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LETTER TO THE EDITOR

On light-induced spectral shifts of F_A bands in mixed alkali halide crystals

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Abstract. Absorption spectra of F_A centres were studied in Li-doped KCl-KBr and KCl-RbCl mixed crystals. In KCl-KBr, light-induced spectral shifts were observed at liquid nitrogen temperature, for the F_{A1} band towards lower energy and for the F_{A2} band towards higher energy. The shifts are thought to be due to structural change where the electron-occupied vacancy finds a new location in relation to the neighbouring chlorine and bromine ions.

The F_A centre in alkali halides consists of an F centre with a smaller alkali cation as one of its nearest neighbours. The break of the cubic symmetry of the F centre leads to two absorption bands, F_{A1} and F_{A2} , relating to optical dipole moments parallel and perpendicular to the symmetry axis, respectively. Two different types, I and II, of F_A centre have been found. Type II, e.g. $F_A(\text{Li})$ in KCl, relaxes to saddle point configuration after optical excitation that leads in emission to a narrow band and high quantum efficiency. Based on these properties, type II can be applied in tunable lasers. From the structural point of view, there has been a continuous interest in the off-axis behaviour of the type-II centres [1].

Asami and Ishiguro [2] have studied optical properties of F_A centres in Li-doped KCl-KBr mixed crystals. They showed that these crystals have both type I and II emissions relating to different excited state (RES) configurations. However, they observed only one pair of absorption bands, F_{A1} and F_{A2} . At 1.6 K they realized an increased peak separation of F_A bands under applied pressure. In the case of $\text{KCl}_{0.78}\text{Br}_{0.22}$ this band splitting showed abrupt changes which the authors related to transitions between off-axis and on-axis configurations.

In the KCl-KBr mixed crystal, the $F_A(\text{Li})$ central electron is surrounded by five K^+ ions and the Li^+ ion. Further, the impurity Li^+ itself is surrounded partly by chlorine and partly by bromine ions, their relative numbers depending on the composition. The arrangement of the ions dictates whether the Li^+ ion is in an off-axis position or not, and also the nature of the RES configuration. Based on their emission measurements, Asami and Ishiguro state that the centre goes to the RES of type II via the RES type I, which is a thermally activated process.

In the present letter we report light-induced spectral shifts of F_A bands in mixed halides which were not recognized in [2]. Five different KCl-KBr (14, 24, 49, 74, and 84 mol% KCl) and two KCl-RbCl (24 and 74 mol% KCl) compositions, as well as 'pure' KCl, KBr and RbCl, all doped with 1 mol% Li in the melt, were crystallized by the Czochralski method in an argon atmosphere. The crystals were coloured additively in a Mollenaer-type heat pipe oven [3] or electrolytically using the method developed in our laboratory [4].

Before measurements were taken the coloured crystals were quenched from 500 °C to room temperature (RT) on a copper plate. The sample was then mounted in an optical cryostat which allowed us to reach every temperature between RT and liquid nitrogen temperature (LNT). The $F \rightarrow F_A$ conversion was carried out at RT or at -20 °C without any significant difference between these two temperatures. The absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer, and for comparing and manipulating the spectra Perkin-Elmer computerized spectroscopy software was applied. The light source for exposures was a projector lamp and to get separate wavelengths, a set of Oriel filters, with a half width of 10 nm and covering the range 400–740 nm with 20 nm intervals, was used.

After $F \rightarrow F_A$ conversion, the crystal was immediately cooled down to LNT and its absorption spectrum was recorded. Then it was exposed for 10 nm to white light and the spectrum was recorded again. For every mixed composition of KCl-KBr, but not for KCl-RbCl and the 'pure' samples, a clear shift of the F_{A1} band towards lower energy and of the F_{A2} band towards higher energy was observed. Figure 1 shows the spectra for the composition of 49 mol% KCl in KCl-KBr. In the energy scale the shifts are of 0.02 eV and 0.01 eV for F_{A1} and F_{A2} bands, respectively.

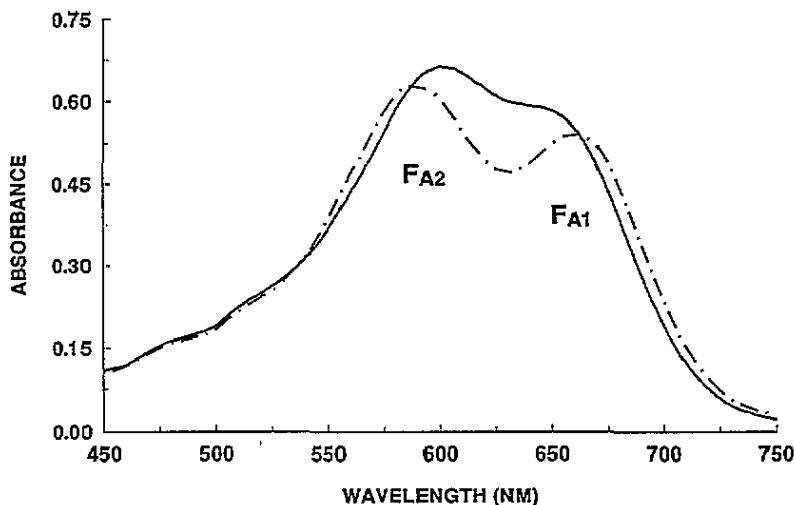


Figure 1. Absorption spectra of F_A centres in KCl-KBr mixed crystals containing 49 mol% KCl. The curves are recorded at LNT before (solid line) and after (dashed line) white light exposure.

It is well known that if F_A centres are exposed at low temperature to monochromatic light, polarized or even unpolarized, the centres will reorientate. After a prolonged exposure with unpolarized light, a steady state is reached where the distribution of reoriented centres is dependent on the exposing wavelength, i.e. to what extent the two F_A bands overlap at that particular wavelength. This phenomenon was applied as follows when searching for the explanation for the energy split.

Firstly an unmixed KCl crystal was cooled down to LNT, its absorption spectrum recorded, and it was successively exposed to a steady state distribution of the wavelengths 540, 580, 600, 660, and 680 nm. Then each spectrum obtained after the exposure was

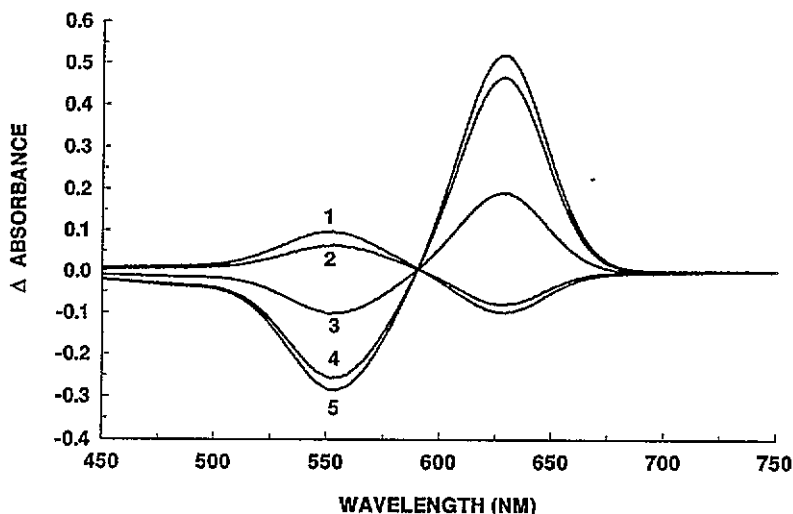


Figure 2. Differences of absorption spectra of oriented F_A centre distributions in unmixed KCl. Curves 1, 2, 3, 4, and 5 present differences between the original F_A spectrum and those obtained with unpolarized light exposure at 540, 580, 600, 620, and 680 nm, respectively.

subtracted from the original LNT one. Figure 2 presents the difference curves all of which have a common intersection point. This means that the exposures induce only reorientational changes for units of equal structure. A similar result was obtained for unmixed KBr and RbCl.

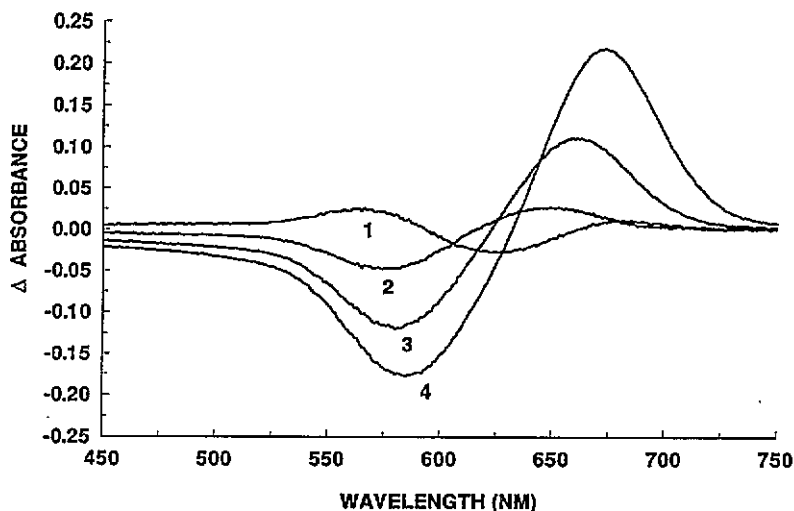


Figure 3. Differences of absorption spectra of F_A centre distributions in KCl-KBr mixed crystal containing 49 mol% KCl. The crystal was exposed with unpolarized light at the wavelengths of 540, 600, 620, 640, and 700 nm. The curves 1, 2, 3, and 4 present differences between the 600 nm spectrum and those of 540, 620, 640, and 700 nm, respectively.

For mixed KCl-KBr crystals, the behaviour was different, as shown in figure 3. A crystal

containing 49 mol% KCl was exposed to a steady state F_A distribution of the wavelengths 540, 600, 620, 640, and 700 nm. Each spectrum was then subtracted from that corresponding to 600 nm. The difference curves no longer intersect at the same point, and neither do their minima or maxima stay fixed, which tells us that the reorientation process must also involve structural changes. For all the KCl-KBr compositions the behaviour was similar.

When heating the KCl-KBr sample, whose behaviour was described in figure 1, back to RT in the dark and measuring its spectrum at LNT, the crystal gave the same spectrum as after the $F \rightarrow F_A$ conversion. Thus the recovery is a temperature-activated process, and remarkably it was observed to start to occur at about -50°C .

Further, we looked for the temperature range where the light-induced shift of the F_A bands can be realized. Our measurements show that starting from -150°C downwards this is possible. Above this temperature the inverse reaction and the formation of F'_A centres cancel the process.

As explained above, the light-induced spectral shift of F_A bands was observed for KCl-KBr, where there are two different types of anion in random order, but the phenomenon did not exist in KCl-RbCl. Thus the shift must be related to a structural change where the electron-occupied vacancy in KCl-KBr finds at low temperature a new energetically favoured position in relation to the neighbouring chlorine and bromine ions. There is no hint that the shift might be due to transitions of the Li^+ ion between on-axis and off-axis positions.

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