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Growth of single crystals of bismuth sulpho iodide in gel

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Single crystals of bismuth sulpho iodide have been grown in sodium silicate gel at room temperature by diffusing suitable reactants. In the first batch of experiments 3 to 7 g solution of $BiCl_3$ was diffused into the gel containing 10 to 15% KI. Platelets of dimensions upto 5 mm were obtained in a period of 30 days. When thiourea of concentration 5 to 10% was used as the inner reactant and 2 to 4 g of BiI_3 dissolved in 50% HI was used as the outer reactant, thin needles of BiSI were obtained. Larger thick needles of BiSI were also obtained when thiourea was used as the inner reactant and solutions of Bi_2O_3 and BiI_3 were used as the outer reactants. Similarly in the next batch of experiments H_2S was used as the inner reactant instead of thiourea and the same outer reactants were diffused. Platelets of dimensions 5 to 8 mm in size were obtained. The effects due to gel density, concentration of the reactants and the neutral gel on nucleation are also discussed.

1. Introduction

BiSI is one of the chalcohalides belonging to $A^{V}B^{VI}C^{VII}$ compounds (where A = Sb, Bi, As; B = S, Se, Te and C = I, Br, Cl, F). Being a ferroelectric crystal BiSI exhibits a number of interesting properties such as electro-optic, electromechanical, photoelectric [1] and is orthorhombic with space group P_{nam} [2]. This crystal has so far been grown from a vapour [3], by slow cooling [4], by Bridgman Stockbarger [5], by the flux technique [6] and by the hydrothermal method [2]. In vapour growth, needles of length 2 cm and thickness varying from 0.5 to 2 mm were obtained. The sublimation method gives rise to needle-shaped single crystals when grown at 450° C for 100 h. Similarly slow cooling of the molten compound (Bi_2S_3 + BiI_3) at the rate of 5° C h^{-1} yields single crystals in the form of characteristic needles upto 2 cm in length. However, no attempt has been made so far to grow single crystals of BiSI by the gel technique. In the present paper the authors report the growth aspects of BiSI single crystals grown by the gel technique at room temperature. The effects of the concentration of the reactants, density of the gel and the introduction of the neutral gel are also investigated and discussed.

2. Experimental details

2.1. KI as inner and $BiCl_3$ in H_2SO_4 as outer reactants

A known quantity of KI solution of 10 to 15% 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). The period of gelation is found to vary from 1 to 24 h depending upon the pH of the gel solution. After gelation, a solution of $BiCl_3$ (3 to 7 g) dissolved in 100 ml of 3 to 4 M H_2SO_4 is poured over the set gel. The outer reactant diffuses into the gel medium and reacts with the inner reactant (KI) giving rise to black platelets with highly shinning surfaces. Fig. 1 shows the crystals obtained in 7 days when the concentration of the inner reactant is 10% KI and that of the outer reactant is 5 g of $BiCl_3$ in 4 M H_2SO_4. The following reactions are expected to take place

$$BiCl_3 + H_2SO_4 \rightarrow BiSCl + 2\,HCl + 2O_2$$

$$BiSCl + KI \rightarrow BiSI + KCl.$$

Fig. 2 shows the SEM photograph of BiSI single crystal harvested in 30 days.

2.2. Thiourea as inner and BiI_3 in HI as the outer reactants

Experiments were also carried out by using thiourea (5 to 10% by weight) as the inner reactant and a solution of BiI_3 (2 to 4 g) dissolved in 25 to 75% HI as the outer reactant. Fig. 3 shows the crystals obtained when the concentration of the inner reactant is 10% thiourea and that of the outer reactant BiI_3 is 3 g in 50% HI.

2.3. Thiourea as inner and Bi_2O_3, BiI_3 as the outer reactants

To improve the size of the crystals of BiSI, a hybrid method has been adopted. Thiourea of concentration 5 to 10% was used as the inner reactant. Initially Bi_2O_3 (8 to 10 g) dissolved in 100 ml of 10 N HCl was taken over the set gel. After 15 days the outer reactant was removed and freshly prepared solution of BiI_3 (2 to 4 g) in 50% HI was taken. Crystallization was found to occur within a few days and grow into larger size needles (Fig. 4). The harvested needles are of 7 mm in size and are as shown in Fig. 5.

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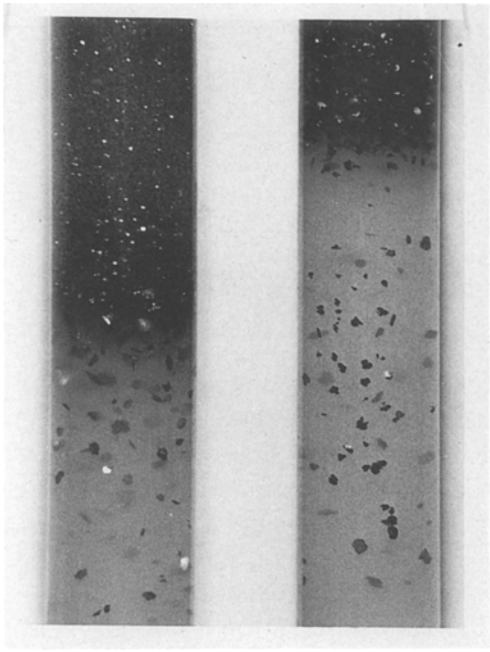

Figure 1 The crystals obtained in 7 days.

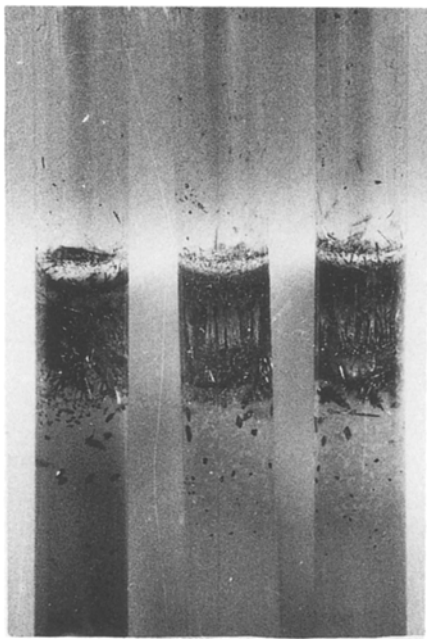

Figure 4 Larger size needles of BiSI grown by hybrid method.

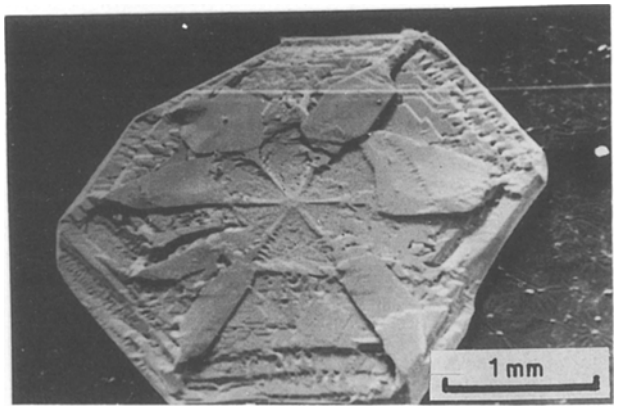

Figure 2 SEM photograph of BiSI single crystal.

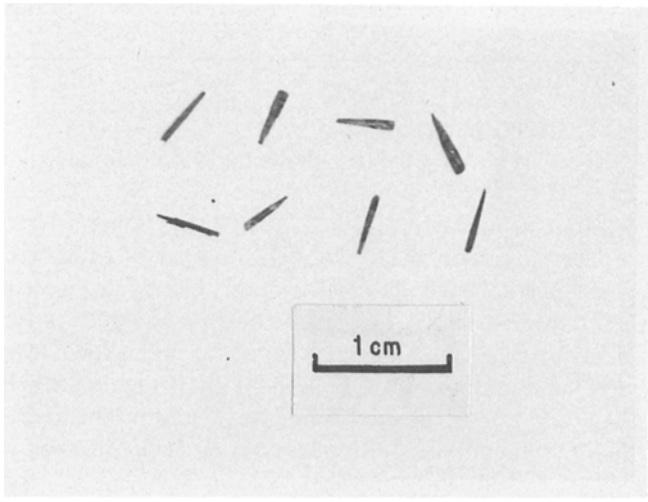

Figure 5 Harvested needles of BiSI.

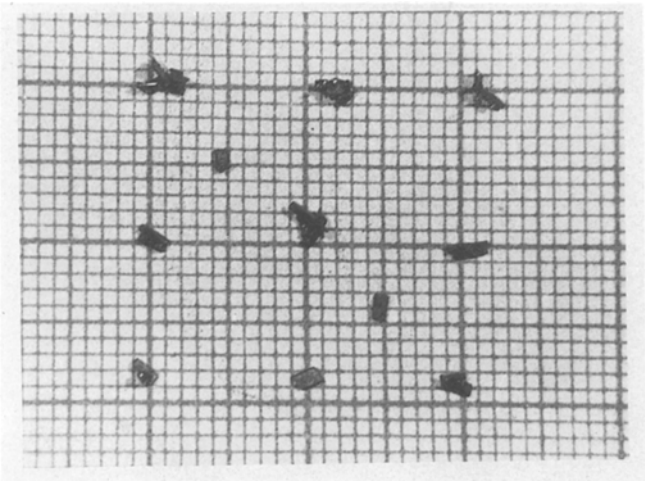

Figure 3 Smaller size needles of BiSI.

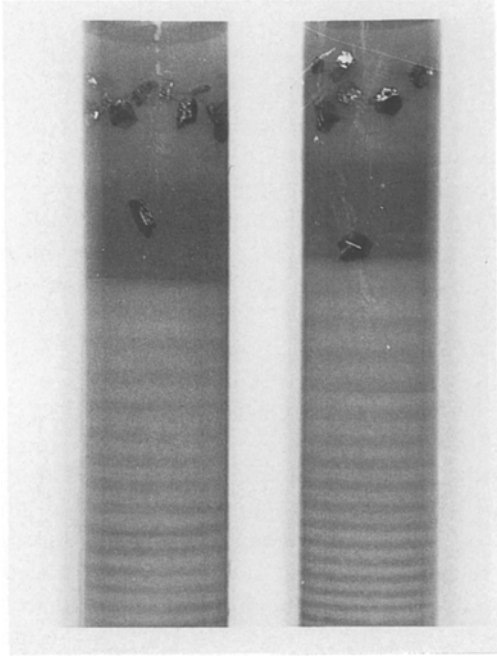

Figure 6 Platelets of BiSI obtained by hybrid method.

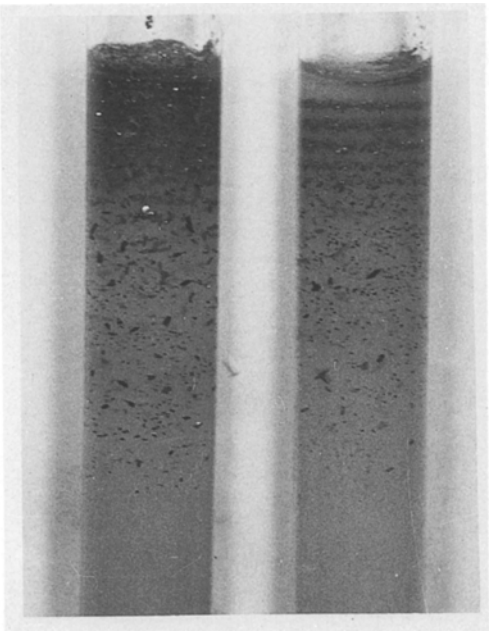

Figure 7 Tiny single crystals of BiSI obtained by second hybrid method.

2.4. H_2S as inner and Bi_2O_3, BiI_3 as the outer reactants

To study the effect of the sulphur donor, thiourea is replaced by H_2S. H_2S gas is passed for about 5 to 10 min into the gel solution. The gel solution is then acidified with 1 N acetic acid for gelation. After gelation the same outer reactants are used as in the previous method (i.e initially 8 to 10 g of Bi_2O_3 in 100 ml of 10 N HCl and later 2 to 4 g of BiI_3 in 50% HI). In this case platelets upto 5 to 8 mm in size were obtained and are as shown in Fig. 6.

2.5. Neutral gel as inner and BiI_3, BiSCl as the outer reactants

Neutral gel of density 1.04 g cm^{-3} was initially set and a solution of BiI_3 (2 to 4 g) in 50% HI was made to diffuse into the gel. The entire gel medium became red in colour within a day or two. This outer reactant was removed and 2 to 5 g of BiSCl crystals dissolved in 100 ml of dilute HCl was taken over the gel. Crystallization was observed in the form of concentric rings. Apart from recrystallization of BiSCl crystals, single tiny crystals of BiSI were also obtained (Fig. 7).

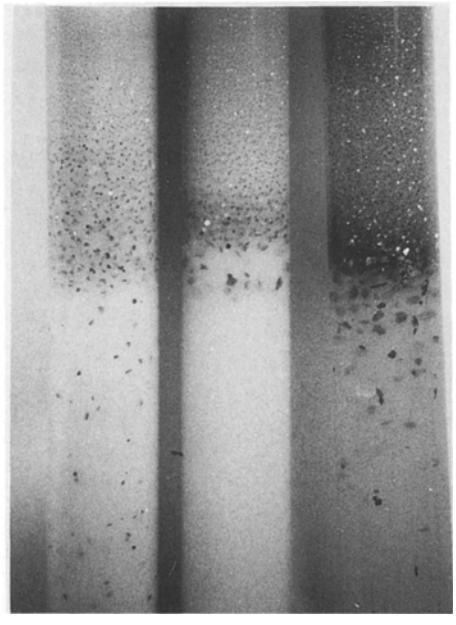

Figure 8 Crystals of BiSI obtained at different gel densities.

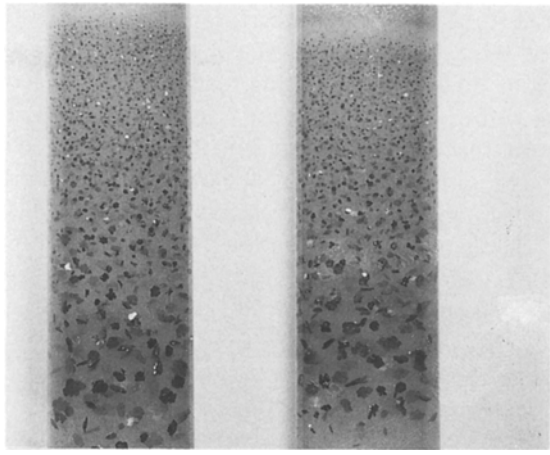

Figure 9 Crystals obtained after the introduction of the neutral gel.

3. Results and discussions

3.1. Crystal growth

In the gel growth technique the gel medium acts as a supporting three-dimensional network to hold the crystal nucleus. The material transport takes place solely by diffusion. Due to the chemical reaction between the inner and the outer reactants of BiSI, initially the gel medium becomes yellow in colour and at a later stage nucleation starts rapidly with glittering dots on the interface. These glittering dots grow daily and black platelets with a highly shining surface were obtained. On the other hand, by the hybrid method as discussed in Section 2.3, black needles upto 7 mm in length were obtained and the nucleation rate was also controlled.

3.2. Effect of reactants

Crystallization takes place for all concentrations of the reactants. In the case of BiSI, good platelets of upto 5 mm were obtained when 10% of KI was used as the inner reactant and 5 g of $BiCl_3$ in 100 ml of 4 M H_2SO_4 was used as the outer reactant. Similarly when 10% of thiourea was used as the inner reactant and 3 g of BiI_3 in 50% of HI was used as the outer reactant, needles of BiSI were obtained.

3.3. Effect of gel density

The effect of density of the gel was studied by changing the density of the gel from 1.03 to 1.06 g cm^{-3} (Fig. 8). Crystallization occurs in the entire range of density of the gel solution, but when the density is more than 1.05 g cm^{-3}, the number of well defined crystals is reduced considerably. The most favourable gel density for obtaining good single crystals is 1.04 g cm^{-3}. The period of gelation has an effective role in the formation of BiSI crystals. When the period of gelation is within 48 h, the gel medium becomes more transparent and better growth results [7].

3.4. Effect of neutral gel

Since the solubility of BiSI is very low, the spontaneous nucleation occurring at the interface is very large. This in turn, affects the size of the crystal. The size of the crystal can in general be increased by decreasing the nucleation. The neutral gel of different heights ranging from 1 to 5 cm were taken over the set gel. The present investigation reveals that though the nucleation rate was controlled to some extent there was no improvement in the size of the crystal (Fig. 9).

4. Conclusions

Thus single crystals of BiSI were grown in sodium silicate gel at room temperature and the growth conditions of the crystal along with the affect of concentration of reactants, density of the gel and the introduction of the neutral gel are also investigated. BiSI single crystals are found to be black in colour with highly shining surfaces and are about 5 mm in size. Needles of this crystal obtained by the hybrid method were about 7 mm in size. X-ray diffraction studies have been done to identify the grown crystals as BiSI.

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