Bull. Mater. Sci., Vol. 32, No. 2, April 2009, pp. 187–192. © Indian Academy of Sciences.

Study of gel grown mixed crystals of $Ba_xCa_{(1-x)}(IO_3)_4$

S L GARUD*, N K MAHAJAN† and K B SARAF
P.G. Department of Physics, Pratap College, Amalner 425 401, India
†Mahajan School of Sciences, Dhule 424 002, India

MS received 18 August 2008; revised 9 April 2009

Abstract. **The growth of mixed crystals of $Ba_xCa_{1-x}(IO_3)_4$ were carried out with simple gel method. The effect of various parameters such as pH of gel solution, gel concentration, gel setting time, concentration of reactants on the growth was studied. Crystals having different morphologies and habits were obtained. The grown crystals were characterized by XRD, FT–IR, EDAX, TGA, DTA and DSC.**

Keywords. **Gel method; $Ba_xCa_{1-x}(IO_3)_4$; mixed crystals; XRD; FT–IR; EDAX.**

1. Introduction

In the field of crystal growth, gel technique has become more popular and has been used more (Joshi and Trivedi 1970; Ittyachen and Kurien 1979; Joshi *et al* 1981). A variety of crystals required for the purpose of research and application can be grown in silica gels. Gel growth technique has been used for the preparation of single crystals of alkaline earth metal iodate crystals (Joshi and Trivedi 1983). Also 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). Gel growth technique has been used for the preparation of single crystals of barium iodate and calcium iodate (Shitole and Saraf 2001). 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 barium calcium iodate are used in medicine and production of other iodates.

The purpose of the present paper is to report the growth and influence of various parameters such as pH of gel, gel reactants, gel concentrations, effect of neutral gel etc on the growth mechanism of mixed iodate crystals of barium calcium iodate in gel.

*Author for correspondence (sl.garud@rediffmail.com)

2. Experimental

The growth of mixed crystals of $Ba_xCa_{1-x}(IO_3)_4$ were carried out in silica gel. Various concentrations of acetic acid and those of sodium metasilicate were used to prepare the gel. For this purpose, 5 cc, 2 N 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, 5 cc solution of barium chloride and calcium chloride 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. Potassium or sodium iodate was used as supernatant. Supernatants having different molarities were carefully poured over the set gels. Experiments having different molarities were carefully poured over the set gels. The chemical reaction inside the gel can be expressed as

$$x\mathrm{BaCl_2} + (1-x)\mathrm{CaCl_2} + 4\mathrm{YIO_3} = \mathrm{Ba}_x\mathrm{Ca}_{(1-x)}(\mathrm{IO_3})_4 + 4\mathrm{YCl},$$

where Y = K or Na.

3. Results and discussion

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

The 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. Fast growth rate in one particular direction leads to the formation of elongated crystals like dendrites.

4. Observations

It was found that the quality of crystals depend upon the different concentrations of reactants. Table 2 summarizes the effects on the habits of single crystals.

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

5. Characterization

Mixed crystals of $Ba_xCa_{1-x}(IO_3)_4$ grown were characterized by XRD, FT–IR, EDAX, TGA, DTA and DSC.

5.1 *X-ray diffraction*

X-ray diffractogram was recorded using Rigaku, Miniflex, Japan with CuKα radiation (1·5418 Å) shown in figure 3. 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 show that the mixed iodate crystals possess monoclinic structure. The ASTM data of $Ba(IO_3)_2$, $Ca(IO_3)_2$ and calculated unit cell parameters of $Ba_{1-x}Ca_x(IO_3)_4$ are given in table 3. The atomic fraction, *x*, of Ba replacing Ca atoms is 0·27, as calculated from the lattice parameters given in table 3 and employing the Vegard's law. The molecular formula of the crystals grown can, therefore, be written as $Ba_{0·27}Ca_{0·73}(IO_3)_4 \cdot nH_2O$ on the basis of XRD and FTIR. Here '*n*' is the number of water molecules.

Table 1. Optimum conditions for growth of barium–calcium iodate crystals.

Parameters	Optimum conditions
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 temp.
Concentration of $NaIO_3$ or KIO_3	0·5 M
Concentration of $BaCl_2$ or $Ba(NO_3)_2$	0·05 M
Concentration of $CaCl_2$ or $Ca(NO_3)_2$	0·5 M
Gel setting time	12 days
Gel aging time	120 h
Period of growth	4 weeks

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

FT–IR is used for structural analysis. In the present study, IR spectrum of barium calcium iodate sample was recorded

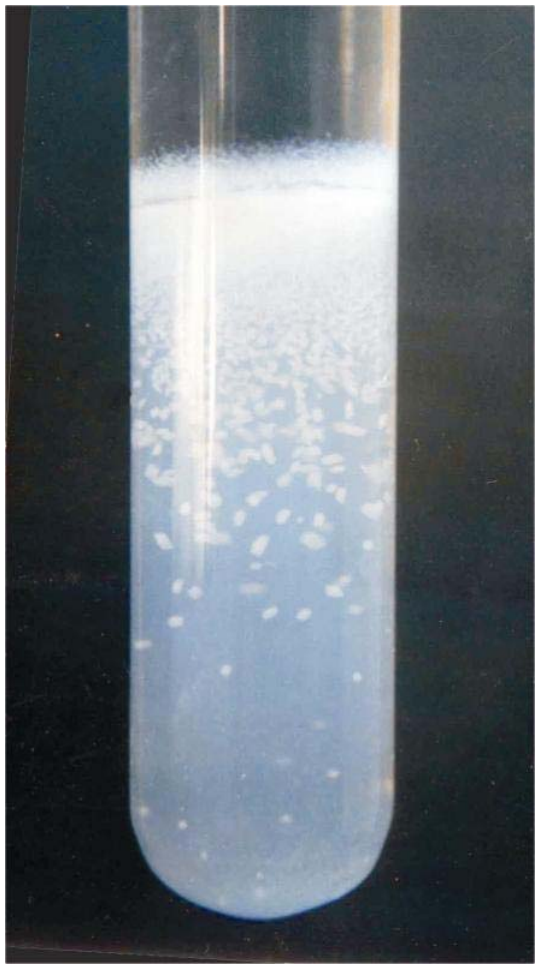

Figure 1. Dendritic growth of barium–calcium iodate crystals.

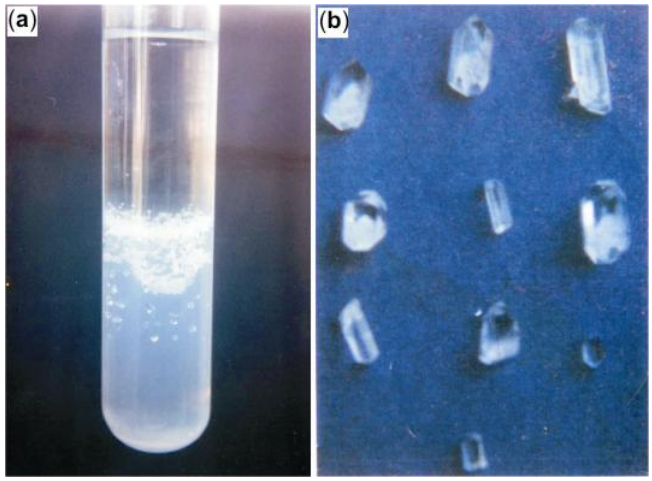

Figure 2. (**a**) Prismatic transparent crystals of barium calcium iodate inside the test tube and (**b**) few prismatic transparent crystals of barium calcium iodate.

Table 2. Effect of concentrations of reactants on habit, quality and size of $Ba_xCa_{1-x}(IO_3)_4$.

Conc. of reactant in gel	Conc. of reactant above gel	Habit	Quality	Size (mm)
$NaIO_3$ or KIO_3, 0·5 M, 3–5 ml	$BaCl_2$ (0·05 M), $CaCl_2$ (0·5 M), 10 ml	Dendritic	Opaque, brittle	10 × 20 × 1
KIO_3, 0·5 M, 8 ml	$BaCl_2$ (0·05 M), $CaCl_2$ (0·5 M), 6 ml	Prismatic	Good	8 × 2 × 2

Table 3. Unit cell parameters.

Parameter	$Ba(IO_3)_2$	$Ca(IO_3)_2$	$Ba_{1-x}Ca_x(IO_3)_4$
System	Monoclinic	Monoclinic	Monoclinic
a	13·63 Å	7·143 Å	12·22 Å
b	7·979 Å	11·29 Å	9·6478 Å
c	9·036 Å	7·280 Å	7·761 Å
β	133·62	106·35	121·10

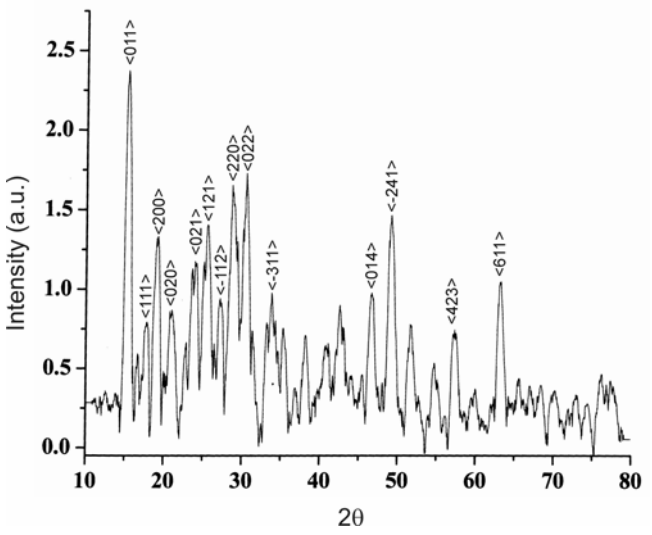

Figure 3. X-ray diffractogram of barium calcium iodate.

using SHIMADZU spectrophotometer at the Department of Chemistry, University of Pune. Figure 4 shows FT–IR spectrum of barium calcium iodate. The IR spectrum was recorded in the wave number range 400–4000 cm^{-1} for KBr line.

The bands at 3435·34 cm^{-1} are due to O–H stretching and at 1678·13 cm^{-1} are due to H–O–H bending. Bands due to vibration involving metal, iodine and oxygen atoms are found predominantly near 750–815 cm^{-1}. Fundamental infrared frequencies, observed in all iodate compounds in general, are also found in present FT–IR analysis, which confirm the iodate group of grown crystals. The bands at 392 cm^{-1} are due to iodate group. Fundamental frequencies that have been observed are ν_1 (symmetric stretching) at 750·30 cm^{-1} and ν_3 (asymmetric stretching) at 815·92 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 barium calcium 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.

5.3 *Energy dispersive analysis (EDAX)*

Elemental analysis was carried out at NCL, Pune. Table 4 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, Ba, Ca and I in the grown crystal measured by EDAX are very close with the values calculated from molecular formula.

5.4 *Thermal analysis ($Ba_{0·27}Ca_{0·73}(IO_3)_4·nH_2O$)*

TGA, DTA and DSC studies of mixed iodate crystals were carried out at NCL, Pune. Figures 5(a), (b) and (c) represent the TGA, DTA and DSC curves, respectively. It shows that compound is stable up to 100°C. The initial 17·664% weight loss occurs due to loss of 9 water molecules in temperature range 100–120°C. Further 5·260% weight loss occurs in the temperature range 220–280°C. This loss of weight is due to loss of coordinated 3 water molecules. There is no further weight loss up to 530°C. Further 68% weight loss in the temperature range 530–650°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 11% weight loss indicating decomposition of reaction producing mixture of BaO and CaO.

Molecular weight of the crystal, $Ba_{0·27}Ca_{0·73}(IO_3)_4·12H_2O$: 982·19
Molecular weight of $Ba_{0·27}Ca_{0·73}(IO_3)_4$: 766·19
Weight of 12 moles of H_2O : 216
Amount of $Ba_{0·27}Ca_{0·73}(IO_3)_4$ in the crystal : 78·0 wt%
Water of crystallization : 22·0 wt%
Wt. loss observed in the first two temperature regime : 16·493 + 5·497 = 21·99%

The calculation shows that the molecular formula of the grown $Ba_{0·27}Ca_{0·73}(IO_3)_4·nH_2O$ crystal as determined from XRD and FTIR can be written as $Ba_{0·27}Ca_{0·73}(IO_3)_4·12H_2O$.

DTA curve of the same compound shows its peaks at 100–120°C, 220–280°C, 530–650°C and 700–760°C.

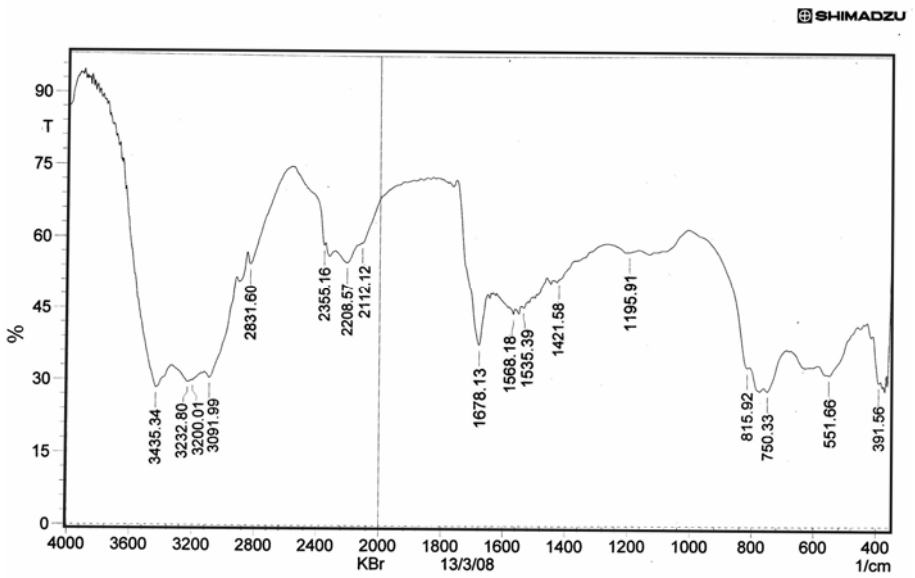

Figure 4. FT–IR spectrum of barium calcium iodate.

Table 4. Values of elemental content of the crystal.

	Content as measured by EDAX		Content as calculated from molecular formula $Ba_{0.27}Ca_{0.73}(IO_3)_4 \cdot 12H_2O$	
Element	wt%	at%	wt%	at%
O	40·32	84·29	40·07	82·75
Ba	3·61	0·53	3·86	0·93
Ca	3·06	2·15	3·04	2·51
I	53·01	13·03	53·00	13·79

Table 5. Values of ΔH and transition temperature, T_r, from DSC of the crystal.

Sample	Wt of the sample	Change in enthalpy, ΔH	Transition temperature, T_r
Barium calcium iodate	0·0154 g	0·4886 kJ/mole	101·52°C
		0·1169 kJ/mole	226·83°C
		–0·03154 kJ/mole	313·46°C

In the DSC study the two endothermic stages are obtained. But at 295°C an exothermic phase transition process was noticed. The thermal effect is –0·0315 kJ/mol. The results of DSC measurements are presented in table 5.

In DSC curve, Step I: The initiation temperature is 96°C and equilibrium temperature is 115°C. At 96°C (initiation temperature), initiation of phase change starts and is completed at peak endo-down temperature of 101·52°C (transition temperature). The temperature at which the sample and reference come to the thermal equilibrium by thermal diffusion appears to be at 115°C: (i) Area under the curve is 7524·214 mJ and (ii) heat of transition, ΔH i.e. enthalpy change of transition is 488·5853 J/g which is 0·4886 kJ/mole. Since molecular weight is 1 g/mole. Therefore, $\Delta H_{tr} = \Delta H_f$ i.e. heat of phase formation is also 0·4886 kJ/mole where ΔH_f is enthalpy change of new phase formation or it is called heat of phase formation.

Step II: At 211·57°C (initiation temperature), initiation of phase change starts and the phase change (i.e. transition) ends at peak endo-down temperature of 226·83°C (transition temperature). The temperature at which the sample and reference come to the thermal equilibrium by thermal diffusion appears to be at 265°C: (i) Area under the curve is 1800·474 mJ and (ii) heat of transition, ΔH_{tr} i.e. enthalpy change of transition is 116·91 J/g which is 0·1169 kJ/mole. Since molecular weight is 1 g/mole. Therefore, $\Delta H_{tr} = \Delta H_f$ i.e. heat of phase formation is also 0·1169 kJ/mole where ΔH_f is enthalpy change of new phase formation or it is called heat of phase formation.

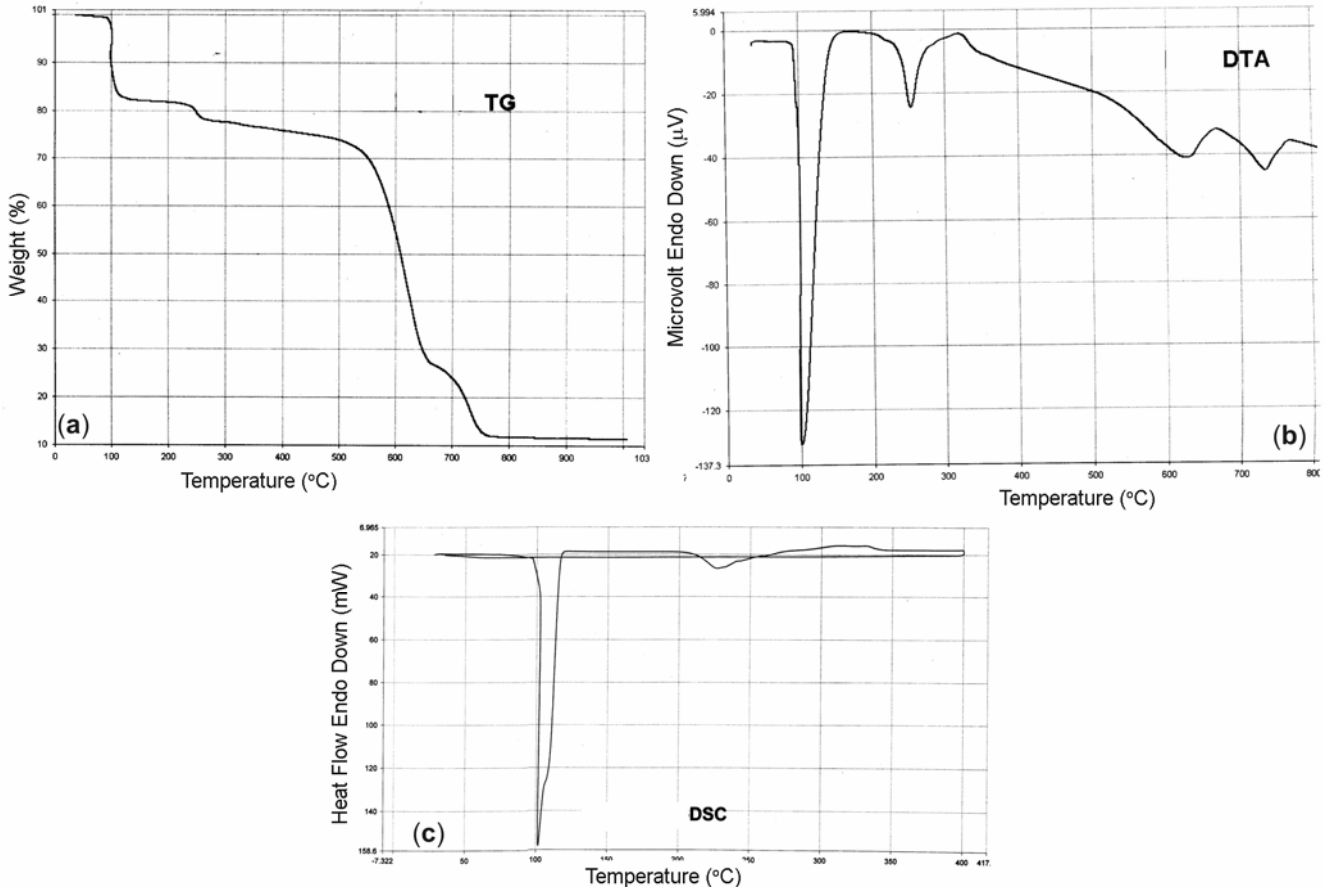

Figure 5. (**a**) TGA curve of barium calcium iodate crystal, (**b**) DTA curve of barium calcium iodate crystal and (**c**) DSC curve of barium calcium iodate crystal.

Step III: At 290°C (initiation temperature), initiation of phase change starts and the phase change (i.e. transition) ends at peak exo-up temperature of 313·54°C (transition temperature). The temperature at which the sample and reference come to the thermal equilibrium by thermal diffusion appears to be at 340°C: (i) Area under the curve is –485·798 mJ and (ii) heat of transition, ΔH_{tr} i.e. enthalpy change of transition is –31·54 J/g which is –0·03154 kJ/mole. Since molecular weight is 1 g/mole. Therefore, $\Delta H_{tr} = \Delta H_f$ i.e. heat of phase formation is also –0·03154 kJ/mole where ΔH_f is enthalpy change of new phase formation or it is called heat of phase formation.

6. Conclusions

From the above studies we observe that
(I) Single diffusion gel growth technique is suitable for growing crystals of mixed barium calcium iodate.
(II) Good quality crystals of mixed barium calcium iodate can be obtained by changing parameters like gel density, gel aging, pH of gel, concentration of reactants, etc.
(III) The observed peaks in diffractogram shows that the mixed iodate crystals possess monoclinic structure.
(IV) The TGA calculation shows that the molecular formula of the grown $Ba_{0·27}Ca_{0·73}(IO_3)_4·nH_2O$ crystal as determined from XRD and FTIR can be written as $Ba_{0·27}Ca_{0·73}(IO_3)_4·12H_2O$.
(V) Chemical compositions of the grown crystal by EDAX match with the theoretical calculation from molecular formula.

Acknowledgements

The authors are grateful to Prof. S A Patil, Department of Physics, Pratap College, Amalner, for providing laboratory facilities. Our thanks to Prof. S R Chaudhari, Principal, Pratap College, Amalner, for constant encouragement. Also we thank Prof. K S Mahajan and Late Prof. R U Vaidya, Pratap College, Amalner, for fruitful discussions. One of the authors (SLG) sincerely thanks the University Grants Commission, New Delhi, for the award of a teacher fellowship under the Faculty Improvement Programme.

References

Armington A F and O'Connar J J 1968 *J. Cryst. Growth* **3/4** 367
ASTM data of $Ba(IO_3)_2$ – Card No. 73-0835
ASTM data of $Ca(IO_3)_2$ – Card No. 70-0636
Bach H and Kuppers H 1978 *Acta Crystallogr.* **B34** 263
Blank Z 1973 *J. Cryst. Growth* **18** 281
Blank Z and Brenner W 1969 *Nature* **222** 79
Blank Z, Brenner W and Okamoto Y 1969 *Mater. Res. Bull.* **3** 829
Ittyachen M A and Kurien K V 1979 *J. Cryst. Growth* **47** 743
Joshi M S and Trivedi S G 1970 *Kryst. Und Technol.* **J5** 1131
Joshi M S and Trivedi S G 1983 *Indian J. Pure & Appl. Phys.* **21** 435
Joshi M S, Mohan Rao P and Antoni A V 1981 *Bull. Mater. Sci.* **2** 127
Kurtz S K and Perry T T 1968 *J. Appl. Phys.* **39** 3798
Morosin B, Bergman J G and Crane G R 1973 *Acta Crystallogr.* **B29** 1067
Nakamoto K 1970 *Infrared spectra of inorganic and coordination compounds* (New York: John Wiley and Sons Inc) 2nd edn
Ranadive D, Blank Z, Brenner W and Okamoto Y 1969 *Nature* **223** 829
Shitole S J and Saraf K B 2001 *Bull. Mater. Sci.* **24** 461