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Growth and study of mixed crystals of Ca–Cd iodate

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Abstract. **Mixed crystals of calcium–cadmium iodate were grown by a simple gel technique using diffusion method. The optimum conditions were established by varying various parameters such as pH of gel solution, gel concentration, gel setting time, concentration of reactants etc. Crystals having different morphologies and habits were obtained. Prismatic, dendritic crystals of calcium–cadmium iodate and prismatic needle shaped, hopper crystals of mixed iodate were obtained. Some of them were transparent, some transluscent and a few others were opaque. The crystals were characterized using FT–IR, EDAX, XRD, TGA and DTA.**

Keywords. **Gel technique; mixed iodate crystals; FT–IR; EDAX; XRD; TGA; DTA.**

1. Introduction

A variety of crystals required for the purpose of research and application can be grown in silica gels. The gel medium prevents turbulence and being chemically inert, it provides a three-dimensional crucible which permits the reagents to diffuse at a desirable controlled rate. Its softness and uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth (Patel and Venkateswara Rao 1978; Shitole and Saraf 2001).

The growth of single crystals in gel at ambient temperature, which are sparingly soluble in water, is a fascinating alternative to the techniques involving high temperature and expensive equipments (Sangwal and Patel 1974). During the last few years, successful application of gel growth technique has been demonstrated by the preparation of single crystals of alkaline earth metal iodate (Joshi and Trivedi 1983). The gel growth technique appeared quite attractive for growing crystals of such compounds on account of its unique advantages in terms of crystals produced and the simplicity of the process (Armington and O'Connar 1968; Blank and Brenner 1969; Blank *et al* 1969; Ranadive *et al* 1969; Blank 1973). Crystals of iodate exhibit nonlinear optical properties (Kurtz and Perry 1968; Morosin *et al* 1973) and piezoelectric properties (Bach and Kuppers 1978). Nonlinear optical phenomena have found a wide variety of applications in many areas of modern science, technology and engineering. The nonlinear devices find large applications in optical communication, image processing and wave-guide coupling. Mixed iodate crystals of calcium cadmium iodate are used in medicine and deodorant.

In the present work, mixed iodate crystals of calcium cadmium iodate were grown by gel technique using diffusion method. Optimum growth conditions for crystals were determined. Optimum conditions were established by varying various parameters such as pH of gel, gel reactants, concentration programming, effect of neutral gel etc.

2. Experimental

Test tubes were used as crystallizing vessels. The silica gel was used as a growth media. Gel was prepared by using glacial acetic acid and sodium meta silicate having different pH values. The chemicals used for growth of mixed iodate crystals were CH_3COOH, $Na_2SiO_3{\cdot}9H_2O$, KIO_3, $NaIO_3$. All chemicals were of AR grade.

Different molar masses were tried to determine the optimum growth conditions. One of the reactants having different concentrations was incorporated into the gel. This solution was then transferred to borosil glass tube of diameter, 2·5 cm and 25 cm in height. The mouth of the tube was covered by cotton plug. After setting of the gel, it was left for aging for different periods of time. Another reactant having different concentrations was then added as supernatant over the set gel. Experiments were carried out by changing different concentrations of the reactants.

The chemical reaction inside the gel can be expressed as

$$x\mathrm{CdCl_2} + (1-x)\mathrm{CaCl_2} + 4\mathrm{YIO_3} = \mathrm{Cd}_x\mathrm{Ca}_{(1-x)}(\mathrm{IO_3})_4 + 4\mathrm{YCl},$$

where Y = K or Na.

3. Results and discussion

The various optimum conditions for growing crystals were found and are given in table 1.

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Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel aging time, etc have considerable effect on growth rate. In the steady state of concentration gradient, growth rate also becomes steady which favours growth of well-developed crystals. However, very slow rate of growth along one direction results in the platy crystals. Fast growth rate in one particular direction leads to the formation of elongated crystals like dendrites or hopper crystals.

4. Observations

Various concentrations of reactants have various effects on the quality of crystals. Table 2 summarizes the effects on the habits of single crystals.

Figure 1 shows dendritic growth of calcium cadmium iodate crystals inside the test tube for high concentration of reactants. Figure 2(a) shows prismatic transparent crystals of calcium cadmium iodate inside the test tube. Figure 2(b) shows a few prismatic transparent crystals of calcium cadmium iodate. At one end, crystals are translucent which is due to the inclusion of silica gel.

5. Characterization

Mixed iodate crystals grown were characterized by FT–IR, EDAX, XRD, TGA and DTA.

5.1 *Fourier transform infrared (FT–IR) spectral analysis*

FT–IR is used for structural analysis. In the present study, IR spectrum of calcium cadmium iodate sample was recorded using SHIMADZU spectrophotometer at the Department of Chemistry, University of Pune. Figure 3 shows FT–IR spectrum of calcium cadmium iodate. The IR spectrum was recorded in the wave number range 400–4000 cm^{-1} for KBr line.

The bands at 3437 cm^{-1} are due to O–H stretching and at 1678 cm^{-1} are due to H–O–H bending. Bands due to vibration involving metal, iodine and oxygen atoms are found predominantly near 748–815 cm^{-1}. Fundamental infrared frequencies, observed in all iodate compounds in general, are also found in the present FT–IR analysis, which confirm the iodate group of grown crystals. The bands at 370 cm^{-1} are due to the iodate group. Fundamental frequencies that have been observed are ν_1 (symmetric stretching) at 748·5 cm^{-1} and ν_3 (asymmetric stretching) at 815 cm^{-1}. The dominant absorption bands are found at 700–815 cm^{-1} in all iodate compounds (Nakamoto 1970) and can be expected to contain ν_1, ν_3 as well as possible splitting of ν_3. From the spectral analysis, it is clear that in case of calcium cadmium iodate crystals the O–H stretch bands in the region 2300–3700 cm^{-1} are much widened. It is due to inclusion of water molecules.

Table 1. Optimum conditions for growth of calcium cadmium iodate crystals.

Conditions	Calcium cadmium iodate
Density of sodium meta silicate solution	1·04 g/cm^3
Amount of 2N acetic acid	5 ml
pH of mixer	4·2
Temperature	Room temperature
Concentration of $NaIO_3$ or KIO_3	0·5 M
Concentration of $CaCl_2$ or $Ca(NO_3)_2$	0·5 M
Concentration of $CdCl_2$ or $Cd(NO_3)_2$	0·5 M
Gel setting time	12 days
Gel aging time	120 h
Period of growth	4 weeks

5.2 *EDAX*

Elemental analysis was carried out at NCL, Pune. Table 3 shows values of elemental content of the crystal by EDAX and theoretical calculation from molecular formula. From the table it is clear that the values (wt % and at %) of O, Ca, Cd and I in the grown crystal measured by EDAX are

Figure 1. Dendritic growth of calcium cadmium iodate crystals.

Table 2. Effect of concentration of reactants of habit, quality and size of $Ca_{1-x}Cd_x(IO_3)_4$.

Conc. of reactant in gel	Conc. of reactant above gel	Habit	Quality	Size (mm)
$NaIO_3$ or KIO_3 0·4 M 3 to 5 ml	$CaCl_2$, $CdCl_2$ 0·5 M 10 ml	Dendritic	Opaque, brittle	10 × 20 × 1
KIO_3 0·4 M 8 ml	$CaCl_2$, $CdCl_2$ 0·4 M 6 ml	Prismatic	Good	8 × 2 × 2

Table 3. Values of elemental content of the crystal.

	Content as measured by EDAX		Content as calculated from molecular formula $Ca_{0·6}Cd_{0·4}(IO_3)_4·12H_2O$	
Element	wt %	at %	wt %	at %
O	41·63	81·77	39·95	82·75
Ca	2·12	5·42	2·49	2·06
Cd	6·91	0·59	4·67	1·37
I	49·34	12·22	52·86	13·79

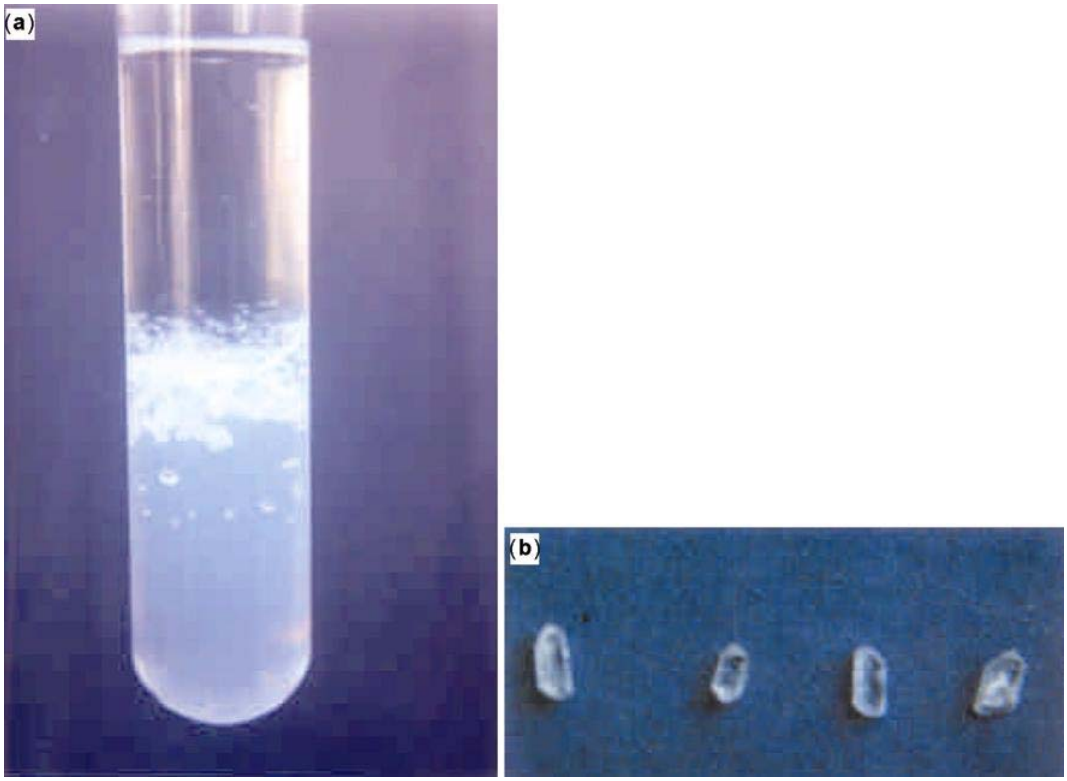

Figure 2. (**a**) Prismatic transparent crystals of calcium cadmium iodate inside the test tube and (**b**) few prismatic transparent crystals of calcium cadmium iodate.

very close with the values calculated from the molecular formula.

5.3 *X-ray diffraction*

X-ray diffractogram was recorded using Rigaku, Miniflex, Japan with CuKα radiation (1·5418 Å) as shown in figure 4. The observed d values and hkl were computed. The computer program, POWD (an interactive Powder Diffraction Data interpretation and Indexing Program version 2.2) was used to calculate d values. The observed peaks in diffractogram shows that the mixed iodate crystals possess monoclinic structure. Calculated unit cell parameters are given in table 4. The atomic fraction, x, of Cd replacing Ca atoms is 0·4, as calculated from the lattice parameters

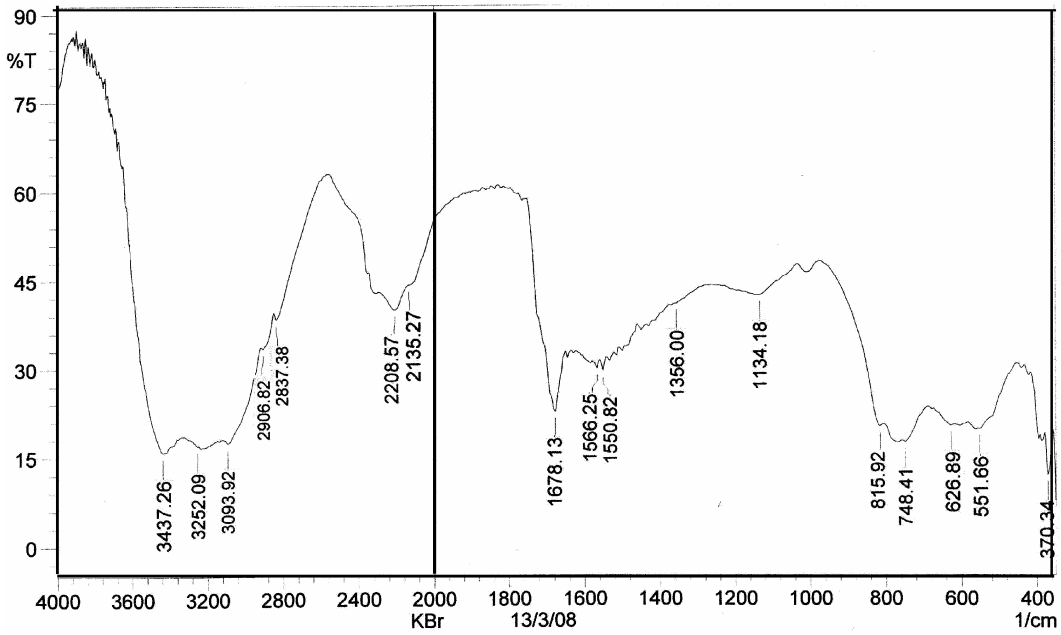

Figure 3. FT–IR spectrum of calcium cadmium iodate.

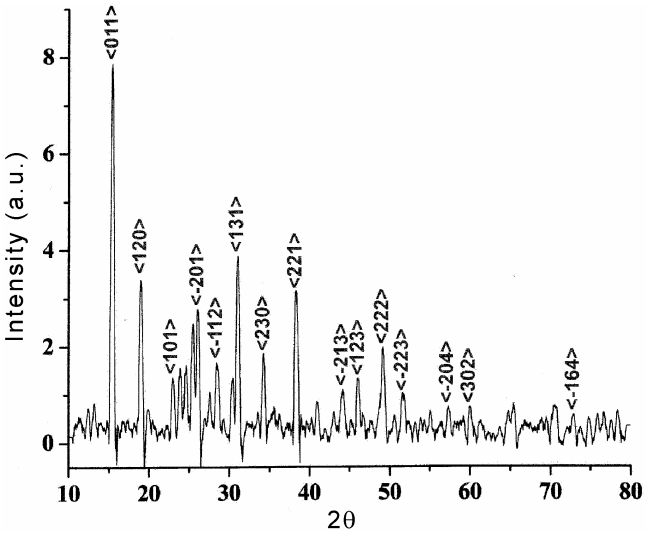

Figure 4. X-ray diffractogram of calcium cadmium iodate.

Table 4. Calculated unit cell parameters.

Parameter	$Ca(IO_3)_2$	$Cd(IO_3)_2$	$Ca_{1-x}Cd_x(IO_3)_4$
System	Monoclinic	Monoclinic	Monoclinic
a	8·509 Å	5·8561 Å	6·931 Å
b	10·027 Å	17·470 Å	12·8759 Å
c	7·512 Å	5·582 Å	6·4784 Å
V	638·213 $(Å)^3$	571·063 $(Å)^3$	578·150 $(Å)^3$

given in table 4 and employing the Vegard's law. The molecular formula of the crystals grown can, therefore, be written as $Ca_{0·6}Cd_{0·4}(IO_3)_4·nH_2O$ on the basis of XRD and FTIR. Here n is the number of water molecules.

5.4 *Thermal analysis*

TGA and DTA studies of mixed iodate crystals were carried out at NCL, Pune. Figures 5(a) and (b) represent the TGA and DTA curves, respectively. It shows that the compound is stable up to 110°C. The initial 18·4% weight loss occurs due to loss of 10 water molecules in the temperature range 110–140°C and a further 3·2% weight loss in the temperature range 220–260°C. This loss of weight is due to loss of coordinated 2 water molecules. There is no further weight loss up to 580°C. Further 65% weight loss in the temperature range 580–670°C is due to decomposition of crystals and may be loss of iodine and some oxygen from the anhydrous mixed iodate crystals. Again in the temperature range 700–760°C, there is 10·19% weight loss indicating decomposition of reaction producing mixture of CaO and CdO.

Molecular weight of the crystal, $Ca_{0·6}Cd_{0·4}(IO_3)_4·12H_2O$	:	985
Molecular weight of $Ca_{0·6}Cd_{0·4}(IO_3)_4$	:	769
Weight of 12 moles of H_2O	:	216
Amount of $Ca_{0·6}Cd_{0·4}(IO_3)_4$ in the crystal	:	78·1 wt%
Water of crystallization	:	21·9 wt%
Wt. loss observed in the first two temperature regimes	:	18·47 + 3·21 = 21·68%

The calculation shows that the molecular formula of the grown $Ca_{0·6}Cd_{0·4}(IO_3)_4·nH_2O$ crystal as determined from XRD and FTIR can be written as $Ca_{0·6}Cd_{0·4}(IO_3)_4·12H_2O$.

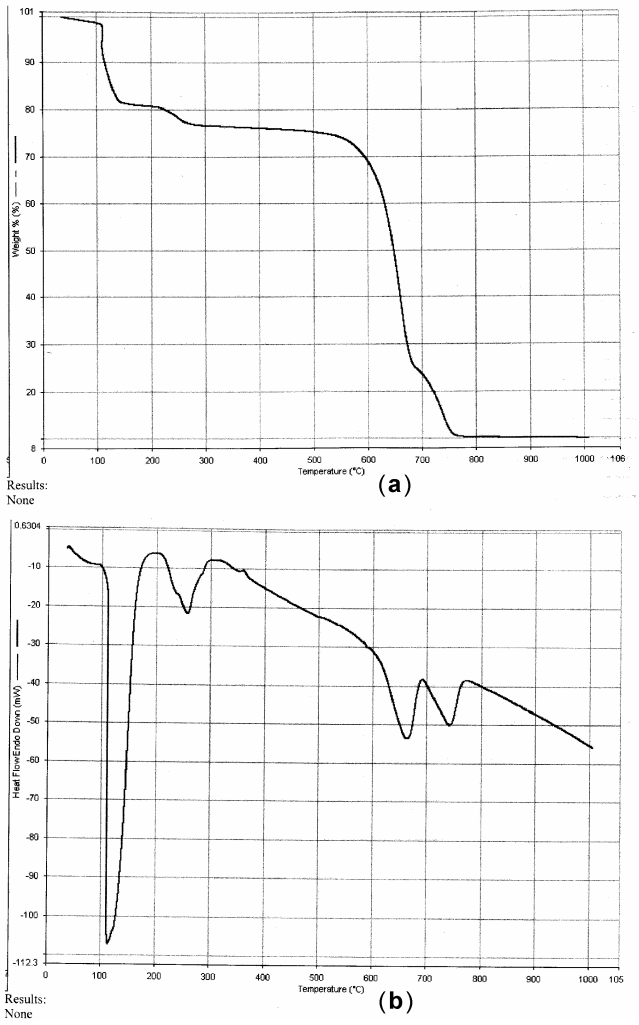

Figure 5. (**a**) TGA curve of calcium cadmium iodate crystal and (**b**) DTA curve of calcium cadmium iodate crystal.

DTA curve of the same compound shows its peaks at 110–140°C, 220–260°C, 580–670°C and 700–760°C.

6. Conclusions

From the above studies we observe that
(I) Gel growth technique is suitable for growing crystals of calcium cadmium iodate.
(II) Different habits of calcium cadmium iodate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, concentration of reactants, concentration of impurities etc.
(III) Well known Liesegang phenomenon is observed in the growth of calcium cadmium iodate crystals.
(IV) Chemical compositions of the grown crystal by EDAX match well with the theoretical calculation from molecular formula.

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