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Comparative study of semicoductors bismuth iodate, bismuth triiodide and bismuth trisulphide crystals

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ABSTRACT

In the present investigation, crystals of Bismuth Iodate[$Bi(IO_3)_3$], Bismuth Iodide[BiI_3] and Bismuth- Tri Sulphide [Bi_2S_3] were grown by a simple gel technique using single diffusion method. The optimum growth conditions were established by varying various parameters such as pH of gel solution, gel concentration, gel setting time, concentration of reactant etc. Gel was prepared by mixing sodium meta silicate ($Na_2SiO_35H_2O$), glacial acetic acid (CH_3COOH) and supernant bismuth chloride ($BiCl_3$) at pH value 4.4 and transferred in glass tube of diameter 2.5 cm and 25 cm in length. The mouth of test tube was covered by cotton plug and kept it for the setting. After setting the gel, it was left for aging. After 13 days duration the second supernant $K(IO_3)$, KI_3 and H_2S water gas solution was poured over the set gel by using pipette then it was kept undisturbed. After 72 hours of pouring the second supernatant, the small nucleation growth was observed at below the interface of gel. The good quality crystals of [$Bi(IO_3)_3$], [BiI_3] and [Bi_2S_3] were grown. These grown crystals were characterized by XRD, FTIR, Chemical Analysis and Electrical Conductivity.

Keywords: Gel Grown [$Bi(IO_3)_3$], BiI_3 and Bi_2S_3 Crystals, XRD, FTIR ,Chemical Analysis and Electrical Conductivity.

INTRODUCTION

Large no of National and International laboratories are busy to grow various types of crystals. Their indusial efforts are to grow Iodate of various compounds similarly various Iodides, Sulphide and Oxalates as well as tartarates at same time some of scientist trying to make study of Iodate of various compounds for example Garud [1-4] Amit Patil [5-6], and Sharda Shitole [7-12] have tried for the comparative study of Iodates, and Bhavsar,Blank and Patel [13-17] had studied Iodide and Sulphide. Also the study of Iodates, Iodide and Sulphide by Nakamoto, Ranadive and Selvarajan [18-23]. In the present work, sincere efforts have been made to concentrate on single antiferromagnetic Bismuth and hence three important compounds of it i.e. crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide have been successfully grown.

However, there are very few reports in the literature on the growth of these crystals by gel method. These three types of crystals were grown by single diffusion gel method in which respective crystals were synthesized by control precipitation. These crystals have been characterized by different techniques. Paper deals with comparative study of all these crystals regarding their growth and characterization. All the results obtained regarding growth and characterization are tried to put at a glance of three types of crystals in the present work.

MATERIALS AND METHODS

Crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide were grown by gel method by using single diffusion techniques. Table 1 gives details about method and chemicals used, different habits of crystals obtained, their transparency, etc.

Monoclinic Bismuth Iodate crystals were obtained. Most of the Bismuth Iodate crystals were transparent, shining, well isolated and very few of them were opaque. Single diffusion method is found more suitable for growth of these crystals.

Table 1: Crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide

Type	Method	Chemicals used	Crystal habits	Quality
Bismuth Iodate [$Bi(IO_3)_3$]	Gel method by using single diffusion techniques	$Na_2SiO_3 5H_2O$, CH_3COOH, $BiCl_3$ and KIO_3	Monoclinic	Transparent, few opaque
Bismuth Iodide [BiI_3]	Gel method by using single diffusion techniques	$Na_2SiO_3 5H_2O$, CH_3COOH, $BiCl_3$ and KI	Hexagonal	Transparent, few opaque, at center
Bismuth Tri-Sulphide [Bi_2S_3]	Gel method by using single diffusion techniques	$Na_2SiO_3 5H_2O$, CH_3COOH $BiCl_3$ and H_2S gas in water solution	Orthorhombic OR Rhombus	Opaque Transparent, Both type

Some of grown Bismuth Iodide crystals found to be hexagonal shaped micro crystals. These crystals were found to be grown near the gel interface. Most of them were opaque and very few of them were transparent crystals. Single diffusion technique proved to be suitable for growth. The structure of Bismuth Tri-Sulphide crystals found to be Orthorhombic or Rhombus. It was found that as the concentration of the reactant $BiCl_3$ in the gel is increased, the size of the spherulites is also increased. Single diffusion method is found more suitable for growth of these crystals.

RESULTS AND DISCUSSION

These crystals possess better habits and better transparency among the grown crystals. Better transparency of Bismuth Tri-Sulphide may be due to presence of more Bismuth. Optimum growth conditions for gel grown crystals established by varying various parameters such as gel density, pH of gel, gel setting time, gel aging time, etc. are reported in Table 2.

Table 2: Optimum growth condition for gel grown Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide crystals

Parameters	Bismuth Iodate	Bismuth Iodide	Bismuth Tri-Suphide
Density of sodium meta silicate solution	1.04gm/cm^3	1.04gm/cm^3	1.04gm/cm^3
Amount of acetic acid	2N, 5 cc	2N, 5 cc	2 N, 5 c c
pH of mixture	4.4	4.4	4.4
Temperature	Room temperature	Room temperature	Room temperature
Gel setting time	13 days	13 days	13 days
Gel aging time	72 hours	72 hours	72 hours
Period of growth	36 days	33 days	31 days

For all these three crystals, suitable value of density of sodium Meta silicate solution is found to be 1.04 gm/cc, pH value for Bismuth Iodate, Bismuth Iodide and Bismuth Tri-Sulphide is found to be 4.4. For pH 4.4, gel took 13 days to set and this gel was allowed to age for 72 hours, Crystals were removed from test tubes after 36, 33 and 31days respectively. Further growth was not noticed. Sometimes crystal became opaque or translucent due to inclusion of silica in them. Reason may be the unnecessary exposure to silica gel. Various concentrations of reactants were tried. Experiments by interchanging the positions of reactants were also carried out. Once the optimum values of concentration of reactants were obtained, experiments of concentration programming were also carried out. All these parameters have more or less effect on growth and habit of these crystals.

5.1 XRD Analysis Crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide were characterized by XRD analysis. X-ray diffractograms were recorded using powder diffraction method at National Chemical Laboratory Pune,

using Miniflex Goniometer model, Regaku, Japan, X-ray diffractometer are as shown in figures 1, 2 and. 3.

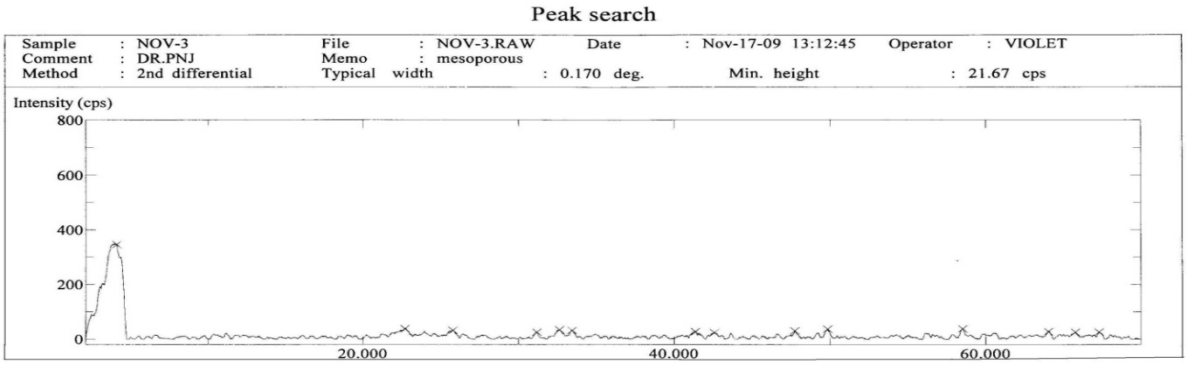

Fig 1 XRD of Bismuth Iodate

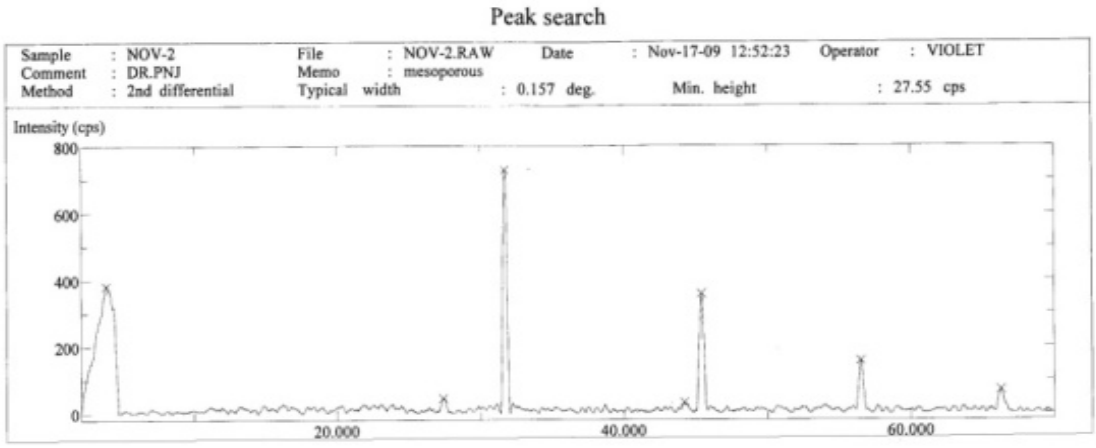

Fig 2 XRD of Bismuth Iodide

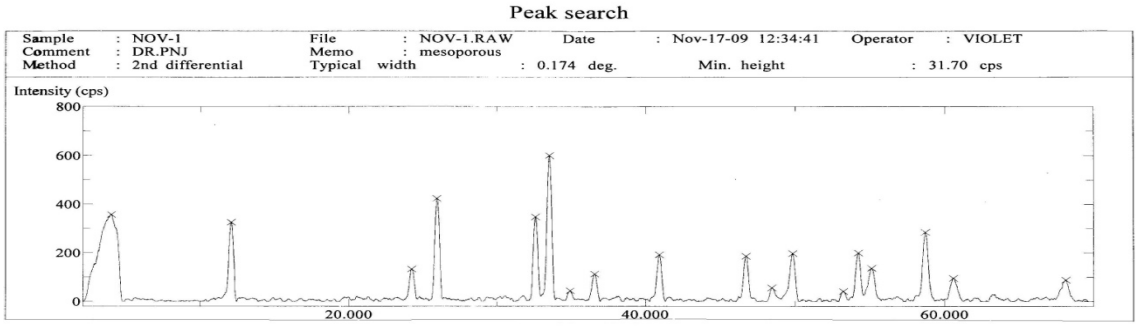

Fig 3 XRD of Bismuth Tri-Sulphide

From these diffractograms, 'd' values were computed. Table 3 represents system of the crystal and unit cell parameters of the three types of Crystals .From the XRD study of crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide it is concluded that Bismuth Iodate is Monoclinic, Bismuth Iodide is Hexagonal and Bismuth Tri-Sulphide is Orthorhombic or Rhombus. Unit cell volume of Bismuth Iodide is 1633.98 $[A^0]^3$ Bismuth Iodate is 784.62 $[A^0]^3$ and Bismuth Tri-Sulphide is 496.84 $[A^0]^3$ If the unit cell volume of grown crystals is compaired the following conclusion can be made**.**

Bismuth Iodide > Bismuth Iodate > Bismuth Tri-Sulphide.

Table 3: Lattice Parameters

Crystals	a A^0	b A^0	c A^0	α	B	γ	$V(A^0)^3$	System
Bismuth Iodate	8.808	5.924	15.044	90.36^0	90.48^0	119.63^0	784.62	Monoclinic
Bismuth Iodide	9.766	9.360	17.875	90.48^0	90.36^0	119.68^0	1633.98	Hexagonal
Bismuth Tri-Sulphide	11.136	11.256	3.968	90.18^0	90.42^0	90.36^0	496.84	Orthorhombic or Rhombus

5.2 Infrared Spectroscopy

FT-IR spectra's of gel grown crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide were scanned by using FT-IR spectrophotometer, SHIMADZU spectrophotometer at the Department of Chemistry, University of Pune. Are as shown in figures 4 , 5 and 6.

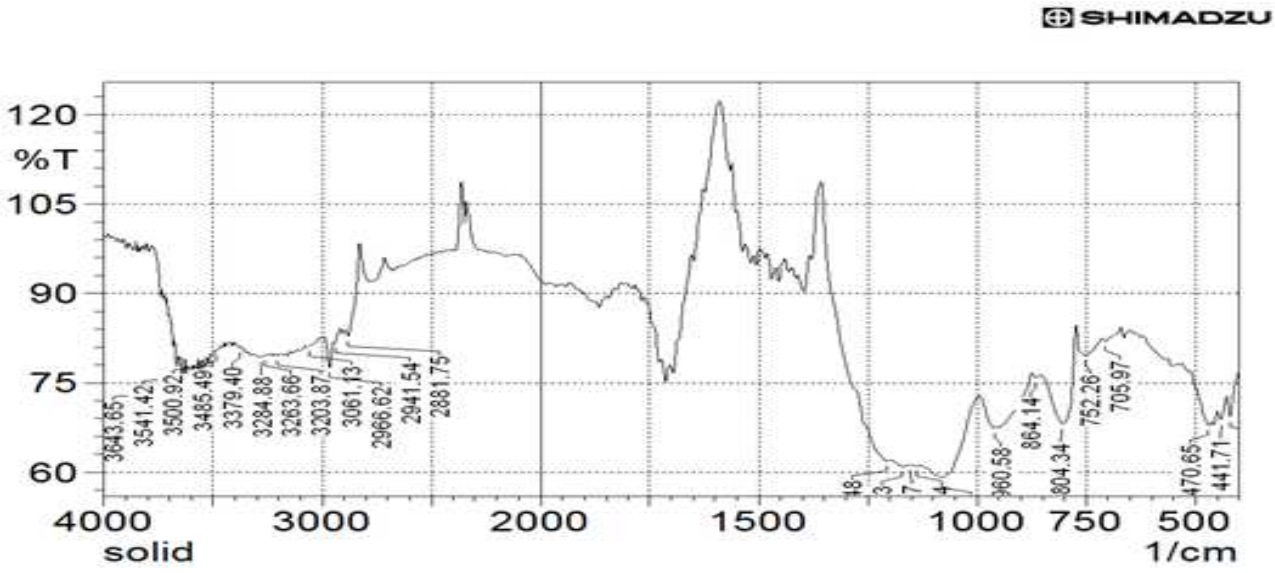

Fig 4. FTIR spectra of Bismuth Iodate [$Bi(I0_3)_3$] Crystals

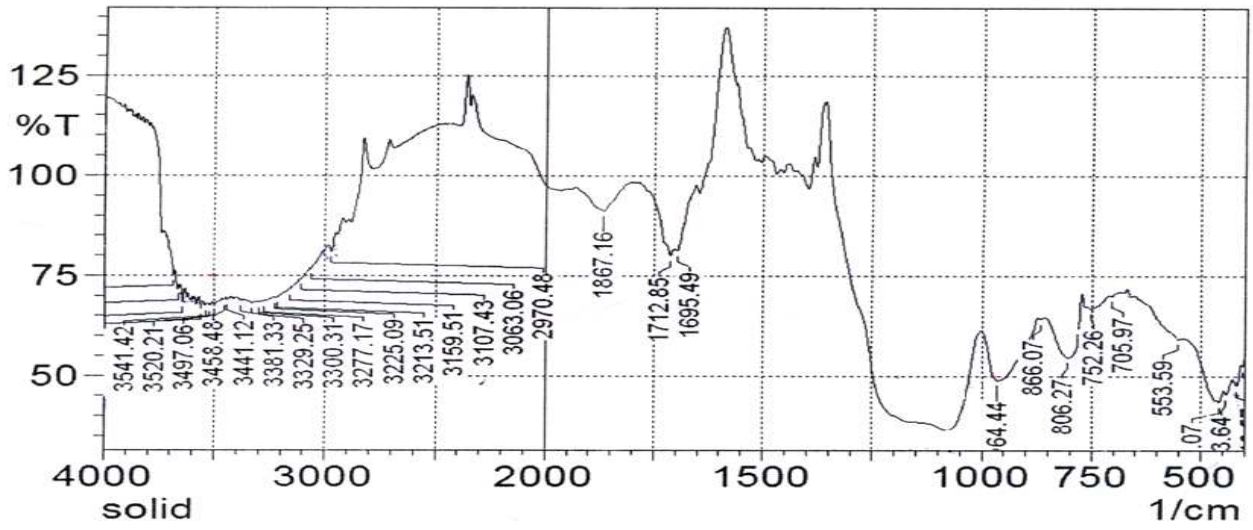

Fig 5. FTIR Spectra of Bismuth Iodide [BiI_3] Crystals

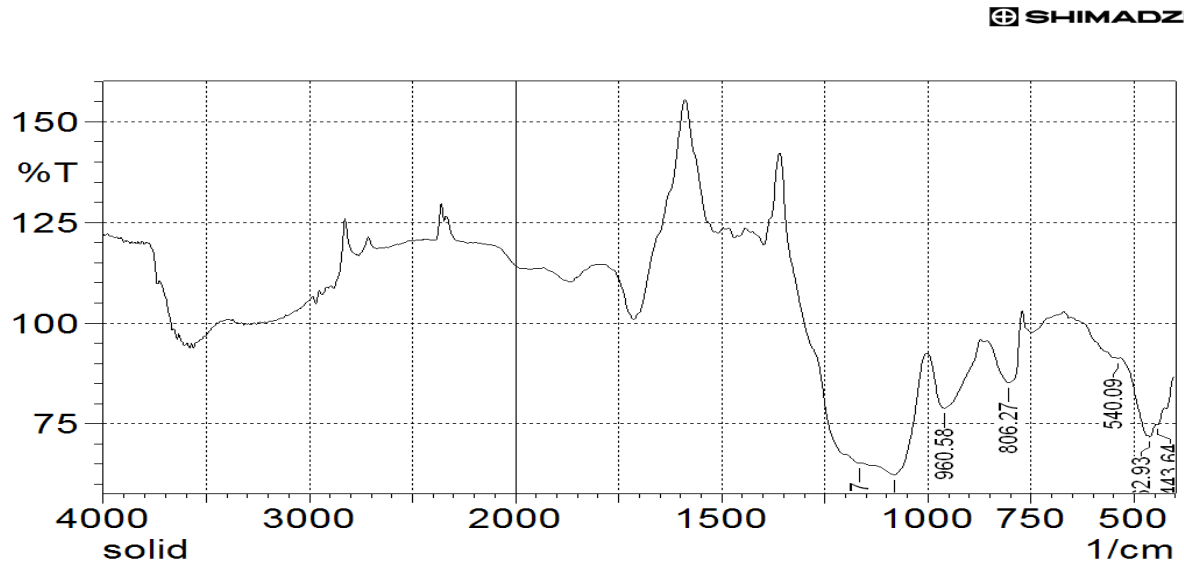

Fig6. FTIR spectra of Bismuth Trisulphide (Bi_2S_3) crystals.

Fundamental frequencies, generally observed in all Iodate, Iodide and Sulphide compounds, are also observed in all three types of crystals. For the comparative study of water content of the sample is established from FT-IR and thermal studies it has been concluded that Bismuth Iodate [10 water molecules] > Bismuth Tri-Sulphide [02 water molecules] > Bismuth Iodide **[**00 water molecules]

Also It may be concluded that, appearent large size of Bismuth Iodate crystals may be due to more water molecules than Bismuth Tri-sulphide and Bismuth Iodide. Strong and sharp intensity band observed in Bismuth Iodate and Bismuth Tri-sulphide at freq 470 cm^{-1} , 462.93 cm^{-1} and 428.21cm^{-1} but at the same frequency weak and sharp intensity band is observed in case of Bismuth Iodide.

5.3 Chemical analysis

Chemical analysis of crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide was carried out at department of chemistry, Smt. G. G. Khadse Science, Art and Commerce Collage Muktainagar Dist Jalgaon. Table 4 shows values of elements present in these gel grown crystals by chemical analysis and theoretical calculation from the molecular formula. From table it is clear that the values (mass %) of constituents in the grown crystals measured by chemical analysis are very close with the values calculated from the molecular formula.

Table 4: Values of elements present in the crystals

Crystal	Element	Content as measured by chemical analysis	Content as calculated from molecular formula
		mass %	mass %
Bismuth Iodate	Bi	27.16	28.48
	I	49.15	51.88
Bismuth Iodide	Bi	33.94	35.43
	I	62.78	64.55
Bismuth Tri-Sulphide	Bi	78.76	81.28
	S	16.86	18.70

The study of chemical analysis and EDAX manifest that the content of Bismuth in all the three compounds is different. The comparison of Bismuth content in the three compounds may be predicated as Bismuth Tri-sulphide [81.28%] > Bismuth Iodide [35.43%] > Bismuth Iodate [28.48%].

If the first stage of decomposition is consider then the range of temperature can be put as follows,

Bismuth Tri-sulphide [35.378 ^{0}C] < Bismuth Iodide [39.246 ^{0}C] < Bismuth Iodate [44.020 ^{0}C]

From the above two observations, It can be predicted that the amount of Bismuth present in the sample is related to initial stability of the sample as the less amount of Bismuth in Bismuth Iodate correspond to its more stability of sample.

If the present of Iodine is consider in Bismuth Iodate and Bismuth Iodide in the above study indicates that presents of Iodine is as follows

Bismuth Iodate [51.88 %] < Bismuth Iodide [64.55 %^{0}C]

From the above two observations, It can be predicted that as the Iodate contain less amount of Iodine make the sample more stable.

5.4 Electrical Conductivity

If Electrical Conductivity of grown sample is considering in the range of Room temperature to 423^{0}K the conductivity can be summarized as follows [Table 5].

Table 5. Electrical Conductivity of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-sulphide

Name of element	Temprature	Current in mA	Coductivity in mho
Bismuth Iodate	Room temperature At 423 ^{0}K	0.05 mA 0.40 mA	75.83 758.83
Bismuth Iodide	Room temperature At 423 ^{0}K	0.04 mA 0.42 mA	65.44 687.39
Bismuth Tri-Sulphide	Room temperature At 423 ^{0}K	0.04 mA 0.2 8 mA	61.52 430.64

Bismuth Iodate, [Room temperature current 0.05 mA, conductivity 75.83] and [423^{0}K current 0.40 mA, conductivity 758.83]. > Bismuth Iodide [Room temperature current 0.04 mA, conductivity 65.44] and [423^{0}K current 0.42 mA, conductivity 687.39].> Bismuth Tri-Sulphide [Room temperature current 0.04 mA, conductivity 61.52] and [423^{0}K current 0.28 mA , conductivity 430.64].

All the three samples show the characteristics of semiconducting materials as the conductivity increases as increase in temperature.

It has been already established that all Sulphides are semiconductors by Azaroff but here Bismuth Iodate and Bismuth Iodide are also found to be semiconductors.

CONCLUSION

1. Gel growth technique is suitable for growing crystals of Bismuth Iodate, Bismuth Iodide and Bismuth Bi-Sulphide.
2. Different habits of Bismuth Iodate, Bismuth Iodide and Bismuth Tri-Sulphide crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
3. Well known Liesegang phenomenon is observed in the growth of Bismuth Iodate and Bismuth Tri-Sulphide crystals.
4. Unit cell parameter values nearly match with the reported ones and the structure of Bismuth Iodate is monoclinic, confirmed by XRD. The structure of Bismuth Iodide is Hexagonal, while the structure of Bismuth Tri-Sulphide is Orthorhombic or Rhombus.
5. Fundamental Infrared frequencies observed in Iodate, Iodide and Sulphide compounds are also found in the present FT-IR analysis, of Bismuth Iodate Bismuth Iodide and Bismuth Tri-Sulphide crystals.
6. Chemical compositions of all the grown crystals by volumetric Analysis and gravimetric Analysis well match with the theoretical calculation from molecular formula.
7. The electrical conductivity of crystals closely related to chemical nature of compound the electrical conductivity increases as increase in temperature. The energy gap of $Bi(IO_3)_3$ is found to be 0.2553 eV ,the energy gap of BiI_3 is found to be 0.2056 eV, the energy gap of Bi_2S_3 is found to be 0.4640 eV which suggest that samples are semiconductor.
8. Crystals are quite transparent, shining and are of good quality.

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