Synthesis and characterization of calcium iodate, monohydrate crystals grown in silica gel

S. J. Shitole

1Department of Physics, Z. B. Patil College, Dhule, Maharashtra, India

E-mail: sjshitole@hotmail.com

Abstract. Simple gel technique was used to grow single crystals of calcium iodate, monohydrate, by single diffusion method. For the growth of crystals, the optimum conditions were established. Morphologies and habit faces like prismatic, prismatic pyramidal crystals were obtained. Few crystals were opaque, some were translucent and some good quality transparent crystals were obtained. Doping of Cu+2 and Fe+3 was done, to study the effect on structure, thermal and nonlinear optical properties. Cell parameters were obtained from the X-ray diffractograms. Structural analysis was done by using FT-IR spectroscopy. TGA and DTA techniques were used to carry out thermal analysis. Nonlinear optical properties were studied using SHG measurements.

1. Introduction

The study of growth and characterization of single crystals is receiving increasing importance due to their various applications in solid-state technology and laser technology. With the absence of crystals, there would be no electronic industry and fiber optic communication. Growth of crystals by gel method is a promising technique for growing single crystals of substances which are sparingly soluble in water and decompose before their melting point [1]. A variety of crystals of high quality can be grown in a large range of solubility and temperature. In gel growth, crystals are mostly formed at ambient temperature and hence are free from strain often present in crystals prepared from melt or vapour. Method is inexpensive and within the scope of small laboratories. Large scale movements like convection currents are almost completely suppressed, which otherwise could be harmful to the quality of crystal [2-7].

Single crystals of calcium iodate, which is non-centro-symmetric, exhibits prominent nonlinear optical property, and piezoelectric property [8]. In the present investigation, Single crystals of calcium iodate, monohydrate was grown by gel method. Since the compound decomposes before its melting point, conventional high temperature methods for its growth are not suitable. It is sparingly soluble in water; hence, gel method is the only alternative technique for growing the crystals of the size and quality as reported here at ambient temperature.

2. Experimental

To carry single and double diffusion experiments, test tubes and U-tubes were used as crystallizing vessels. Silica gel is used as growth medium. Acetic acid is used to acidify the gel. Proper chemical reaction is selected to get the desired product. The two soluble reactants are diffused into a gel, where they react to form an insoluble product. Dopants are incorporated either in gel or above the gel along with the supernatant. Optimum conditions were obtained by varying parameters such as density of gel, pH of gel, gel aging, concentration of reactants, concentration programming, concentration and
amounts of dopants. Various concentrations of acetic acid and those of sodium metasilicate were used to prepare gel. For this purpose, 5cc, 2N acetic acid was taken in a beaker, to which sodium metasilicate solution having different densities was added drop by drop with constant stirring by using magnetic stirrer. It avoids premature local gelling. To this mixture, 5cc of potassium or sodium iodate solution was added with constant stirring. The pH of the mixture was maintained at 4.2. Experiments were performed to optimize suitable pH value for growth of good quality crystals. This mixture was then transferred to the test tube and it was closed with cotton plug. The gel was allowed to set. It took nearly 12 days for setting. This set gel was aged for 5 days. Aging helps in nucleation control due to reduction in the diameter of the capillaries in gel. Calcium chloride or calcium nitrate was used as supernatant. Supernatants having different molarities were carefully poured over the set gels. Experiments were also performed by interchanging positions the reactants.

The chemical reactions inside the gel can be expressed as,

\[ \text{XCl}_2 + 2\text{YIO}_3 \rightarrow \text{X(IO}_3)_2 + 2\text{YCl}, \]
\[ \text{X(NO}_3)_2 + 2\text{YIO}_3 \rightarrow \text{X(IO}_3)_2 + 2\text{Y(NO}_3)_2, \]

Where X = Ca and Y = K or Na.

### 3. Result and discussion

Parameters such as gel density, gel setting time, gel aging time, concentration of reactants, pH of gel, concentration of impurities have considerable effect on growth of crystals. Crystals having different morphologies were obtained. Prismatic crystals of size 3 x 2 x 2 mm\(^3\) far away from gel interface and prismatic pyramidal crystals of size 5 x 2 x 2 mm\(^3\) away from gel interface were obtained. It was observed that the number of crystals growing diminished with the increase in the distance from gel interface. It may be due to reduced rate of diffusion of supernatant. Second reason may be attributed to the aging of gel, since crystals in this region nucleate in a comparatively older gel. High concentration of reactants results into either needle shaped crystals of size 8 x 2 x 2 mm\(^3\) or hopper crystals of size 10 x 3 x 2 mm\(^3\) near the gel interface. The reason may be high diffusion gradient near the gel interface. Less concentration of reactants leads to the formation of platy crystals due to slow diffusion rate and insufficient supply of reactants. Figure 1 shows few transparent needle shaped crystals, observed away from gel interface, at somewhat more concentration of reactants. Figure 2 shows hopper shaped crystals, grown inside the test tube near gel interface, due to higher concentration of reactants. Figure 3 shows different habits of calcium iodate crystals. Figures 4 and 5 show needle shaped crystal and its schematic. Figures 6 and 7 show prismatic pyramidal crystal and its schematics, resp.
4. Characterization
Calcium iodate crystals were characterized by XRD (X-Ray diffractometry), FTIR (Infrared), and Thermal Analysis [TGA (Thermo Gravimetric Analysis), DTA (Differential Thermal Analysis) to study structure, and SHG Measurements to study NLO property.

4.1. XRD (X-Ray Diffractometry)
X-ray diffraction (XRD) is an excellent analysis technique for identifying unknown solid materials. The XRD pattern can act as a fingerprint to identify unknown materials in crystal and semi crystalline samples. The atoms are arranged in a regular pattern, and there is as smallest volume element, that by repetition in three dimensions describes the crystal. This smallest volume element is called a unit cell. The dimensions of the unit cell are described by three axes: a, b, c and the angles between them alpha, beta and gamma.

X- Ray diffractograms were recorded using powder rotation photograph method. The specifications of diffractometer are, Cukα radiation λ = 1.5418 Å, 20 range = 10° to 90° and scanning speed = 10° / min. Figures
8, 9, and 10 show diffractograms of undoped, Cu-doped and Fe-doped calcium iodate crystals respectively.

From diffractograms, it is clear that impurities are induced only in certain planes, but it does not change the structure of crystal. Impurities only cause a slight change in lattice parameters. Change in volume of unit cell of doped crystals may be attributed to ionic radii of doped impurities (Cu$^{2+}$, Fe$^{3+}$). These crystals belong to monoclinic system with $a \neq b \neq c$ and $\alpha = 90^\circ \neq \beta$. The calculated values of $a$, $b$, $c$, and $\beta$ are in good agreement with the reported ones [13]. The calculated values of lattice parameters, $\beta$, and volume of undoped and doped crystals with respect to reported values are represented in table 1.

**Table 1.** Lattice parameters of calcium iodate, monohydrate
4.2 FT-IR analysis

FTIR is an important technique for identification and characterization of a substance. Infrared Spectroscopy gives information on the vibrational and rotational modes of motion of a molecule.

In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the dipole. A permanent dipole is not necessary, as the rule requires only a change in dipole moment. A molecule can vibrate in many ways, and each way is called a vibration mode. For molecules with N atoms in them, linear molecules have $3N - 5$ degrees of vibrational modes, whereas nonlinear molecules have $3N - 6$ degrees of vibrational modes, also called vibrational degrees of freedom. Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, the band is not observed in the IR spectrum, but only in the Raman spectrum. Asymmetrical diatomic molecules, absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex.

FT-IR spectra of undoped and doped iodate crystals were scanned by using FT-IR spectrophotometer, Spectrum 2000, Perkin Elmer model by placing sample KBr pellet in the sample beam in two ranges, 300 \text{ cm}^{-1} \text{ and } 400 \text{ cm}^{-1}. FT-IR spectra of undoped, Cu-doped, and Fe-doped calcium iodate crystals represented in figures 11, 12 and 13 respectively.

| parameters | Reported | Observed | (Observed) | (Observed) |
|------------|----------|----------|------------|------------|
| $a$ Å      | 8.509    | 8.494 (1)| 8.543 (7)  | 8.554 (4)  |
| $b$ Å      | 10.027   | 10.033 (2)| 10.136 (7)| 10.049 (2) |
| $c$ Å      | 7.512    | 7.512 (2)| 7.549 (6)  | 7.501 (3)  |
| $\beta$    | 95.27    | 95.00    | 94.00      | 95.00      |
| $V$ (Å$^3$)| 638.213  | 637.457  | 651.673    | 642.349    |

Figure 11. FT-IR spectra of undoped calcium iodate in the range 4000-400 cm$^{-1}$ & 710-300 cm$^{-1}$
Fundamental frequencies of the pyramidal iodate ions as have been reported earlier by Nassau et al [14], Dasent and Waddington [15], Balicheva and Petrova [16], Niquist and Kagal [17], Rocchiccioli [18], Dratovsky and Pacesova [19], and Nakamoto [20] are in good agreement with the observed values in the present investigation. Vibrational frequencies of undoped, Cu-doped, and Fe-doped calcium iodate crystals are given in table 2.

**Table 2.** Vibrational frequencies of undoped, Cu-doped, and Fe-doped calcium iodate crystals

| Fundamental Frequencies                      | Calcium iodate |
|----------------------------------------------|----------------|
|                                              | Undoped (cm⁻¹) | Cu-doped (cm⁻¹) | Fe-doped (cm⁻¹) |
| Symmetric stretching frequency, γ₁           | 759.15         | 759.15           | 759.15           |
| Symmetric bending frequency, γ₂               | 396.77         | 396.74           | 396.72           |
| Asymmetric stretching frequency, γ₃           | 818.83         | 815.86           | 818.85           |
| Asymmetric bending frequency, γ₄              | 335.04         | 335.47           | 335.15           |

4.2. Thermal Analysis

The principle of thermogravimetry is based on the simple fact that, the sample is weighed continuously as it is being heated to elevated temperature. In DTA, the study depends on the measurement of difference in heat content of a sample with reference to a standard substance as a function of temperature or time.
Thermal studies were carried doped out using Mettler Toledo Star system. Definite amount of sample was taken and heating was carried out from ambient to 900°C for TGA and DTA at the rate of 5°C/min in an air medium. Figure 14 includes TGA curve [Figure 14 (a)] and DTA curve [Figure 14 (b)] of undoped calcium iodate. Figures 15 includes TGA [Figure 15 (a)] and DTA curve [Figure 15 (b)] of Cu-doped calcium iodate and Figures 16 includes TGA [Figure 16 (a)] and DTA curve [Figure 16 (b)] of Fe-doped calcium iodate crystals, respectively.

Figure 14(a). TGA curve of undoped calcium iodate

Figure 14(b). DTA curve of undoped calcium iodate

Figure 15(a). TGA curve of Cu-doped calcium iodate

Figure 15(b). DTA curve of Cu-doped calcium iodate
These crystals exhibit three steps explicitly. Table 3 shows kinetic data from TGA of these crystals. Results obtained are in good agreement with the reported one [21]. The compound is stable up to 220°C. The weight loss begins at 220°C. There is 3.2% weight loss in the temperature range 220 - 280°C. This is the first step and is suggestive of loss of one water molecule from the crystal. This water loss step is not very sharp but extends over a wide temperature range of about 60°C and indicates that lattice water is strongly hydrogen bonded with iodate group, showing that calcium iodate crystals are monohydrated.

For Cu-doped and Fe-doped calcium iodate crystals, almost similar results are obtained with slight changes in the temperature range of decomposition reactions and values of % weight loss. Thus doping has no effect on the structure of crystal. Kinetic data from dynamic TGA of undoped, Cu-doped, and Fe-doped calcium iodate is shown in table 3.

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

| Compound                     | Step | Temp. Range (°C) | % Weight loss | Probable product formed (solid) |
|------------------------------|------|-----------------|---------------|---------------------------------|
| Undoped calcium iodate, monohydrate | I    | 220 – 280       | 3.2           | Ca(IO₃)₂                         |
|                              | II   | 580 – 640       | 58            | Ca₅(IO₆)₂                       |
|                              | III  | 750 – 800       | 18            | Ca₅(IO₆)₂                       |
| Cu-doped calcium iodate, monohydrate | I    | 240 – 280       | 2             | Ca(IO₃)₂                         |
|                              | II   | 450 – 600       | 60            | Ca₅(IO₆)₂                       |
|                              | III  | 720 – 750       | 18            | Ca₅(IO₆)₂                       |
| Fe-doped calcium iodate, monohydrate | I    | 220 – 270       | 3.2           | Ca(IO₃)₂                         |
|                              | II   | 500 – 620       | 58            | Ca₅(IO₆)₂                       |
|                              | III  | 750 – 780       | 18            | Ca₅(IO₆)₂                       |
4.3. Powder SHG measurements

Powder SHG technique [22, 23] makes it possible to predict the magnitude of the nonlinear coefficients of the powder samples in a very simple manner, should provide a substantial increase in the number of new materials for use in nonlinear optic applications.

In SHG, an optical beam of frequency $2\omega$ can be generated from the interaction of a high power laser beam of frequency $\omega$ with a suitable material either in the form of crystal or powder sample. It cannot occur in isotropic medium or in centrosymmetric crystals. Hence, a noncentrosymmetric crystal is a must to get SHG [24, 25].

For performing experiments, sample plates were prepared from powder samples of KDP, undoped, Cu-doped, and Fe-doped calcium iodate. All the samples were sieved by a 75 $\mu$m sieve, in order to maintain uniform particle size. Each sample plate was placed in front of Nd: YAG laser beam. Before sample plate, beam splitter splitted the input signal into reference signal, collected by photo detector and second signal on sample plate, which in turn generated second harmonic signal. Reference signal and second harmonic signal were both applied to digital storage oscilloscope. V ($\omega$) of reference signal and V ($2\omega$) of SHG signal were recorded as a function of arc lamp voltage. Conversion efficiency was calculated by taking ratio $V(\omega)/V(2\omega)$. Graphs of arc lamp voltage versus conversion efficiency were plotted and $\tan\theta$ has been found. Nonlinear coefficients were calculated by using the relation,

$$d^2_{known}/d^2_{unknown} = \tan \theta_{known}/\tan \theta_{unknown}$$

Where, $d_{known}$ = nonlinear coefficient of KDP
$d_{unknown}$ = nonlinear coefficient of the sample under test, to be found out
$\tan \theta_{known}$ = slope of graph of arc lamp voltage versus conversion efficiency of reference sample (KDP)
$\tan \theta_{unknown}$ = slope of graph of arc lamp voltage versus conversion efficiency of sample under test

Table 4 gives the results of calculations of nonlinear coefficients ($d_s$). Cu and Fe doped samples of calcium iodate do not show any nonlinear property. Output from these sample plates was completely stopped.

Table 4. Nonlinear coefficients of KDP and undoped calcium iodate crystals

| Substance              | Nonlinear coefficient ($d_s$) m/v |
|------------------------|-----------------------------------|
| KDP                    | $6.3 \times 10^{-13}$             |
| Undoped calcium iodate | $1.2535 \times 10^{-13}$          |

5. Conclusions

Gel technique can be successfully employed for the growth of calcium iodate crystals. In case of gel method, various habits can be obtained by changing various parameters. Well known Liesegang phenomenon has been observed in case of calcium iodate crystals. Calcium iodate crystals exhibit the phenomenon of efflorescence. Suitable value of pH for calcium iodate crystals is 4.2. Doping of impurities has no significant effect on the morphology of crystals. XRD results match very well with the standard JCPDS data. Dopants have been incorporated only in certain planes. No major changes in structure have been observed. IR analysis confirms the presence of fundamental IR frequencies observed in all iodate compounds. Thermal analysis exhibits three steps explicitly on heating the samples. The first step involves dehydration at 250°C, second step shows decomposition at 580°C, and the third step involves again decomposition at 640°C. Powder second harmonic generation experiments exhibit the nonlinear nature of the substance. But the
intensity of SHG is very small. Cu$^{2+}$ and Fe$^{3+}$ doped samples have negative effect on SHG property. These samples do not show nonlinear effect.

References

[1] Armington AF and O Connor JJ 1968 Gel growth of cuprous halide crystals J. Cryst. Growth 3-4 367-71
[2] Shitole SJ and Saraf KB 2001 Growth and study of some gel grown group II single crystals of iodate Bull. Mater. Sci. 24(5) 461-68
[3] Shitole SJ and Saraf KB 2002 Growth, Structural and microtopographical studies of calcium iodate, monohydrate crystals grown by silica gel. Cryst. Res. Technol. 37(5) 440-45
[4] Shitole SJ and Saraf KB 2007 Spherulitic growth of cadmium iodate in silica gel and its XRD and FTIR analysis. J. Adv. Sci. And Tech. 10(I & II) 42-55
[5] Joshi MS and Trivedi SG 1981 Growth of single crystals of barium iodate and strontium iodate in silica gels. Cryst. Res. Technol. 16(1) 19-26
[6] Garud SL, Mahajan NK and Saraf KB 2009 Study of gel grown mixed crystals of BaxCa (1-x)(IO3)4. Bull. Mater. Sci. 32(2) 187-92
[7] Garud SL and Saraf KB 2008 Growth and study of mixed crystals of Ca Cd iodate. Bull. Mater. Sci. 31(4) 639-43
[8] Morosin B, Bergman JG and Crane GR 1973 Crystal structure, linear and nonlinear optical properties of Ca (IO3)2.6H2O. Acta. Crysta. B29 1067-72
[9] De Kock and AJR 1980 Handbook on Semiconductors vol3, ed Kellar SP and Moss TS (Amsterdam: North Holland) p 247
[10] Nyrit J 1982 Industrial Crystallization (Amsterdam: Elsevier) p 203
[11] Dennis J and Henisch HK 1967 J. Electrochem. Soc. 114-263
[12] Dake HC 1938 Quartz family minerals: a handbook for the mineral collector (New York: Whittlesey House)
[13] JCPDS Card for X-ray Diffraction Data No. 26 p 1405
[14] Nassau K, Shiever JW and Prescott BE 1973 Transition metal iodates. I. Preparation and characterization of the 3d iodates. J. Solid State Chem. 7 186-204
[15] Dasent WE and Waddington TC 1960 Iodine Oxygen Compounds. Part I. Infrared Spectra and Structure of Iodates J. Chem. Soc. 2429-32
[16] Balicheva TG and Petrova VA 1973 Vibrational spectra of the IO3-ion in alkali iodates. J. Structural Chem. 14(3) 424-30
[17] Nyquist RA and Kagal RD 1971 Infrared Spectra of Inorganic Compounds (New York: Academic Press)
[18] Rocchiccioli, C. Compt. Rend. 250 (1960) 1232.
[19] Dratovsky, M. and Pacesova, L. Russian Chemical Reviews, Ed. Uspekhi Khimji (1968).
[20] Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds, 2nd Ed., Wiley Interscience (1970).
[21] Sanyal GS and Nag K 1977 Thermal studies on the dimesoperiodates and iodates of Ca (II), Sr (II) and Ba (II) preparation and characterization of hexavalent iodates. J. Inorg. Chem. 39 1127-30
[22] Chemla DS and Zyss J 1987 Nonlinear Optical Properties of Organic Molecules and Crystals (New York: AcademicPress)
[23] Kurtz SK and Perry TT 1968A powder technique for the evaluation of nonlinear optical materials. J. Appl. Phys. 39(8) 3798-813
[24] Bloembergen N, Armstrong JA, Ducuing J and Pershan PS 1962 Interactions between light waves in a nonlinear dielectric. Phys. Rev. Lett. 127 1918-39
[25] Franken PA, Hill AE, Peters CW and Wernreich G 1961 Generation of Optical Harmonics Phys. Rev. Lett. 7 118-9