

# Growth and study of barium oxalate single crystals in agar gel

P V DALAL\* and K B SARAF

PG Department of Physics, Pratap College, Amalner 425 401, India

MS received 15 December 2005; revised 22 May 2006

**Abstract.** Barium oxalate was grown in agar gel at ambient temperature. The effect of various parameters like gel concentration, gel setting time and concentration of the reactants on the growth of these crystals was studied. Prismatic platy shaped spherulites and dendrites were obtained. The grown crystals were characterized by X-ray powder diffractometry, infrared spectroscopy, thermogravimetric and differential thermal analysis. An attempt is made to explain the spherulitic growth mechanism.

**Keywords.** Barium oxalate; agar gel; XRD; IR; TGA/DTA.

## 1. Introduction

Crystal growth is a heterogeneous chemical process in which conversion from one phase to another phase of a compound is involved. In the field of crystal growth, gel technique has become more popular and has been used by several investigators (Joshi and Trivedi 1970; Ittyachen and Kurien 1979; Joshi *et al* 1981). Due to its simplicity (Armington and O'Connar 1968; Ranadive *et al* 1969), it can be successfully used at room temperature to suppress nucleation centres (Arora 1981) and is suitable for crystals having low solubility (Dennis and Henisch 1967).

The ferroelectric and ferroelastic properties of rare earth oxalates and molybdates have wide applications in electro and acousto optical devices (Barkley *et al* 1971, 1972; Sapriel and Vacher 1977). Synthesis of superconducting compounds by the controlled precipitation of oxalates followed by calcinations has been reported (Caillaud *et al* 1988).

Oxalate crystals are insoluble in water and they decompose before the melting point (Prasad *et al* 1996). Synthesis of rare earth oxalates has been carried out using the gel method (Jayakumari *et al* 1995; Sushma Bhat *et al* 1995; Raju *et al* 1998). Transition metal oxalates were also grown by this method (Arora and Tony Abraham 1981). Barium copper oxalate crystal was grown in silica hydrogel (Bangera and Mohan Rao 1992) and barium oxalate crystal was grown by precipitation of alkaline earth metal oxalate powders from its aqueous solution (Pactor 1977). The work on barium oxalate is reported only in silica hydrogel. Hence the purpose of the present paper is to report the growth and influence of various parameters on the growth mechanism of single crystals of barium oxalate in agar gel at ambient temperature.

## 2. Experimental

The growth of barium oxalate crystal was carried out in agar gel. All chemicals such as acetic acid, barium chloride, oxalic acid and agar-agar were of AR grade.

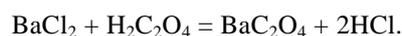
In the present work, agar-agar gel (Brezina and Harvan-kova 1991; Agrawal *et al* 1999) was preferentially used for the growth of crystals by single and double diffusion techniques.

A test tube having 25 cm in length and 2.5 cm in diameter was employed. In single diffusion, hot aqueous agar gel and oxalic acid solution were thoroughly mixed and kept in the test tube for setting. After setting and aging, the gel, barium chloride, was added to the above gel.

Now on reversing the reactants, in single diffusion, hot aqueous agar gel and barium chloride solutions were thoroughly mixed and kept in the test tube for setting. After setting and aging the gel, oxalic acid, was added.

In double diffusion, the U tube was filled up to proper heights with hot agar-agar solution and kept for setting and aging. Oxalic acid solution was poured into one limb and barium chloride solution was poured into the other limb of the U tube.

The reaction, which leads to the growth of crystals, was expressed as



## 3. Results and discussion

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

In single diffusion, after a few days, dendritic and spherulitic growths were observed. The dendritic growth of barium oxalate is as shown in figure 1, while figure 2 shows prismatic platy shaped transparent crystals at the

\*Author for correspondence (yash\_paresh@yahoo.co.in)

**Table 1.** Optimum conditions for growth of barium oxalate crystals.

Conditions	Single diffusion	Double diffusion
% of gel	1.5	1.5
Concentration of barium chloride	1 M	1 M
Concentration of oxalic acid	1 M	1 M
Gel setting period	6 days	12 days
Gel aging	48 h	48 h
Period of growth	80 days	60 days
Temperature	Room temp.	Room temp.
Quality	Transparent, opaque	Opaque
Size	17 × 4 × 2, 4 × 3 × 2 and 4 mm diameter	4 mm diameter

**Figure 1.** Dendritic growth of barium oxalate.**Figure 2.** Prismatic platy shaped transparent crystals at the interstitial and spherulites inside the gel.

interstitial and spherulitic growth well inside the gel on reversing the reactant in single diffusion. In double diffusion, spherulitic growth was observed as shown in figure 3. Figure 4 shows some good quality transparent as well as spherulite crystals.

Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time etc have considerable effect on growth rate. In the steady state of concentration gradient, growth rate also becomes steady which favours growth of spherulite crystals. However,

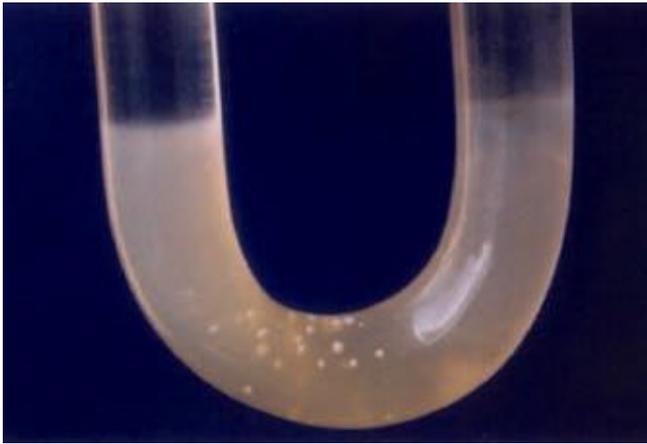


Figure 3. Spherulite crystals of barium oxalate in U-tube.

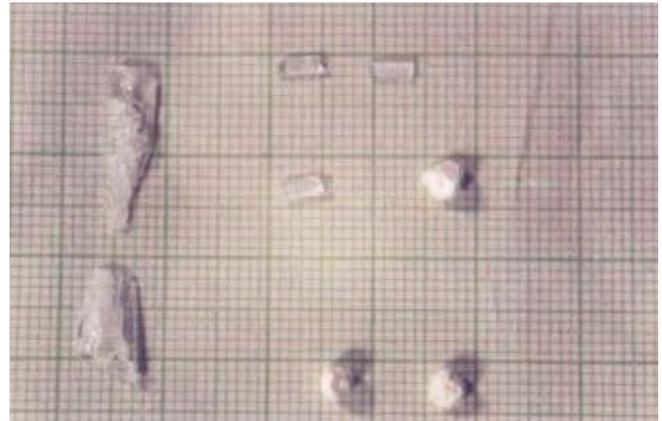


Figure 4. Some good quality transparent as well as spherulite crystals.

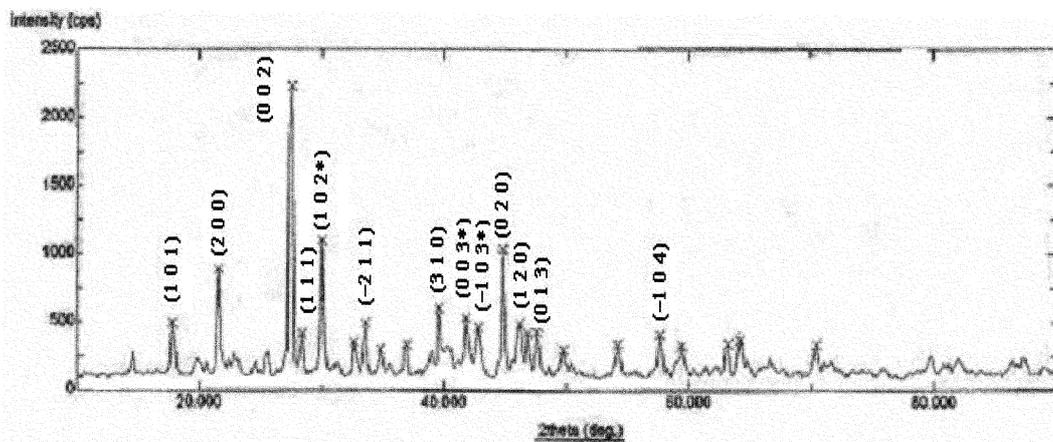


Figure 5. X-ray diffractogram of barium oxalate.

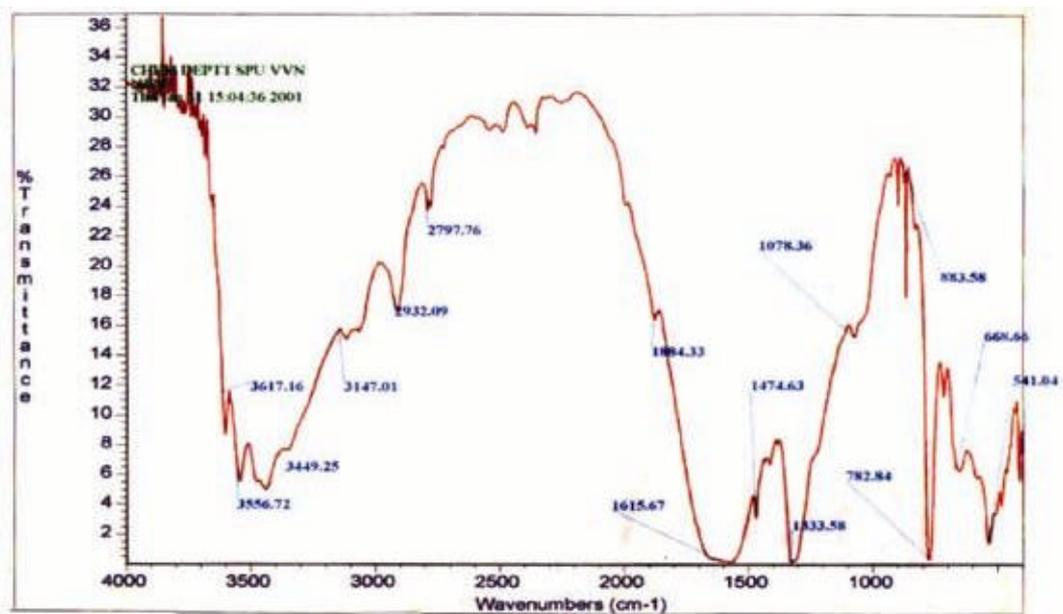


Figure 6. Infrared spectra (IR) of barium oxalate.

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 dendrite crystals.

### 3.1 Growth mechanism of spherulite

Spherulites are formed in the crystallization process of many substances, which are especially characteristic of substances consisting large molecules, particularly, polymers. This characteristic feature of a spherulite is due to no coincidence of one of the crystallographic axes with the direction of the molecule chains lying along the radius of spherulite (Sheftal 1968).

Spherulite shapes may be explained perfectly satisfactorily via a model of a sheet of paper crumpled into folds, the edges being compressed toward the centre, giving the crystal a spherical shape (Sheftal 1968).

## 4. Characterization

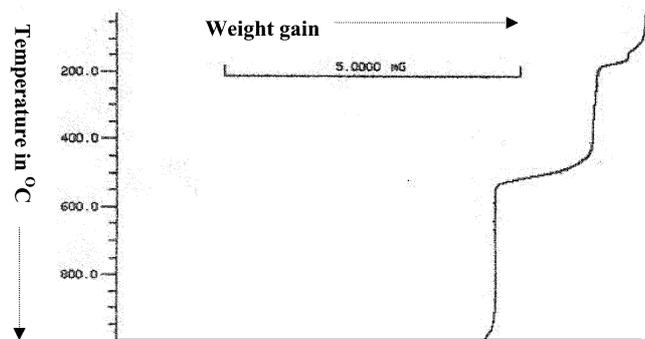
### 4.1 X-ray diffraction

X-ray powder diffractograms were recorded using Minislex model, Rigaku (CuK $\alpha$  radiation, scanning speed, 10°/min). Figure 5 shows X-ray diffractogram of barium oxalate.

From the diffractograms,  $d$ -values for different  $h k l$  were computed. The computer program, POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) was used to calculate ' $d$ ' values. Calculated ' $d$ ' values matched with reported values. Table 2 shows calculated unit cell parameters.

**Table 2.** Calculated unit cell parameters.

Parameters	Barium oxalate
System	Monoclinic (P)
$a$	8.2426 Å
$b$	4.0458 Å
$c$	6.4706 Å
$b$	92.319 Å
$V$	215.60 Å <sup>3</sup>



**Figure 7.** Thermogravimetric analysis (TGA) of barium oxalate.

### 4.2 Infrared spectra

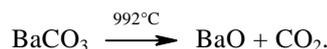
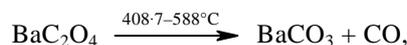
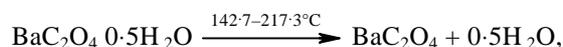
IR absorption spectrum of barium oxalate crystals (figure 6) shows a well pronounced broad intense peak at 3556.72 cm<sup>-1</sup>, which is attributed to asymmetric and symmetric O–H stretching and the peak at 1615.67 cm<sup>-1</sup> is related to O–H bending vibration, which established the presence of water of crystallization. The sharp peak at 782.84 cm<sup>-1</sup> may be attributed to metal–oxygen bond.

### 4.3 Thermal analysis

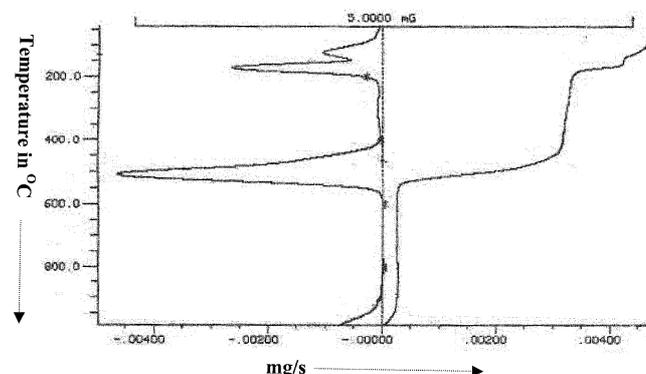
TGA and DTA of grown crystals were carried out at the National Chemical Laboratory, Pune, by Mettler TA4000 system.

TGA curves (figure 7) show that the compound is stable up to 54°C. It loses 2% in weight in the temperature range 54–142°C which may be due to loss of moisture. The 3.75% loss in weight may be due to dehydration of 0.5 water molecule in the temperature range 142.7–217.3°C. There is no further weight loss up to 408.7°C and hence barium oxalate is completely dehydrated.

The 11.701% losses in weight, in the temperature range 408.7–558°C, suggest loss of CO. The compound remains stable up to 992°C, and then starts to decompose. It may be due to loss of CO<sub>2</sub>. This thermal behaviour in terms of scheme (Raju *et al* 1998) may be explained as below:



The weight loss of the grown sample is further supported by DTA (figure 8) analysis at the respective temperatures.



**Figure 8.** Thermal analysis (DTA/TGA) of barium oxalate.

## 5. Conclusions

From the above studies we observe that:

- (I) Gel growth technique is suitable for growing crystals of barium oxalate.
- (II) Single and double diffusion methods show variation in the growth mechanisms.
- (III) XRD results obtained, especially 'd' values, matched with the standard JCPDS data.
- (IV) The study of characteristic peaks obtained (IR) reveals the presence of metal oxygen bond.
- (V) Loss of 0.5 water molecule by dehydration around 142.7–217.3°C (endothermic), the evolution of CO around 408.7–558°C and CO<sub>2</sub> around 992°C (exothermic) and yielding stable residual barium oxide beyond 992°C are seen.

## Acknowledgements

The authors thank the Head, Department of Physics, Pratap College, Amalner, for providing laboratory facilities, Dr N R Shah, Department of Chemistry, Pratap College, Amalner, for fruitful discussion on IR and Prof. P P Patil, Director, North Maharashtra University, Jalgaon, for providing characterization facilities.

## References

Agrawal B P, Chauhan K M and Bhadbhade M M 1999 *Indian J. Pure & Appl. Phys.* **37** 395

- Armington A F and O'Connar J J 1968 *J. Cryst. Growth* **3/4** 367
- Arora S K 1981 *Prog. Crystal Growth Charact.* **4** 345
- Arora S K and Tony Abraham 1981 *Indian J. Pure & Appl. Phys.* **19** 199
- Bangera Kasthuri V and Mohan Rao P 1992 *Bull. Mater. Sci.* **15** 339
- Barkley J R, Brixner L H and Hogan E M 1971 *IEEE symposium on the application of ferroelectrics* (New York: York Town Heights)
- Barkley J R, Brixner L H, Hogan E M and Waring R K 1972 *J. Ferroelectrics* **3** 191
- Brezina B and Harvankova M 1991 *Mater. Res. Bull.* **87** 537
- Caillaud F, Baumard J F and Smith A 1988 *Mater. Res. Bull.* **23** 1273
- Dennis J and Henisch H K 1967 *J. Electrochem. Soc.(USA)* **114** 263
- Ittyachen M A and Kurien K V 1979 *J. Cryst. Growth* **47** 743
- Jayakumari Isac, Raju K S and Ittyachen M A 1995 *Bull. Mater. Sci.* **19** 495
- Joshi M S and Trivedi S G 1970 *Kryst. Und Technol.* **15** 1131
- Joshi M S, Mohan Rao P and Antoni A V 1981 *Bull. Mater. Sci.* **2** 127
- Pactor A 1977 *Krist. & Technol.* **12** 729
- Prasad N V, Prasad G, Bhimasankaram T, Suryanarayana S V and Kumar G S 1996 *Bull. Mater. Sci.* **19** 639
- Raju K S, Varughese John and Ittyachen M A 1998 *Bull. Mater. Sci.* **21** 375
- Ranadive D, Blank Z, Brenner W and Okamoto Y 1969 *Nature* **223** 829
- Sapriel J and Vacher R 1977 *J. Appl. Phys.* **48** 1191
- Sheftal N N 1968 *Growth of crystals* (New York: Consultants Bureau)
- Sushma Bhat, Kotru P N and Raju K S 1995 *Curr. Sci.* **69** 607