Asian Journal of Chemistry Vol. 15, No. 1 (2003), 71–74

Growth and Spectral Investigation of BiSCl Crystals

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Bismuth sulphochloride (BiSCl) has been prepared by the reaction of $BiCl_3$ dissolved in H_2SO_4 and acetic acid in silica gel. The IR and Raman spectra were recorded in the range of 600–50 cm^{-1}. The IR spectra reveal that the frequency bands are sensitive to sulphur substitution and the Raman spectra show that the bands below 200 cm^{-1} are halogen sensitive.

Key words: Growth, Spectral, BiSCl crystals.

INTRODUCTION

Ferroelectric materials have gained much importance due to their use as sonar detectors and photographic pickups[1]. They also find application in high capacity computer memories due to large dielectric constant under ordinary conditions in the reversible spontaneous polarization[2].

Among the V-VI-VII group compounds BiSCl has alone been reported as useful material for device applications and this material has been used in light modulation, time controlling devices and IR radiation converters[3]. It is a semiconducting crystal which exhibits a number of interesting properties such as electrooptic, electromechanical, photoelectric, etc. This crystal has so far been grown from vapour, slow cooling and by gel technique[4]. In the present paper the authors report the growth and spectral investigations on BiSCl crystals.

EXPERIMENTAL

A known quantity of thiourea solution of concentration ranging from 8 to 10% by weight was mixed with 100 mL sodium silicate gel solution of density 1.04 g/cm^3. The gel solution impregnated with the inner reactant was acidified with 1 N acetic acid and taken in straight tubes of different diameters (1–3 cm) and length (10–25 cm) and allowed to set. The period of gelation was varied from 1–24 h and by changing the pH value of the solution. After gelation, solution of Bi_2O_3 (5–10 g) dissolved in 100 mL of 10 N HCl was taken over the set gel. The outer reactant diffused into the gel medium and reacted with the inner reactant giving rise to single crystals of BiSCl.

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Crystals of BiSCl are grown is U-tubes like counter-diffusion thiourea with Bi_2O_3 in 10 N HCl. The size of the crystals is restricted because of the continuous depletion of the reactants and the limited volume of the gel medium.

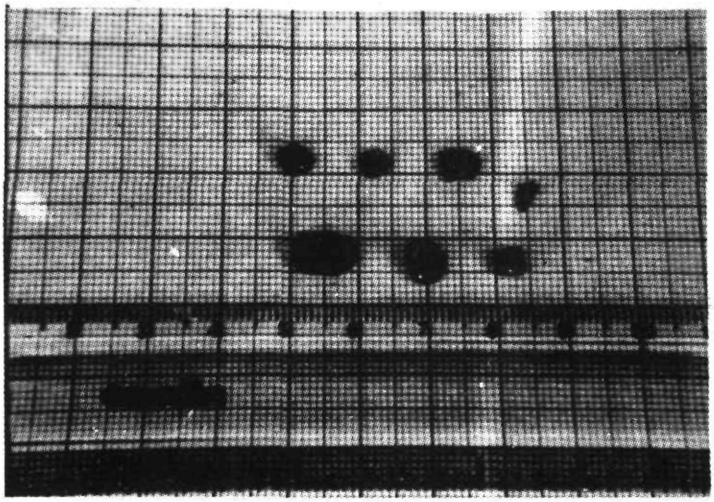

Fig. 1. Gel grown crystals of BiSCl.

RESULTS AND DISCUSSION

In the present investigation crystals with different morphologies were obtained at different depths in the test tube and at different growth conditions. The growth will be affected by the nucleation of crystals just below the gel interface. They start growing from a bunch of nucleation with the diffusion of field solution into the gel. With lapse of time, the thickness of the crystal increases with faster rate along (001) direction. This is due to the presence of diffusion field around the crystal tips of the needle and the crystals grow into the supersaturated solution whereas the sides of the crystals are in contact with a largely exhausted solution.

In the absence of neutral gel, spontaneous nucleation occurring at the interface is very large. This, in turn affects the size of the growing crystals. A solution of Bi_2O_3 in 10 N HCl was poured over the set gel as the outer reactant, pH range between 4.5 and 7.0, gave rise to prismatic needle-shaped crystals.

The IR and Raman spectra of BiSCl have been extensively investigated[5], whereas little is known about the optical measurements of the other bismuth components. Teng *et al.*[6] have analyzed the symmetrical coordinates of SbSI using group theory. The overall phonon spectrum of this material is explained in which the crystal is formed by atomic change along c-axis interacting weakly between them[7].

The IR spectrum of BiSCl shows a peak at 68 cm^{-1} which is similar to the vibrational frequency of BiI_3. The peaks lying below 150 cm^{-1} are assigned to Bi-Cl stretching modes. As the Bi-S modes are very broad, chlorine sites might contribute largely to the intermolecular forces of binding in the solid state. A peak at 167 cm^{-1} is a characteristic peak of Bi-S Bond[8]. The broad band around 126

cm^{-1} may be assigned to sulphur stretching vibration. Its stretching band positioned below 100 cm^{-1} can trace the interaction between the bands. When antimony is replaced with bismuth, the band below 100 cm^{-1} is well sharpened. This sharpening is due to large reduction in the vibrational degrees of freedom of chlorine. When smaller antimony in the crystal lattice is replaced with larger bismuth then it can fit well into the voids formed by the chlorine lattice. Although BiSCl exhibits peaks below 150 cm^{-1} the intermolecular force forms the bonding interaction between bismuth and chlorine and it will be due to overtones[9]. The Raman spectra are given in Fig. 1, while Raman peaks due to voids in BiSCl crystals are given in Fig. 2.

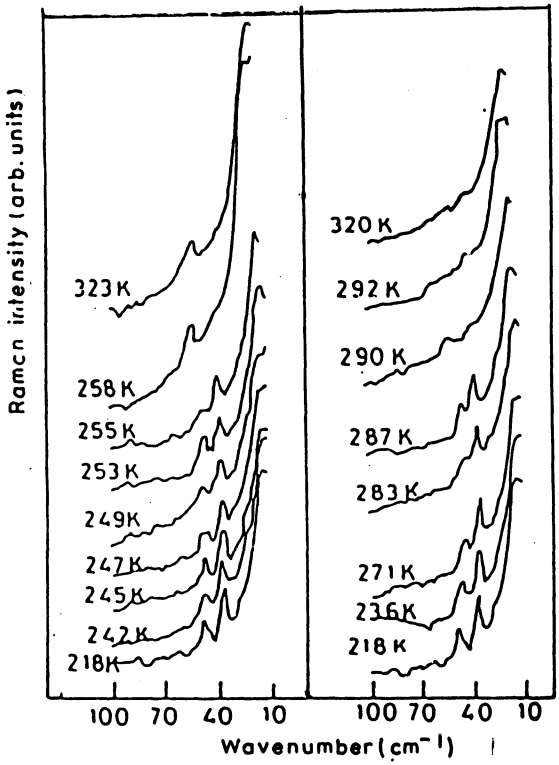

Fig. 1. Raman spectra of BiSCl crystals.

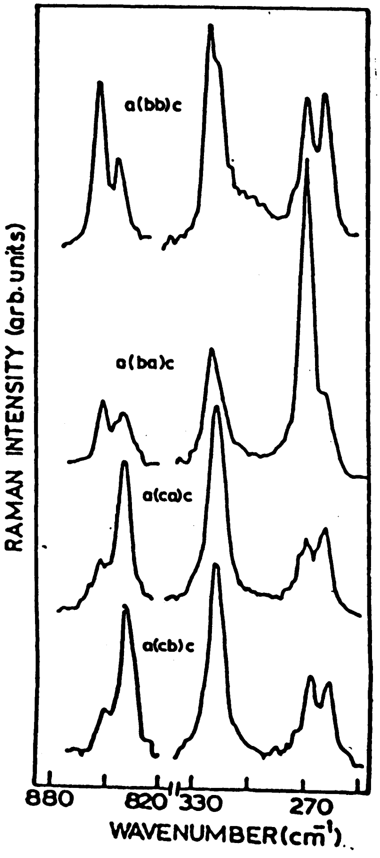

Fig. 2. Raman peaks due to voids in BiSCl crystals.

The present study of IR spectra of BiSCl give a clear picture of the structure of single molecule in the unit cell. Three fundamental absorption bands have been observed at 549, 380 and 148 cm^{-1}. The vibrational representation of angular XYZ molecule is represented as $\nu = 3$ Å and all the vibrations are found to be active in both IR and Raman spectra[10]. The appearance of high frequency IR bands at 540 cm^{-1} in the spectrum of BiSCl suggests that these vibrations correspond to Bi-S stretching vibrations[11]. The rest of the observed frequency results from the allowed combination of the stretched frequencies[12].

Conclusion

The IR spectra were taken in polytex FIR-30 in the region 700–50 cm^{-1}; the frequencies for all sharp bands are expected to be accurate to ±1 cm^{-1}. The band ionicity of the compound will decrease when other atoms are replaced[13]. Hence it is concluded that the potential energy distribution will be used to check the validity of the assignments.

ACKNOWLEDGEMENT

The authors (KS) and (TR) are thankful to the University Grants Commission for awarding the Minor Research Project.

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(*Received*: 29 April 2002; *Accepted:* 6 July 2002) AJC-2797

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MAY 7, 2003

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