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High-pressure optical studies of doped alkali halides. IV. Mixed crystals*

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Optical excitation and emission studies have been made on various compositions of mixed crystals of $KCl_{1-x}Br_x$:In, $KCl_{1-x}Br_x$:Tl, and $NaCl_{1-x}Br_x$:Tl. For the potassium salts measurements were made in both the NaCl and CsCl phases. In general, excitation peak locations were measurably below the prediction from linear interpolation, while emission peak locations deviated so far as to provide a minimum in peak location and a maximum in the Stokes's shift at an intermediate composition. The half-widths were greater than a linear interpolation would predict. This last result can be explained in terms of the number of different isostructures with which the impurity ion interacts in a mixed crystal. Although the analytical relation between Stokes's shift and dielectric constant does not give a quantitative correlation, it is of interest that one can quantitatively relate the deviation from linearity of the Stokes's shift and the dielectric constant using a single scaling parameter for both the $KCl_{1-x}Br_x$:Tl and $NaCl_{1-x}Br_x$:Tl systems.

In this paper we report optical excitation and emission spectra of the mixed-crystals systems $KCl_{1-x}Br_x$: In at 8 and 40 kbars, $KCl_{1-x}Br_x$: Tl at 18 and 40 kbars, and $NaCl_{1-x}Br_x$: Tl at 10 kbars. For the first two systems there is a phase transition (fcc to sc) at ~19 kbars so that results are presented for both phases. The experimental techniques including sample preparations have been described elsewhere[1] and will not be discussed here.

It has been shown[2] that such mixtures follow Vegard's law. X-ray measurements on our samples show this also. Many properties, however, deviate from linearity with composition. Heats of solution,[3,4] the bulk modulus,[5] and dielectric constant[6] all show marked deviations, in some cases exhibiting maxima or minima. The dielectric studies are especially useful in discussing our optical results.

There exist very little data on the optical properties of impurities in mixed ionic crystals. One study indicates that the A-absorption band in KCl-KBr: Tl solutions changes monotonically between the locations in the pure components, but varies nonlinearly with composition, favoring the lower-energy KBr: Tl band location.[7] The A-band half-width displays a maximum at low concentrations (near 20%) of KCl. Line-shape broadening due to the mixing is surely due to a statistical averaging of various site configurations surrounding the impurity, leading to a band which is a composite of bands from several types of sites. A similar behavior has been observed for the A-absorption band in the KCl-KBr: Pb system.[8]

The correlation between the bulk dielectric constant and the measured optical properties may be understood by using results derived from studies of the effects of solvents on electronic transitions. Generally, dipole-dipole interactions and polarization effects between a solute molecule and a solvent are shown to influence optical transitions. A review of such effects is given by Becker.[9]

To apply the results of solvation effects on electronic transitions, one can assume that the "polar solvent" is the host lattice whose dielectic constant depends on composition; the "polar solute molecule" becomes the highly polarizable Tl^+ impurity and its nearest-neighbor anions. The solvent is "fluid" in the sense that vibrational relaxation ("dipole reorientation") occurs rapidly compared to the emission process. For such a system, the Stokes shift δ_S for the optical transitions may be approximated as[9]

$$\delta_S = h\nu(\mathrm{abs}) - h\nu(\mathrm{emis}) = \frac{A}{a^3}\left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right), \qquad (1)$$

where A is a positive constant, ϵ is the solvent static dielectric constant, n is the solvent (optical) refractive index, and a is the solute dipole cavity radius.

For a mixed crystal, one can write the Lorentz-Lorenz equation as

$$J(x) = \frac{n^2(x) - 1}{n^2(x) + 2} = \frac{4\pi}{3} N\left[\alpha_a^e + (1-x)\,\alpha_b^e + x\alpha_c^e\right] \qquad (2)$$

for a mixed crystal of composition $ab_{1-x}c_x$. N in (2) is the concentration of cations or anions, and α_i^e is the electronic polarizability for ions of type i. Assuming that the electronic polarizabilities of the crystal ions are the same in both pure and mixed crystals, one finds that $J(x)$ can be written in terms of the electronic polarizabilities of the pure crystals, as found from the pure-crystal refractive indices. Thus,

$$J(x) = (1-x)J(0) + xJ(1). \qquad (3)$$

Using known values for the static dielectric constant $\epsilon(x)$ as a function of mixture x, Eq. (1), and $a(x)$ from Vegard's law, one can solve for the expected Stokes shift $\delta_S(x)$ as a function of mixture by using (1), where all the parameters (except for A) are functions of x.

RESULTS

Typical experimental results for $NaCl_{1-x}Br_x$: Tl are shown in Fig. 1. Peak location and half-width data for all three systems appear in Table I. In general, the excitation peak energies for the mixed crystals were below the values predicted by linear interpolation from the pure materials; the emission peak energies were much below—sufficiently to provide a minimum peak energy at an intermediate composition. The half-widths were greater than predicted by linear interpolation with some tendency for the maximum deviation to occur for $x < 0.5$. It is of interest to note that the behavior in the high-pressure (sc) phase is essentially identical to that in the NaCl phase.

For $KCl_{1-x}Br_x$: In the two Jahn-Teller–split emission components were observed at some compositions at 8 kbars. All other systems exhibited only the single high-energy (A_T or $A_{T'}$)[10] peak at the pressure studied. In this discussion the position of the A_T (or $A_{T'}$) peak is used throughout.

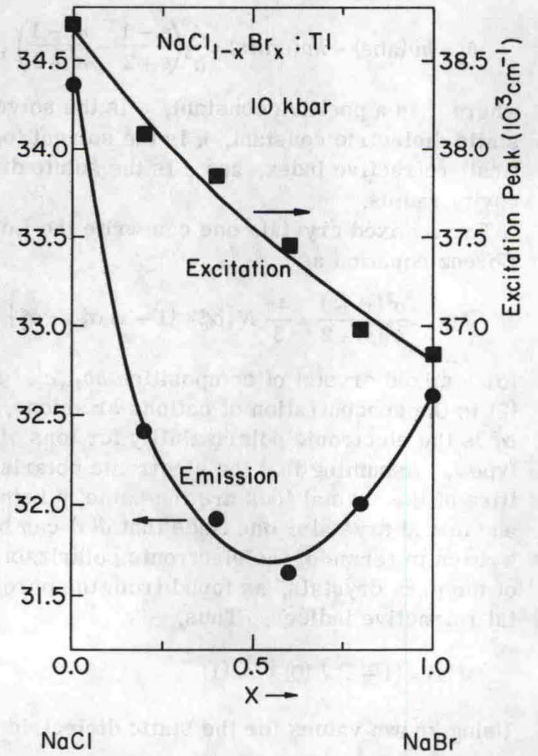

FIG. 1. Excitation and emission peak location vs composition—$NaCl_{1-x}Br_x$: Tl at 10 kbars.

An interesting result of the emission energy depression due to mixing is that one might expect to find both emission bands in mixed crystals formed from component crystals which displayed only one band. This was observed by Kleeman and Fischer[7] but left unexplained. They found two emission bands in $KBr_{0.83}I_{0.17}$: Tl at 20 K, while KBr : Tl displayed only the higher-energy emission. Increasing the temperature caused the growth of the low-energy band at the expense of the higher one, which indicates the bands are the Jahn-Teller A_X and A_T peaks.

We observed, in addition, a low-energy emission at 8 kbars in the room-temperature emission spectrum of $KCl_{0.9}Br_{0.1}$: In, but not in $KCl_{0.5}Br_{0.5}$: In or KCl : In. This, and Kleeman and Fischer's observation, can be explained by the following argument. It has been shown earlier[1,10] that A_X and A_T bands tend to shift to higher energy with pressure and that pressure causes a redistribution of the intensity of the doublet, with increasing pressure, favoring the high-energy emission. An extrapolation of these results is that, if some perturbation caused the emission band(s) to shift to lower energy, one might observe a redistribution favoring the lower-energy emission (if such a state existed). The effect of mixing is to drastically lower the emission energy and could, therefore, also induce A_X emission from materials which, based upon the pure-component spectra, would be expected to show only A_T emission. Such appears to be the case for $KBr_{0.83}I_{0.17}$: Tl at zero pressure and 20 K and for $KCl_{0.9}Br_{0.1}$: In at 8 kbars and room temperature. This means that an A_X excited state probably exists in pure KCl : In, though it has never been observed because of the large potential barrier between it and the A_T state.

DISCUSSION

The deviation from linearity of the half-widths is caused by a broadening due to a spectral averaging over different impurity isostructures and was also observed in $KCl_{1-x}Br_x$ F bands[11] and in $KCl_{1-x}Br_x$: Tl.[7]

An attempt was made to correlate the optical spectra parameters to the variation of the dielectric constant with mixing, using the results of solvation theory. The motivation is that the mixture dependence of the observed Stokes shift deviates from linearity much like the measured dielectric constants. Further, mixed-crystal studies of F centers[11] indicate that a dielectric continuum model may be appropriate, and solvation theory might apply.

Using (1) and (2) of the previous section, one can solve for the constant A in (1). This was