Growth and Characterization of Noval ABX_3 type crystal using Metal halide ($BaBr_2$) by Slow Evaporation method

Mrs. S. Valli [1], Sandra. K. Saji[2]

[1] *Assistant Professor, Department of Chemistry, Nirmala College for Women, Coimbatore - 641018*
[2] *Department of Chemistry, Nirmala College for women, Coimbatore - 641018*

Abstract - A noval ABX_3 type crystal were grown using benzyltriethylammonium chloride and barium bromide by slow evaporation method at room temperature. Highly good quality crystals were grown within five days. The grown crystals were characterized by CHN analysis, UV spectroscopic study, FT-IR study, XRD analysis and TGA. CHN elemental analysis was done to identify the presence of carbon, hydrogen and nitrogen presnt in the complex. The characteristics and crystalline nature were analyzed using X-ray diffraction (XRD) study. The presence of various functional group in the crystals were identified by FT-IR spectral analysis. UV spectral studies were done to find the quality and purity of crystals. Thermal stability of the crystals were analyzed using TGA studies which reveals the crystals are stable to 957ºC.

Key Words: CHN elemental analysis, XRD, FT-IR, UV, TGA

1. INTRODUCTION

Crystal is considered as the building block of solid materials. The growth of newer and good quality crystals for future techniques is inevitably important. Crystal growth has become important in today's technological system in the field of Chemistry, physics, engineering, transportation, medical and safety technologies.[1] The basic condition for the growth of crystal is the process of "super saturation and nucleation". Super saturation is the state in which more solute is dissolved in solvent. When super saturated solution is cooled certain temperature is reached where nucleation of crystals occur. Nucleation is the development of the nuclei of crystal from solution or other crystals. Then further the size of crystal increases and thus crystal growth occurs.

The method we are using is slow evaporation solution growth technique. It is one of the most oldest, convenient, easiest and economic crystal growth method. In this method, the solution loses particles, which are weakly bound to other components, and therefore the volume of the solution decreases. In this method, an excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and solute. In almost all cases, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and, therefore the solvent evaporates more rapidly and the solution becomes supersaturated.

2. MATERIAL SYNTHESIS

Barium bromide complex crystal of ABX_3 type were prepared by mixing Benzyltriethylammoniumchloride and Barium bromide ($BaBr_2$) in 1:1 molar ratio respectively using triple distilled water. The two solutions were mixed together thoroughly in acidic medium by using 1ml of HCl. Then the resulting solution was filtered through whatmann42 filter paper. The solution was kept at room temperature for preparation of solids by slow evaporation method. A colorless transparent crystalline product was obtained and shown in **Figure-1**.

$$[C_6H_5CH_2N(C_2H_5)_3]Cl + BaBr_2 \longrightarrow [C_6H_5CH_2N(C_2H_5)_3]BaBr_2Cl$$

Figure-1

3. CHARACTERIZATION

The elemental analysis of the compound was carried out by CHN analysis. It is used to determine carbon, hydrogen and nitrogen contents in crystal. Quality of the compounds in a crystal lattice can be verified by elemental analysis study. UV spectroscopic studies give information about the electronic transition in the compound. UV spectrum is helpful to detect the purity of the grown crystal. UV spectrum shows the transmittance range of the crystal. FT-IR is an analytical technique used to identify absorption band associated with lattice vibration of crystals. FT-IR is a main technique to identify the types of chemical bond in an organic molecule. It is also used to identify the purity of crystal. The crystallinity of the compound can be confirmed by X-ray diffraction studies.

X-ray diffraction studies offer the clear analysis of crystal structure and orientation of crystals for the successful use of single crystals in their technological applications. The % Crystallinity of the crystal can be calculated using Hinrichsen's formula,

$$\% \text{ Crystallinity} = I_c / (I_c + I_a) * 100$$

Where,k

I_a & I_c are the integrated intensities corresponding to the amorphous and crystalline phases, respectively.

The thermal stability of the compound can be confimed by thermogravimetric analysis. In TGA, the sample is heated in a given environment at controlled rate. The change in the weight of substance is recorded as a function of temperature.

4. RESULTS AND DISCUSSION

Solubility

The crystal of barium bromide complex of ABX_3 type are soluble only in water and are found to be insoluble in Ether and Dimethyl sulphoxide while testing for solubility. The solubility test for the complex is tabulated in **Table -1.**

Table-1: Solubility test of Barium bromide complex crystal

(++ = Soluble, – – = Insoluble)

SOLVENT	OBSERVATION
Water	++
Ether	– –
DMSO	– –

Elemental Analysis

Composition of the grown crystal is verified by using results obtained from the elemental analysis (C, H, N).[2] The result of elemental analysis (Carbon, Hydrogen and Nitrogen) of [BTEATC-Ba] crystal is given in **Table-2.** For the comparison, theoretical values are also given.

Table- 2: Elemental analysis of barium bromide complex crystal

Sample name	Carbon %		Hydrogen %		Nitrogen %	
	Exp	Theo	Exp	Theo	Exp	Theo
[BTEATC-Ba]	33.42	37.98	5.02	5.35	5.24	4.56

UV Spectroscopic studies

The UV spectrum in **Figure-2** shows that the grown crystal of ABX_3 type barium bromide complex is highly pure in nature as no peak is obtained near adsorption value of water. It also confirms the presence of aromatic compound present in the crystal.[3]

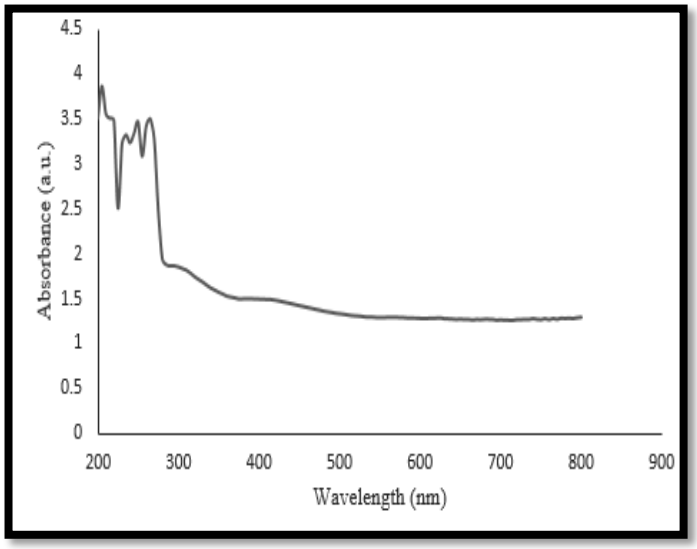

Figure-2: UV spectrum of Barium bromide complex crystal

FT-IR studies

The observed stretching frequency and the corresponding type of bonds are given in **Table -3**. [4] The FT-IR spectrum of ABX_3 type Barium bromide Complex crystals is shown in **Figure-3.**

S.NO	ABSORPTION PEAK [cm^{-1}]	POSSIBLE GROUPS
1	3363.86	N-H stretch
2	2985.81	C-H stretch (Methyl group)
3	1635.84	C-C stretch
4	1481.33	C-C Stretch (Aromatic)
5	1396.46	C-H bend

6	1157.29	C-N-C stretch
7	1211.30	C-N stretch
8	1010.70	C-H out of plane
9	902.69	C-C stretch
10	756.10	C-N-C and C-C-N deformation
11	702.09	C-Cl bond

Table-3: FT-IR peak value of Barium bromide complex crystal

The N-H stretching appears at 3363.86 cm^{-1} due to the presence of NH^{4+} ions. The peak appears at 2985.81 cm^{-1} is due to C-H stretching of methyl group. The peak at 1635.64cm^{-1} is due to C-C stretchingof aromatic group. The absorption peak appears at 1481.33cm^{-1} is due to methyl and methylene scissoring. The C-H bend due to methyl and methylene group occurs at 1396.46 cm^{-1}.

The peak at 1157.29 cm^{-1} is due to C-N-C stretching vibrations. The peak at 1211.30 cm^{-1} is due to the C-N stretching. The C-H out of plane occurs at 1010.70 cm^{-1}. The alkane symmetric C-C stretching vibrations occurs at 910.40 cm^{-1}. The C-N-C and C-C-N deformation vibration occurs at 756.10 cm^{-1}. The vibrational frequencies of C-Cl bond occurs at 702.09 cm^{-1}.

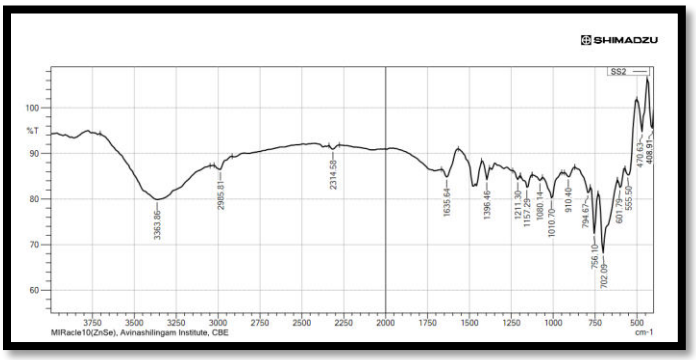

Figure-3: FT-IR spectra of barium bromide complex crystal

XRD analysis

X-ray powder diffraction pattern of the ABX_3 type Barium bromide complex crystals is shown in **Figure-4.** Bragg's peaks of high intensity are obtained at specific 2Θ angles. This shows that the compound is crystalline in nature.[5]

We can evaluate %Crystallinity of grown crystals of barium bromide complex using Hinrichson's formula

% Crystallinity = Ic/ (Ic+Ia) * 100

Where, Ic and Ia are integrated intensities corresponding to the amorphous and crystalline phase.

Therefore %Crystallinity of Barium bromide complex is given by,

%Crystallinity = 410.5633 / (410.5633+32.7885) * 100

= 410.5633 / 443.3518 * 100

= 92.60%

The %Crystallinity of Barium bromide complex is **92.60%.**

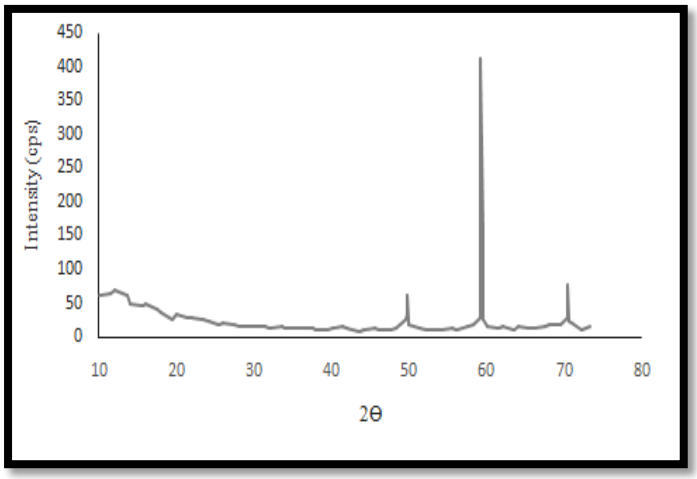

Figure-4: XRD of barium bromide complex crystal

Thermal analysis

The TGA curve in **Figure-5** shows the two stage weight loss when heated between the room temperature and 957.45ºC. [6] The first stage decomposition starts at 95.34ºC and end at 234.82ºC the weight loss noted at this temperature is 16.75%. It is assumed that Cl will get evolved first followed by the decomposition of hydrocarbons and nitrogen gas.

$$[C_6H_5CH_2N(C_2H_5)_3]BaBr_2Cl \longrightarrow [C_6H_5CH_2N(C_2H_5)_3]Cl + BaBr_2$$

When the complex undergoes decomposition as above, one mole of complex decomposed to one mole of benzyltriethylammoniumchloride and one mole of barium bromide. In the second stage, the decomposition of barium bromide starts at 750.60ºC and ends at 957.45ºC with the weight loss of 5.105% the weight loss can be accounted for formulating the following decomposition reaction.

$$BaBr_2 \longrightarrow Ba + Br_2 \uparrow$$

The decomposition takes place between 95.34ºC and 957.45ºC. The total weight loss during this period is calculated as 26.01%.

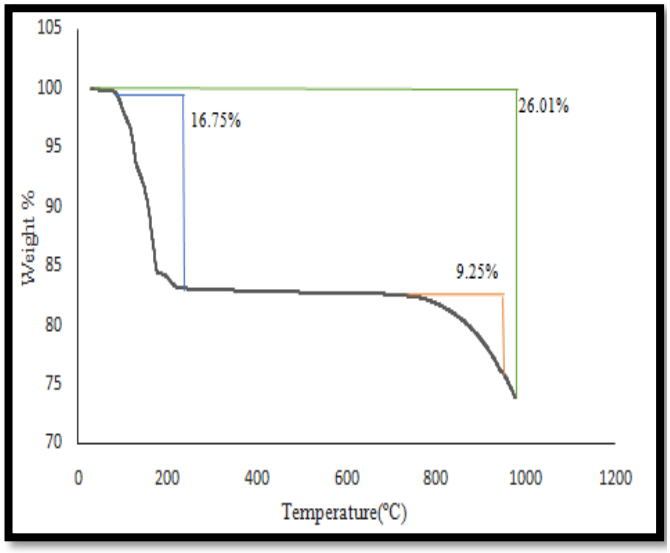

Figure-5: TGA of barium bromide complex crystal

5. CONCLUSION

The noval ABX_3 type crystals were grown using benzyltriethylammonium chloride and barium bromide by slow evaporation method at room temperature. The grown crystals of barium bromide complex crystals were harvested after five days. The grown crystals were characterized by CHN elemental analysis, UV spectroscopic study, FT-IR analysis, XRD analysis and TGA. The CHN analysis of the barium bromide complex crystal confirms their molecular formula. The FT-IR spectra confirms the presence of methyl group, methylene group and benzyl group. It also confirms C-C and C-N bonds and C-Cl bond.

The UV spectra of the compound confirms the absence water and confirms the high purity of crystals. The powder XRD pattern shows the sharp peaks which are characteristics of the crystals. The crystalline nature of the prepared compounds is confirmed by getting well defined peaks at different 2θ values and %crystallinity was also calculated. It also shows double stage decomposition in the TG thermogram. It confirms the higher stabilities of these compounds.

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