VITA

Mr. R. Roop Kumar was born on 24th March 1962 in Madras, India. He did his early education in D.A.V. Hr. Sec. School, Madras. He received Bachelor of Science and Master of Science degrees in Physics from the University of Madras in 1983 and 1985. He joined as a full time research scholar in Physics Division, Chemical Engineering Department, Alagappa College of Technology, Anna University in March 1987, to work on the growth aspects of V-VI-VII group compounds. He is an author of eight papers in the International journals and he has also presented nine papers in National/International Conferences. The author presented one of his papers in the Eighth American Conference on Crystal Growth held at Colorado, USA 1990 with the financial assistance of 500 US dollars. He has visited USA, London and Paris. He has been awarded CSIR - Senior Research Fellowship in Materials Science to pursue research on V-VI-VII group compounds. He is a member of Indian Association for Crystal Growth, Indian Physical Society and American Association for Crystal Growth.
1. Introduction
BiSI is one of the chalcogenides belonging to A₂B₃C₇⁺⁺ 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 Pmnm[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: S + BiI₃) at the rate of 5°C h⁻¹ yields single crystals in the form of characteristic needles up to 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 BiCl₃ in H₂SO₄ 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 BiCl₃ (3 to 7 g) dissolved in 100 ml of 3 to 4 M H₂SO₄ 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 shining 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 BiCl₃ in 4 M H₂SO₄. The following reactions are expected to take place:

BiCl₃ + H₂SO₄ → BiSO₄Cl₂ + 2 HCl

BiSO₄Cl₂ + KI → BiSI + KCl.

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

2.2. Thiourea as inner and BiOCl 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 BiOCl (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 BiOCl is 5 g in 50% HI.

2.3. Thiourea as inner and Bi₂O₃, BiI₃ 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 BiOCl (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 BiOCl (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.
The crystals obtained in 7 days.

Larger size needles of BSI grown by hybrid method.

Smaller needles of BSI.

Platelets of BSI obtained by hybrid method.
2.4. H$_2$S as inner and Bi$_2$O$_3$, Bil$_3$ as the outer reactants

To study the effect of the sulphur donor, thiourea is replaced by H$_2$S. H$_2$S 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$_2$O$_3$ in 100 ml of 10 N HCl and later 2 to 4 g of Bil$_3$ in 50% H$_2$SO$_4$). 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 Bil$_3$, BiSCI as the outer reactants

Neutral gel of density 1.04 g cm$^{-3}$ was initially set and a solution of Bil$_3$ (2 to 4 g) in 50% H$_2$SO$_4$ 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 BiSCI crystals dissolved in 100 ml of dilute HCl was taken over the gel. Crystalization was observed in the form of concentric rings. Apart from recrystallization of BiSCI crystals, single tiny crystals of BiSI were also obtained (Fig. 7).

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$_2$SO$_4$ was used as the outer reactant. Similarly when 10% of thiourea was used as the inner reactant and 3 g of Bil$_3$ in 50% of H$_2$SO$_4$ 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.

References

Received 1 September 1988
and accepted 13 February 1989.
Growth of single crystals of bismuth sulpho chloride in gel

R. ROOP KUMAR, G. RAMAN AND F. D. GNANAM
Crystal Growth Centre, Anna University, Madras-25, India

Single crystals of the sparingly soluble compound, BiSCI 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 BiSCI upto 10 mm in size have been grown in a period of 20 to 25 days. The crystals grown have been identified as BiSCI 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 $D_{2h}^5$. BiSCI 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 BiSCI crystals and has given the crystal data. The present work describes the growth conditions of single crystals of BiSCI 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:O$_3$ (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 BiSCI. 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 BiSCI are also grown in U-tubes by counter diffusing thiourea solution and Bi:O$_3$ dissolved in 10 N HCl. The problem in growing this crystal 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>
<thead>
<tr>
<th>Method</th>
<th>Concentration of reactants</th>
<th>Bi:O$_3$ in 100 ml 10 N HCl (g)</th>
<th>Growth period (days)</th>
<th>Max. size (mm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight tube</td>
<td>10.0</td>
<td>5.0</td>
<td>50-60</td>
<td>4.0</td>
<td>Good single crystals with controlled nucleation</td>
</tr>
<tr>
<td>U-tube</td>
<td>8.0</td>
<td>8.0</td>
<td>25-30</td>
<td>3.0</td>
<td>Controlled nucleation but crystal size limited</td>
</tr>
<tr>
<td>Modified U-tube (Fig. 1)</td>
<td>10.0</td>
<td>5.0</td>
<td>25-30</td>
<td>10.0</td>
<td>Controlled nucleation good morphology</td>
</tr>
<tr>
<td>Single and double tube system (Figs 3a and 3b)</td>
<td>10.0</td>
<td>5.0</td>
<td>15-20</td>
<td>3.0</td>
<td>Spurious nucleation, clusters at the gel boundary</td>
</tr>
</tbody>
</table>

0022-2461/89 $03.00 + .12 $ 1989 Chapman and Hall Ltd.
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 temperature 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 Bi₂O₃ 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 CaSO₄·2H₂O 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 Bi₂O₃ (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 Bi₂O₃ in 100 ml of 10 N HCl as outer reactant yielded larger crystals 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 1 Modified U-tube apparatus](image1)

![Figure 2 Single crystals of BiSCl grown in modified U-tube](image2)

![Figure 3 (a) Single tube system, (b) Double tube system](image3)
Crystallization occurs in the entire range of density of the gel solution, but at 1.04 g cm\(^{-1}\) 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 BiO\(_3\) 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\(_{3h}^3\).

References

3. V. I. Popolitov, Kristalllografia, 13 (1968) 375.
7. Ibid. ibid. 75 (1980) 466.

Received 1 September 1988
and accepted 13 February 1989
Effect of Seeding on the Growth of BiSCl Single Crystals in Gel

1. Introduction

Members of V-VI-VII family belong to the rhombic-bipyramidal system with space group Pnma. BiSCl, a semiconducting ferroelectric crystal, is one of the members of this family. This crystal has so far been grown from melt (NITSCHE, MERZ), hydrothermal (POPOLITOV), vapour (DONGES) and gel (ROOP KUMAR et al.). The present work deals with the effect of seeding on the growth of BiSCl single crystals in sodium silicate gel at room temperature. The effects due to the change in the concentration of the reactants and that of the gel density are also investigated and discussed.

2. Experimental

Experiments were performed by using straight tubes and modified U-tube apparatus. Thiourea solution of concentrations ranging from 8 to 10 percent by weight was used as the inner reactant and a solution of Bi$_2$O$_3$ (3-10 g) dissolved in 100 ml of 10 N HCl was used as the outer reactant. By modified U-tube apparatus (ARORA) single crystals of BiSCl of dimensions up to 10 mm were obtained in a period of 15-25 days when 10% thiourea was used as the inner reactant and 10 g of Bi$_2$O$_3$ dissolved in 10 N HCl was used as the outer reactant. When experiments were performed in straight tubes with similar conditions time delay was observed for nucleation, compared to U-tube method and hence the growth time also gets extended. To improve the size of the crystals, seeding of BiSCl was performed. Initially the gel solution with the inner reactant thiourea (8-10% by weight) was allowed to set. At the time of gelation, seeding of BiSCl at different depths (2-10 cm) was performed (Fig. 1). After gelation the outer reactant Bi$_2$O$_3$ (3-10 g) dissolved in 100 ml of 10 N HCl was poured over the set gel. It was observed that seeding at a depth of 4 cm yielded controlled growth of BiSCl (Fig. 2). When seeding depth is more, dendritic growth has been observed. Seeding...
at different time interval was also performed and observed that this factor does not have striking effect on the growth of BiSCl.

Fig. 1. Seeding of BiSCl at different depths
Fig. 2. Controlled growth of BiSCl after seeding

3. Results and discussion

Materials having low solubility can be grown by gel. The growth process in gel occurs as a sequence of controlled diffusion of ions through the inner gel medium, the reaction of ions at some favourable rate to form crystal nuclei and finally growth of the nuclei into crystals of larger size. In the case of BiSCl when Bi\(_2\)O\(_3\) dissolved in HCl reacts with the inner reactant thiourea the entire gel medium initially turns into greenish yellow in colour and after a long period of 50-60 days, single crystals of BiSCl of red colour sizes upto 4 mm were obtained in straight tubes (Koop Kumar et al.). To improve the size of the crystals, seeding of BiSCl crystals in straight tubes was performed and observed that seeding at a depth of 4 cm induced no further nucleation and good single crystals of size nearly 10 mm were obtained in a period of 20 to 25 days.

Experiments were performed by varying the concentration of thiourea (inner) from 8 to 15 percent by weight and that of the outer reactant Bi\(_2\)O\(_3\) (10% w) in 10 N HCl. It has been observed that crystallisation occurs in the entire range of concentrations. But when 10% thiourea and 10% of Bi\(_2\)O\(_3\) in 10 N HCl were used as the reactants, larger size BiSCl single crystals of well defined morphology were obtained.

The density of the sodium silicate gel was varied from 1.03 to 1.06 g/ml and it was observed that gel density of 1.04 g/ml was optimum to yield well defined single crystals of BiSCl.
4. Conclusion

Single crystals of BiSCl of sizes up to 10 mm have been grown in sodium silicate gel at room temperature after seeding, when 10 percent thiourea was used as the inner and 10 g of $\text{Bi}_2\text{O}_3$ in 10 N HCl as the outer reactant. The grown crystals were red in colour.

References


(Received April 12, 1990, accepted April 30, 1990)

Authors' address:

c/o Dr. P.D. GNANAM
Alagappa College of Technology
Anna University
Madras - 600 025, India
Effect of Neutral Gel on the Growth of Single Crystals of Bismuth Sulfo Iodide

Introduction
BISI is one of the chalcocahilde belonging to \( \text{AB}_2\text{Cl}_4\text{I}_7 \) compounds (where \( \text{A} = \text{Sb, Bi, As}; \text{B}=\text{S,Se,Te} \text{ and } \text{C}=\text{I,Cl,Br,F} \)). It is a semiconducting crystal which exhibits a number of interesting properties such as electro-optic, electro-mechanical, photoelectric etc. (SASAKI). It is orthorhombic with space group \( \text{Pnam} \) (POPOLOV). This crystal has been so far grown from vapour (ARIVUGLI et al.), by slow cooling (NITSCHE, MERZ), by Bridgman Stockbarger (HORAK, CERMAK), by flux technique (NASSUE et al.), by hydrothermal method (POPOLOV), and by gel (ROOP KUMAR et al.). In the present paper the authors report the effect of neutral gel on the growth of single crystals of bismuth sulfo iodide.

Experimental
10-15 % of KI solution is mixed with 100 ml of sodium silicate gel solution of density 1.04 g/ml. The gel solution impregnated with the inner reactant is acidified with 1 N acetic acid and taken in straight tubes of different diameters (1-3 cm) and lengths (10-25 cm). The period of gelation is found to vary from 1 to 24 hours. After gelation, solution of \( \text{BiCl}_3 \) (3-7 g) dissolved in 100 ml of \( \text{H}_2\text{SO}_4 \) of concentrations of 3-4 % is poured over the set gel. The outer reactant diffuses into the gel medium and reacts with inner reactant (KI) giving rise to black platelets of highly shining surfaces.

Figure 1 shows the SEM photograph of BISI single crystal harvested in 30 days. Similar experiments were performed with thiourea and \( \text{H}_2\text{S} \) as the inner reactants and a mixture of \( \text{Bi}_2\text{S}_3 \) and \( \text{BiI}_3 \) as the outer reactants. Needles of BISI crystals were obtained when \( \text{H}_2\text{S} \) was used as the inner electrolyte and \( \text{BiI}_3 \) in HI as the outer electrolyte.
Results and discussion

In gel growth technique the gel medium acts as a supporting three-dimensional network to hold the crystal nucleus. The material transport is taking place solely by diffusion. Regarding BiSI due to the chemical reaction between inner and outer reactants, initially the gel medium becomes yellow in colour and at a later stage nucleation starts rapidly with glittering dots. These dots grow day by day and after a few days black platelets of highly shining surface of BiSI were obtained.

Effect of neutral gel

In the absence of neutral gel, spontaneous nucleation occurring at the interface is very large. This spontaneous nucleation in turn affects the size of the growing crystals and thereby only 3 mm size platelets of BiSI single crystals were obtained. The size of the crystal can in general be increased by decreasing the nucleation. Ultimately to improve the size of growing crystals and also to control the rate of nucleation, experiments were performed by pouring neutral gel of various heights ranging from 0-8 cm. Initially the gel impregnated with the inner reactant KI of particular concentration was allowed to set. After gel set, neutral gel of different heights was poured over the set gel. Later, after the gel set of neutral gel, a solution of BiCl₃ dissolved in 3-4 cm of H₂SO₄ was poured over to set neutral gel as the outer reactant. It was observed that the greater the height of the neutral gel, the larger the size of the growing crystal. But the present investigation reveals that when the height of the neutral gel was 4 cm, good single platelets of BiSI of dimensions upto 7-9 mm were obtained with controlled nucleation in a period of 30 - 40 days (Fig. 2).
Pig. 2. Optimised growth condition of BiSI after the introduction of neutral gel

**Effect of reactants**
Crystallisation takes place for all concentrations of the reactants. In the case of BiSI, good platelets of sizes upto 7-9 mm were obtained when 10% KI were used as the inner reactant and 5 g of BiCl₃ in 4 M H₂SO₄ as the outer reactant.

**Effect of gel density**
Experiments were performed by varying the gel density from 1.03 to 1.06 g/ml. It was observed that the crystallisation occurs in the entire range of density of gel solution. When the density is more than 1.05 g/ml the number of well defined crystals is reduced considerably. Hence, the most favourable gel density for getting good single platelets of BiSI is 1.04 g/ml.

**Conclusion**
Thus single crystals of BiSI were grown in sodium silicate gel at room temperature and the effect of neutral gel in the growth of BiSI is studied and found that after the introduction of neutral gel, platelets of BiSI of sizes nearly 7-9 mm were obtained in a period of 30-40 days, when 10% KI were used as the inner reactant and 5 g of BiCl₃ in 4 M H₂SO₄ as the outer reactant. The grown crystals were confirmed by X-ray analysis.
ROOP KUMAR et al.: Effect of Gel on the Growth of BiSI Crystals

References


(Received July 23, 1990, accepted August 30, 1990)

Authors' address:
c/o Prof. P.D. GNANAM
Alagappa College of Technology
Anna University
Madras - 600025, India
Great attention is at present being devoted to ternary compounds, which show semiconducting properties. To this group belong also substances of the type $A^V B^{VI} C^{VI}$ where $A^V$ being antimony or bismuth, $B^{VI}$ being sulphur, selenium or tellurium and $C^{VI}$ being chlorine, bromine or iodine. BiSCI is one of the members of this family belonging to rhombic-bipyramidal system with space group Pnam. This crystal has so far been grown from melt (Nitsche and Merz 1960) by hydro-thermal (Popolitov 1969) and from vapour (Donges 1950). The present work describes the effect of growth parameters that affect BiSCI single crystals in sodium silicate gel at room temperature.

Known quantity of thiourea solution of desired concentration was mixed with 100 ml of sodium silicate gel solution of density 1.04 gm/ml. The gel solution impregnated with inner reactant was acidified with 1 N acetic acid and taken in straight tubes of different diameters (1-3 cm) and lengths (10-25 cm) and allowed to set. The period of gelation was varied from 1 to 24 hours by adjusting the pH value of the solution. After gelation, solution of Bi$_2$O$_3$ (3-10 gm) dissolved in 100 ml of 10 N HCl was taken over the gel. The reactant on reaction with the inner gives rise to single crystals of BiSCI of sizes upto 4 mm in a period of 50-60 days. Similar procedure has been successfully employed by Raman et al (1984, 1986) to grow single crystals of antimony sulpho halides in gel.

A modified version of the U-tube as shown in Figure 1 was carried out to improve the size of the crystals. The neutral gel of density 1.04 gm/ml was set using acetic acid. Thiourea of concentration 10 percent by weight was poured over the set gel and a solution of Bi$_2$O$_3$ in HCl were taken on either sides of the limbs. Crystals started growing initially on the boundary of the gel. Later nucleation sites were also observed on either sides of the limbs. These nucleation normally originate on the top surface of the reactant until they attain some critical size and then sink to the boundary of the gel and grow further. These crystals have high morphological perfection as compared to those grown on the boundary of the gel. Experiments were repeated by varying the concentration of thiourea from 8 to 15 percent by weight and that of Bi$_2$O$_3$ from 3 to 10 gms in 100 ml of 10 N HCl. Good single crystals of about 10 mm in size were obtained in a period of
Effect of growth parameters on BiSCI single crystals in gel

Figure 1. Modified U-tube apparatus used to grow BiSCI single crystals.

15-25 days when the concentrations of thiourea was 10 percent by weight and that of bismuth oxide was 10 gm in 100 ml of 10 N HCl. The harvested crystals are shown in Figure 2.

Figure 2. Single crystals of BiSCI.

Single tube and double tube systems were performed to grow single crystals of BiSCI (Roop Kumar et al 1989) as adopted by Patel and Bhat (1972) to grow single crystals of BaSO₄ and SrSO₄. Similar results have been observed by Butler.
and Bouchard (1971) in the growth of CuSO₄·2H₂O crystals. The additional advantage of this system is that it provides a good facility for seeded growth in gel.

![Figure 3. BISCl crystals grown under seeding at a depth of 4 cm.](image)

![Figure 4. Dendritic growth of BISCl when the seeding depth is more than 4 cm.](image)

To improve the size of the crystals and to reduce the growth period seeding was adopted in straight tubes. Initially the gel solution with the inner reactant thiourea of concentration 10 percent by weight was allowed to set. At the time of gelation seeding of BISCl at different depths starting from 2 cm to 10 cm were performed. After gel set the outer reactant (3-10 gm of Bi₂O₃ in 10 N HCl) was poured over the set gel. It was observed that seeding at a depth of 4 cm yielded controlled growth of BISCl (Figure 3). When the seeding depth was less
Effect of growth parameters on BiSCI single crystals in gel

than 4 cm, there was no improvement in the size of the seeded crystals and greater the depth of the seed dendritic growth has been observed (Figure 4). Seeding at different time intervals was also performed and observed this factor does not have

Table I. Results obtained by different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Concentration of reactants</th>
<th>Maximum size in mm</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight tube (without seeding)</td>
<td>10 5 50-60 4</td>
<td></td>
<td>Good single crystals</td>
</tr>
<tr>
<td>(with seeding)</td>
<td>10 10 20-25 10</td>
<td></td>
<td>Large size crystals</td>
</tr>
<tr>
<td>U-tube</td>
<td>8 8 25-30 3</td>
<td></td>
<td>Controlled nucleation with crystal size limited</td>
</tr>
<tr>
<td>Modified U-tube (Figure 1)</td>
<td>10 10 15-25 10</td>
<td></td>
<td>Controlled nucleation with high morphological perfection</td>
</tr>
<tr>
<td>Single and double tube systems</td>
<td>10 5 15-20 3</td>
<td></td>
<td>Spurious nucleation with clusters at the gel boundary</td>
</tr>
</tbody>
</table>

striking effect on the growth of BiSCI. The growth period was just 20-25 days and the size of the crystals obtained were 10 mm. The results obtained by different methods are summarised in Table 1.

References

Butler S R and Bouchard R J 1971 J. Crystal Growth 10 163
Patel A R and Bhat H L 1972 J. Crystal Growth 12 286
Popolitov V I 1969 Kristallografiya 13 376
Raman G, Gnanam F D and Ramasamy P 1984 J. Crystal Growth 69 404
------1986 J. Crystal Growth 75 466
Growth and microhardness studies of bismuth sulphochloride

R. ROOP KUMAR, G. RAMAN, F. D. GNANAM
Alagappa College of Technology, Anna University, Madras 25, India

Sulphohalogenides of antimony and bismuth have drawn much attention because of their optical, photoconducting and ferroelectric properties [1]. Bismuth sulphochloride is one among this group of materials having orthorhombic structure with space group Pnam [2]. This crystal has been grown from melt [3], hydrothermally [4], from vapour [5] and by gel [6]. The structure determination of this material has been extensively worked by Kramer [7]. Since BiSCl is very sparingly soluble in water, it cannot be grown from solution by the conventional technique. This letter deals with the growth aspects of BiSCl single crystals in acid solution by the counterdiffusion technique. The microhardness and work-hardening coefficient of this material are also reported.

10 g Bi₂O₃ was dissolved in 100 ml 7 m HCl. To this solution 10% thiourea (100 ml) was added and it was maintained at a temperature of 305 K in a constant-temperature bath. Slow evaporation resulted in spontaneous nucleation. Good single crystals of BiSCl of size nearly 8–10 mm were obtained in a period of 15–20 days. These crystals were used as seed crystals for obtaining large BiSCl crystals. When experiments were carried out the liberation of sulphur from thiourea was observed with time. This could be prevented by counterdiffusing water through a gel medium similar to the one adopted by Varga and Vannay to grow β-Agl single crystals [8].

Fig. 1 is a schematic diagram of the apparatus used. This apparatus consisted of an inner container of 1 l capacity fitted with a sintered disc of different grades (G₁ to G₅) having different porosity in the range 5–170 μm and an outer beaker. Sodium silicate gel was set with acetic acid over the sintered disc to a height of 0.7 cm. A freshly prepared BiSCl solution was placed in the inner container and a seed of optimum size was suspended. Water was placed in the outer beaker. The water level in the outer beaker was maintained at 1 cm above the inner solution. The whole set-up was kept in a constant-temperature bath maintained at 305 K. The diffusion of water from the outer container to the inner through the gel medium maintained the required supersaturated condition for the growth process. Seed crystals 5 mm in size were suspended in the solution. The seed rotation was maintained at 60 r.p.m. Crystals of size up to 15 mm were grown in a period of 30 days (Fig. 2).

The growth rate and perfection of a crystal grown from solution depends primarily on the degree of supersaturation. In the case of BiSCl the optimization of supersaturation of the solution was obtained by varying the concentration of any one of the components, viz. thiourea, Bi₂O₃ or HCl. In the first batch of experiments the concentration of thiourea was maintained at 10 wt% and 10 g Bi₂O₃ was dissolved in HCl of different molarities (5 m to 10 m). In the second set of experiments the concentration of thiourea was varied from 8 to 12 wt% whereas the concentration of Bi₂O₃ (10 g) in HCl (7 m) was maintained constant. Similarly, the concentration of Bi₂O₃ was varied from 5 to 10 g, keeping the concentration of HCl (7 m) and thiourea (10 wt %) constant. Single crystals of good structural perfection were obtained when the concentrations of thiourea and Bi₂O₃ were 10 g each and the HCl concentration was 7 m. When the concentration of the reactants were less than the optimum concentrations the growth rate was very poor, and when the concentrations were increased spurious nucleations occurred, affecting the seeds.
The diffusion of water through the gel column was controlled by the height of the gel column. The height of the gel column was varied from 0.2 to 1.5 cm and it was observed that when the height of the gel column was 0.7 cm and the pressure height difference between the solution and water was 1 cm, no additional nucleation was observed and the growth was practically undisturbed. Single crystals of BiSCI of size up to 15 mm were obtained in a period of 30 days.

Microhardness is primarily used to study the mechanical strength of a material [9]. Selected smooth surfaces of BiSCI single crystals were subjected to static indentation test at room temperature. A Leitz Wetzlar hardness tester fitted with a diamond pyramidal indentor attached to an incident light microscope was used in the present work. The load \( P \) was varied from 2 to 100 g and the time of indentation was kept constant at 10 s for all of the trials. The diagonal length \( (d) \) of the indented impressions obtained at various loads were measured using a micrometer eyepiece. Several indentation trials at each load were carried out and the average value of the diagonal lengths of the indentation mark in each trial was calculated. The microhardness value \( H_w \) was calculated using \( H_w = 1.8544 \frac{P}{d^2} \) kg mm\(^{-2} \), where \( H_w \) is the Vickers microhardness number, \( P \) is the applied load in kg and \( d \) is the average diagonal length of the indentation impression in mm. The relationship between \( P \) and \( d \) is given by \( P = K_1 d^n \), where \( K_1 \) is the standard hardness and \( n \) is a constant. The value of \( n \) represents the work-hardening coefficient. The microhardness value was found to decrease with increasing load (Fig. 3). The work-hardening coefficient \( (n) \) was determined using the least-squares fit method and found to be equal to 1.9 (Fig. 4).

To summarize, it has been established experimentally that single crystals of BiSCI can be grown from acid solution, coupled with the counterdiffusion technique. Reddish crystals of BiSCI of size up to 15 mm have been obtained in a period of 30 days. The grown crystals have been confirmed by X-ray analysis. Microhardness studies reveal the work-hardening coefficient of BiSCI to be 1.9.

**References**


Received 19 October and accepted 20 December 1990