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Atomic substitution and ferroelectric phase transition in $Bi_xSb_{1-x}SI$

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In order to characterize the effect caused by the atomic substitution on the ferroelectric phase change in $A_VB_{VI}C_{VII}$ compounds, we have studied a series of $Bi_xSb_{1-x}SI$ mixed crystals. The Raman scattering, together with dielectric constant data, indicate that the Curie temperature T_C falls from 293 K to a nearly zero value when the Bi concentration x is raised from 0 to 0.75. Within this Bi concentration range, the ferroelectric phase transition in the mixed crystal is associated with a SbSI-like soft-mode behavior. The effect of the Sb by Bi substitution is, in many aspects, very comparable to that caused by hydrostatic pressure.

I. INTRODUCTION

The physical properties of the $A_VB_{VI}C_{VII}$ compounds (A = Sb or Bi, B = S or Se, C = I or Br) have been thoroughly investigated[1-5] and continue to raise a great deal of interest. The most intensely studied member of this family is SbSI. Interest has been particularly centered on the optical-mode instability associated with the displacive ferroelectric phase transition in the crystal. From investigation on specific heat,[6] pyroelectric current,[7] x-ray reflection,[8] and phase boundaries,[9] it is found that the ferroelectric phase transition at 293 K in SbSI is first order. In the paraelectric phase, SbSI is orthorhombic[10] and belongs to the D_{2h}^{16} space group with four molecules in the unit cell. Below 293 K, it becomes ferroelectric with the C_{2v}^{9} space group. It has been shown[11] that all the lattice dynamics can be accounted for if one assumes that the material is formed of double linked chains along the $\vec{c}$ axis. In this assumption, the space group is C_{2h}^{2} and the interaction between atoms perpendicular to the chains is neglected. Thus the unit cell contains only two molecules.

Very little is known about BiSI. It is believed that at room temperature it exhibits the same orthorhombic structure as SbSI.[12] A ferroelectric phase transition at 115 K was reported[13,14] but the existence of such a transition has not been confirmed by more recent dielectric constant measurements on pure BiSI crystal.[15]

The phonon spectrum of both SbSI and BiSI has been determined by Raman scattering[16] and also by far infrared reflectivity measurements.[17] One found a similarity between the Raman spectra of those two compounds. Nevertheless, whereas near the ferroelectric phase transition temperature, SbSI exhibits a soft-mode behavior, there are rather strong indications at the present stage of experimentation that this is not the case for BiSI.

In view of this fundamental difference, it seemed interesting to undertake a detailed study on the $Bi_xSb_{1-x}SI$ mixed crystals. In addition to the inherent interest on soft mode in relatively disordered structure such as mixed crystals, this study should bring information on the eventual phase change in BiSI. Raman scattering measurements have been made for a series of samples with concentrations $0 \leq x \leq 1$. From these data, it results clearly that the mixed crystal maintains a soft-mode behavior for the Bi concentration lower than 0.70. On the contrary, for $x > 0.70$, no appreciable temperature dependence of the phonon frequency is observed within a temperature range extending from 7 to 300 K. The highest-frequency mode in SbSI shows two-mode behavior in the $Bi_xSb_{1-x}SI$ mixed crystal in contrast with all the other optical modes which exhibit one-mode behavior.

From dielectric measurements, it is found that the influence of the Bi concentration on the Curie temperature is very comparable to the hydrostatic pressure effect as reported by Peercy.[18]

II. RAMAN SCATTERING AND SOFT MODES IN $Bi_xSb_{1-x}SI$

In this section, we present the Raman data of a series of $Bi_xSb_{1-x}SI$ mixed crystals with x varying from 0 to 1. For each Bi concentration, Raman spectra are studied as a function of temperature. The experimental setup is the same as that described in an earlier work.[16] The incident beam is supplied by a yttrium-aluminum-garnet laser emitting at 1.06μm so that all the spectra are excited by transmission Raman spectroscopy. In the analysis of the experimental results, the fol-

lowing aspects will be discussed: (i) behavior of the highest-frequency mode, (ii) variation of the Curie temperature, and (iii) soft mode in the mixed crystal.

A. Behavior of the highest-frequency mode

The Raman spectrum of a mixed crystal contains generally the contribution of the normal modes of the two end members in addition to the spectrum specific to the mixed crystal. In such two-mode behavior, the mode frequencies in the mixed crystal are close to those of the single modes in the two end members. In contrast with this, it is usually found that in highly ionic crystals only one set of modes appears in the mixed crystal with its frequency gradually changing from that of one end member to its counterpart in the other end member. In such a case, one refers to a one-mode behavior.

Figure 1 shows the evolution of a typical Raman spectrum at 300 K as the Bi concentration varies from $x=0$ to $x=1$. The striking fact emerging from examination of Fig. 1 is that the highest-frequency mode, which occurs at 322 cm^{-1} in SbSI and at 286 cm^{-1} in BiSI,[16] obviously shows a two-mode behavior in the mixed crystal. On the contrary, all the other optical modes exhibit a one-mode behavior.

Bearing in mind the empirical criterion discussed

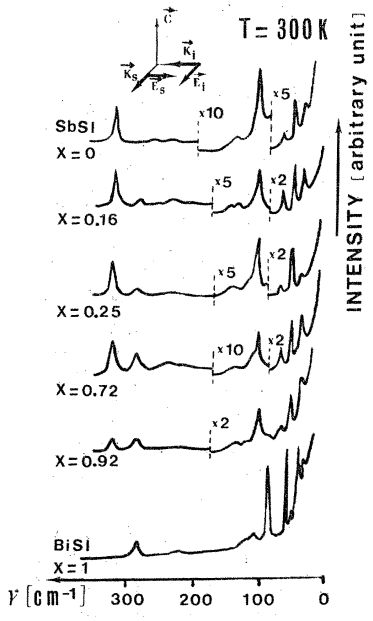

FIG. 1. Raman spectra as a function of Bi concentration x in $Bi_xSb_{1-x}Si$ mixed crystals. $\vec{k}_i$ and $\vec{k}_s$ are the incident and scattered wave vectors and $\vec{E}_i$ and $\vec{E}_s$ designate the incident and scattered polarizations.

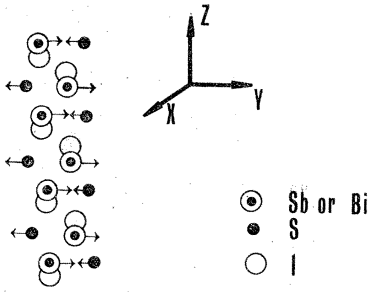

FIG. 2. Representation of the eigenvector of the highest-frequency normal mode in SbSI. The z axis is chosen parallel to the ferroelectric $\vec{c}$ axis.

in the above paragraph, the two-mode behavior of the highest-frequency mode can be understood in terms of the analysis of the normal-mode function. We have indeed assigned this mode to the stretching of the Sb (or Bi) sublattice against the S sublattice (Fig. 2). The absence of the motion of iodine in this mode has been justified by the consideration that the substitution of iodine by bromine leaves its frequency unchanged.[16] On the assumption that the Sb (or Bi) atom is bound to the S atom by strong covalent bonds, this highest-fre-

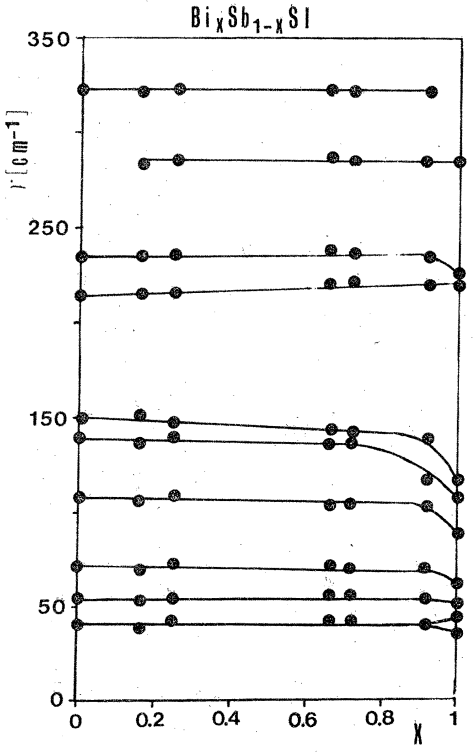

FIG. 3. Variation of the Raman-active phonon frequencies with different Bi concentration x in $Bi_xSb_{1-x}SI$ mixed crystals.

quency mode has an accentuated covalent character which favors two-mode behavior. All the other modes invoking vibrations of iodine have ionic or partially ionic character which favors, on the contrary, one-mode behavior.

In a recent lattice-dynamic calculation based on a simple Born–van Kármán model, Furman, Brafman, and Makovsky[19] have used a set of eigenvectors in which the 319-cm^{-1} mode in SbSI contains also vibrations of iodine, but the central Sb and S groups have the same scheme as those we proposed; they also noticed that the Sb-S bond represents the largest force constant and determines solely the frequency of this mode. Hence, there is no fundamental contradiction between our argument and this calculation.

In Fig.3, the phonon frequencies as a function of Bi concentration are displayed. One can state that the modes which show accidental degeneracy at 40 cm^{-1} in the mixed crystal and in SbSI are well split in BiSI. This observation may be due to an increase of the interchain interaction in BiSI as compared with SbSI which exhibits a nearly one-dimensional structure.

B. Variation of the Curie temperature with concentration

In order to investigate the influence of the substitution of Sb by Bi on the ferroelectric phase change, we have determined the Curie temperature T_C in the mixed crystal by two methods: Raman scattering and dielectric constant measurement. The last method will be discussed in Sec. III. For the former case, we have used the fact that from selection rules, the soft mode is Raman active in the ferroelectric phase but inactive for this process in the paraelectric phase. Then, by following the soft mode when the temperature is raised and by extrapolating its frequency toward zero, one can estimate the temperature for which the crystal passes from one phase to other. In Fig. 4, the variation of T_C with Bi concentration x is shown. For comparison, some values which have been reported in Ref. 15 are also represented by the full circles on the same figure. One can state that T_C follows a rapid linear decrease when x is increased from 0 to 0.75, with a slope of about 40 K per 0.1 Bi concentration.

It clearly appears that the T_C vs concentration x curve is, in many aspects, very similar to the T_C vs hydrostatic pressure curve as determined by Peercy.[18] This close resemblance of the effect on T_C caused by these two parameters suggests also that the elastic properties of the mixed crystal would contribute greatly to the change of its ferroelectric properties.

Another remark on the variation of T_C is that

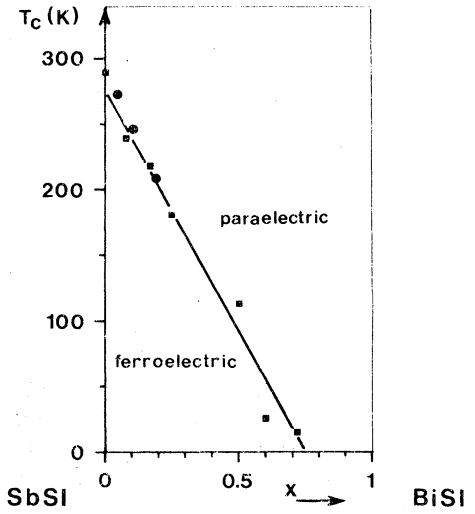

FIG. 4. Curie temperature as a function of the Bi concentration x in $Bi_xSb_{1-x}SI$ mixed crystals. Squares: our data; full circles: data taken from Ref. 15.

the extrapolation of the T_C-vs-x curve shows that T_C may become negative for x higher than 0.75. This fact may explain why we failed to observe in BiSI the SbSI-like displacive type ferroelectric transition even down to 7 K.

C. Soft-mode behavior

SbSI has a somewhat complicated soft-mode behavior[2,4] which is associated with the first-order ferroelectric transition at 293 K. It is the first ferroelectric material in which anticrossing between energies of soft phonon and other optical phonons has been observed. In contrast with this, the temperature-dependent Raman spectra of BiSI does not reveal any soft-mode evidence down to 7 K. In order to find out how the Bi substitution influences the soft-mode behavior in a $Bi_xSb_{1-x}SI$ mixed crystal and till what Bi concentration x the phase transition remains a first-order displacive type, the Raman spectrum is studied as a function of temperature for each value of x extending from 0 to 1. Our attention is focused on the Γ_1 low-frequency spectrum which is also the symmetry of the soft mode in SbSI. It is found that as far as a phase transition may exist in mixed crystal, this is true for x increasing from 0 to 0.75; the ferroelectric transition is associated with a softening of at least one of the optical modes.

In Fig. 5, we show a typical evolution of the Γ_1 low-frequency spectrum as the temperature is approaching T_C, while in Fig. 6, the frequency shift versus temperature curves of several Bi concentrations x are shown. Since it is difficult to discriminate accurately between the two coupled

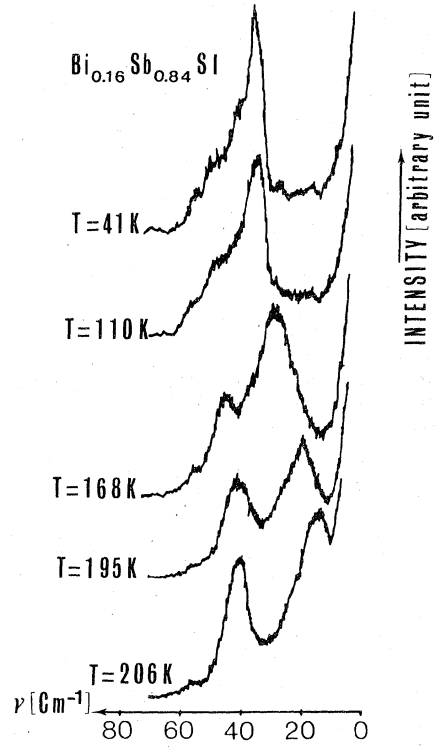

FIG. 5. Typical Raman spectrum change showing the decrease in frequency of the soft mode with temperature.

modes during the anticrossing process, first, because of their unequal intensities in the resultant large band structure, and second, because of the rapid lowering of T_C as x increases, nevertheless, it is true that anticrossing between the soft-phonon and other optical-phonon energies exists even in the mixed crystal, as evidenced by Fig. 7 for a small concentration x.

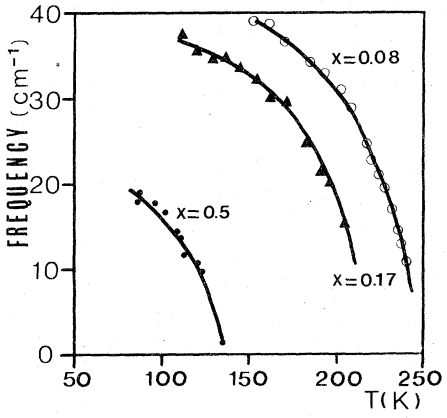

FIG. 6. Frequency-vs-temperature plot of several Bi concentrations x in $Bi_xSb_{1-x}SI$.

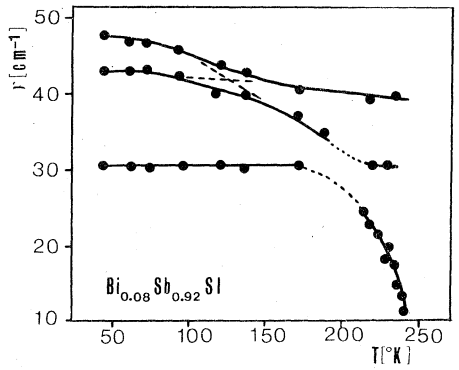

FIG. 7. Typical evolution of the three lowest-frequency modes showing anticrossing between vibrational energies as the temperature is approaching T_C.

Since the soft-mode behavior is closely related to the lattice dynamics, we think that the elaboration of a realistic model would be worthwhile. In the calculation presented by Furman *et al.*,[19] this point of view is not taken into account since the long-range Coulomb forces are neglected. This approximation may be justified in the paraelectric phase far away from the ferroelectric transition; it is certainly inadequate near the transition.

III. DIELECTRIC PROPERTIES OF $Bi_xSb_{1-x}SI$

In addition to the inherent interest which allows the ferroelectric transition to be characterized, the measurements of the dielectric constant may yield precious information about the order of the transition. Dielectric constant data were taken at 1 kHz, using a GR 1615A capacitance bridge. Gold electrodes were applied perpendicularly to the $Bi_xSb_{1-x}SI$ $\vec{c}$ axis. The variation of the capacitance C for different values of x extending from 0 to 0.75 is plotted as a function of the temperature in Fig. 8. One remarks that all the curves exhibit a maximum whose position coincides with the Curie temperature given by the Raman data within an error of ±2 K. On the contrary, for x greater than 0.75, we did not find any singularity of the capacitance down to 7 K. In Fig. 9, the reciprocal of the capacitance is displayed in the vicinity of T_C for several Bi concentrations x.

Owing to the method used by Draegert and Singh,[20] one can establish that if the transition is first order, the ratio of the slope of the reciprocal dielectric constant just below to just above T_C would have a value inferior or equal to −4, whereas for a second-order transition, this ratio must be higher than −4. We have found that this ratio lies between −0.2 to −0.3 for a Bi concentration varying from 0.25 to 0.60. This suggests that the transition may be a second-order one. Based on

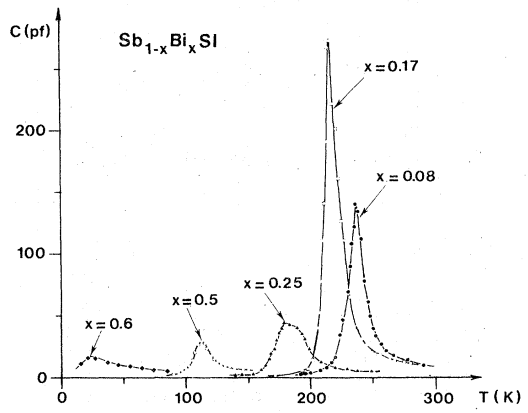

FIG. 8. Electrical capacitance of $Bi_xSb_{1-x}SI$ as a function of temperature for different Bi concentrations x.

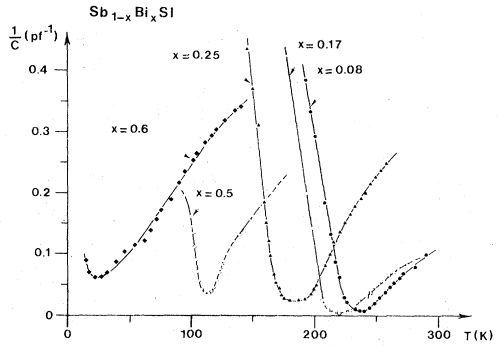

FIG. 9. Reciprocal capacitance of $Bi_xSb_{1-x}SI$ near the phase transition temperature for different Bi concentrations x.

their dielectric data, Ishikawa, Shikata, and Toyoda[15] have observed the same change of the order of transition in $Bi_xSi_{1-x}SI$ even though the critical Bi concentration x is reported to have a value less than 0.25. A last comment about Fig. 9 concerns the curve for 0.25, where the minimum shows a considerable broadening. This plateaulike minimum may be due to mixture of domain orientations.

IV. DISCUSSION

In order to test the presence of any low-frequency vibrations in SbSI and BiSI, we also used the technique based on the diffuse scattering of x rays and compared the diffuse streak pattern of these two materials. It is shown[21] that the diffuse scattering intensity $I(s)$ due to the disorder caused by a harmonic vibration $\vec{u}$ is proportional to $(\vec{s}\cdot\vec{u}_0)^2$

$$I(s)\sim(\vec{s}\cdot\vec{u}_0)^2,$$

where $\vec{s}$ is the scattering vector and $\vec{u}_0$ the magnitude of the vibration which is assumed to have the following form:

$$\vec{u}=\vec{u}_0\sin(\omega t+\phi).$$

On the other hand,

$$m\omega^2\langle u^2\rangle=\frac{\hbar\omega}{\exp(\hbar\omega/kT)-1}\sim kT \quad \text{if } \hbar\omega\ll kT .$$

Hence

$$I(s)\sim T/\omega^2,$$

and the diffuse scattering intensity is enhanced by the presence of low-frequency vibrations. In particular, if the mode is soft, $\omega^2\sim T-T_C$ and

$$I(s)\sim T/(T-T_C) .$$

Our measurements indicate that an intense diffuse scattering of x rays is found in the case of SbSI, in agreement with its well-known soft-mode behavior. On the contrary, no trace of this kind of scattering has been observed in BiSI.

V. CONCLUSION

From Raman data, it turns out that the highest-frequency mode shows two-mode behavior in mixed $Bi_xSb_{1-x}SI$ crystals. This observation is in contrast with all the other optical modes which exhibit one-mode behavior. Furthermore, for the range $0<x<0.5$, the mixed crystal undergoes a ferroelectric transition, indicated by the existence of SbSI-like soft-mode behavior. For a Bi concentration higher than 0.5, the Curie temperature becomes too low to allow a study of the soft mode in the ferroelectric phase.

With respect to Raman selection rules, as well as from dielectric constant measurements, the Curie temperature is found to follow a linear decrease with increasing Bi concentration. The similarity of the Curie temperature change between the effects caused by Sb-Bi substitution and by hydrostatic pressure suggests that the former acts like an internal pressure which increases in the mixed crystal as x increases. For a more detailed interpretation, it would be interesting to see whether a lattice-dynamics calculation based on the Cochran theory on ferroelectrics is possible. The knowledge of the change in elastic properties will be a great help to elaborate a more quantitative interpretation of the soft-mode behavior in these mixed crystals.

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