

Topic Code:

Influence of trivalent non-magnetic ion on structure, optical, magnetic and dielectric properties of $YCrO_3$ perovskite

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Abstract: In this report, effect of Bi^{3+} doped on structural, optical, magnetic and dielectric properties is studied. Upon Bi substitutions, unit cell volume shows an evolution and the average grain size is elongated. The optical band gap of the prepared samples decreases with increasing Bi content. The maximum magnetization (M_s) value decreases and coercivity (H_c) increases that can be attributed to the increasing structural distortion with Bi content. There is an anomaly observed at around magnetic transition in the temperature dependent dielectric study. The dielectric permittivity is enhanced upon Bi substitutions.

1. INTRODUCTION

In past few decades, there has been significant interest in perovskite type rare earth chromite family due to its intriguing magnetic and transport properties. In recent years, rare earth orthochromites (general formula $RCrO_3$, R= rare earth metal) have received huge attention in enormous fields of applications such as interconnected material of solid oxide fuel cells, negative temperature coefficient thermistors and humidity sensors. $YCrO_3$ is an important material in the class of rare earth chromites. It exhibits orthorhombic perovskite structure with $Pnma$ space group. The centrosymmetric nature of this compound has attracted considerable attention due its potential applications as a magnetoelectric material. It exhibits a well-accepted canted antiferromagnetic ordering with a weak ferromagnetic moment below $T_N = 140$ K and a relaxor-type dielectric behaviour with presence of an anomaly around 473 K [1, 2]. In this report, a detailed investigation of structural, magnetic and dielectric properties of polycrystalline samples $Y_{1-x}Bi_xCrO_3$ ($x = 0.00, 0.05, 0.10, 0.15$) is carried out.

2. EXPERIMENTAL DETAILS

A series of $Y_{1-x}Bi_xCrO_3$ ($x = 0.00, 0.05, 0.10, 0.15$) polycrystalline samples are synthesized through sol-gel auto combustion route [3]. For the phase confirmation XRD technique is adapted. FESEM technique used to study the surface morphology. UV spectroscopy is used to study the band gap of all the samples. For magnetic study, VSM is used and to know the dielectric behavior, impedance analyzer is adopted.

3. RESULTS AND DISCUSSION

XRD spectra along with Rietveld refinement shows the pure phase formation of all the compounds and crystallize in distorted orthorhombic perovskite structure ($Pnma$ space group). FESEM morphology depicts that grain size is increased with Bi substitution due to the cationic size mismatch as shown in Fig.1. Energy band gap is reduced upon Bi substitution confirm from UV study. The maximum magnetization (M_s) value decreases and coercivity (H_c) increases can

be attributed to the structural distortion with Bi content shown in Fig.2. Dielectric permittivity is enhanced with increasing Bi content and a dielectric anomaly is found near magnetic transition.

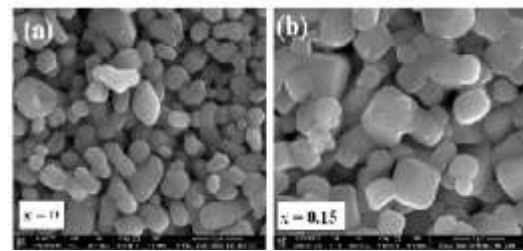


Fig.1. (a-b) FESEM morphology of $Y_{1-x}Bi_xCrO_3$ ($x = 0.00$ & 0.15).

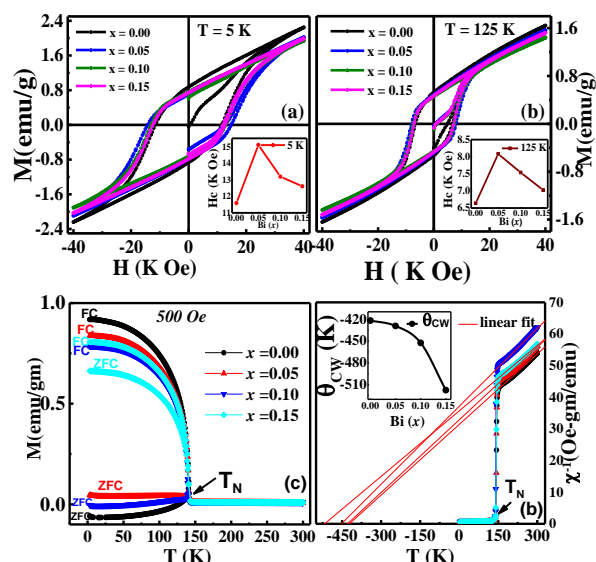


Fig.2. (a-b) M-H, (c-d) M-T plots and Curie Weiss fitting of $Y_{1-x}Bi_xCrO_3$ ($x = 0.00, 0.05, 0.10, 0.15$).

REFERENCES

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- [2]. A. K. Mall et al J. Euro. Ceram. Soc. **38** (2018) 5359.
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Abstract: In this report, effect of Bi^{3+} doped on structural, optical, magnetic and dielectric properties is studied. Upon Bi substitutions, unit cell volume shows an evolution and the average grain size is elongated. The optical band gap of the prepared samples decreases with increasing Bi content. The maximum magnetization (M_s) value decreases and coercivity (H_c) increases as compared to parent sample that can be attributed to the increasing structural distortion with Bi content. It is observed that energy band gap decreases with increasing Bi substitution. There is an anomaly observed at around magnetic transition in the temperature dependent dielectric study. The dielectric permittivity is enhanced upon Bi substitutions and all the compounds show relaxor like ferroelectric behavior.

Introduction

CHARACTERISTICS

- Biferroic material
- High melting point
- High thermal & chemical stability
- Low resistivity
- P-type semiconductor

Applications

- solid oxide fuel Cell
- humidity sensor
- thermistor
- magnetolectric material

Objectives

In this report, a detailed investigation of structural, optical, magnetic and dielectric properties of polycrystalline samples $\text{Y}_{1-x}\text{Bi}_x\text{CrO}_3$ ($x = 0.00, 0.05, 0.1, 0.15$) is carried out. As Bi^{3+} contains a $6s^2$ lone pair of electrons, which can be intended to enhance the polarization and it will be affected the other physical properties.

Parameters	x = 0	x = 0.05	x = 0.10	x = 0.15
a (Å)	5.5157 (6)	5.5114 (7)	5.5198 (1)	5.5182 (6)
b (Å)	7.5215(1)	7.5227 (1)	7.5393 (4)	7.5409 (8)
c (Å)	5.2341 (5)	5.267 (7)	5.2340 (7)	5.2461 (1)
V (Å ³)	217.14 (4)	217.010 (5)	218.32 (7)	218.38 (4)
χ^2	1.79	3.15	2.89	3.79

Surface Morphology

FESEM

The average grain size of YCrO_3 and $\text{Y}_{0.85}\text{Bi}_{0.15}\text{CrO}_3$ is calculated from ImageJ software are found to be $(0.412 \pm 0.009) \mu\text{m}$ and $(0.561 \pm 0.084) \mu\text{m}$ respectively.

- grain growth takes place and the grains are elongated with Bi-substitution.

Dielectric Study

$\epsilon' \sim f$ & $\tan \delta \sim f$

• With increase in frequency dielectric constant decreases and attains a constant value at higher frequency.

• Obeys Maxwell-Wagner and Koops phenomenological theory.

• the dielectric constant increases and tangent loss decreases as compared to parent sample.

$\epsilon' \sim T$ & $\tan \delta \sim T$

- Parent and doped sample show relaxor like ferroelectric behavior.
- Shows an anomaly around magnetic transition.

Experimental Details

Synthesis

Precursors solution

$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Continuous stirring at 90°C for 40 min. pH = 7. NH_3 sol.

Pellet formation, sintering (1100°C , 10h)

Calcination (900°C , 2 h)

Grinding → Fluffy ashes → Drying → Gel formation

- XRD – Rigaku Ultima-IV X-ray Diffractometer
- FESEM- FEI NOVA nanoSEM450
- UV spectroscopy- JASCO V-750
- VSM- 9T-PPMS-VSM (M/s. QD, USA)
- Impedance Analyzer- IM3570 (HIOKI)

Optical Study

Kubelka-Munk (KM) function $F(R)$ as $F(R) = \frac{(1-R)^2}{2R}$

The optical band gap E_g can be evaluated using the relation, $ah\nu = A(h\nu - E_g)^n$, $h\nu$ is the photon energy in eV, a is absorption coefficient, A is material constant and E_g is energy band gap.

- with increasing Bi^{3+} content, the energy band gap decreases ranges from 3.15 to 2.72 eV and 2.04 to 2.00 eV.

Magnetic study

M-H

Temperature (K)	5 K				125 K			
Bi concentration	x = 0	x = 0.05	x = 0.1	x = 0.15	x = 0	x = 0.05	x = 0.1	x = 0.15
M_{max} (emu/g)	2.23	2.00	1.94	1.99	1.64	1.56	1.42	1.52
H_c (kOe)	11.58	15.10	13.18	12.60	6.64	8.08	7.53	7.02
M_r (emu/g)	0.87	0.71	0.75	0.78	0.52	0.48	0.45	0.47

M-T

Curie Weiss (CW) law, $\chi^{-1} = \frac{C}{T - \theta_{CW}}$

The negative θ_{CW} value shows in all the compositions is attributed to AFM interaction exist.

Result and discussions

XRD

- Structure – Orthorhombic
- Space group - $Pnma$
- JCPDS card no.- 34-0365

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