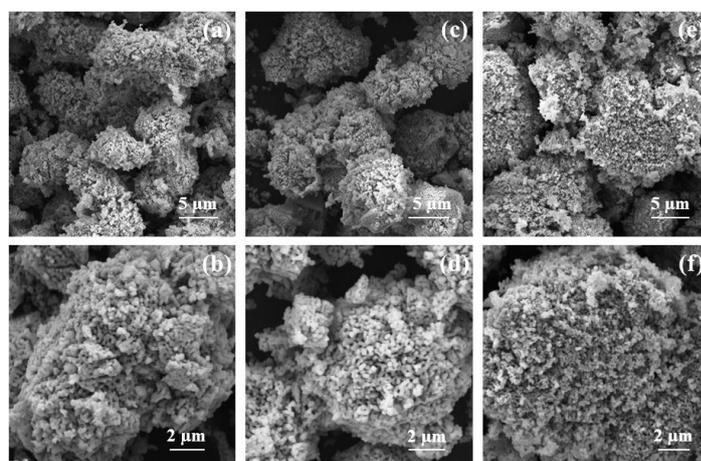


Fig. 2. SEM images of (a-b) pure, (c-d) 1% of Cr doped and (e-f) 5% of Cr doped SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> nanoparticles

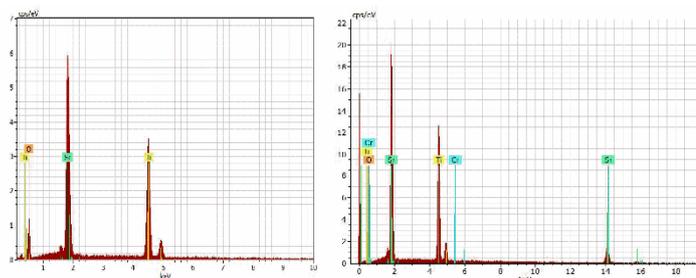


Fig. 3. EDS spectrum of (a) pure and (b) 5 % of Cr doped SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> nanoparticles

### 3.3. UV-vis and FTIR Analysis

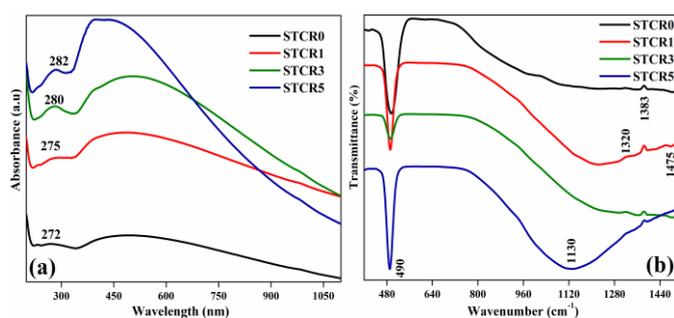


Fig. 4. (a) UV-vis absorbance and (b) FTIR spectra of SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> nanoparticles

The UV-vis spectra of undoped and Cr doped STO nanoparticles are shown in Fig. 4(a). It is observed that while increasing dopant concentration, the absorption maximum shifted towards higher wavelength indicating the strong optical absorption behavior of Cr doped STO. The Cr doped nanoparticles shows a red-shifted onset of absorption in the UV region.

FTIR is a technique used to obtain the information chemical bonding, band positions, and absorption peaks are depends on crystalline structure, chemical composition of the materials. The characteristic peaks exhibited by FTIR spectra of Cr doped STO nanoparticles are shown in Fig. 4(b).

The IR spectra for different doping levels are very similar, indicating the same organic compounds to be present after synthesis.

The broad absorption bands around 1474 cm<sup>-1</sup> is attributed to normal polymeric O-H stretching vibration of H<sub>2</sub>O in Sr-Ti-O lattice. The normal characteristic IR peaks below 1000 cm<sup>-1</sup> features the possibilities of Sr-O/Ti-O/Cr-O bonds and the functional groups.

Absorption bands observed in the range of 420–680 cm<sup>-1</sup> attributed to the stretching modes of metal oxides (M-O). The splitting of sub-bands around 500–400 cm<sup>-1</sup> are due to the presence of Ti<sup>4+</sup> and Cr<sup>3+</sup> ions [1].

The peak at 1130 cm<sup>-1</sup> is attributed to the C-O-C bond and around peaks at in the range of 1300-1400 cm<sup>-1</sup> attributed to C=C stretching bond, due to the synthesis.

### 3.4. Dielectric measurement

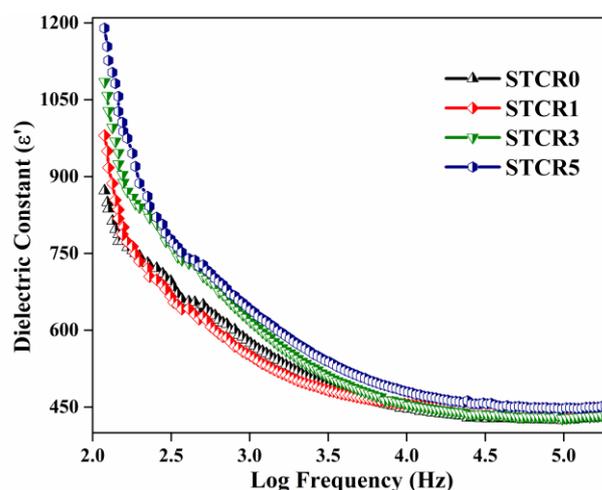


Fig. 5. Dielectric spectra of SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> nanoparticles

The results of the low-frequency dielectric measurements are shown in Fig. 5. Dielectric constant or dielectric permittivity is calculated from  $\epsilon' = \frac{Cd}{\epsilon_0 A}$  where d is the

sample thickness, A is the surface area of the sample, and  $\epsilon_0$  is the free space permittivity ( $8.854 \times 10^{-14}$  F cm<sup>-1</sup>). Dielectric behaviour of Cr-doped STO samples is qualitatively similar to that of undoped STO and reveals no anomalies.

The dielectric constants increases with the Cr<sup>3+</sup> ion substituted in Ti<sup>4+</sup> site. However, there is a remarkable increase of the low-frequency dielectric constant (ε') from 875 to 1190 for 5% Cr. The observed increase of the dielectric permittivity can be due to intrinsic effects, related to the incorporation of Cr on the STO host lattice or due to extrinsic effects that include the development of Schottky barriers between semi-conductive grains at insulating grain boundaries (interfacial/grain boundary effect), composition stoichiometry variations and density of the ceramics.

### 4 Conclusions

In summary, perovskite STO nanoparticles were prepared by co-precipitation method, and the effect of different Cr ion content on the structural, morphological, optical, and electrical properties have been investigated in detail. Cr doping enhanced the dielectric constant in STO nanoparticles. Here increased concentration of Cr increase the dielectric constant unlike other dopants due to dominant contribution from orientation and electronic polarization which is achieved here by the method of preparation.

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