

F bands in KCl-KBr mixed crystals

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Abstract. Gamma ray-induced *F* bands in melt grown mixed crystals of KCl and KBr are studied at room temperature. The effect of dislocations on *F*-centre density in mixed crystals has been discussed. In addition, the influence of composition of mixed crystals on *F* band parameters has been studied. The behaviour of observed *F* bands is correlated to local strained regions and to the configuration of *F* centre in mixed crystals.

Keywords. Mixed crystals; colour centres; dislocation density; optical density; absorption spectra.

1. Introduction

Of the many impurities that can be substitutionally added to the alkali halides, one of the most simple systems results from the substitution of alkali or halide ions that are foreign to the host crystal. Since most of the alkali halides are mutually soluble over a large concentration range, studies can easily be made of the effect of large concentrations of these impurities. Smakula *et al* (1963) made a systematic study of the effects of these monovalent impurities upon the location and half-width of different colour centres. Similar observations on colour centres in mixed crystals have been made by other workers also (Gaikazyan *et al* 1960; Gaikazyan and Zavadovskaya 1960; Thyagarajan 1966).

Arends *et al* (1965) studied the *F*-centre growth curves in KCl-KBr mixed crystals and observed that the *F*-centre density decreases while the dislocation density increases for the mixed crystals compared to pure components (see also Smakula *et al* 1962, 1963). The above results show that the influence of composition on dislocation density and *F*-centre concentration is just the opposite. It has been observed by Mizuno and Inoue (1960) that dislocations do play a role in the annihilation of *F*-centres which accounts for the decrease in optical density of mixed crystals.

In the background of these existing results we have made an attempt to study the effect of dislocations on the variation of *F*-centre parameters with composition in KCl-KBr mixed crystals. The crystals were, therefore, grown by a different technique so as to have a different type of dislocation distribution compared to those reported earlier. Its variation with composition was in a random manner (Subramaniam and Bansigir 1980).

2. Experiment

Single crystals of pure KCl, KBr and mixed crystals of KCl-KBr have been grown from melt using a technique described by Subramaniam and Bansigir (1980). Samples of 10 mm × 15 mm × 1 mm were cleaved from as-grown crystals and irradiated with a gamma dose of 10⁶R from ⁶⁰Co source at room temperature. The absorption spectra were recorded using carry-14 spectrophotometer immediately after irradiation, in the range of 300 nm to 700 nm. Such high doses (≈ 10⁶ R) were necessary for mixed crystals as it was difficult to colour these crystals. Freshly cleaved samples were used for recording absorption spectra and care was taken to avoid moisture contamination on the surface of the samples. The spectra were recorded on a number of samples cleaved from different portions of the ingot to take care of variation in composition within the ingot.

Quantitative estimate of dislocation density in various samples has been included in table 1. Impurity contents are those which are present in the Sarabhai Chemicals of GR grade and are same in all the compositions; impurities are not added deliberately in these crystals.

3. Results

Optical absorption spectra of pure KCl, KBr and mixed crystals of KCl-KBr are shown in figure 1a to j where optical absorbance ($\log I_0/I$) is plotted against the photon energy in eV. All these studies are confined to the well-known and prominent *F* band which is observed in the visible region for these alkali halides. Compiled in table 1 are the observed *F* band parameters such as *F* band peak position, half-width, number of *F* centres per cm³ along with the dislocation density.

Figure 2 illustrates the variation of *F* band peak position with composition for KCl-KBr mixed crystals. It is clear from the figure that the *F* band deviates from Mollwo relation towards lower energies. This observation is similar to those of earlier workers (Smakula *et al* 1963).

Table 1. *F* band parameters and dislocation density of KCl-KBr mixed crystals.

Crystal	ϵ_{\max} (eV)	Half width (eV)	No. of <i>F</i> - centres cm ⁻³ N_f (10 ¹⁸)	Dislocation density (10 ⁶ cm ⁻²)
KCl (pure)	2.16	0.400	11.6	>100
KCl _{0.98} Br _{0.14}	2.13	0.425	6.2	20
KCl _{0.79} Br _{0.31}	2.10	0.445	3.0	14.5
KCl _{0.71} Br _{0.29}	2.09	0.435	2.7	24.5
KCl _{0.61} Br _{0.39}	2.06	0.450	2.2	36
KCl _{0.53} Br _{0.48}	2.05	0.443	2.6	39
KCl _{0.41} Br _{0.59}	2.02	0.430	4.0	33
KCl _{0.39} Br _{0.71}	2.01	0.426	5.4	25
KCl _{0.15} Br _{0.85}	1.98	0.415	6.6	20
KBr (pure)	1.97	0.410	7.9	>100

Impurity content: same in all the samples.

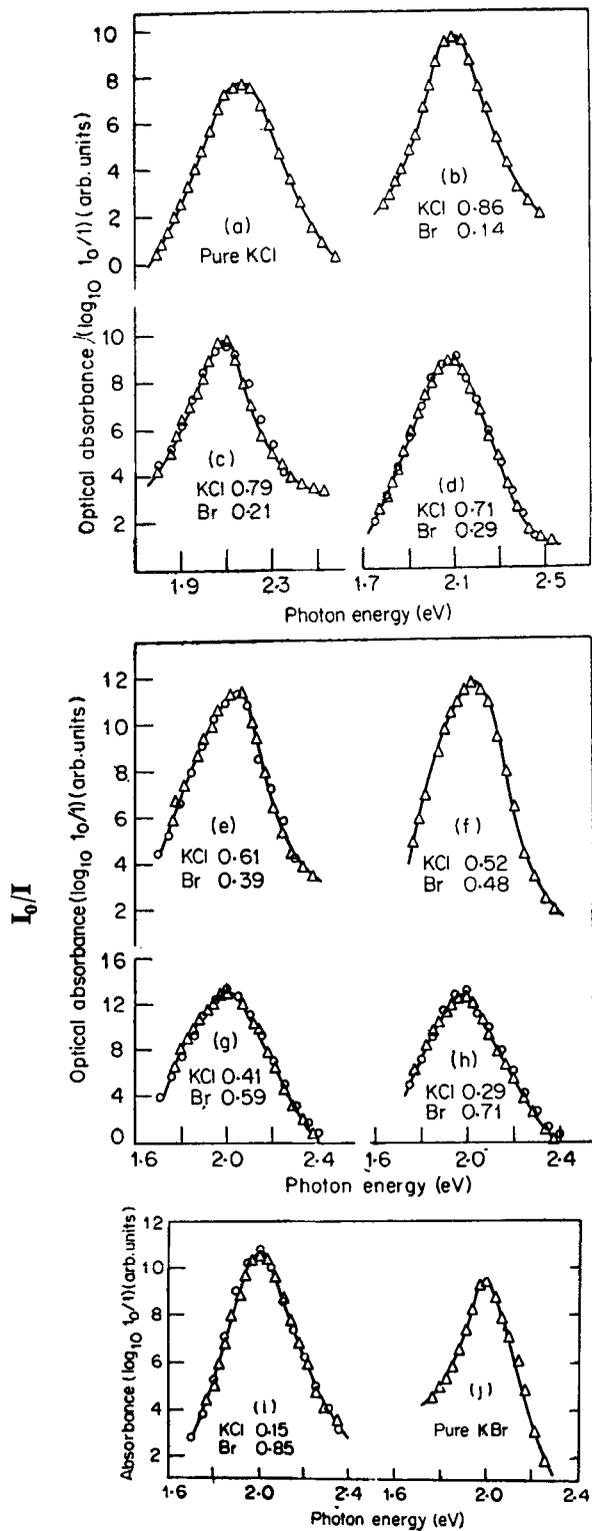
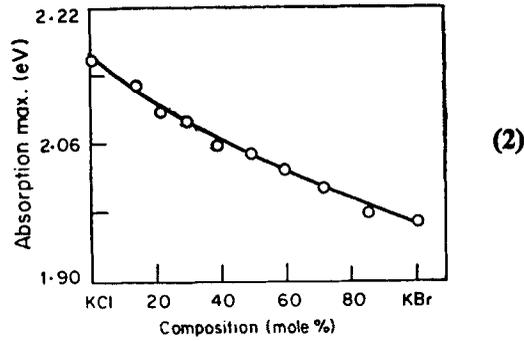
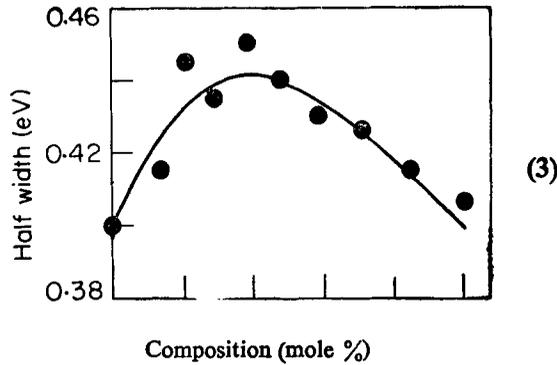


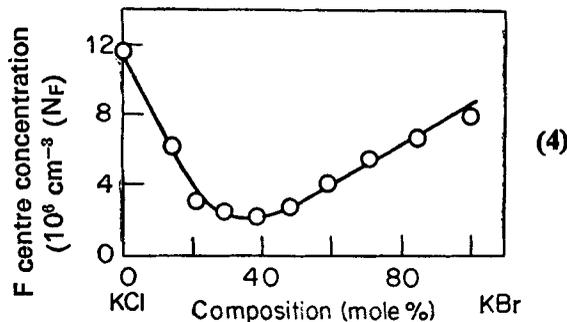
Figure 1. Represents the variation of optical absorbance ($\log I_0/I$) with photon energy in eV.



(2)



(3)



(4)

Figure 2. Influence of composition on the spectral position of the F band.

Figure 3. Influence of composition on the half-width of the F band.

Figure 4. F centre density dependence on the composition.

A Gaussian fit to these spectra was made. The open triangle ($-\Delta-\Delta-$) in figure 1a to j refer to actually observed spectra and the open circle ($-\circ-\circ-$) refer to spectra obtained after making the Gaussian fit to these curves. The overlapping of the curves indicates that the Gaussian fit to these spectra is a good approximation as suggested by Dexter (1956).

Half-width of mixed crystals is plotted as a function of composition (figure 3). A non-linear variation with a maximum for the equimolar composition *i.e.* $\text{KCl}_{0.55}\text{Br}_{0.45}$ was observed and a decrease towards end components on both sides. We have also calculated the number of F centres per cm^3 using the expression (Schulman and Compton 1963)

$$N_F \times f = 0.87 \times 10^{17} \frac{n}{(n^2 + 2)^2} a_{\max} W, \quad (1)$$

where N_F = number of F centres per cm^3 ; f = oscillator strength, a factor which is related to the probability of optical transition producing the absorption; n = refractive index of the crystal; W = half-width of the absorption band; and a_{max} = the absorption coefficient in cm^{-1} at the peak of the absorption band.

Figure 4 illustrates the variation of concentration of F centre with composition for KCl-KBr solid solution, the dose rate being same for all the crystals. It exhibits a nonlinear variation with a minimum for the equimolar composition. (Arends *et al* 1965).

Although the crystals for the present study are grown in a way such that the variation of dislocation density with composition is different from the earlier reported results (see table 1) (Arends *et al* 1965; Smakula *et al* 1962) even then the variation of F band parameters with composition is similar to those reported earlier. This comparative study illustrates the influence of dislocations on absorption spectra as discussed below.

4. Discussion

When alkali halides are exposed to gamma rays various colour centres are formed; one giving the strongest absorption is the F band which is an electron trapped at negative ion site. Mixed crystals acquire much less colouration compared to pure crystals when exposed to gamma rays, hence a dose nearly $\sim 10^6\text{R}$ was necessary to produce F bands of sufficient intensity. In the present study the following three observations were made: (i) A lower concentration of F centres in mixed crystals (ii) shift of F band peak position towards lower energies and (iii) broadening of half-width.

4.1 Role of dislocations

Crystals for the present study were grown in a different manner so as to have a random variation of dislocation density with respect to composition. Although the variation of dislocation density in this mixed system are different from those reported earlier (Smakula *et al* 1962; Arends *et al* 1965) as is clear from the data given in table 1, the variation of F band parameter such as F centre concentration, half-width and F band peak position remain the same. These observations show that the presence of dislocations is not playing a major role.

It was observed by Miessner (1953) and Mizuno and Inoue (1960) that the disorder present in the vicinity of dislocations in solid solutions favour the rate of diffusion of both the F centres and holes and leads to an increased annihilation of F centres. This was supposed to be a reason for the decrease in optical density of mixed crystals near the equimolar composition where dislocation density was observed to be maximum (Arends *et al* 1965). According to these observations the F centre density in pure KCl and KBr should be less compared to that in mixed crystals in the present system as the dislocation density is very high in pure KCl and KBr ($\sim 10^6/\text{cm}^2$) and is low in mixed crystals ($\sim 10^4/\text{cm}^2$). We have observed a similar type of variation in F centre density as pointed out by earlier workers (Arends *et al* 1965; Gaikazyan *et al* 1960) with a minimum value of F centre density for the intermediate composi-

tion. Thus we can say that the dislocations do not play a major role in the production of F centres.

4.2 Size effect

In a KCl-KBr mixed system inclusion of ions of larger ionic radii (Br^-) in place of ions of smaller radii (Cl^-) produces strain of tensile nature. A support to this idea was provided by the work of Kumar *et al* (1980).

In this system it has been observed (Subba Rao and Hari Babu 1978) that the lattice parameter increases with the addition of Br^- ions to a KCl lattice and follow Vegard's law. The ionic distance changes linearly with composition in mixed crystals but the F band peak position deviates towards lower energies with a maximum deviation for the equimolar composition and they do not follow the Mollwo-Ivey relation. This leads to the hypothesis that lattice constant is not the only parameter in determining the shift in the position of F absorption band. Jacobs (1954) studied the effect of hydrostatic pressure on absorption spectra and observed that the peak of the F band shifts to shorter wavelength with increasing pressure *i.e.* under compression. In accordance with this observation the shifts in F band peak position in KCl-KBr mixed crystals towards longer wavelength or lower energy side are due to internal stresses which are tensile in nature. This is justified also by the fact that inclusion of a Br^- ion with larger radii in a KCl lattice produces tensile strain in the lattice. Thus we can say that the local strained regions due to difference in ionic size as interpreted theoretically by Kataoka and Yamada (1977) cause spectral shift.

It is known that the optical width of a band depends on the interaction of lattice vibrations with an electron trapped in a defect site. If there are defects in the lattice a perturbation of local vibrations takes place and changes in optical width are to be expected. Theoretical significance for this assumption was given by localized mode approximation (Schulman and Compton 1963). If it is assumed that the electron is strongly localized in the anion vacancy site, interaction with all but the six nearest neighbours can be reasonably neglected. In addition, the motion of ions at right angles to the line joining an ion with the vacancy will have much less influence upon the energy of the system than the motion parallel to this line. Further, the strongest effects will occur when the radial motion of all the six neighbouring ions are in phase that is when they all move in or out from the vacancy which is known as the breathing mode of the centre. Half-width of F band has been related to the frequency characteristic of the breathing mode (Schulman and Compton 1963). The physical state of the six neighbouring ions of the vacancy where an electron is trapped is different in mixed crystals compared to pure KCl and KBr. This difference is due to the presence of two kinds of anions of different radii. Frequency of the breathing mode of the centre will therefore be different in mixed crystals which is responsible for the change in half-width of the F band. Conductivity experiments have shown that the defect concentration in mixed crystals is not very high and is of the same order as compared to pure crystals (Bhima Sankaram and Bansigir 1978; Hari Babu *et al* 1975). The presence of two kinds of anions creating localized strains in the lattice is therefore responsible for the F band broadening rather than the defect concentration as reported earlier by Gaikazyan *et al* (1960) and Gaikazyan and Zavadovskaya (1960).

Thus, from these observations we may conclude that it is not the presence of dislocations which plays a major role but it is the presence of local strained region due to

difference in ionic size of the anions in KCl-KBr mixed crystals which affects the *F* band parameters such as peak position half-width and their concentration in these crystals.

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