

# Study of XRD, FTIR, Thermal Analysis and Nonlinear Optical Properties of Barium, Calcium, Cadmium Iodate Crystals Grown in Silica Hydro Gel

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## ABSTRACT

In the present work, technologically important crystals of barium, calcium, and cadmium iodate were grown. These crystals exhibit nonlinear optical property and piezoelectric property. Crystals of barium, calcium, and cadmium iodate were grown by gel method. Optimum growth conditions for gel grown crystals were established by varying various parameters such as gel density, pH of gel, gel setting time, gel aging time, etc. are reported. These crystals were characterized by XRD analysis, Infrared spectroscopy and Thermal analysis. Powder SHG experiments were carried out to determine nonlinear optical coefficients. Present work deals with study of all these crystals regarding their growth and characterization. All obtained results are presented at a glance.

## Keywords

Gel growth, XRD, FTIR, Thermal analysis, NLO property.

## 1. INTRODUCTION

Liesegang, Bradferd, and Holmes studied the formation of 'Liesegang rings' [1-3]. The growth of crystals in gels was recorded in 1913. Afterwards many co-workers [4-8] extensively discussed the mechanism of crystal growth which accelerated the mechanism of growth and characterization of crystals in gels.

For production of high quality crystals, gel growth in aqueous solution is now a wide spread technique in a large range of solubility and temperature [9-11]. Crystals are free from strain, and are mostly formed at ambient temperature in gel growth [12]. Large scale movements like convection currents are almost completely suppressed, in this method. Two soluble reactants are diffused into a gel where they react to form an insoluble product. The rate of diffusion of crystallizing species and the related crystal growth kinetics is not affected by the presence of gel [13]. Crystallization occurs by diffusion of reactants to a small number of nucleation centers, due to suppression of turbulence and nucleation [14]. In the present work, technologically important crystals of barium, calcium and cadmium and lithium iodate were grown. These crystals exhibit nonlinear optical property [15, 16] and piezoelectric property [17].

## 2. EXPERIMENTAL DETAILS

Gel was prepared from aqueous solution of sodium meta silicate. The gel was acidified by acetic acid. A series of experiments having different pH values for the gel and the different concentration for reactants were arranged. In case of test tubes, out of the two reactants, one was incorporated in gel and the other one, either  $\text{KIO}_3$  or  $\text{NaIO}_3$  was used as supernatant. Experiments were also carried out by changing the position of reactants. In case of U-tubes, solutions of the reactants were placed on top of the acetic acid set gel, in two separate limbs of the tube. The chemical reaction inside the

gel for the growth of said crystals can be expressed as,  $\text{XCl}_2 + 2\text{YIO}_3 = \text{X}(\text{IO}_3)_2 + 2\text{YCl}$ , where  $\text{X} = \text{Ca, Ba or Cd}$  and  $\text{Y} = \text{K/Na}$ .

## 3. RESULTS AND DISCUSSION

Crystals of barium, calcium, and cadmium iodate were grown by gel method by using single and double diffusion techniques. Optimum growth conditions for gel grown crystals were established by varying various parameters such as gel density, pH of gel, gel setting time, gel aging etc. are reported in Table 1.

Table 1. Optimum growth conditions for gel grown iodate crystals

Parameters	Ba ( $\text{IO}_3$ ) <sub>2</sub> , H <sub>2</sub> O	Ca ( $\text{IO}_3$ ) <sub>2</sub> , H <sub>2</sub> O	Cd ( $\text{IO}_3$ ) <sub>2</sub>
Density of sodium meta silicate solution	1.04 gm/cm <sup>3</sup>	1.04 gm/cm <sup>3</sup>	1.04 gm/cm <sup>3</sup>
Amount of 2N acetic acid	5 cc	5 cc	5 cc
pH of mixture	4.2	4.2	3.68
Temperature	Room temperature	Room temperature	Room temperature
Gel setting time	12 days	12 days	15 days
Gel aging time	120 hours	120 hours	144 hours
Period of growth	4 weeks	4 weeks	5 weeks
Preferred diffusion method	Single diffusion method	Single diffusion method	Double diffusion method

Dendritic (10 to 20 x 1 mm<sup>2</sup>), prismatic pyramidal (3 x 2 x 2 mm<sup>3</sup>), and prismatic (2 x 2 x 1.5 mm<sup>3</sup>) shaped crystals of barium iodate were obtained. Most of them were opaque and few of them were transparent. Single diffusion method is found more suitable for growth of these crystals. In case of calcium iodate crystals, hopper (15 x 3 x 2 mm<sup>3</sup>), needle shaped (10 x 2 x 2 mm<sup>3</sup>), prismatic pyramidal (5 x 2 x 2 mm<sup>3</sup>), and prismatic (2 x 2 x 2 mm<sup>3</sup>) crystals were obtained. Few of them were translucent and some of them were transparent. Few transparent crystals were opaque at their one end. That might be due to inclusion of silica gel. In this type also, single diffusion technique proved to be suitable for growth. Cadmium iodate crystals of spherulitic shape having 2 to 2.5 mm diameter were obtained. They were cream colored. In this case, double diffusion method was preferred over single diffusion.

Figure 1 shows prismatic, transparent crystals of barium iodate and figure 2 shows few transparent crystals of calcium iodate. Figure 3 shows transparent needles of calcium iodate and figure 4 shows spherulites of cadmium iodate.



Figure 1: Prismatic, transparent crystals of barium iodate

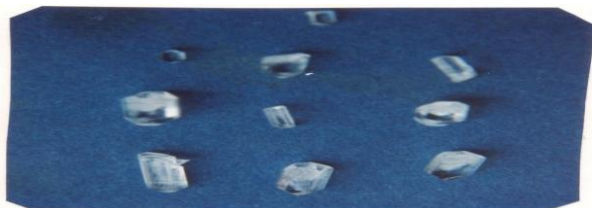


Figure 2: Transparent crystals of calcium iodate

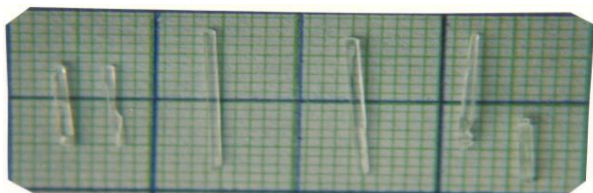


Figure 3: Needle shaped crystals of calcium iodate



Figure 4: Spherulites of Cadmium iodate

### 3.1 XRD Analysis

Crystals of barium, calcium, cadmium, and lithium iodate were characterized by XRD analysis. X-ray diffractograms were recorded using powder diffraction method using Miniflex model, Rigaku, Japan, X-ray diffractometer. From these diffractograms, 'd' values were computed. The unit cell parameters a, b, c, and  $\beta$  along with 'd' values of all the three types of crystals are in good agreement with the reported values.

Table 2 represents system of the crystal, unit cell parameters,  $\beta$ , and volume of the three types of crystals. The X-ray diffractograms of barium, calcium and cadmium iodate crystals are shown in figures 5 to 7. From these diffractograms, intensity ratios  $I / I_0$ , 'd' values, and hkl were computed. Results from these diffractograms are reported in table, are in good agreement with the reported values [18].

Table 2. Lattice parameters

Type of crystal		a Å <sup>0</sup>	b Å <sup>0</sup>	c Å <sup>0</sup>	$\beta$ °	V (Å <sup>0</sup> ) <sup>3</sup>	System
Barium iodate, monohydrate	i) Reported	9.061	7.988	9.918	92.10	-	Monoclinic $a \neq b \neq c$ , $\alpha = 90^\circ \neq \beta$
	ii) Observed	9.014 (7)	8.017 (1)	9.932 (4)	91.00	717.495	
Calcium iodate, monohydrate	i) Reported	8.509	10.027	7.512	95.27	-	Monoclinic $a \neq b \neq c$ , $\alpha = 90^\circ \neq \beta$
	ii) Observed	8.494 (1)	10.033 (2)	7.512 (2)	95.00	637.457	
Cadmium iodate	i) Reported	5.856	17.470	5.582	90.00	-	Orthorhombic $a \neq b \neq c$ , $\alpha = \beta = \gamma = 90^\circ$
	ii) Observed	5.855 (1)	17.467 (8)	5.591 (2)	90.00	571.730	

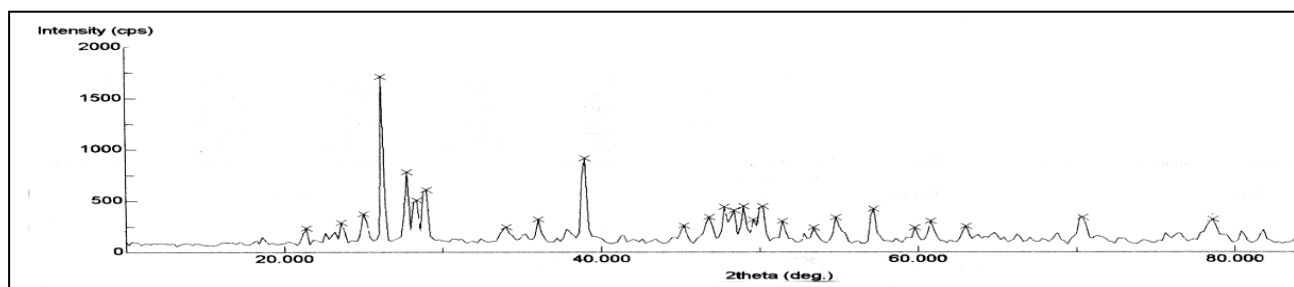


Figure 5: X-ray diffractogram of barium iodate

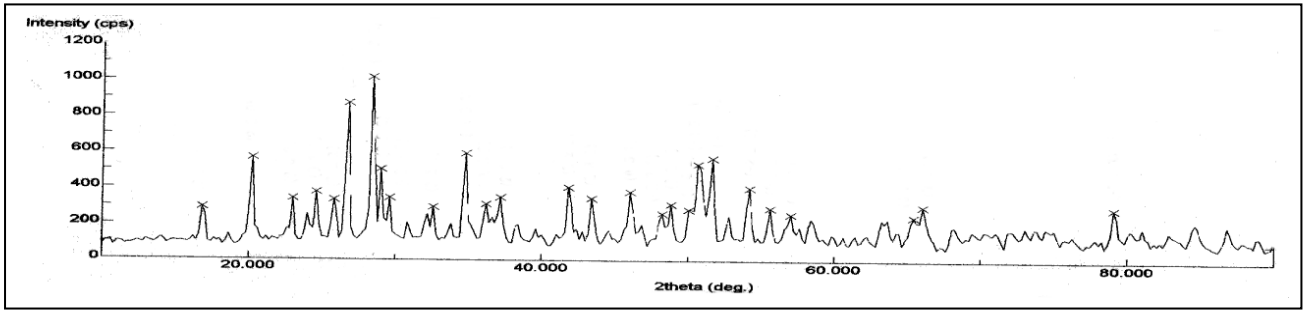


Figure 6: X-ray diffractogram of calcium iodate

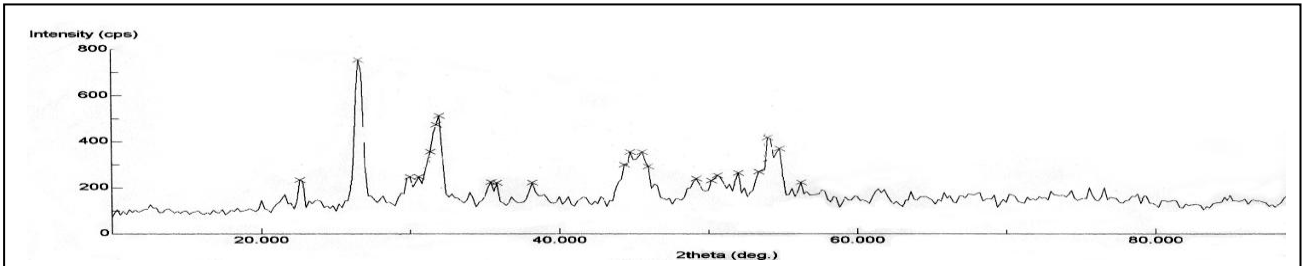


Figure 7: X-ray diffractogram of cadmium iodate

### 3.2 Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) gives detailed information about the absorption bands due to presence of water molecules, metal ions, hydroxyl ions, organic molecules, etc. In the present investigation, FT-IR spectra of barium, calcium and cadmium iodate were scanned by using FT-IR spectrophotometer, Spectrum-2000, Perkin-Elmer model, by placing sample KBr pellet in the sample beam in two ranges, 4000 – 400  $\text{cm}^{-1}$  and 710–300  $\text{cm}^{-1}$ . These spectra are represented in figures 8 to 10. Observed

values of the fundamental frequencies of the iodate ions are in good agreement with the reported values [19-22]. Fundamental frequencies, generally observed in all iodate compounds, are also observed in all four types of crystals. These are represented in Table 3. In case of barium and calcium iodate, bands due to O-H stretching in the range 3390-3470  $\text{cm}^{-1}$  and bands due to H-O-H bending in the range 1590-1610  $\text{cm}^{-1}$  are also observed, which indicates that both of these crystals are monohydrated.

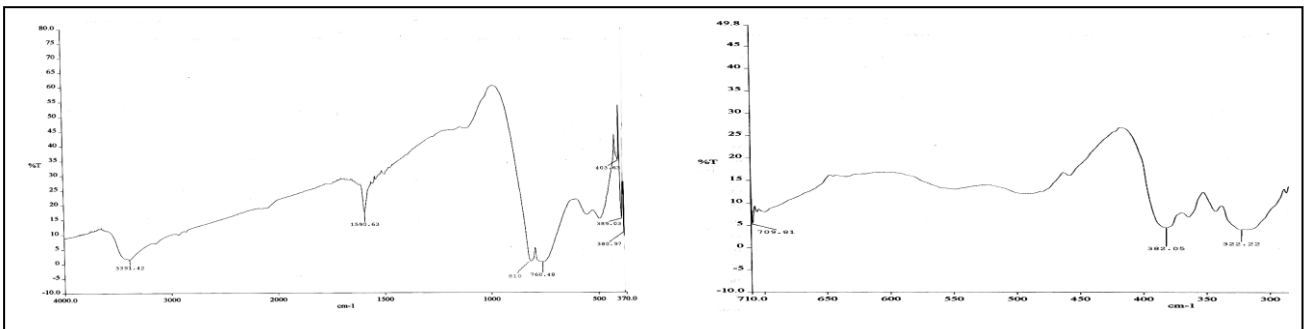


Figure 8: FT-IR spectra of barium iodate in the range (a) 4000-400  $\text{cm}^{-1}$  (b) 710-300  $\text{cm}^{-1}$

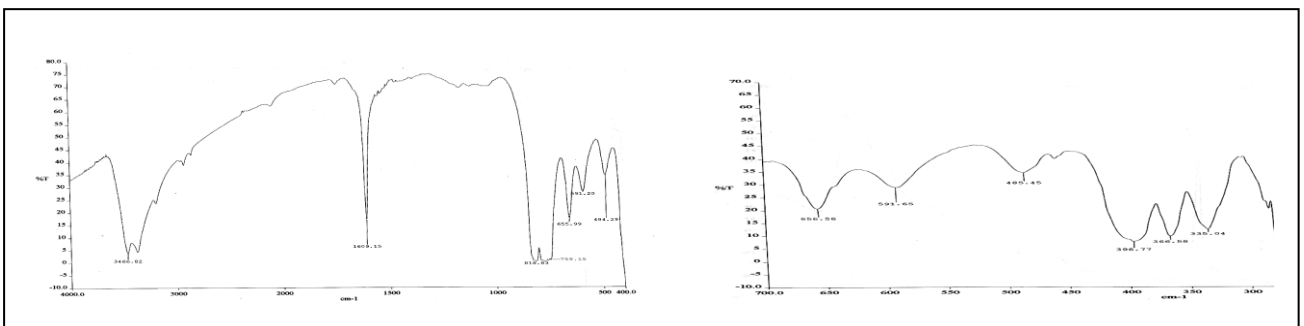


Figure 9: FT-IR spectra of calcium iodate in the range (a) 4000-400  $\text{cm}^{-1}$  (b) 710-300  $\text{cm}^{-1}$

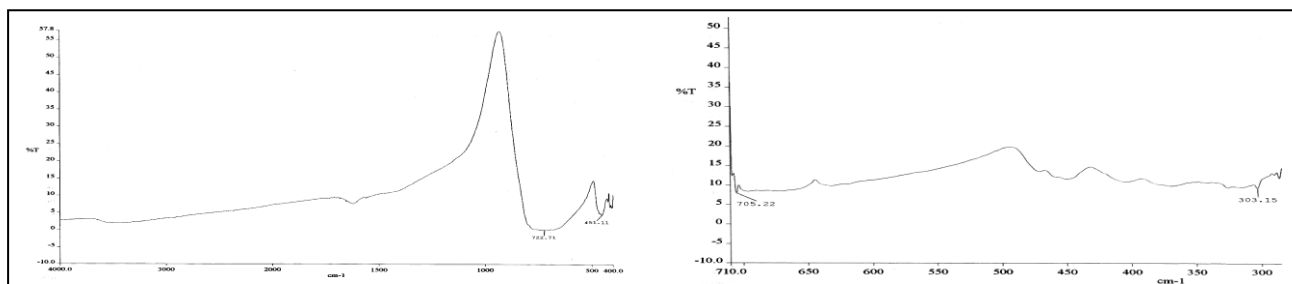


Figure 10: FT-IR spectra of cadmium iodate in the range (a) 4000-400  $\text{cm}^{-1}$  (b) 710-300  $\text{cm}^{-1}$

Table 3. Vibrational infrared frequencies

Fundamental frequencies	Ba(IO <sub>3</sub> ) <sub>2</sub> , H <sub>2</sub> O ( $\text{cm}^{-1}$ )	Ca(IO <sub>3</sub> ) <sub>2</sub> , H <sub>2</sub> O ( $\text{cm}^{-1}$ )	Cd(IO <sub>3</sub> ) <sub>2</sub> ( $\text{cm}^{-1}$ )
Symmetric stretching frequency, $\gamma_1$	760.48	759.15	705
Symmetric bending frequency, $\gamma_2$	382.05	396.77	451
Asymmetric stretching frequency, $\gamma_3$	810.0	818.83	722
Asymmetric bending frequency, $\gamma_4$	322.22	335.04	303

### 3.3 Thermal Analysis

Barium, calcium, cadmium, and lithium iodate crystals were characterized by TGA, DTA, and DSC thermal analysis, because a single thermal analysis method does not provide complete information of a system.

However, additional information may be provided by other thermal methods, if required. In case of barium, calcium, and cadmium iodate, all three methods provide similar results. TGA, DTA and DSC thermo grams are shown in Figures 11 - 19.

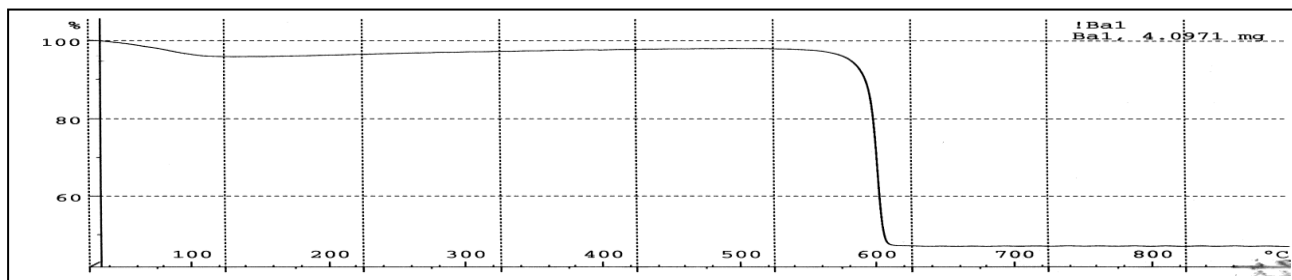


Figure 11: TGA curve of barium iodate

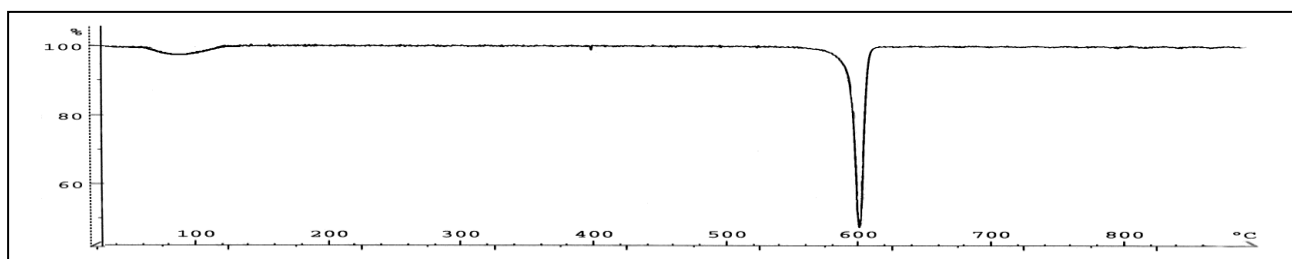


Figure 12: DTA curve of barium iodate

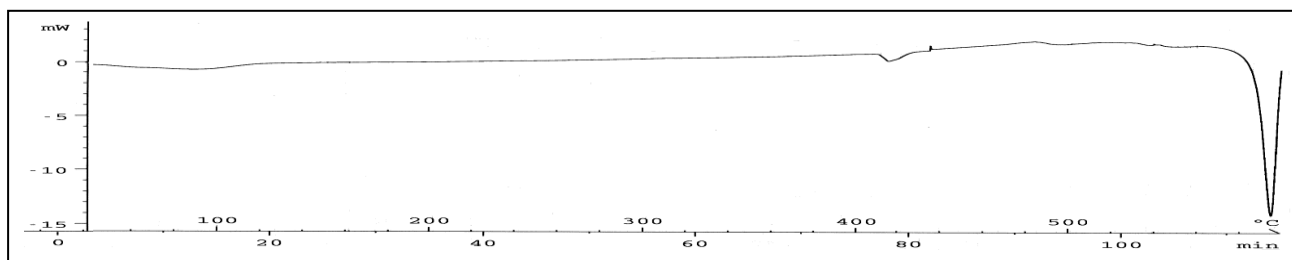


Figure 13: DSC curve of barium iodate

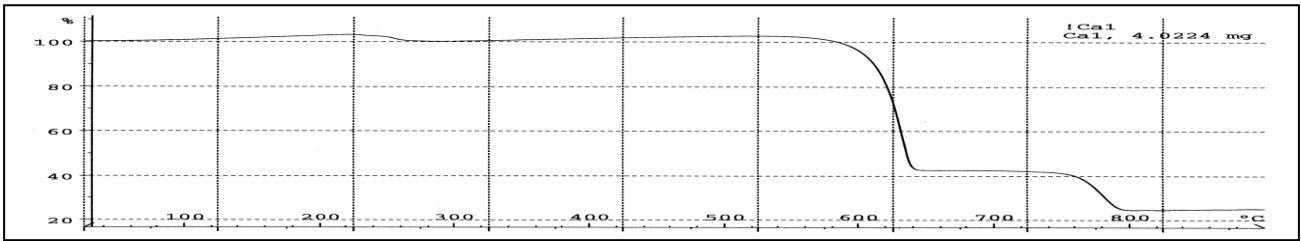


Figure 14: TGA curve of calcium iodate

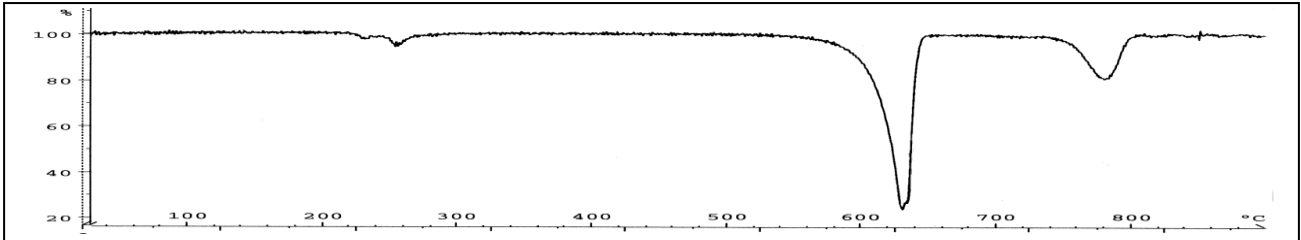


Figure 15: DTA curve of calcium iodate

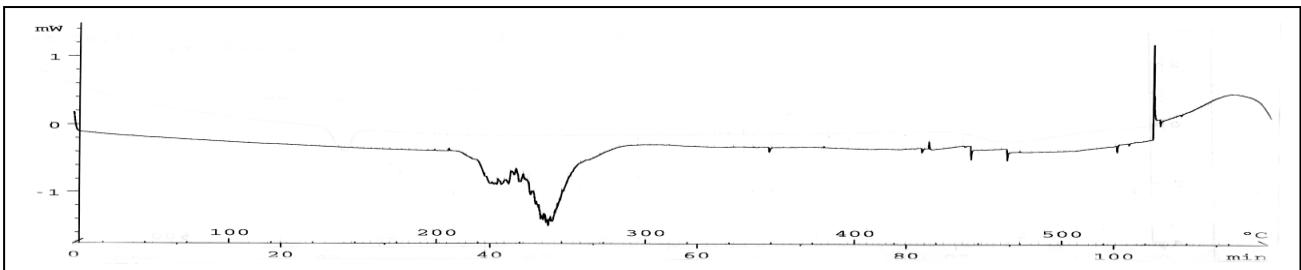


Figure 16: DSC curve of calcium iodate

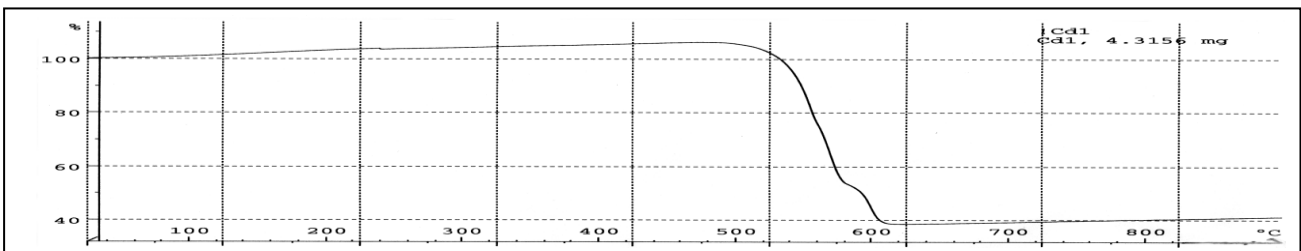


Figure 17: TGA curve of cadmium iodate

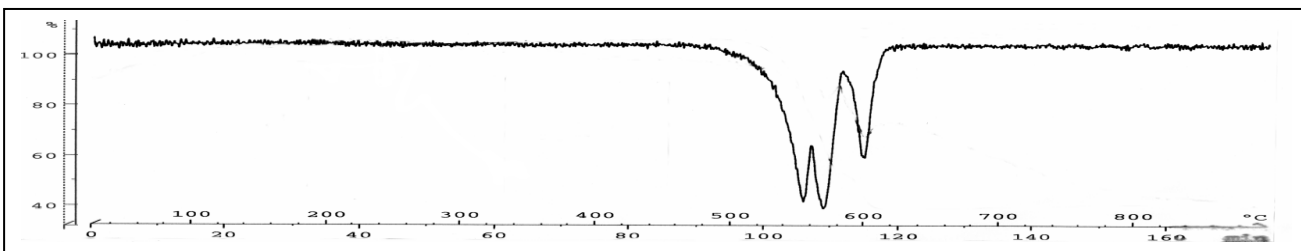


Figure 18: DTA curve of cadmium iodate

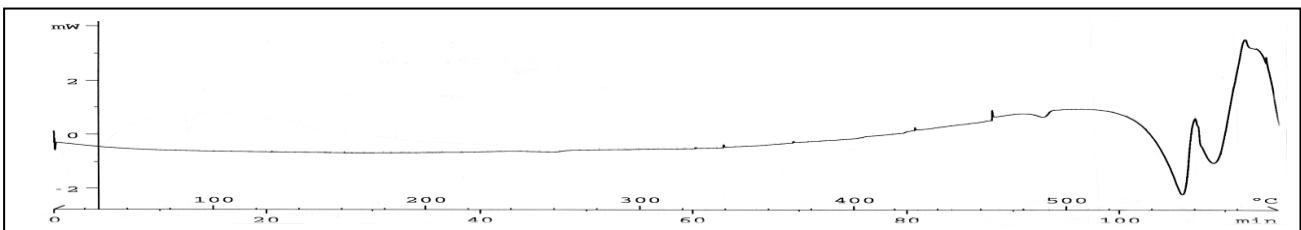


Figure 19: DSC curve of cadmium iodate

Barium iodate crystals exhibit two steps, first of dehydration and second of decomposition. Calcium iodate crystals show three steps, first step of dehydration, second of decomposition, and third step again of decomposition. Cadmium iodate crystals show two steps, both of which

indicate decomposition reactions [23-24]. Table 4 represents kinetic data of TG analysis of these crystals. Definite amount of sample was heated from ambient to 900°C for TGA and DTA, and up to 600°C for DSC studies.

**Table 4. Kinetic data of TG analysis**

Compound	Step	Temperature range °C	% Weight loss	Probable product formed	Nature of reaction
Barium iodate, monohydrate	I	50 – 100	4	Ba(IO <sub>3</sub> ) <sub>2</sub>	endothermic
	II	560 – 610	50	Ba <sub>5</sub> (IO <sub>6</sub> ) <sub>2</sub>	
Calcium iodate, monohydrate	I	220 – 280	3.2	Ca(IO <sub>3</sub> ) <sub>2</sub>	endothermic
	II	580 – 640	58	Ca <sub>5</sub> (IO <sub>6</sub> ) <sub>2</sub>	
	III	750 – 800	18	Ca <sub>5</sub> (IO <sub>4</sub> ) <sub>2</sub>	
Cadmium iodate	I	500 – 580	50	Cd <sub>5</sub> (IO <sub>6</sub> ) <sub>2</sub>	endothermic
	II	580 – 620	16	Cd <sub>5</sub> (IO <sub>4</sub> ) <sub>2</sub>	

### 3.4 Powder SHG Measurements

By using powder SHG technique [25-26], conversion efficiencies of barium, calcium, cadmium, and lithium iodate have been measured with respect to KDP. Values of nonlinear coefficients (d's) are represented in Table 5. These iodates, i.e. barium, calcium, and cadmium iodate exhibit nonlinear optical property. But conversion efficiency of cadmium iodate is maximum, followed by barium iodate and then calcium iodate.

**Table 5. Nonlinear coefficients of KDP and iodate crystals**

Compound	Nonlinear coefficients (d) pm/V
Barium iodate, monohydrate	0.1935
Calcium iodate, monohydrate	0.08754
Cadmium iodate	0.2940
KDP	0.44

### 4. CONCLUSIONS

Gel technique can be successfully employed for growth of barium, calcium and cadmium iodate crystals. Single diffusion method is found to be convenient for the growth of barium and calcium iodate crystals while double diffusion is suitable for the growth of Cadmium iodate crystals.

X-ray diffraction studies suggest that the calculated unit cell parameters,  $\beta$ , and d values are in good agreement with the standard JCPDS data. FTIR analysis confirms the presence of fundamental infrared frequencies, generally observed in all iodate compounds. Thermal analysis exhibits two steps explicitly on heating the samples of Ba and Cd iodate. The first and second steps involve decomposition reaction. In case of calcium iodate, the first step involves dehydration reaction; second and third steps involve decomposition reaction. Cadmium iodate exhibits good nonlinear optical property and its 'd' value is even more than that of barium and calcium iodate.

### 5. REFERENCES

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