

Growth of strontium oxalate crystals in agar–agar gel

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Abstract. Single crystals of strontium oxalate have been grown by using strontium chloride and oxalic acid in agar–agar gel media at ambient temperature. Different methods for growing crystals were adopted. The optimum conditions were employed in each method by varying concentration of gel and reactants, and gel setting time etc. Transparent prismatic bi-pyramidal platy-shaped and spherulite crystals were obtained in various methods. The grown crystals were characterized with the help of FT–IR studies and monoclinic system of crystals were supported with lattice parameters $a = 9.67628 \text{ \AA}$, $b = 6.7175 \text{ \AA}$, $c = 8.6812 \text{ \AA}$, $\beta = 113.566^\circ$, and $V = 521.84 \text{ \AA}^3$ calculated from X-ray diffractogram.

Keywords. Crystal growth; strontium oxalate; X-ray spectroscopy; FT–IR.

1. Introduction

The growth of single crystals of various substances has gained considerable attention of several investigators. Sophisticated and strenuous equipments have been developed and employed for growing a wide variety of crystals; either may be due to lack of natural crystals or their nonavailability in the required purified form. The growing methods are to be selected, depending on the nature of crystals for which it has to be used for specific purpose. Oxalate crystals are insoluble in water and decompose before melting; therefore, single crystals of these materials cannot be grown by either slow solvent evaporation or melt techniques (Prasad *et al* 1996). However, they can be suitably grown by gel method. In recent years, crystal growth in gel medium has attracted much attention because of its simplicity (Armington and O’Cornnar 1968; Ranadive *et al* 1969), and shown special characteristics of suppression of nucleation centres (Arora 1981). Most oxalates and molybdates have wide applications in electro- and acousto-optical devices (Barkley *et al* 1971, 1972; Sapriel and Vacher 1977). Oxalates play a vital role in increasing the hardness of barium titanate and to achieve decreased layer thickness in multilayer ceramic capacitors (Bera and Sarkar 2003). They also have good ionic conductivity (George *et al* 1990), exhibit applications as precipitation agent (Mullens *et al* 1993) as well as used in nano particle synthesis, in magnetic and luminescent devices (Vos *et al* 1992; Ye *et al* 1999; Ahmad *et al* 2004). Synthesis of rare earth oxalates (Bhat *et al* 1995; Jayakumari *et al* 1995; Raju *et al* 1998) and transition metal oxalates has been

carried out using gel method (Arora and Tony 1981). Barium copper oxalate crystal in silica hydrogel (Bangera and Mohan Rao 1992), barium oxalate in silica (Dharmaprakash and Mohan Rao 1986; Moses *et al* 2008) and in agar gel (Dalal and Saraf 2006), cadmium oxalate in silica (Shedam and Venkateswara Rao 2006) and in agar gel (Chauhan and Arora 2009) were performed. Strontium was used in doping (Suryanarayana *et al* 1998), and in mixed oxalate crystals (Trifa *et al* 2007). However, strontium oxalate crystals grown in gel media are not so far reported. The purpose of the present work is to report the growth and influence of various parameters on the growth mechanism of strontium oxalate.

2. Experimental

The growth of strontium oxalate crystals was carried out in agar–agar gel by adopting the similar techniques as reported (Dalal and Saraf 2009). Two vessels, one U-tube of length 25 cm and diameter 2.5 cm, and other a single glass tube of length 20 cm and diameter 2.5 cm were used.

In double diffusion, the U-tube was filled with hot agar–agar solution and was kept for setting. After setting and aging of gel, one limb was filled with 20 ml (0.5–1 M) oxalic acid solution and other with 20 ml (0.5–1 M) strontium chloride. Nucleation was observed inside and at the interstitial of the gel after one week. As the reactant solution diffused deep into the gel, spherulite crystals were found to be growing. The growth was completed in about 80 days. The maximum size of grown spherulite crystals was 4 mm in diameter.

In single diffusion, hot aqueous agar–agar gel solution and a 5 ml oxalic acid solution (0.5–1 M) were mixed and kept in test tube for setting. After setting and aging the gel, a 20 ml strontium chloride solution (0.5–1 M) was added over

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Table 1. Summary of optimum conditions established for growth of strontium oxalate.

Conditions	Single diffusion	Double diffusion
% of gel	1.5	1.5
Concentration of strontium chloride	1 M	1 M
Concentration of oxalic acid	1 M	1 M
Gel setting period	3 days	6 days
Gel aging	24 h	24 h
Period of growth	60 days	80 days
Temperature	Room temp.	Room temp.
Quality	Transparent prismatic bi-pyramidal Platy shaped	Opaque, spherulite
Size	6 × 6 × 3 mm	4 mm in diameter

**Figure 1.** Spherulite crystals were obtained at interstitial and inside test tube.

the set gel. Initially a thin precipitation layer was formed on the surface of the gel. This white precipitate band increased gradually as the diffusion proceeded into the gel.

On reversing the reactant, hot aqueous agar-agar gel solution and a 5 ml strontium chloride solution (0.5–1 M) were mixed and kept in test tube for setting. After setting and aging the gel, a 20 ml oxalic acid solution (0.5–1 M) was added over the set gel. Nucleation was started readily at the interstitial and inside the test tube. Heavy nucleation was observed in the test tube, which was further increased.

To control heavy nucleation, in single diffusion, other technique was tried. A mixer of strontium chloride solution and agar-agar gel was set as per the previous method. And a neutral gel was set over the above set gel by introducing 30 ml hot agar-agar solution without any reactant. Then a 1 M, 20 ml oxalic acid solution was poured over the set gel. It

**Figure 2.** Some large size spherulite crystals in double diffusion.

is observed that neutral gel has reduced the number of nucleation but did not change the size of the crystal. However, spherulite and bi-pyramidal crystals were obtained.

To improve the size of the crystal, again one more method was adopted. A gel was set by mixing a solution of different concentrations and quantities of ammonium chloride as an additive with strontium chloride and agar-agar solution as per previous method. Then 1 M, 20 ml oxalic acid

solution was poured over the set gel. Transparent prismatic platy shaped bi-pyramidal crystals of maximum size $6 \times 6 \times 3$ mm and spherulite crystals were separated after 60 days.

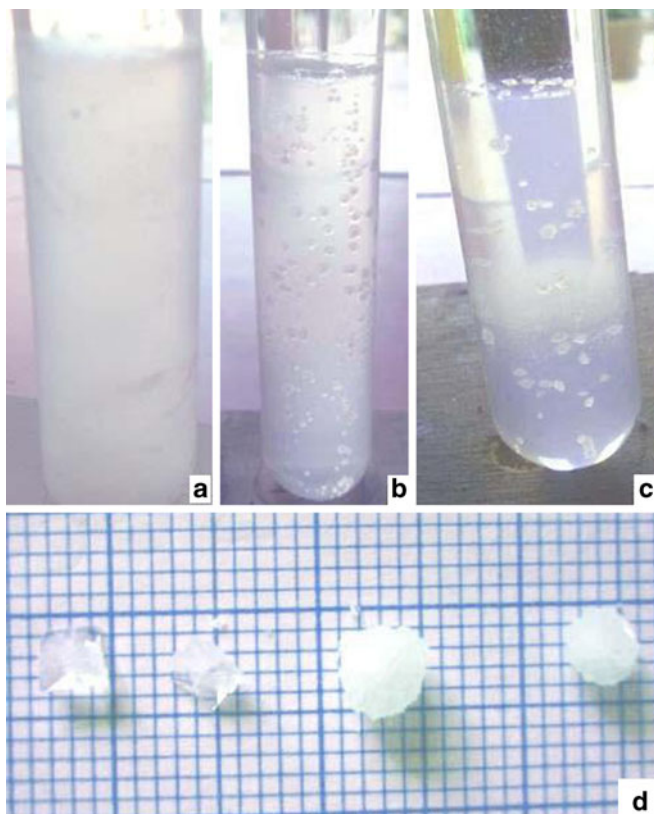


Figure 3. a. White precipitate, on taking strontium chloride as supernatant and oxalic acid as one reactant with gel, b. spherulite crystals at interstitial and well inside gel on reversing reactants, c. spherulitic, and transparent prismatic bi-pyramidal crystals at interstitial and well inside in neutral gel and d. bi-pyramidal and spherulite crystals in single diffusion.

The powder X-ray diffraction studies of grown crystals were carried out using an X'pert MPD, "Philips", Holland, using $\text{CuK}\alpha$ radiation. The FT-IR spectra of the material in the frequency range of $400\text{--}4000\text{ cm}^{-1}$ were recorded on Perkin-Elmer spectrophotometer.

3. Results and discussion

The optimum conditions for growing crystals are given in table 1. In double diffusion, spherulite crystals were obtained at the interstitial and inside the test tube as shown in figure 1. In double diffusion, spherulites obtained at the interstitial were of larger size than obtained inside in single diffusion. Some large size grown spherulite crystals are shown in figure 2.

In single diffusion, white precipitate was observed on allowing strontium chloride as supernatant and oxalic acid with set gel as shown in figure 3(a), while spherulite crystals were observed at the interstitial and well inside the gel on reversing the reactants as shown in figure 3(b). Figure 3(c) shows spherulitic, transparent and bi-pyramidal growth of crystals at the interstitial and well inside the neutral gel. Neutral gel has controlled nucleation up to certain extent but could not improve the size of crystals. Some good quality bi-pyramidal crystals with maximum size $4 \times 4 \times 3$ mm grown in neutral gel are shown in figure 3(d). NH_4Cl was used as an additive for the purpose to suppress the nucleation density and to increase the size of the crystals. Transparent, platy-shaped crystals at the interstitial and spherulite crystals well inside the test tube were obtained when 4 M, 8 ml NH_4Cl solution was used in the gel (figure 4a). Some good quality and large size ($6 \times 6 \times 3$ mm) strontium oxalate crystals were obtained in the presence of NH_4Cl as shown in figure 4(b).

Spherulite crystals were obtained in double diffusion technique. Similar spherulite crystals were also separated in a single diffusion technique in which the gel medium does

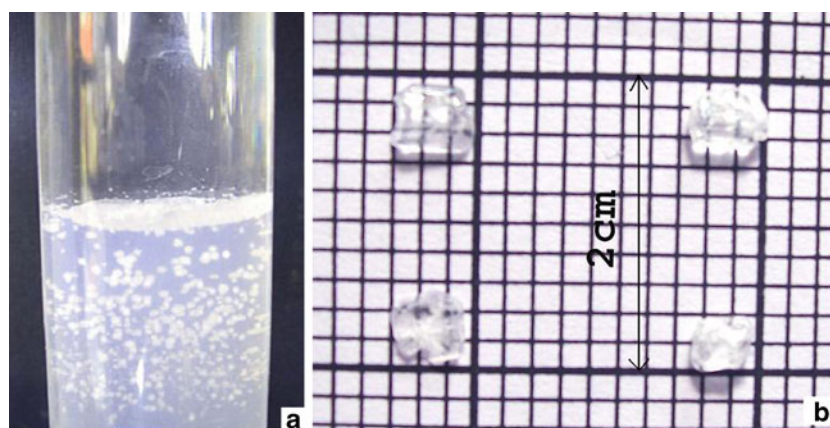


Figure 4. a. Transparent prismatic bi-pyramidal platy shaped crystals at interstitial and spherulite crystals well inside test-tube using NH_4Cl additive in single diffusion and b. some good quality crystals obtained using NH_4Cl as additive in single diffusion.

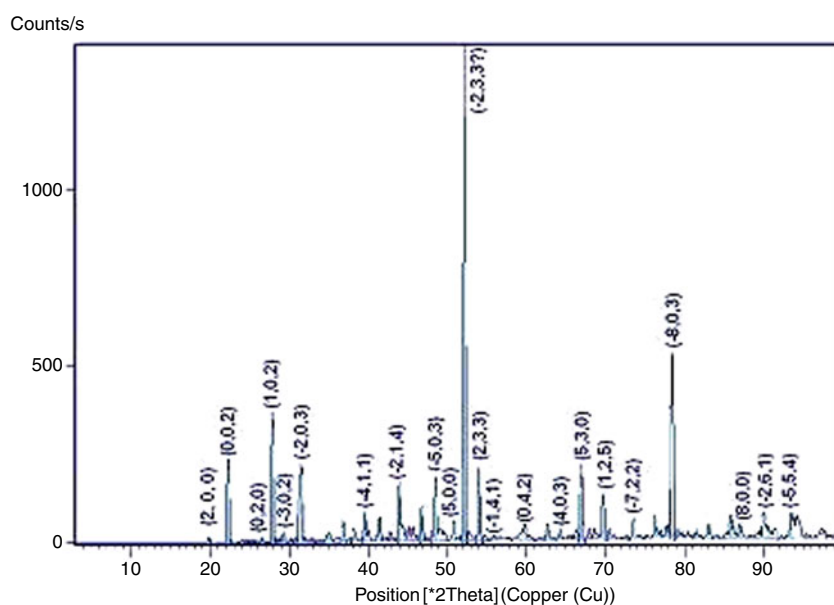


Figure 5. X-ray diffractogram of strontium oxalate.

Table 2. Comparison of unit cell parameters of strontium oxalate.

Parameters	Calculated	JCPDS data
System	Monoclinic (P)	Monoclinic
<i>a</i>	9.67628 Å	6.4500 Å
<i>b</i>	6.7175 Å	7.5000 Å
<i>c</i>	8.6812 Å	10.240 Å
β	113.566°	105.30°
<i>V</i>	521.84 Å ³	477.80 Å ³

not contain additive ammonium chloride or no neutral gel was used. However, bi-pyramidal platy-shaped transparent and large size crystals were found in a single diffusion technique when ammonium chloride was used in the gel media. This might be due to the common chloride ion effect, which reduced the rate of nucleation to improve the size and shape of the crystal. Similar bi-pyramidal crystals were also found in single diffusion technique, when the rate of nucleation was controlled by neutral gel, used in between the diffusing reactants.

3.1 Powder X-ray diffraction results

The indexed powder X-ray diffraction pattern of the grown crystals are shown in figure 5. The computer program, POWD (Interactive Powder Diffraction Data Interpretation and Indexing Program, version 2.2) was used to calculate '*d*' values and unit cell parameters. Calculated unit cell parameters are compared with the JCPDS data (T.No. 19-1282) and are shown in table 2. From the calculated parameters, it can be concluded that strontium oxalate crystallizes under monoclinic system.

3.2 FT-IR results

FT-IR spectrum in the range 400–4000 cm⁻¹ of the grown strontium oxalate crystals is shown in figure 6. A strong sharp band appeared at 3294.88 cm⁻¹ attributed to O–H stretching and a weak band at 3004.20 cm⁻¹ may be due to intra-molecular hydrogen bonded O–H stretching vibration. A medium and sharp band at 1724.07 cm⁻¹ can be attributed to carbonyl stretching vibration but very strong band at 1607.55 cm⁻¹ may be due to partial double bond character of carbonyl group stretching vibration. This may be due to one >C=O group and other >C=O group with coordinated bond from carbonyl oxygen to strontium. Strong and very sharp band at 714.79 cm⁻¹ may be due to oxygen–metal bond (Packter and Omon 1984). The presence of O–H group may be due to coordinated water molecule in the crystal.

4. Conclusions

From systematic investigation of strontium oxalate, best conditions have been established to get good quality crystals. Following are the pointwise conclusions:

- (I) Agar–agar gel does not require maintaining of pH, while silica hydro gel requires appropriate condition of pH. Therefore, agar–agar gel is the better media than silica hydro gel.
- (II) In double diffusion method, spherulite crystals of about 4 mm diameter were collected whereas in single diffusion transparent prismatic bi-pyramidal platy shaped crystals of about 6 × 6 × 3 mm³ in size were collected.
- (III) Neutral gel has controlled the nucleation up to certain extent, but does not improve the size. However, NH₄Cl used

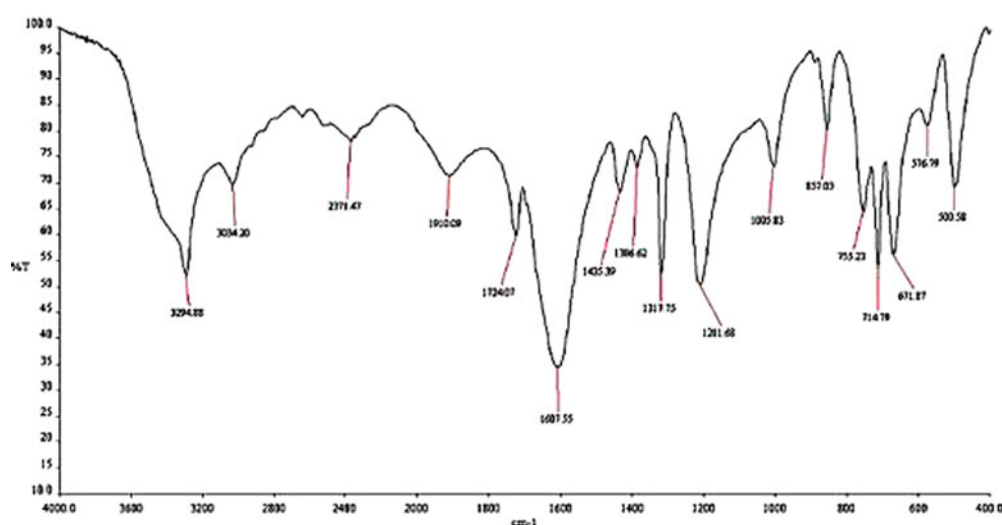


Figure 6. FT-IR spectra of strontium oxalate crystals grown in agar-agar gel.

in the gel has improved the increasable size and transparency of the crystal.

(IV) The results obtained from the XRD data have confirmed the monoclinic structure of strontium oxalate.

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References

- Ahmad T, Ramanujachary K V, Lofland S E and Ganguli A K 2004 *J. Mater. Chem.* **14** 3406
- Armington A F and O'Connar J J 1968 *J. Cryst. Growth* **3** 367
- Arora S K 1981 *Prog. Crystal Growth Charact.* **4** 345
- Arora S K and Tony A 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
- Bera J and Sarkar D 2003 *J. Electroceram.* **11** 131
- Bhat S, Kotru P N and Raju K S 1995 *Curr. Sci.* **69** 607
- Chauhan K M and Arora S K 2009 *Cryst. Res. Technol.* **44** 189
- Dalal P V and Saraf K B 2006 *Bull. Mater. Sci.* **29** 421
- Dalal P V and Saraf K B 2009 *Cryst. Res. Technol.* **44** 36
- Dharmaprakash S M and Mohan Rao P 1986 *Bull. Mater. Sci.* **8** 511
- George V, Ittyachen M A and Jayakumari Issac 1990 *Cryst. Res. Technol.* **25** K-153
- Jayakumari Isac, Raju K S and Ittyachen M A 1995 *Bull. Mater. Sci.* **19** 495
- Moses Ezhil Raj A, Jayanthi Deva D, Jothy Bena V, Jayachandran M and Sanjeeviraja C 2008 *Cryst. Res. Technol.* **43** 1307
- Mullens J, Vos A, De Backer A, Franco D, Yperman J and Van Poucke L C 1993 *J. Therm. Anal.* **40** 303
- Packter A and Omon A 1984 *Cryst. Res. Technol.* **19** 467
- Prasad N V, Prasad G, Bhimasankaram T, Suryanarayana S V and Kumar G S 1996 *Bull. Mater. Sci.* **19** 639
- Raju K S, Varughese J 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
- Shedam M R and Venkateswara Rao A 2006 *Bull. Mater. Sci.* **16** 309
- Suryanarayana K, Dharmaprakash S M and Sooryanarayana K 1998 *Bull. Mater. Sci.* **21** 87
- Trifa Chahrazed, Bouhali Amira, Boudaren Chaouki, Bouacida Sofiane and Bataille Thierry 2007 *Acta Crystallogr.* **E63** i102
- Vos A, Mullens J, Carleer R, Yperman J and Van Poucke L C 1992 *Bull. Soc. Chim. Belg.* **101** 187
- Ye X R, Jia D Z, Yu J Q, Xin X Q and Xue Z L 1999 *Adv. Mater.* **11** 941