Growth and characterization of barium copper oxalate single crystals in gels

KASTHURI V BANGERA and P MOHAN RAO*

Department of Physics, K R E College, Surathkal, Srinivasnagar 574 157, India

*Department of Physics, Mangalore University, Mangalagangothri 574 199, India

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Abstract. Barium copper oxalate was grown in silica hydrogel at ambient temperature. The effect of various parameters like gel pH, gel density, gel aging and concentrations of reactants on the growth of these crystals was studied. The crystals grown were characterized by chemical analysis, X-ray powder diffractometry, infrared spectroscopy, thermogravimetric and differential thermal analysis. The results of these observations are described and discussed.

Keywords. Barium copper oxalates; silica hydrogel; gels.

1. Introduction

In recent years crystal growth in gel medium has attracted the attention of many investigators (Venkateswara Rao 1985; Dharma Prakash and Mohan Rao 1986; Kotru *et al* 1986; Narayana Kalkura and Deva Narayan 1987). The principle relies on the slow migration of crystal constituents (ions) through silica hydrogel so that a very slow reaction occurs with the formation of a sparingly soluble compound. When the concentration of this compound exceeds the solubility limits, crystals will be formed, the main function of the gel being to control the flow of reacting ions.

Mixed crystal growth has scarcely been studied by employing the gel technique (Joshi *et al* 1980; Dharma Prakash and Mohan Rao 1986) and the field is in an early stage of development with many opportunities to create new species. The purpose of the present paper is to report the growth of single crystals of barium copper oxalate in silica hydrogel at ambient temperature.

2. Experimental

The growth process involved diffusion of barium chloride and copper chloride solutions into a gel in which oxalic acid was impregnated before hand. Crystal growth experiments were carried out in corning glass tubes (length 200 mm, inner diameter 25 mm). The chemicals used were commercial sodium metasilicate (water glass) solution, oxalic acid (AnalaR), barium chloride (AnalaR) and copper chloride (AnalaR). The gel was set by mixing sodium meta silicate solution of specific gravity 1.04 with aqueous 1.0 M oxalic acid in proper ratio such that the pH of the resulting solution was around 3.1. After the gel was set a mixture of barium chloride and copper chloride solution of varying strengths (0.25–1 M) was slowly poured above the set gel down the walls of different test tubes. The crystals grown were characterized

*For correspondence

by chemical analysis, X-ray powder diffraction, infrared spectroscopy, thermogravimetric and differential thermal analyses.

3. Observations and discussion

In terms of clarity of gel mixture and separation between the crystals, the combination of pH 2.9 to 3.2 gel mixture and 0.5 M supernatant feed solution (barium chloride and copper chloride) gave the best results. The specific gravity of the sodium meta silicate solution used was 1.04. The gelling time was about one week. Nucleation was observed within a day after adding the chloride solutions to the gel set with 1.0 M oxalic acid just below the gel interface. It was observed that barium copper oxalate crystals are grown in the form of transparent blue crystals of cubic shape near the interface. As the mixed chemical solution diffuses deep into the gel, transparent colourless crystals of different morphology were found to grow. These transparent blue and colourless crystals are henceforth referred to as types I and II crystals respectively. A typical experimental tube where types I and II crystals were grown is shown in figure 1. The growth was completed in about three weeks. The average size of the type I crystals was about 5×3 mm and that of type II crystals was about 10×3 mm. Some of the crystals grown are shown in figures 2 and 3.

3.1 pH

It is found that the initial pH values of 2.9–3.1 give the optimum condition for the growth of barium copper oxalate crystals. When the pH was increased above 3.4, irregularly shaped and opaque dendritic crystals were obtained along with the formation of Leisgang rings. On the other hand it was observed that only few blue crystals were formed below pH 2.6.

Figure 1. A typical growth tube ($\times 3$).

Figure 2. Transparent blue crystals of $\text{Ba}_x\text{Cu}_{1-x}\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (type I) ($\times 5.5$).

Figure 3. Well-developed colourless crystals of $\text{Ba}_x\text{Cu}_{1-x}\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (type II).

3.2 Gel density

In general, very dense gels produce poor crystals. On the other hand, gels of insufficient density take a longer time to form and are mechanically unstable. The present observations agree with this general rule. Generally, for growing crystals, gel density from 1.03 to 1.06 can be used. It is observed that nucleation density decreases as the gel density increases. A greater gel density implies smaller pore size and poor communication among the pores thus decreasing the nucleation density (Helberstadt *et al* 1969).

3.3 Gel aging

Aging of gels decreases the pore size and hence decreases the diffusion and nucleation density. The longer a gel is set at room temperature, the greater the amount of water which evaporates from the gel. The effect of evaporation of water should be considered before and after the formation of gel framework. Before the gel is set, the evaporation of water causes an increase in gel density which in turn decreases the diffusivity of Ba^{2+} and Cu^{2+} ions in the gel, thereby decreasing the number of nucleation sites. After the gel is set, evaporation of water causes not only the lack of ionic carriers in the channel of gel framework, but also discontinuities in the channel due to the shrinkage of the gel. Both these effects would adversely affect the diffusion of Ba^{2+} and Cu^{2+} and hence the number of nucleation sites.

3.4 Concentration of reactants

It is seen that as the concentration of the feed solutions increases, the nucleation density also increases. This may be due to the enhanced availability of Ba^{2+} and Cu^{2+} ions. To grow good crystals, the concentration of feed solution suitable is 0.5 M. Similarly the concentration of oxalic acid suitable for the growth of good quality crystals is 1.0 M.

3.5 Chemical analysis

Both varieties of crystals, viz. types I and II crystals were subjected to chemical analysis. The results are shown in table 1.

3.6 X-ray powder diffractometric studies

X-ray powder diffraction pattern of these crystals was recorded with X-ray diffractometer (JEOL, JDX OP) using FeK_α radiation. The samples were scanned over a 2θ range of 10° to 100° at $2^\circ/\text{min}$. The observed d values with relative intensities for the two varieties of crystals are given in tables 2 and 3.

3.7 Infrared absorption spectra

Infrared absorption spectra of both these gel grown crystals were recorded on a spectrophotometer (Shimadzu IR-408) using KBr pellet technique. The infrared spectra for the two varieties of crystals are shown in figures 4 and 5.

Table 1. Chemical composition of types I and II crystals.

Sample	Ba^{2+}	Cu^{2+}
Type I (bluish) crystal	28.24%	16.38%
Type II (colourless) crystal	47.77%	12 ppm

Table 2. Observed d values with relative intensities for type I barium copper oxalate crystal.

$d(10^{-8} \text{ cm})$	Intensity	$d(10^{-8} \text{ cm})$	Intensity
6.277	S	2.967	S
5.899	S	2.684	W
5.577	W	2.405	W
5.340	VS	2.347	W
4.519	VW	2.240	VW
4.249	S	2.126	W
3.969	W	1.737	VW
3.773	VW	1.694	W
3.471	S	1.527	S
3.185	VVW	1.291	VS

VW, very weak; W, weak; S, strong; VS, very strong.

Table 3. Observed d values with relative intensity for type II barium copper oxalate crystal.

$d(10^{-8} \text{ cm})$	Intensity	$d(10^{-8} \text{ cm})$	Intensity
6.689	VW	2.960	W
6.295	VS	2.845	VS
5.930	VW	2.441	S
5.316	S	2.315	VS
4.492	S	2.184	VS
4.226	W	1.967	W
3.754	VS	1.890	S
3.313	VS	1.772	W
3.177	VS	1.524	VS

VW, very weak; S, strong; W, weak; VS, very strong.

Figure 4. Infrared spectra of $\text{Ba}_x\text{Cu}_{1-x}\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (type I).

Figure 5. Infrared spectra of $\text{Ba}_x\text{Cu}_{1-x}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (type II).

Table 4. Assignment of IR band frequencies (cm^{-1}).

$\text{BaCu C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (type I crystal)	$\text{BaCu C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (type II crystal)	Assignment
3400	3350	(OH) stretch
1650	1600	(HOH) bend
1425	—	
1295	1310	(C—O) asymmetric stretch
	1215	
	1020	
810	840	(M—O)
	715 } 645 }	(O—C—O)

Simple oxalate salts consist of a metal cation and the oxalate anion. Therefore, the infrared spectra of these crystals are considered to arise from the oxalate ion and from the crystallization water present in the crystal. IR studies on various oxalates have been carried out by several investigators (Freeberg *et al* 1967; Shippy 1980a). The observed infrared bands and their assignments are shown in table 4.

In agreement with Shippy (1980b), the bands above 3000 cm^{-1} are assigned to OH stretching vibrations of water molecules. The H—O—H bending mode has been assigned to the IR band at about 1600 cm^{-1} . These two bands for the two crystals are almost similar, suggesting that the bonding of water molecules in the two crystals is similar and the O—H...O distances may be almost the same. The bands around 1300 cm^{-1} correspond to the asymmetric stretching mode of C—O bond. A slight difference in the frequencies of this band in the crystals indicates that the Ba—O and Cu—O bond lengths in the two structures are not similar. The observed IR bands around 715 and 645 cm^{-1} are assigned to various fundamental modes of vibrations of O—C—O bond.

The IR band observed at 840 cm^{-1} in type II crystals and at 810 cm^{-1} in type I crystals has been assigned to M—O bond (Packter and Omon 1984) where $\text{M} = \text{Ba} + \text{Cu}$.

The infrared spectral studies described above confirm the general crystal structure for simple metal oxalates (Fujita 1957) and represented schematically as:

where $\text{M} = \text{Cu} + \text{Ba}$.

3.8 Thermogravimetric and differential thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of these gel-grown barium copper oxalate crystals were carried out simultaneously by employing an automatic recording apparatus (Shimadzu DTA-30) at a heating rate of $10^\circ\text{C min}^{-1}$. The typical TGA and DTA curves are shown in figures 6 and 7.

The number of water molecules present and the purity of the crystals were determined from thermogravimetric analysis. Taking either the weight percentage of the end product or the initial weight as standard, the course of decomposition was analysed comparing it with the molecular weight. It is observed that types I and II crystals of barium copper oxalate contain 4 and 2 molecules of water respectively.

TGA and DTA data of various oxalates (Dollimore *et al* 1963, 1970) showed that most oxalates decompose in nitrogen producing the respective metals as final products in a single reaction. Since the present decomposition study was carried out in air, the end product would certainly not reach the stage of metals barium or copper.

The DTA curve of type II barium copper oxalate (figure 7) shows endothermic peak at about 170°C , two sharp exothermic peaks at around 235°C and 435°C and a small endothermic peak at 780°C .

Figure 6. TGA plot of barium copper oxalate.

Figure 7. DTA plot of barium copper oxalate.

The endothermic peak at 170°C must correspond to the liberation of water molecules from the dehydrated $\text{Ba}_x\text{Cu}_{1-x}\text{C}_2\text{O}_4$ which undergoes decomposition to form BaCO_3 and CuO . The exothermic peak at around 235°C corresponds to the formation of CuO and the peak around 435°C indicates the formation of BaCO_3 . The endothermic peak at 780°C is associated with the decomposition of BaCO_3 to BaO .

Similarly, the DTA curve of type I crystals (figure 7) shows endothermic peak at about 90°C and a exothermic peak at 220°C and a small endothermic peak at about 770°C.

The endothermic peak at 90°C in the DTA curve (figure 7) corresponds to dehydration of the mixed oxalate crystals. The exothermic peak around 220°C must be due to the transformation of copper oxalate into copper oxide. The small endothermic peak at 770°C corresponds to the decomposition of barium oxalate into barium oxide. It may be noted here that as the copper concentration in the mixed crystal increases (i.e. I type of crystals), the DTA peak corresponding to the decomposition of barium oxalate into barium carbonate is absent. This may be attributed to the fact that, the initial decomposition reaction to copper oxide is so exothermic that the subsequent decomposition of unreacted barium oxalate is accelerated.

4. Conclusion

Barium copper oxalate mixed crystals in silica hydrogel have been grown successfully at ambient temperature. It is found that well-developed single crystals are obtained at 0.5 M concentrations of feed solution in the pH range 2.9 to 3.1 of the gel.

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References

- Dharma Prakash S M and Mohan Rao P 1986 *J. Mater. Sci. Lett.* **5** 769
Dollimore D, Griffiths D L and Nicholson D 1963 *J. Chem. Soc.* **2** 617
Dollimore D and Griffiths D L 1970 *J. Therm. Anal.* **2** 229
Freeberg F E, Hartman K O, Hisatune I C and Schempf J M 1967 *J. Phys. Chem.* **71** 397
Fujita M 1957 *J. Phys. Chem.* **61** 1014
Helberstadt E S, Henisch H K, Nickl J and White E W 1969 *J. Colloid Interface Sci.* **29** 469
Joshi M S, Mohan Rao P and Antony A V 1980 *Bull. Mater. Sci.* **2** 127
Kotru P N, Raina K K and Koul M L 1986 *J. Mater. Sci.* **21** 393
Narayana Kalkura S and Deva Narayanan S 1987 *J. Cryst. Growth* **83** 446
Packter A and Omon A 1984 *Crystal Res. Technol.* **19** 467
Shippy T A 1980a *J. Mol. Struct.* **63** 157
Shippy T A 1980b *J. Mol. Struct.* **67** 223
Venkateswara Rao A 1985 *Bull. Mater. Sci.* **7** 83