Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.8 No.6, 2016

Preparing $CaBi_2O_4$ by Solid State Method and Studying Its Structural Properties

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The research is financed by Asian Development Bank. No. 2006-A171(Sponsoring information)

Abstract
The compound $CaBi_2O_4$ was synthesized by solid state reaction and studied by X-ray powder diffraction method, Infra-red spectroscopy (IR) , Differential thermal analysis (DTA) .The values d and hkl indexes were calculated. The discussion indicate that, the compound belongs to monoclinic type of crystallization.The parameters a= 14.007 (A^o) ,b=11.551(A^o), c=12.264 (A^o),the volume of unit cell was V= 1944.064 $(A^o)^3$, theoretical and experimental densities were identified. Z=8.
Keywords: x-rays, calcium bismuths , solid state..

1. Introduction:

The study of hybrid oxides in different proportions and inferring their physical and chemical and optical properties have received considerable attention recently [1], and so methods to obtain these types of compounds developed as of ceramic method (thermal, synth mixed powders) to the way of common deposition and method Sol- gel and then move on to the method of thermal synth by high pressure water vapor (Hydrothermal synthesis). Compounds resulting from the oxide of bismuth and oxides of alkali elements and earth alkaline occupy important place in the field of solid electrolytes industry that operate in a wide range of temperatures [2]. It is known that Bi_2O_3 exist in four polymorphic forms at normal atmospheric pressure, and all of these crystalline forms are structurally studied "[9]. The unilateral tendency figure α- Bi_2O_3 is stable and steady until the degree 729℃ at atmospheric pressure, and after this degree δ - Bi_2O_3 turns into cubic shape, and stays steady until melting point 824℃, the polymorphic moderation Quartet shapes β-Bi_2O_3 and cubic ones α - Bi_2O_3 can appear during the cooling phase at the degree 650℃ and 639℃ respectively [10].

$$\delta - Bi_2O_3 \rightarrow \alpha-Bi_2O_3 \rightarrow \beta-Bi_2O_3 \rightarrow \text{ک}- Bi_2O_3$$
$$639\ ℃ \rightarrow 650\ ℃ \rightarrow 729\ ℃ \rightarrow 824\ ℃$$

Many compounds containing bismuth were studied and focus was on the metaphase balances of compounds consisting of bismuth and barium oxides, and examined their case in detailed schemes [3]. In addition, researcher Borjersson and others have focused on the study of some of the electrical properties of solid solutions containing bismuth [4] and activates $CaBi_2O_4$ optical stimulation and oxidation of persistent organic pollutants under visible light where it was used in the decomposition of both the Blue Methylen (MB) and Ethanal (CH_3CHO) in its state of gas where the stability of the catalyst is very important in terms of catalytic oxidation which $CaBi_2O_4$ has compared to [TiO_2] [5] and it enters the super-conductor industry, excavators oxidants, dyes, catalysts , sensors [6]

2. Idea of the Search*:*

The synthesis of binary strings consisting of bismuth oxide and calcium oxide Bi_2O_3-CaO by solid state method and studying the properties of the structural and crystal x-ray diffraction way XRD and spectroscopy IR and a thermal analysis differential DTA, this issue falls under the framework of the preparation of the hybrid and the important oxides compounds synthetically out "of metal oxides .

3. The goal of the research project:

Preparing mixed oxide $CaBi_2O_4$ by solid state beginning of the following raw materials $CaCO_3$, Bi_2O_3 and study its phase analysis by X-rays, and then studying its structural characteristics and crystalline in an attempt to synthesize different ways of preparation and access to the best way and the least expensive.

4. Devices and required tools for synthesis:

We have been using various tools and devices, including:

- Balance analytical accuracy up to 0.0001 gr.
- Glass different tools.
- Ceramic crucibles can withstand temperatures up to 1100 ℃

- Dryer to dry the samples, one of the brand (memmert).
- Incinerator to burn samples and a type (Carbolite) up space even class 1100 ℃.
- X-ray diffraction of the powder X-Ray Powder Diffractometer model Philips-PW-1840 device differential thermal analysis to study the thermal behavior of the samples from the DTA type Chimadzu.
- Red nice subcutaneous device IR-Spectrometer type Jasco-FT / IR-41000
- Ceramic mortar to grind samples to get a fine powder as possible.

5. Necessary materials for the synthesis:

- bismuth Bi_2O_3 99% (Alfa).
- calcium carbonate $CaCO_3$ 95% (RIEDEL-DE HAEN AG SEELZE-HANNOVER).
- Actone 99.8% (Eurolab).
- and this purity is necessary to obtain accurate results in a diffraction X ray, where we know that the presence of impurities affect the results and its accuracy on the hand and the presence of secondary reactions or additional materials lead to the emergence of peaks in the spectra produced.

6. Practical section:

6.1.Artificiality solid state:

Ceramic method is used effectively when it is intended to get mixed oxides, and this method involves sampling and mechanical grinding flour mixture oxides and repeat the process of crushing weight of the samples in order to get the mutual influence of active material in the solid state.

Materials were taken Bi_2O_3, $CaCO_3$ and dried to get rid of suspended impurities and then took the necessary weights according to the molar ratio $CaCO_3$: Bi_2O_3 = 1: 1

The weights required for the preparation of composite raw materials $CaBi_2O_4$ according to the ratio (1: 1) in order to obtain 5 gr of that compound in accordance with the table below

Table(1): Weights of incoming raw materials in the reaction:

	$CaCO_3$	Bi_2O_3
Mass of(gr)	0.884019	4.3045

The weighted materials were mixed and crushed in a mortar casserole for a period of 15 min with the addition of acetone to increase the possibility of the homogeneity of the mixture, and the process repeated three times in succession. Then samples were pressed using mechanical compression tool for tablets in a thickness of 2mm and 5mm diameter. The goal of getting these discs is that they give the results of the synthesis better than the powder particles for the fact that they are very close to each other and this gives it greater potential for interaction.

Samples were transferred to crucibles ceramic bear even temperature 1100ºC of incinerated at different temperatures, and enable us to obtain diffraction of X-rays, we have adopted in the next step to repeat the crushing process and the pressure and heating for three consecutive times in order to increase homogeneity. This process continues and is repeated even get Output includes a single phase only and this definitive guide to complete the synthesis process and constitute a composite $CaBi_2O_4$ with the absence of spectral lines belonging to the raw materials of any individual oxides. The inference of the existence of a single phase in the output process is that all the peaks belong to one type of index Miller and corresponding to a certain crystallized pattern , since the mere presence of one peak of more than magnitude 50% do not belong to this supposed required pattern makes us cancel the assumption and follow another assuming . It must be noted that the presence of a peak of the diffraction pattern is not consistent with the index Miller for the supposed pattern is attributed to one of the following reasons:

- Either that belongs to one of the raw materials.
- Either assumption is incorrect and must be changed.
- The presence of impurities resulting from the lack of precision in the preparation and artificiality.

6.2. Results and discussion

6.2.1. Instant analysis of X-ray:

sample of burned $CaBi_2O_4$ was examined at a temperature of 750 ºC for a period of 3 hours by X-ray diffraction device XRD using cathode copper with a wavelength λ = 1.54056 Aº, and the following figures show a spectrum of X-ray diffraction to sample $CaBi_2O_4$ with identifying the most important crystalline levels and the following diffraction diagram shows the values of 2θ, the intensity of diffraction associated with the electronic level in the crystal density.

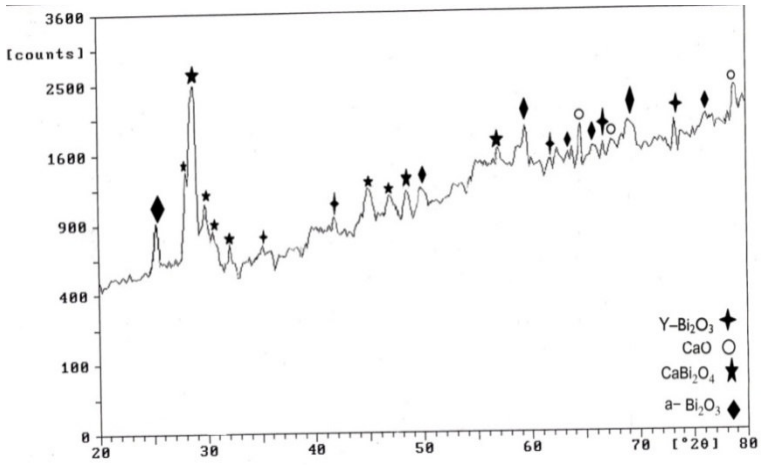

Figure 1: X-ray diffraction diagram of the result of the synthesis of the sample where $CaBi_2O_4$

We note an emergence of many peaks with high intensities belong to bismuth oxide of the sort α- Bi_2O_3 that appears when the process of calcination at the temperature 727 °C and three peaks with low intensities belong to calcium oxide CaO take 2θ values = (64.151,67.371,79.661) denote the lack of artificiality which will decrease in their turn when increasing the duration of the burning period and we noticed the beginning to form a compound where $CaBi_2O_4$ few peaks appeared with low intensities. 2θ = (28.775,29.885, 33.073, 38.670, 50.921, 52.431,56.670).

(T = 750 °C) and time of calcination 3 hours

and a $CaBi_2O_4$ sample was examined when burned at a temperature of 750 °C for a period of 10 hours by x-ray diffraction XRD device and the following figures show the spectra of x-ray diffraction to $CaBi_2O_4$sample with identifying the most important crystalline levels were calculated from the relationship Prague nλ = 2d sin θ, see Figure2 .

it was observed that the increase in the burning time lead to increased interaction and the possibility of completion.

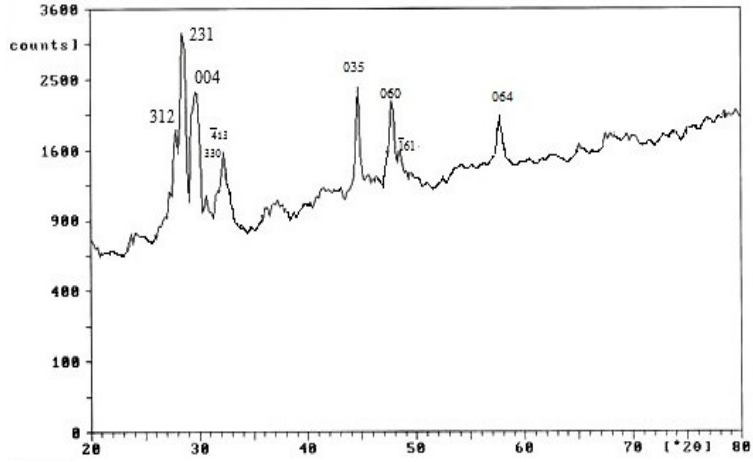

Figure 2: X-ray diffraction diagram of the result of the synthesis of the sample $CaBi_2O_4$ where (T = 750°C)

From the figure 2 we note that this degree is the best degree in terms of the synthesis where the synthesis of this compound completed and peaks sharply appeared with high intensities

The calculation of basic cell dimensions a, b, c and the average account for each static lattice constants was done according to the following relationship:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} + \frac{2hl\cos\beta}{ac}\right)$$

As a result of the calculation it shows that the basic cell dimensions monoclinic are as follows:

a = 14.007 (A°), b = 11.551 (A°), c = 12.264 (A°), β = 101.551°

The basic cell size was calculated according to the monoclinic pattern of crystallization as in the following relationship:

$$V = a*b*c*\sin\beta\ (A^o)^3$$

After measuring the experimental density by becknometre and re-measurement three times and taking its arithmetic , it turned out to be $\rho_{exp} = 3.573$ gr / cm^3 and this was Z = 8.0155 replacing the value of Z relationship of density theory, we find that $\rho_{ther} = 3.572$gr / cm^3

Table (4): Basic cell of experimental and theoretical density and the number of formulas included in one basic cell, calculated for a compound where $CaBi_2O_4$ size (T = 750 °C)

Volume $(A)^3$	Theoretical Density (gr/Cm^3)	Exp Density (gr/Cm^3)	Z
1944.064	3.572	3.573	8

6.2.2. Studying infrared spectroscopy (IR) for a sample $CaBi_2O_4$ when burning at 750°C temperature for 10 hours: The test was done using the infrared device on a sample of $CaBi_2O_4$ when the ratio Ca: Bi = 1: 1

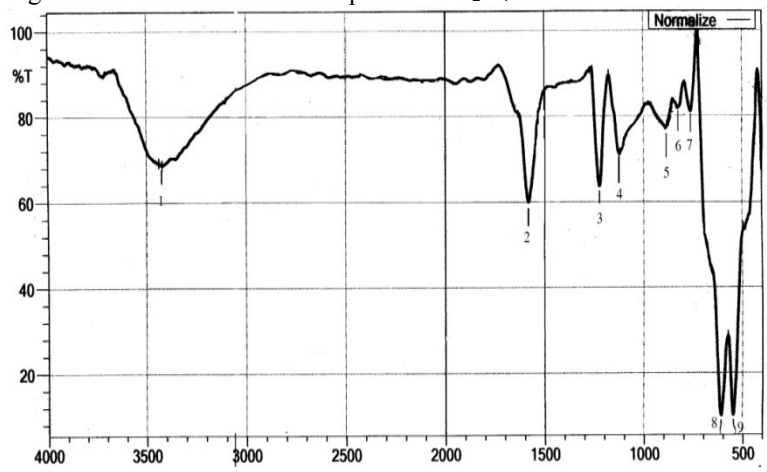

Figure 3: infrared spectrum of a sample $CaBi_2O_4$ prepared in a manner of solid state (T = 750°C)

it shows an appearance of the vibration due to the bound OH at (3425.58) cm^{-1} and vibration of bend molecules of water within the crystal structure at the value (1583.65) cm^{-1} and three stretch vibrations Bi-O bonds belonging to the group BiO_3 pyramidal shape [7] [12] at the values (715,831, 1224) cm^{-1} and stretch vibration Bi-O outside spinel structure at the value (1120) cm^{-1} and stretch vibration Ca-O bonds at (896) cm^{-1}.

Two stretch vibrations Bi-O bonds , non-bridge oxygen group,distorted $[BiO_6]$ octahedrons [7] at values (574.78, 609) cm^{-1}.

6.2.3.Studying the thermal behavior using a differential thermal analysis (DTA) for a $CaBi_2O_4$ sample burned at 75 °C temperature for 10 hours:

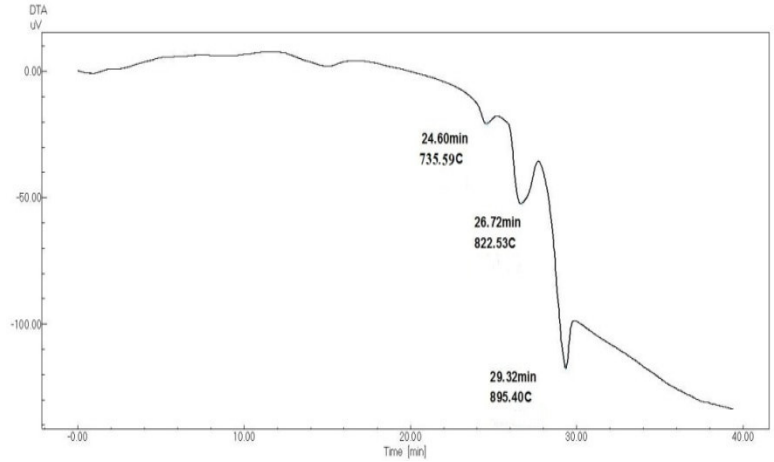

Figure 4:curved DTA differential thermal analysis of the compound $CaBi_2O_4$

A thermal decomposition test was done for the compound $CaBi_2O_4$, the resulted DTA scheme for the sample showed several peaks of endothermic where the peak was recorded 735.59 °C indicating a shift polymorphism for bismuth oxide α-$Bi_2O_3 \rightarrow \delta$-$Bi_2O_3$. Another peak was recorded at degree 822.53 °C indicating the emergence of a turning Eutictic between several phases of which, appeared out of disintegration at heat 760.59 °C other phases emerged at the heat 822.53 °C and thus pointed to the continuing disintegration process and a peak appeared 895.40 °C endothermic indicated the final and full disintegration for calcium Bismuths where no Exdo peaks appeared heat belong to the change of the structure of the compound, which refers to the high thermal stability of the compound synthesized

Conclusions:

After completion of the synthesis and studying of resulting compounds, we conclude the following results:

1- The compound $CaBi_2O_4$ was prepared by solid state method and the temperature was set at 750 °C,

synth.

2- The synthesis was controlled and its result was figured out by using x-ray diffraction device.
3- We were able to calculate index Miller in a way of trials and errors and found that the compound crystallizes according "Monoclinic" pattern and the number of formulas included in one basic cell, Z = 8 and dimensions of the basic cell of a = 14.007 (A^o), b = 11.551 (A^o), c = 12.264 (A^o) , β = 101.551 and cell volume V = 1944.064 $(A^o)^3$.
4- The infrared spectrum supports the formulation of the desired compound.
5- The thermal behavior of the composite output was examined by a differential thermal analysis DTA and show the emergence of three thermal effects.

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