



SYNTHESIS AND CHARACTERIZATION OF THE $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ CRYSTAL

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ABSTRACT

In the present investigation, synthesis and characterization of the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound has been reported. This compound is synthesized by solid state reaction technique. Crystallizing nature and surface morphology of the compounds are investigated by Scanning Electron Microscope (SEM) image and X-ray analysis. Crystallizing and melting temperature of the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound is studied by thermal analysis and band gap was also analyzed by DRS. Single phase formation of the compound $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ is also confirmed by XRD analysis. Result of the investigation show that the newer compound, $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$, behaves as a semiconductor at room temperature.

Key words: Synthesis, Characterization XRD, DRS, TGA, DTA, SEM, EDA

INTRODUCTION

Conducting materials plays an important role in the technological development of science. Rare earth based oxide superconducting compounds have been widely used in various devices based upon its lower resistivity nature. In this context, the synthesis of newer materials with low resistivity is more important. Superconductivity has flourished as a field of scientific endeavour over years and is an area of vital interest since 1911, the discovery of the phenomenon of superconductivity by Kamerlingh Onnes. It has emerged as a technology, contributing to advances in medicine, electronics, astronomy, transportation and other experimental sciences. Mercury was found to be superconducting at 4.17 K. Later, the discovery in Ba-La-Cu-O system around 40 K has been found by Bednorz and Muller in 1986, many researches for rare-earth-alkali earth metals- copper oxides system have been

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carried out. A large number and wide variety of metals, alloys, binary and ternary chemical compounds have been found to show superconductivity at low temperatures. As a result, several groups have reported transition temperature above the liquid nitrogen temperature in the Y-Ba-Cu-O system. Usually yttrium, calcium, bismuth, barium etc elements are conducting material¹⁻⁴. Hence, the authors planned to investigate the rare earth oxide as the conducting materials like $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound.

EXPERIMENTAL

Method

In the present investigation, yttrium-calcium-bismuth barium oxide compound was prepared by mixing dry powders of high purity yttrium oxide (Y_2O_3), calcium carbonate ($CaCO_3$), bismuth oxide (Bi_2O_3) and barium carbonates ($BaCO_3$) in the proper molecular ratios. Synthesis can occur in four steps: Mixing of chemicals, initial sintering, intermediate sintering and final annealing. After the chemicals were thoroughly mixed, with the aid of an agate and mortar, the sample was placed in a suitable alumina container for firing. Then the sample was allowed for initial sintering in a furnace at about $850^\circ C$ for 24 hours. This process forms the basic crystal structure and eliminates the CO_2 from $BaCO_3$ and $CaCO_3$ by the following chemical reaction⁵ -



This initial firing results in a porous blackish green powder. Then the sample was reground into fine powder and placed again in the furnace. Now the material was heated at about $910^\circ C$ for 24 hours. The rate of cooling in the final annealing was kept as it does not exceed 100 degree per hour until the temperature of the material is below $500^\circ C$. The final process of sintering was carried out for an extended period of time to a temperature that is below the melting point of the material. Hence, the particles are fused together with respect to the molecular ratio, which results with hard sintered and high crystallinity in the prepared compound. The newer inorganic compound, $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$, has been prepared by solid-state reaction technique.

The compound was characterized with powder X-ray diffraction, UV-VIS absorption spectrophotometer (Diffused Reflectance Spectrometer), thermal analysis and scanning electron microscope to find out its structural, optical, thermal and crystallizing nature of the compound.

RESULTS AND DISCUSSION

Powder X-ray diffraction study

The well sintered $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound was characterized by X-ray diffraction technique using Cu- K_α radiation. It is a very useful technique used for identifying crystalline structure of the compounds⁶. The numbers of counts with respect to 2θ were recorded from 5° to 80° . The resultant powder XRD pattern is shown in Fig. 1.

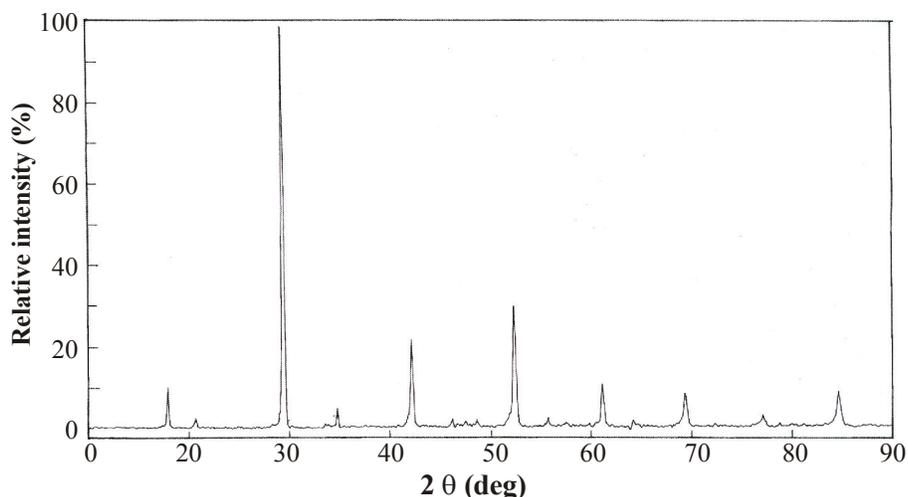


Fig. 1: Powder XRD pattern of the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound

From the XRD pattern, the compound is identified in a single phase formation and its lattice parameters were calculated by using AUTOX-93 programme with respect to d-spacing values for each intensity peaks. Observed and calculated value of d and h k l parameters of each reflection is tabulated in Table 1. The comparison of lattice parameters with respect to its parent compounds are also given in Table 2. This shows that due to the substitution of calcium and bismuth in yttrium site of $Y_4Ba_3O_{9-y}$ compound, the system changes from hexagonal to orthorhombic and the lattice parameters were slightly altered. Hence, the volume difference also arises due to the variation of atomic radius of the substitutional atoms.

Table 1: XRD result of the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ Compound

S. No	d_{obs} (Å)	d_{cal} (Å)	h	k	l	I/I ₀
1	4.9502	4.9504	0	0	5	9

Cont...

S. No	d_{obs} (Å)	d_{cal} (Å)	h	k	l	I/I ₀
2	4.2946	4.3001	1	1	0	2
3	3.0278	3.0269	2	0	0	100
4	2.6704	2.6631	1	2	2	1
5	2.5823	2.5824	2	0	5	5
6	2.1406	2.1420	2	2	1	25
7	1.9638	1.9602	3	0	3	2
8	1.8721	1.8687	3	0	5	1
9	1.7481	1.7482	1	3	6	34
10	1.6488	1.6497	3	2	3	1
11	1.5136	1.5135	4	0	0	11
12	1.4481	1.4473	4	0	5	1
13	1.3542	1.3541	4	0	5	1
14	1.2367	1.2420	4	2	8	3
15	1.1445	1.1445	5	0	7	10

Table 2: Comparison between parent and the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound

Compound	a (Å)	b (Å)	c (Å)
$Y_4Ba_3O_9$	6.110	6.110	25.184
$Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$	6.053 (6)	6.108 (2)	24.751 (3)

Diffused reflectance spectroscopy study

In the DRS study, the percentage of reflectance of the compound was recorded for the wavelength range from 200 nm to 800 nm and is shown in Fig.2. From the spectrum, the energy gap value of the compound at room temperature was found to be 3.1745 eV, which shows that the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound exhibits semiconducting nature at room temperature condition^{7,8}.

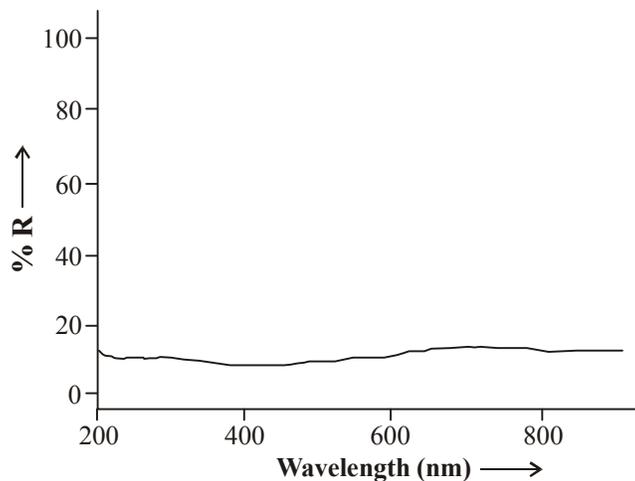


Fig. 2: Diffused reflectance spectrum of $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$

Thermal studies

The combined spectrum of TGA and DTA curve of the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound is shown in Fig. 3. These techniques are effective tools to determine the crystallization temperature (TGA) and percentage of weight loss (DTA).

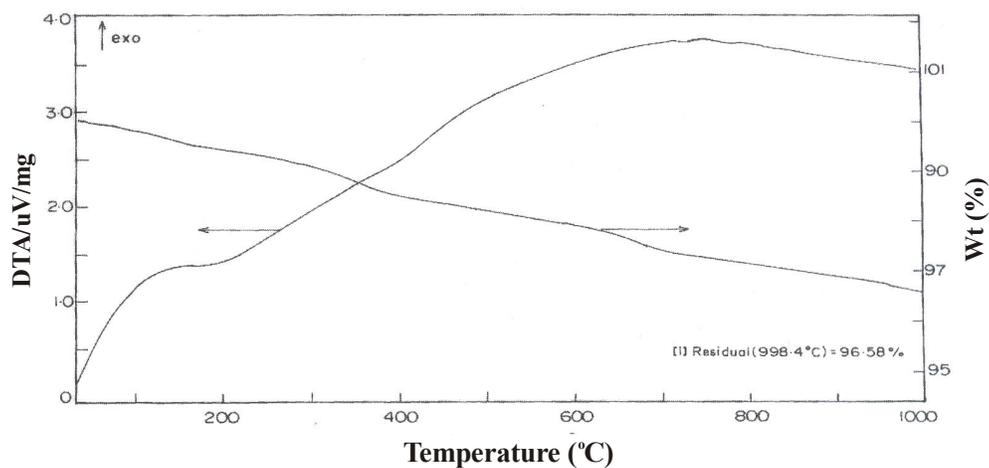


Fig. 3: Combined TGA and DTA curve of $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound

The TGA analysis reveals that the crystallization temperature is $745.3^{\circ}C$ and DTA reveals that the percentage of weight loss for the compound is 3.46% at $998.4^{\circ}C$ and stabling of the compound is found to be 96.58% .

SEM Study

The recorded scanning electron microscope images (X10,000 and X20,000 magnification) of the prepared $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound are given in Fig. 4.

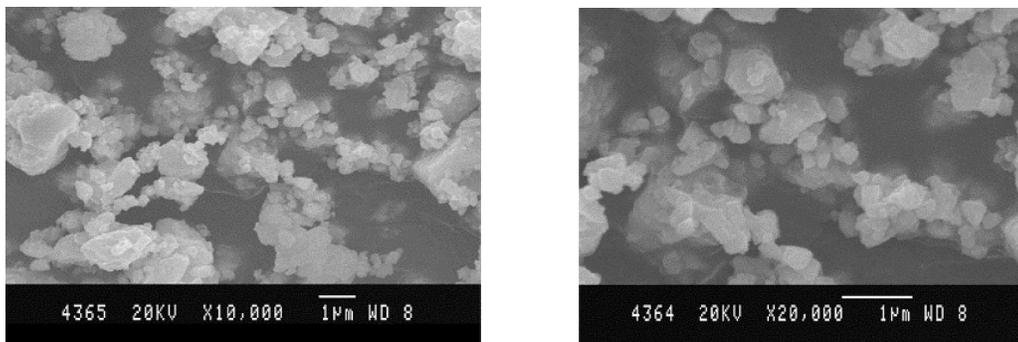


Fig. 4: SEM images of the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound

From the SEM images, it is observed that the sample is formed with a well crystalline nature with oriented planes¹⁰. Also some particles are in the initiative state of gathering together to form a regular pattern at higher temperatures and forms a unique crystal system, when it is allowed for slow cooling.

EDS Analysis

The energy dispersive X-ray analysis spectrum of the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound is shown in the Fig. 5. This pattern confirms that the substituted yttrium, calcium and bismuth atoms are present with the regular barium oxide crystal system.

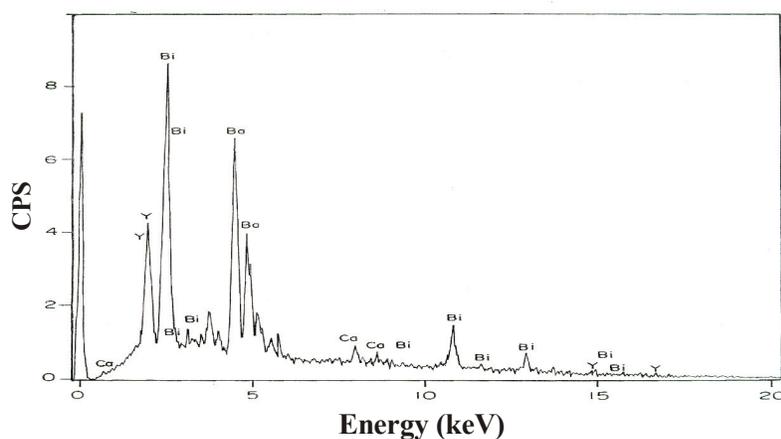


Fig. 5: EDS spectrum of $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ compound

CONCLUSION

Conclusions are drawn from the above characterization results and these are -

- The single phase formation of the compound is confirmed from the XRD study.
- The compound is crystallized in orthorhombic structure with lattice parameters: $a = 6.053$ (6) Å, $b = 6.108$ (2) Å and $c = 24.751$ (3) Å.
- From the TGA, the total weight loss of the compound up to 998.4°C is calculated as 3.46 %. From DTA, it is also observed that material is started to crystallize at 745°C and become well crystalline around 900°C.
- SEM and EDS confirms the well crystallizing nature and the presence of substituted calcium and bismuth atoms with the regular yttrium-barium oxide crystal system of the compound.
- The present study concluded that at room temperature condition, the $Y_{1.5}Ca_{0.5}Bi_2Ba_3O_{9-y}$ crystal behaves as the semiconductor and its energy gap value is found to be 3.1745 eV.

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