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Growth of single crystals of bismuth sulpho chloride in gel

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Single crystals of the sparingly soluble compound, BiSCl have been grown in sodium silicate gel using straight tube and U-tube methods. Thiourea and bismuth trioxide dissolved in 10 N HCl are used as the reactants. The optimum conditions for growth of this crystal have been determined by studying the effect of the concentrations of the inner and outer reactants and that of the gel density. Single crystals of BiSCl upto 10 mm in size have been grown in a period of 20 to 25 days. The crystals grown have been identified as BiSCl by X-ray diffraction analysis.

1. Introduction

From a wide variety of current techniques for the growth of single crystals, the gel technique has gained considerable importance due to its simplicity and the effective growth of single crystals of compounds which cannot be easily grown by other methods. The work of Henisch [1] stimulated many workers to use the gel technique to grow crystals of variety of compounds which are sparingly soluble in water.

Members of the V–VI–VII family belong to the rhombic–bypyramidal system with space group D_{2h}^{16}. BiSCl is one of the members of this family and is a semiconducting ferroelectric crystal. This crystal has so far been grown from melt [2], hydrothermal growth [3] and from vapour [4]. Kramer [5] has extensively worked on BiSCl crystals and has given the crystal data. The present work describes the growth conditions of single crystals of BiSCl in sodium silicate gel at room temperature and the effects due to the change in concentration of the reactants and change in gel density are also investigated and discussed.

2. Experimental details

A known quantity of thiourea solution of concentration ranging from 8 to 10% by weight is mixed with 100 ml of sodium silicate gel solution of density 1.04 g cm^{-3}. The gel solution impregnated with the inner reactant is acidified with 1 N acetic acid and taken in straight tubes of different diameters (1 to 3 cm) and lengths (10 to 25 cm) and allowed to set. The period of gelation is varied from 1 to 24 h by changing the pH value of the gel solution. After gelation, solution of Bi_2O_3 (5 to 10 g) dissolved in 100 ml of 10 N HCl is taken over the set gel. The outer reactant diffuses into the gel medium and reacts with the inner reactant giving rise to single crystals of BiSCl. Similar procedure has been successfully employed by the authors [6, 7] to grow single crystals of SbSI, SbSCl, SbSBr and SbSF in gel.

Crystals of BiSCl are also grown in U-tubes by counter diffusing thiourea solution and Bi_2O_3 dissolved in 10 N HCl. The problem in growing this cystal in U-tube is that the size of the crystal is restricted because of the continuous depletion of the reactants and the limited volume of the gel medium.

A modified version of the U-tube as shown in Fig. 1 was carried out to improve the size of the crystals. The larger volume of the neutral gel (in the beaker) as compared to the U-tube prehaps serves to yield relatively larger crystals and also minimizes gel disruption and this in turn facilitates for the growth of large size crystals [8]. The crystals grown by this method are shown in Fig. 2.

The double diffusion process as shown in Fig. 3a and 3b was carried out to improve the size of the crystal. The crystallization apparatus used in the present investigation are (i) single tube system and (ii) double tube system as suggested by Patel and Bhat

TABLE I Optimum concentration of the reactants, growth period and maximum size of the BiSCl crystals. Gel density is 1.04 g cm^{-3}

Method	Concentration of reactants Thiourea (wt %)	Bi_2O_3 in 100 ml 10 N HCl (g)	Growth period (days)	Max. size (mm)	Remarks
Straight tube	10.0	5.0	50–60	4.0	Good single crystals with controlled nuleation
U-tube	8.0	8.0	25–30	3.0	Controlled nuleation, but crystal size limited
Modified U-tube (Fig. 1)	10.0	5.0	25–30	10.0	Controlled nuleation, good morphology
Single and double tube system (Figs 3a and 3b)	10.0	5.0	15–20	3.0	Spurious nucleation, clusters at the gel boundary

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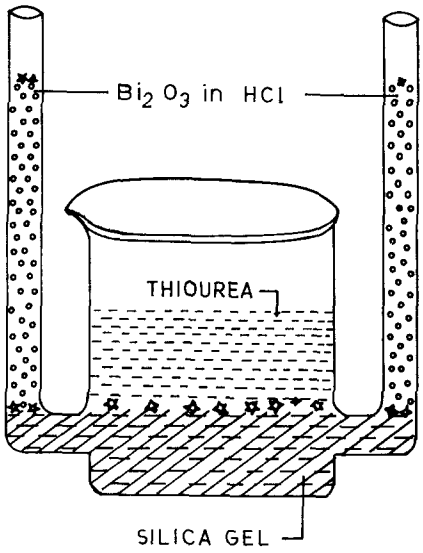

Figure 1 Modified U-tube apparatus.

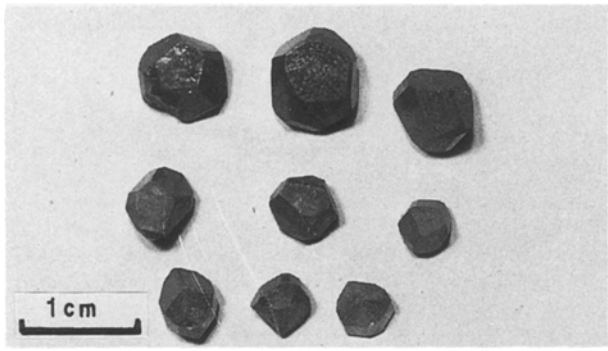

Figure 2 Single crystals of BiSCl grown in modified U-tube.

[9]. It was verified that smaller tubes have been found to impair the size of the crystals. The two systems (Figs 3a and 3b) have the additional advantage of providing a reasonably good facility for seeded growth in gel.

3. Results and discussion

3.1. Crystal growth

The growth of single crystals in gels at ambient temperatures is very effective for those materials having low solubility in water. The crystal growth in gel occurs as a sequence of controlled diffusion of ions through the inert gel medium, the reaction of the ions at some favourable rate to form crystal nuclei and finally growth of the nuclei into crystals of larger size. The crystal density is limited by diffusion of the reactants in the gel. In the case of BiSCl when Bi_2O_3 dissolved in HCl reacts with the inner reactant thiourea, the entire gel medium initially becomes greenish yellow. After 20 days some glittering dots were observed in the gel medium. These dots started growing day by day and after 50 to 60 days single red crystals of BiSCl up to 4.0 mm in size were obtained in straight tubes. The results obtained by different methods are summarized in Table I. In the case of the single tube and double tube system it was observed that the crystallization occurred on the top surface of the gel medium and not within the gel medium. A similar result has been observed in the growth of $CaSO_4 . 2H_2O$ crystals by Butler and Bouchard [10]. In the case of the modified version of the U-tube (Fig. 1) crystals initially started growing on the top surface of the gel. Then it was observed that nucleation occurred on either sides of the limbs. These nucleations normally originate on the top surface of the reactants and keep floating until they attain some critical size and then sink to the surface of the gel medium and grow further. These crystals have high morphological perfection as compared to those crystals grown within the gel medium.

3.2. Effect of reactants

The effect of concentration of the reactants on crystal size and nucleation density was studied by varying the concentration of thiourea (inner) from 8 to 12% by weight and that of the outer reactant Bi_2O_3 (5 to 10 g) in 10 N HCl. It has been observed that crystallization occurred in the entire range of concentrations. However 10% thiourea as inner reactant and 10 g of Bi_2O_3 in 100 ml of 10 N HCl as outer reactant yielded larger cystals of BiSCl with well defined morphology.

3.3. Effect of gel density

The effect of density of gel was studied by changing the density of the gel from 1.03 to 1.06 g cm^{-3}.

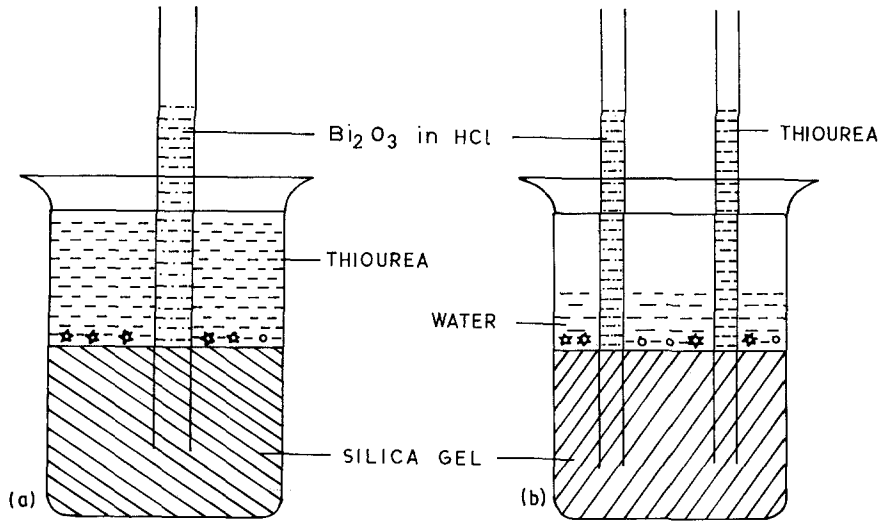

Figure 3 (a) Single tube system. (b) Double tube system.

Crystallization occurs in the entire range of density of the gel solution, but at $1.04\,g\,cm^{-3}$ gel density well defined single crystals of BiSCl were obtained. Regarding the period of gelation, the gel becomes more transparent and aids crystal growth when the period of gelation is within 48 h.

4. Conclusions

Single crystals of BiSCl of size upto 1 cm have been grown in sodium silicate gel at room temperature. 10% thiourea and 10 g of Bi_2O_3 in 100 ml of 10 N HCl yields good crystal of large dimensions. The grown crystals were found to be orthorhombic with space group D_{2h}^{16}.

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