Synthesis and characterization of some doped and undoped Cadmium iodate crystals grown in silica gel

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Abstract:

Cadmium iodate [Cd $(IO_3)_2$] crystals were grown by single diffusion gel technique. Growth conditions were optimized. Optimum growth conditions are reported. The crystals were doped by impurities such as Cu^{+2} and Fe^{+3}. Structure of crystals was confirmed by X-ray powder diffraction method. Effect of doping on structure is studied. Slight change in lattice parameter values is reported. Thermal studies of doped and undoped crystals are reported. Thermal analysis exhibits two steps explicitly on heating the samples. The first step involves decomposition reaction in the temperature range 500 - 580^0C, giving products Cd_5 $(IO_6)_2$, I_2, and O_2. In the second step, decomposition reaction in the temperature range 580 - 620^0C, yields solid product, Cd_5 $(IO_4)_2$ after reaction. Powder second harmonic generation experiments prove nonlinear nature of the substance. Nonlinear coefficient values,'d' of doped and undoped samples are reported. Cu^{+2} doped samples stop the generation of second harmonic signal. Fe^{+3} doped samples generate second harmonic signal, but the value of nonlinear coefficient is smaller than undoped sample.

Keywords

Silica gel; Cadmium iodate; Doping; XRD; TG/DTA; NLO; SHG.

1. Introduction

Gel growth in aqueous solution is now a wide spread technique for production of high quality crystals in a large range of solubilities and temperatures [1-3]. In gel growth, crystals are mostly formed at ambient temperature and hence are free from strain often present in crystals prepared from the melt or from the vapour [4]. In this method, two soluble reactants are diffused into a gel where they react to form an insoluble product. This is achieved by incorporating one of the reactants with the gel before setting in a test tube and adding the reactant in solution above the gel as supernatant. In this method, large scale movements like convection currents are almost completely suppressed, which otherwise could be harmful to the quality of crystal. The presence of gel does not considerably affect the rate of diffusion of crystallizing species [5] and the related crystal growth kinetics. The principle role of gel appears to be the suppression of turbulence and nucleation, [6] due to which crystallization occurs by diffusion of reactants to a small number of nucleation centres.

In recent years, very few attempts have been made to study growth and characterization of iodate crystals in general and cadmium iodate crystal in particular [7-9]. All these researchers have used slow evaporation method for growing the crystals. There are no reports in the literature on the growth of these crystals by gel method. Recently attention was drawn to different salts of iodic acid in view of their piezoelectric and electro-optical applications [15]. Hence, the growth of cadmium iodate crystals by gel technique by single diffusion method is attempted and reported in the present paper. These crystals were also grown by doping impurities like copper and iron. Experiments were carried out by varying different parameters like density of gel, gel aging, pH of gel, concentration of reactants and concentration of impurities which considerably affect the

growth of crystals. Optimum growth conditions were determined and are reported in the present paper.

2. Experimental

Single diffusion experiments were attempted. Test tubes of diameter 2.5 cm and height 25 cm were used as crystallization apparatus. All experiments have been carried out in silica gel. Gel was prepared from aqueous solution of sodium meta silicate. The gel was acidified by acetic acid. The chemical used for growth of doped and undoped cadmium iodate crystals were CH_3COOH, Na_2SiO_3, $CdCl_2$, $NaIO_3$, $CuCl_2$, $FeCl_3$. All chemicals used were of AR grade.

A series of experiments using different pH values (3 to 4 pH) for the gel and the different concentrations for reactants (0.2 M to 0.6 M) were carried out. In case of test tubes, out of the two reactants, $CdCl_2$ was incorporated in gel and $NaIO_3$ was used as supernatant over the gel. These experiments yield Spherulitic crystals of Cd $(IO_3)_2$ of few mm size. Experiments were also carried out by interchanging the position of reactants. These experiments do not yield any crystals at all.

Solutions of impurities having different concentrations, $CuCl_2$ (0.1 M to 0.3 M) or $FeCl_3$ (0.1 M to 0.3 M) and amounts (1 cc to 3 cc) were incorporated in gel. The chemical reaction inside the gel for the growth of said crystals can be expressed as,

$$CdCl_2 + 2NaIO_3 = Cd\ (IO_3)_2 + 2NaCl$$

Grown crystals inside the test tube can be seen in Fig. 1. In the present investigation, the crystal structure of undoped and doped crystals was determined by using Miniflex model, Rigaku, Japan diffractometer with Cukα radiation (λ= 1.5418 A^0). Thermal studies were carried out using Mettler Toledo Star system. Nonlinear optical studies were carried out using Kurtz Powder method.

Fig. 1. Cadmium iodate crystals grown inside the test tube

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Fig. 2. Spherulites of Cadmium iodate

3. Results and discussions

Spherulite shaped crystals of 2 to 6 mm size were obtained. Some of the grown spherulites outside the test tube are as shown in Fig. 2. The optimum growth conditions for various parameters were found and are given in Table 1.

Table 1. Optimum conditions for growth of $Cd(IO_3)_2$ crystals

Parameter	Optimum condition
Density of sodium meta silicate solution	1.04 gm/cm^3
Amount of 2N acetic acid	5 cc
pH of mixture	3.68
Temperature	Room temperature
Concentration of $NaIO_3$ / KIO_3	0.4M
Concentration of $CdCl_2$	0.5M
Gel setting time	15 days
Gel aging time	144 hours
Period of growth	4 weeks
Concentration of impurity solution ($CuCl_2$ / $FeCl_3$)	0.1M
Amount of impurity solution ($CuCl_2$ / $FeCl_3$)	1cc in test tube 2cc in U-tube

Less concentration of reactants does not yield any crystals at all. High concentration yields crystals of smaller size with increased nucleation centres. Reported concentration of reactants when used yields smaller spherule near the gel interface with more number of nuclei. This may be due to high diffusion gradient near the gel interface. As the distance from gel interface increases, number of nuclei reduces and size of spherule increases due to smaller concentration gradient. Slow diffusion should lead to better nuclei, which because of their higher energy content should be less likely to reach their critical size.

Very less amount and low concentration of impurity does not affect the growth and morphology of crystals. Higher concentration of copper impurity, when incorporated in gel reduces the size of

spherules, while iron impurity does not affect the size at all. Cu induces light blue colour, while Fe induces light brown colour in cream shade of undoped crystals.

3.1 X-Ray Diffractometry

Excellent experimental verification for the crystal structures is available through the X-Ray Diffractometry. [10-14].The X-ray diffractograms of gel grown undoped and doped barium iodate crystals were recorded using powder diffraction method. Miniflex model, Rigaku, Japan, X-ray diffractometer, having wavelength (λ) of CuKα radiation = 1.5418 A0

The Figs 3, 4 and 5 show X-ray diffractograms of Cd $(IO_3)_2$, Cu-doped Cd $(IO_3)_2$, and Fe-doped Cd $(IO_3)_2$, respectively. . From diffractograms, it is clear that impurities are induced only in certain planes, since the intensity of radiation is enhanced only in certain planes. Impurities cause a slight change in lattice parameters. The calculated values of lattice parameters, β, and volume of undoped and doped crystals along with the reported values are represented in Table 2. The calculated values are in good agreement with the reported ones [15]. It has been observed that volume of unit cell changes according to the ionic radius of doped impurity.

Volume of unit cell of Cu-doped crystals > Volume of unit cell of Fe-doped crystals > Volume of unit cell of undoped crystals

Ionic radius of Cu^{+2} is 0.73 A0, and that of Fe^{+3} is 0.645 A0. These crystals belong to orthorhombic system with $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^0$.

Table 2. Lattice parameters of cadmium iodate crystals

Lattice parameters	Undoped		Cu-doped (observed)	Fe-doped (observed)
	reported	observed		
a A^0	5.856	5.855 (1)	5.827 (8)	5.859 (6)
b A^0	17.470	17.467 (8)	17.678 (8)	17.421 (3)
c A^0	5.582	5.591 (2)	5.573 (1)	5.592 (6)
β^0	90.00	90.00	90.00	90.00
V $(A^0)3$	-	571.730	574.061	570.766

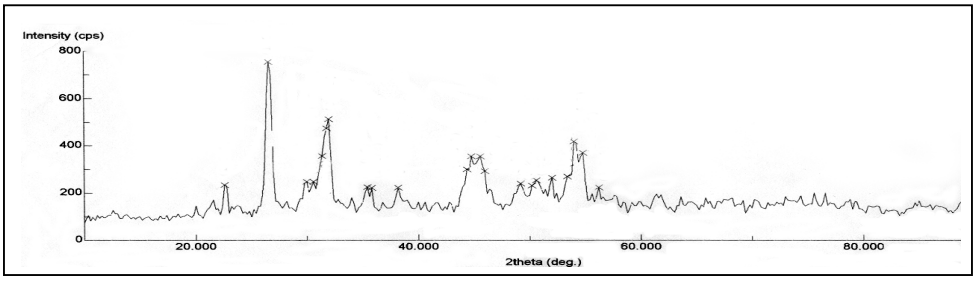

Fig. 3 X-ray diffractogram of undoped cadmium iodate

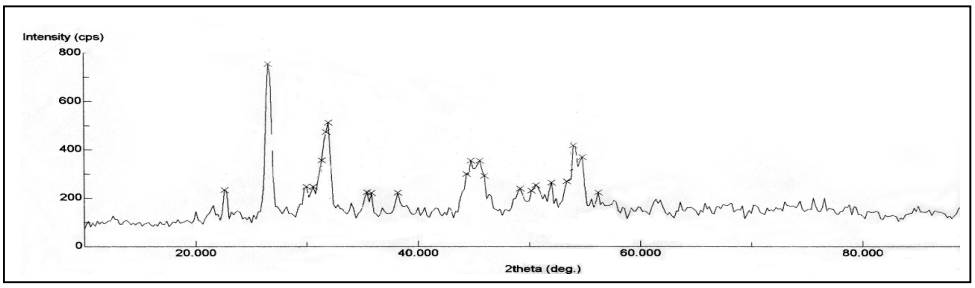

Fig. 4 X-ray diffractogram of Cu-doped cadmium iodate

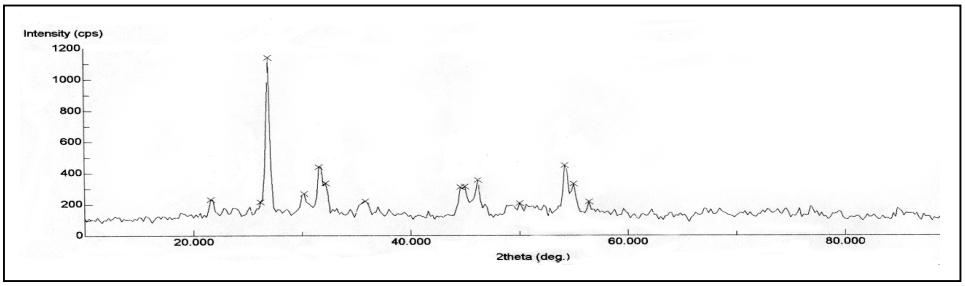

Fig. 5 X-ray diffractogram of Fe-doped cadmium iodate

3.2 Thermal analysis

Thermal analysis, mainly, Thermo Gravimetry (TG), Differential Thermal Analysis (DTA) are widely used in the investigation of both physical and chemical phenomena. Numbers of reviews are available on applications of thermo analytical methods [16-20]. Definite amount of sample was taken and heating was carried out from ambient to 900^0C for TGA and DTA in air medium. Thermal spectra of undoped Cd $(IO_3)_2$, Cu-doped Cd $(IO_3)_2$, and Fe-doped Cd $(IO_3)_2$ are represented in Figs. 6, 8, and 10 respectively. DTA spectra of undoped Cd $(IO_3)_2$, Cu-doped Cd $(IO_3)_2$, and Fe-doped Cd $(IO_3)_2$ are represented in Figs. 7, 9 and 11 respectively.

Table 3 lists TGA data for various ions of Cd $(IO_3)_2$. From the table, these crystals exhibit two steps.

Table 3. Kinetic data from dynamic TGA of undoped, Cu-doped, and Fe-doped cadmium iodate crystals

Compound	**Step**	**Temperature range ^{0}C**	**% Weight loss**	**Probable product formed (solid)**
Undoped cadmium iodate	I	500 – 580	50	$Cd_5(IO_6)_2$
	II	580 – 620	16	$Cd_5(IO_4)_2$
Cu-doped cadmium iodate	I	500 – 570	50	$Cd_5(IO_6)_2$
	II	570 – 600	16	$Cd_5(IO_4)_2$
Fe-doped cadmium iodate	I	500 – 580	48	$Cd(IO_6)_2$
	II	580 – 610	16	$Cd_5(IO_4)_2$

DTA of this compound clearly exhibit the following reactions:

i) A strong endotherm in the temperature range 500 - 580^{0}C, resulting products are Cd5 $(IO_6)_2$, I_2, and O_2. This DTA endotherm splitted in the form of two shoulder peaks may indicate first the formation of solid products and then discharge of oxygen and iodine.

ii) The third sharp short but strong endotherm within the temperature range 580 - 620^{0}C, indicates second decomposition reaction. The products formed are Cd_5 $(IO_4)_2$, and O_2.

For undoped, Cu-doped and Fe-doped cadmium iodate crystals, similar results are obtained. Doping thus has no effect on the structure of crystal.

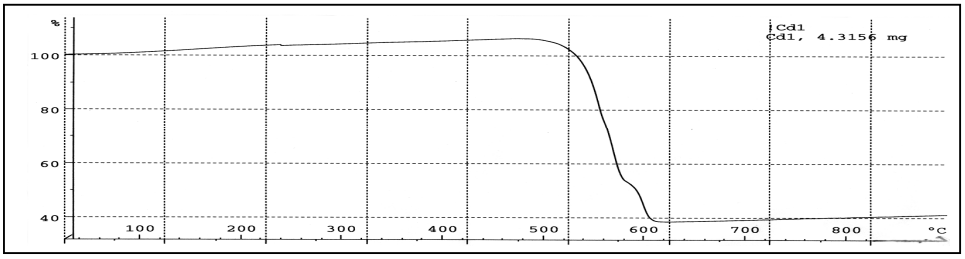

Fig. 6 TGA curve of undoped cadmium iodate

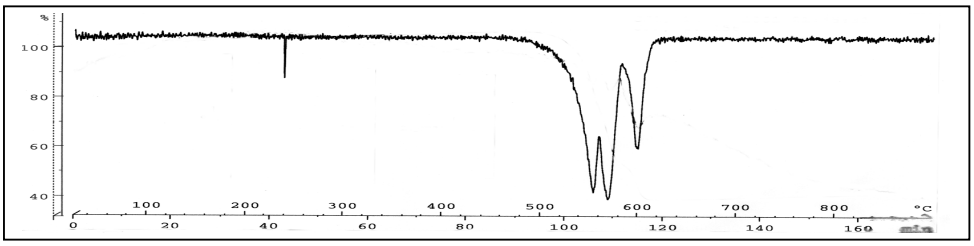

Fig. 7 DTA curve of undoped cadmium iodate

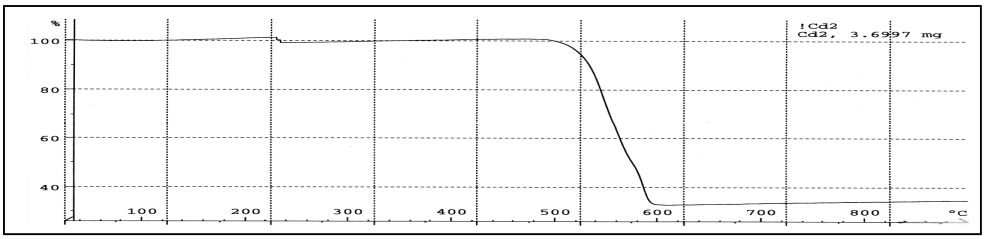

Fig. 8 TGA curve of Cu-doped cadmium iodate

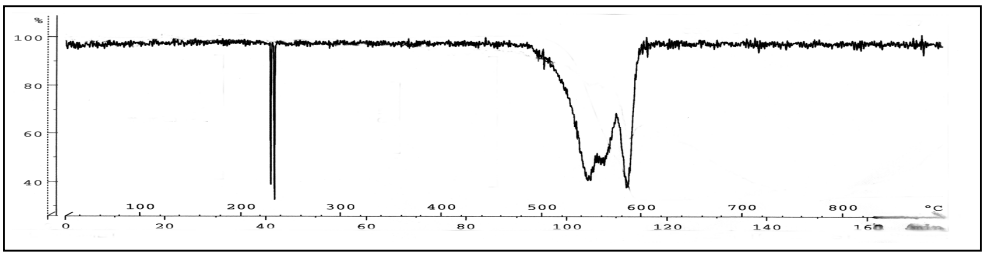

Fig. 9 DTA curve of Cu-doped cadmium iodate

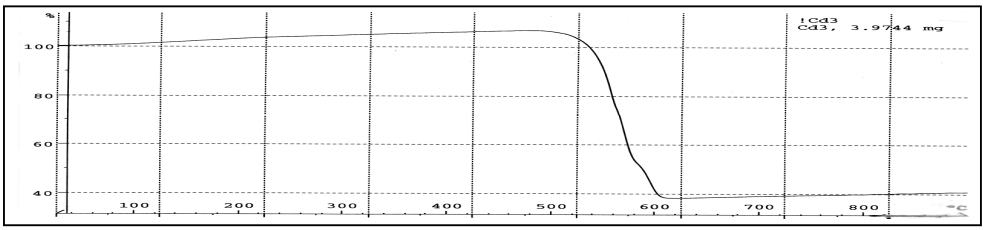

Fig. 10 TGA curve of Fe-doped cadmium iodate

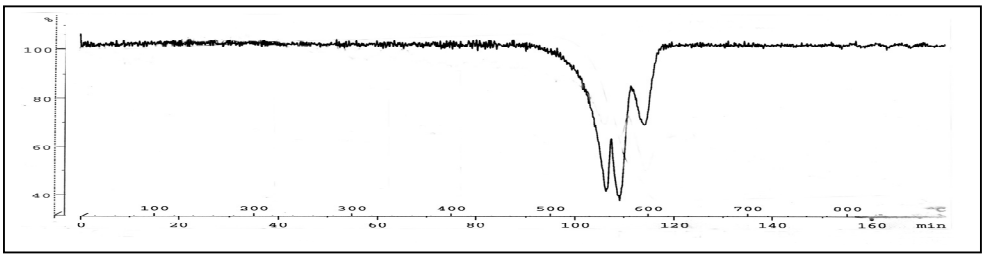

Fig. 11 DTA curve of Fe -doped cadmium iodate

3.3 Powder SHG measurements

The rapid development of optical communications systems has led to a demand for nonlinear optical materials of high performance for use as components in optical devices. The search for new material has identified novel organic and inorganic systems of considerable potential and high performance [21]. Powder SHG technique [22] is a simple and quick experimental technique, which requires the materials in powder form. It is a very simple method with a reasonably high reliability, which enables one to check whether the material is having nonlinear optical property or not. This powder technique enables one to predict the magnitude of the nonlinear coefficients, should provide a substantial increase in the number of new materials for use in nonlinear optic applications. From Table 4, it can be observed that conversion efficiency of KDP is highest among the four substances. Conversion efficiency of undoped cadmium iodate is smaller than that of KDP. For Cu-doping, it is the least and for Fe-doping, it is somewhat more than that for Cu-doping.

Table 4. Nonlinear coefficients

Substance	Nonlinear coefficient (d's) m/v x 10^{-13}
KDP	6.3
Undoped cadmium iodate	4.2098
Fe-doped cadmium iodate	2.2799

4. Conclusions

Following conclusions can be drawn from the above discussion.

Spherulite shaped cadmium iodate crystals can be grown by single diffusion gel technique. Gel density, gel aging, pH, concentration of reactants, and impurities affect the growth in a limited manner. Unit cell parameter values match very well with the reported ones. Small change in unit cell parameter values due to doping is noticed.

Thermal analysis exhibits two steps explicitly on heating the samples. Both steps involve decomposition reactions in the temperature ranges 500 - 580^0C and 580 - 620^0C respectively. Product after reaction is $Cd_5 (IO_4)_2$. Powder second harmonic generation technique has proved the nonlinear nature of the substance. Value of nonlinear coefficient is determined. Doping of Cu^{+2} inhibits nonlinear behaviour of the substance, while Fe^{+3} doping of has less negative effect as compared to Cu^{+2} doping.

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