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Thermal and optical studies of gel grown cobalt iodate crystal

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ABSTRACT

Cobalt iodate crystals were grown in silica gel at ambient temperature. The effect of various parameters like gel concentration pH of gel, gel setting time, concentration of the reactants on the growth of these crystals were studied prismatic, platy shaped and dendrites were obtained. The grown crystals were characterized by FT IR. Thermogravimeteric and differential thermal analysis and UV.

Key words. Cobalt iodate, TGA/DTA, FT-IR and UV.

INTRODUCTION

Crystal growth is a heterogeneous chemical process in which conversion from one phase to another phase of compound is involved. In the field of crystal growth, gel technique has become more popular and has been used by several investigator [1-3].Due to simplicity[4-5],it can be successfully used at room temperature, to suppress nucleation centers [6].In gel method suitable for crystals having low solubility [7].

Modern technologies such as optoelectronics, acoustic- optics etc has exploited the versatile properties of crystals. With the development of electronic devices much attention has been paid to role of foreign particles in crystallization process, particularly in semiconductor industries. Most of iodate compounds are insoluble in water and decompose before their melting point. Hence crystals of such type of compounds cannot be grown by either slow evaporation or melt technique. In this situation gel method is the appropriate one for their growth. The gel growth technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals. Gel growth is an alternative technique to solution growth with controlled diffusion and the growth rate process is free from convection.

In this paper, we report a method of growing cobalt iodate crystals by single diffusion of chemical reaction in silica gel medium. The cobalt iodate crystals characterized by studying its FT-IR, TGA/DTA and optical properties.

MATERIALS AND METHODS

Experimental

Good quality crystals can be grown in gels in a variety of ways; the single diffusion method was employed in the present work for growth of cobalt iodate crystals. The silica gel was used as a growth media. The chemicals used for growth of cobalt iodate crystals were, acetic acid, sodium meta silicate, cobalt chloride and KIO_3. All chemicals were of AR grade. To grow the cobalt iodate crystals the required silica gel medium was prepared by adding the sodium meta silicate solution of specific gravity is 1.04gm/cc drop by drop with constant stirring by using magnetic stirrer into 5ml (2N) acetic acid till the pH value of solution is 4.5 was set for the mixture. To the above sodium meta silicate solution of pH 4.5.Then added 5ml aqueous solution of 0.5M cobalt chloride as inner reagents with constant stirring. This mixture is transferred to the test tube of length 25 cm and 2.5cm diameter. To keep the solution free from dust and impurities, care was taken to cover the test tube with cotton plug. It would take about 3days for the gel to set in summer (28^0 -35^0c);where as it would taken even 3-5 days for gel set in winter (18^0 – 25^0c).It was left for two more days for ageing and then outer reagent, the aqueous solution of 0.1M KIO_3 was added on to the top of the gel. The outer reagent was added down the sides of the test tube using a pipette and not directly on to the gel medium. Due to the diffusion of the outer reagent into the gel medium and its reaction with inner reagents, crystals started to grow. Nucleation was observed within 36 hours of addition of the outer reagent. Circular shaped, opaque, crystals were observed as shown in fig. (1).In fig. (2) crystals are shown in the test tube. All experiments carried at room temperature. The reaction that takes place in the gel medium is given below.

$$COCl_2 + 2KIO_3 \longrightarrow CO(IO_3)_2 + 2KCL$$

RESULT AND DISCUSSION

The optimum conditions for growing crystals are given in table (1).

In single diffusion after a few days spherulitic, opaque and good quality crystals growth of cobalt iodate observed as shown in figure (1).While figure (2) shows the inside the test tube.

Table, 1, Optimum condition for growth of cobalt iodate crystal

Conditions	Single diffusion
Density of sodium meta silicate	1.04gm/cm^3
Amount of 2N acetic acid	5ml
pH of the gel	4.4
Temperature	Room temperature
Concentration of $COCl_2$	0.5M
Concentration of KIO_3	0.1M
Gel setting period	7days
Growth of period	3 weeks
Size	2,3,4,mm diameter

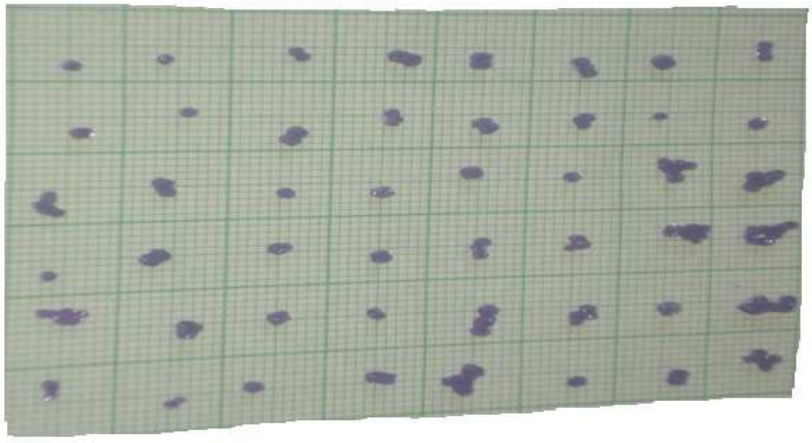

Figure 1.Violet coloured opaque crystals of cobalt iodate crystals

Figure 2.Crystal growth in the test tube

Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting period etc have considerable effect on growth rate. In the steady state of concentration gradient growth rate also becomes steady which favors' growth of good quality crystals.

3.1 FT – IR analysis of cobalt iodate crystal

FT – IR is used for structural analysis. In the present study FT – IR spectrum of cobalt iodate sample has recorded using SHIMADZU spectrophotometer at Department of chemistry, university of pune. FT – IR spectrum was recorded in the wave number range 400 – 4000cm^{-1} for KBr line. The FT – IR spectrums shown in fig.(3).The band frequencies along with the suggested assignments were summarized in table (2).

Table ,2, FT – IR spectral and vibrational assignments of cobalt iodate

Wave number cm^{-1}	Intensity	Assignments
3640 - 3610	S, Sh	O-H stretch
3500 - 3200	S,B	O – H stretch
3000 - 2850	M	C –H stretch
1760 - 1665	S	C = O stretch
1470 - 1450	M	C –H bend
1370 - 1350	M	C – H rock
1335 – 1250	S	C – N stretch
1300 - 1150	M	C –H wag
1000 - 650	S	= C – H bend
690 -515	M	C – Br stretch

M = medium, W = weak, S = strong, N = narrow, B = broad, Sh = sharp,

The FT – IR spectrum shows the identification of O –H bending. The peaks were identified in comparison with reports. [8-10].Fundamental FT – IR frequencies observed in all cobalt iodate compound in general are also found in this analysis with confirms the cobalt iodate grown crystals. The sample has water of crystallization as evidenced by broad band 3616cm^{-1}(O – H stretching) and at 932cm^{-1} (O –H bending).

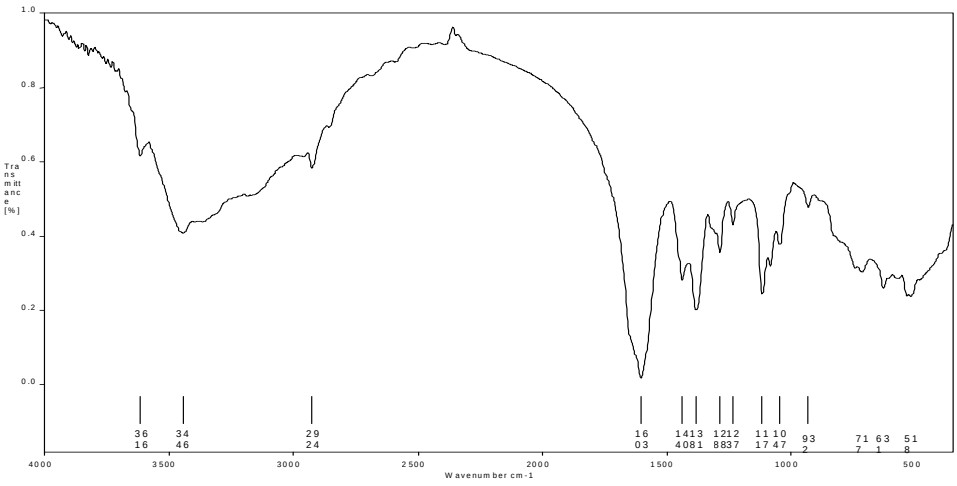

Figure 3. FT - IR of cobalt iodate

3.2 Thermal analysis of cobalt iodate crystal

The thermo gravimetric analysis provides a quantitative measurement of any mass changes associated with thermally induced transitions. For example TG can record directly the loss in mass as a function of temperature or time for transition that involve dehydration or decomposition.TG curves are characteristics of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges.

In the present investigation TGA, DTA were conducted. The thermo gravimetric analysis and differential thermal analysis were performed on powdered sample using a Diamond TGA/DTA analyzer. The thermo gram was obtained by heating the sample from room temperature to 1000^0C in an atmosphere of nitrogen with a heating rate of 30^0 C min^{-1}.The TGA and DTA Plots are shown in fig.(4) and (5) respectively.

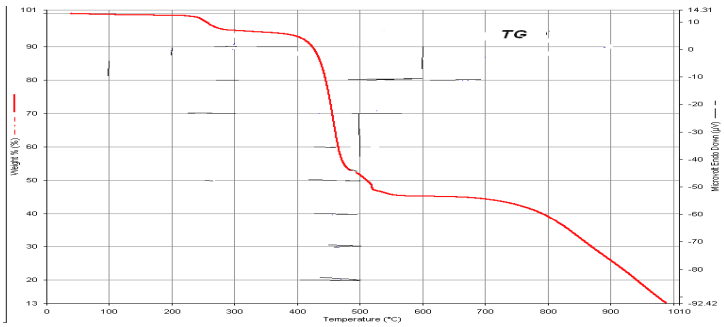

Figure 4.TGA curve of cobalt iodate

The TGA curve shows the loss of all water molecules in the first step of decomposition around 220^0C .

I) The compound is stable up to 45^0C to 220^0C.

II) 5% weight loss in the temperature range 220^0C to 270^0C may due to adsorbed water molecule.

III) Then the sample is remaining stable from 270^0C to 400^0C and thermo graph is parallel to temperature axis.

IV) 50.4% loss in weight in the temperature range 400^0C to 515^0C.Due to the loss of oxygen molecule

V) Again the sample is remaining stable from 515^0C to 750^0C.

VI) In the temperature range750^0C to 1000^0C weight loss is up to 32%. It may be due to loss of remaining iodine or oxygen molecule.

The TGA data of cobalt iodate crystal summarize table (3) And table (4) shows DTA data.

Table. 3. TGA data of Cobalt iodate crystal

Stage	Temperature range	Observed % weight loss	Calculated % weight loss	Loss of molecule in stage
I	250^0c to 270^0c	5%	5.2%	H_2O
II	400^0c to 515^0c	50.4%	50.7%	I or O
III	750^0c to 1000^0c	32%	31.1%	Remaining Ior O

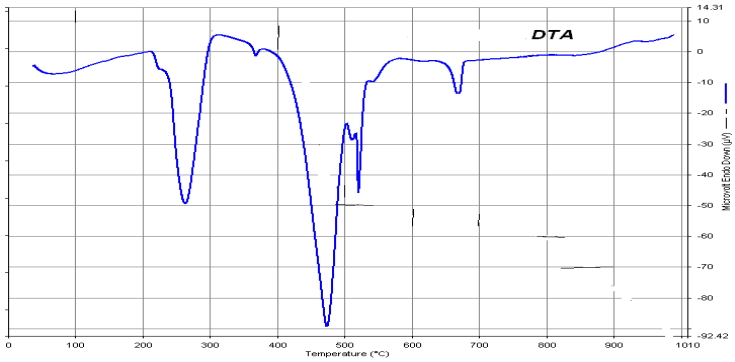

Figure 5. DTA of cobalt iodate crystal

Table .4. The data of DTA of cobalt iodate crystal

Peak recorded	Peak height	Nature	On set temperature
270^0c	-40.00	Endothermic	230^0c
481^0c	-92.00	Endothermic	410^0c
520^0c	-20.00	Endothermic	510^0c
675^0c	-12.00	Endothermic	682^0c
380^0c	-2.00	Exothermic	370^0c
510^0c	-6.00	Exothermic	500^0c

3.3 UV Absorption spectroscopy

Absorption spectra of cobalt iodate crystals were recorded using a SHIMADZU UV- 2450 UV-Vis spectrophotometer over the wavelength range 200 -650 nm at Nano Research Laboratory, Department of Physics; Pratap college Amalner. Figure (6) shows UV absorption spectra of cobalt iodate crystals .From the spectrum, it has been inferred that cobalt iodate crystal has sufficient transmission in the entire visible and IR region. The absorption coefficient is high at lower wavelength and wide transparency from 450 nm suggesting their suitability for second and third harmonic generation's radiation. [11 -12].

The band gap energy of the cobalt iodate crystals with the obtained wavelength are calculated using the following simple conversion equation;

Band gap energy (eV) = 1240/wavelength (nm).Band gap Energy is represented in table (5).

Table .5.Band gap energy of cobalt iodate crystals

Crystal	Λ(nm)	Band gap Energy (eV)
Cobalt iodate	375	3.306

The band gap energy of cobalt iodate crystals is found to be 3.306eV.

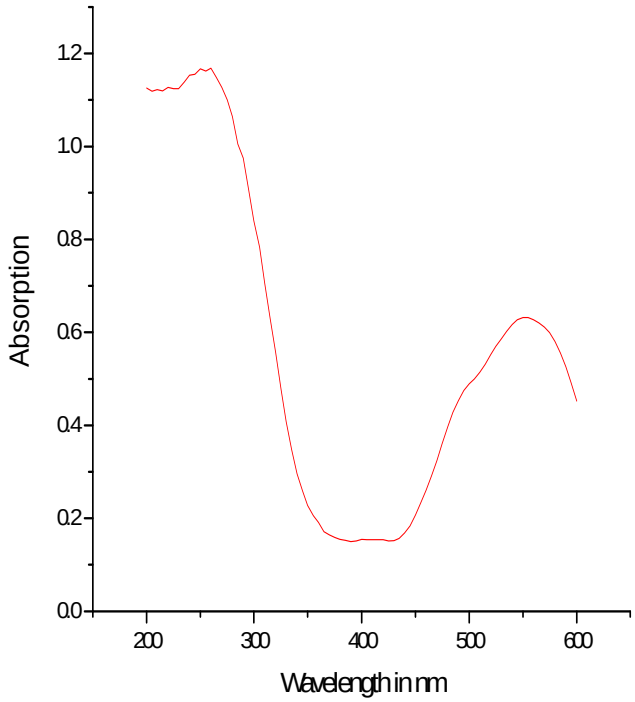

Figure 6, Optical absorption spectra of cobalt iodate

CONCLUSION

1) Gel method is found suitable for growing cobalt iodate crystals.
2) The growth of single crystals of cobalt iodate was accomplished using single test tube diffusion method. Optimum conditions for growth were worked out.
3) Different habits of cobalt iodate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, concentration of reactants, etc.
4)TGA/DTA analysis of cobalt iodate crystals have been investigated. The decomposition temperature and percentage of weight loss of grown are recorded by TGA/DTA analysis.
5) It is investigated that Cobalt iodate crystals have NLO properties.

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