Note added in proof: The theoretical values calculated by Hildebrandt, Stephenson & Wagenfeld (1973) can only be considered as an approximation for low-Z elements since they use averaged screening constants. Improved calculations have been published by Stephenson (1976) for $Z = 2$ to 23. However, the results for silicon differ very little from those quoted in the present work.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1979). A**35**, 857–858

Sign reversal of piezo-optic birefringence in mixed crystals of KCl–KBr. By G. S. KUMAR, R. ETHIRAJ and V. G. KRISHNA MURTY, *Department of Physics, Osmania University, Hyderabad* 500 007, *India*

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Abstract

The dispersion of stress–optical coefficient C_{001} of mixed crystals of KCl–KBr is measured in the wavelength range 250–520 nm. Sign reversal of C_{001} is observed in all crystals studied.

Recently, Ethiraj, Krishna Murty & Bansigir (1978) have studied the dispersion of piezo-optic birefringence characterized by the stress–optical coefficients C_{001} (stress along a cube axis and observation along another axis) and C_{110} (stress along a face diagonal and observation along a cube axis) in mixed crystals of KCl–KBr in the wavelength range 300–620 nm. They found that the values of these coefficients decrease more rapidly with decrease of wavelength (dispersion larger) than in the case of pure crystals. In earlier studies on piezo-optic dispersion, a reversal in the sign of the coefficients C_{001} and C_{110} has been observed in the ultraviolet region in the case of some alkali halide crystals (KCl, KBr and KI: Srinivasan, 1959; Rahman & Iyengar, 1967; RbBr, RbI, CsCl and CsI: Laiho & Korpela, 1968). In order to see whether the stress–optical coefficients, C_{001}, of mixed crystals of KCl–KBr undergo reversal in sign as in the case of pure crystals, their dispersion was measured in the wavelength range 250–520 nm and the results obtained are reported in this paper.

The experimental method described by Ethiraj, Krishna Murty & Bansigir (1978) was employed for evaluating the coefficient C_{001} at different wavelengths of KCl, KBr and five mixed crystals of KCl–KBr. The crystals grown by Ethiraj, Krishna Murty & Bansigir (1978) were used in the present investigation. The dispersion curves for all the crystals studied are shown in Fig. 1. As can be seen from Fig. 1, the value of C_{001} of each crystal decreases slowly at first and then rapidly with the decrease of wavelength and undergoes a reversal in its sign at a particular wavelength ($\lambda_{\rm rev}$) depending on the composition of the crystal. In KCl and KBr, the sign reversal occurs at 251 nm and 273 nm, respectively. These values are in good agreement with the values 255 nm and 276 nm reported by Srinivasan (1959) for these crystals. In Fig. 2 are plotted the reversal wavelengths as a function of mol% of KBr for all crystals. It is interesting to note that the $\lambda_{\rm rev}$ varies non-linearly with mol% of KBr

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with a maximum value around equimolar concentration. This may be explained as follows.

It is known that a uniaxial stress in a crystal causes a shift in the position and a change in the intensity of the fundamental absorption peaks resulting in a change in the electronic polarizability. In addition, a uniaxial stress also splits the absorption peaks and each of these split components contributes to the electronic polarizability. If the resultant polarizabilities for light polarized in directions parallel and perpendicular to the direction of stress are not equal, piezo-optic birefringence occurs. The magnitude and sign of birefringence at any wavelength depend on the relative contributions of the split components of the absorption peaks.

In KCl, KBr and KI, the piezo-optic birefringence (coefficient C_{001}) decreases rapidly as the first fundamental absorption peak is approached and undergoes sign reversal in the neighbourhood of this peak. In these crystals, as the size of the halide ion increases the absorption peaks shift to longer wavelengths. Since the sign reversal of birefringence takes place in the vicinity of the first absorption peak, the $\lambda_{\rm rev}$ of these crystals should also shift to longer wavelengths. Studies on dispersion of piezo-optic birefringence confirm this. For instance, the first absorption peak in KCl, KBr and KI occurs at 162 nm, 187 nm and 219 nm, respectively (Hilsch & Pohl, 1930), while the piezo-optic birefringence in these crystals undergoes sign reversal at 255 nm, 276 nm and 338 nm. Thus the value of $\lambda_{\rm rev}$ of a crystal depends on the positions of the absorption peaks in the ultraviolet.

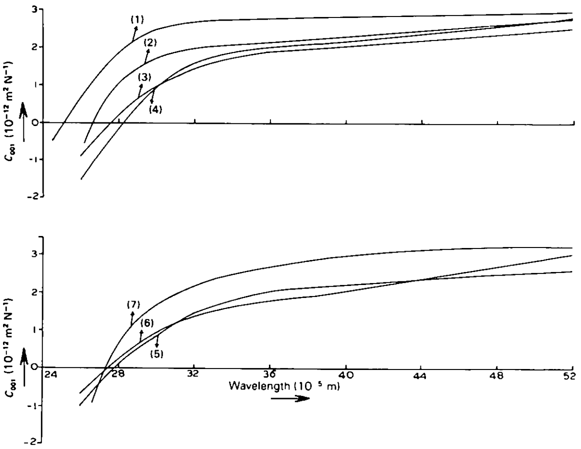

Fig. 1. Dispersion of the stress–optical coefficients C_{001}. (1) KCl, (2) $KCl_{0.86}KBr_{0.14}$, (3) $KCl_{0.69}KBr_{0.31}$, (4) $KCl_{0.59}KBr_{0.41}$, (5) $KCl_{0.43}KBr_{0.57}$, (6) $KCl_{0.21}KBr_{0.79}$, (7) KBr.

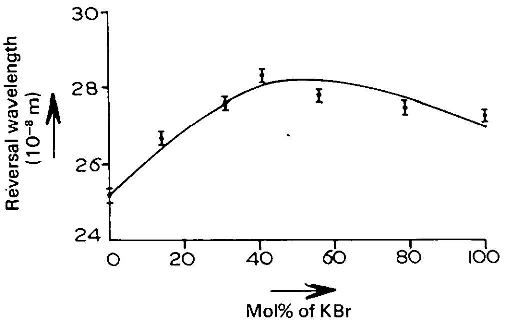

Fig. 2. Reversal wavelength *versus* mol% of KBr.

The variation of C_{001} of each mixed crystal with wavelength (Fig. 1) is quite similar to that of a pure crystal. In all mixed crystals except $KCl_{0.86}KBr_{0.14}$, the value of $\lambda_{\rm rev}$ is larger than that of pure KBr (Fig. 2). The ultraviolet absorption studies in mixed crystals of KCl–KBr (Mahr, 1961) show the presence of both Cl^- and Br^- peaks, their heights and positions depending on the relative concentration of the ions in the mixture. However, around equimolar concentration, both KCl and KBr peaks are prominently present but with increasing concentration of KBr, all the absorption peaks shift to longer wavelengths. It is possible that all these peaks are split on the application of uniaxial stress and contribute to birefringence.

One may therefore expect the values of $\lambda_{\rm rev}$ of mixed crystals to be larger than those of pure crystals, as is observed in the present investigation, because of the presence of both KCl and KBr peaks and their shift towards longer wavelengths. For a given mixed crystal, the positions and relative heights of the absorption peaks determine the value of its $\lambda_{\rm rev}$. The maximum value of $\lambda_{\rm rev}$ around equimolar concentration may be due to the presence of both the series of peaks prominently. Thus the behaviour of $\lambda_{\rm rev}$ in the mixed crystals of KCl–KBr is similar to the behaviour of other properties like microhardness, dislocation density, ionic conductivity (Subba Rao & Hari Babu, 1978), dielectric constant (Kamiyoshi & Nigara, 1971) and thermal expansion (Venudhar *et al.*, 1979), which show a non-linear variation with mol% of KBr, the deviation from linearity being maximum around the equimolar concentration.

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