

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 $\text{KCl}_{1-x}\text{Br}_x:\text{In}$, $\text{KCl}_{1-x}\text{Br}_x:\text{Tl}$, and $\text{NaCl}_{1-x}\text{Br}_x:\text{Tl}$. 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 $\text{KCl}_{1-x}\text{Br}_x:\text{Tl}$ and $\text{NaCl}_{1-x}\text{Br}_x:\text{Tl}$ systems.

In this paper we report optical excitation and emission spectra of the mixed-crystals systems $\text{KCl}_{1-x}\text{Br}_x:\text{In}$ at 8 and 40 kbars, $\text{KCl}_{1-x}\text{Br}_x:\text{Tl}$ at 18 and 40 kbars, and $\text{NaCl}_{1-x}\text{Br}_x:\text{Tl}$ 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 elsewhere¹ and will not be discussed here.

It has been shown² 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 constant⁶ 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 interac-

tions 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 dielectric 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 as⁹

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

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

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

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,

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

Using known values for the static dielectric con-

stant $\epsilon(x)$ 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 $\text{NaCl}_{1-x}\text{Br}_x : \text{Tl}$ 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 $\text{KCl}_{1-x}\text{Br}_x : \text{In}$ 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.

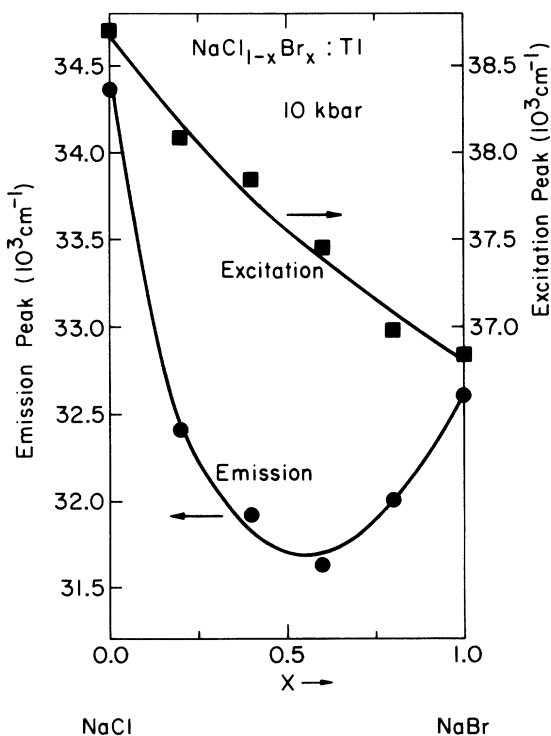


FIG. 1. Excitation and emission peak location vs composition— $\text{NaCl}_{1-x}\text{Br}_x : \text{Tl}$ at 10 kbars.

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 Fischer⁷ but left unexplained. They found two emission bands in $\text{KBr}_{0.83}\text{I}_{0.17} : \text{Tl}$ at 20 K, while $\text{KBr} : \text{Tl}$ 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 $\text{KCl}_{0.9}\text{Br}_{0.1} : \text{In}$, but not in $\text{KCl}_{0.5}\text{Br}_{0.5} : \text{In}$ or $\text{KCl} : \text{In}$. This, and Kleeman and Fischer's observation, can be explained by the following argument. It has been shown earlier^{11,10} 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 $\text{KBr}_{0.83}\text{I}_{0.17} : \text{Tl}$ at zero pressure and 20 K and for $\text{KCl}_{0.9}\text{Br}_{0.1} : \text{In}$ at 8 kbars and room temperature. This means that an A_X excited state probably exists in pure $\text{KCl} : \text{In}$, 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 $\text{KCl}_{1-x}\text{Br}_x$ F bands¹¹ and in $\text{KCl}_{1-x}\text{Br}_x : \text{Tl}$.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 centers¹¹ 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

TABLE I. Peak locations and half-widths—mixed crystals.

Compound	Mode ^a	Fraction Br (<i>x</i>)						
		0	0.1	0.25	0.5	0.75	0.9	1.0
Peak Locations ^b								
KCl _{1-x} Br _x :In								
8 kbars	Ex	34.75	34.5	34.1	33.70	33.6	33.55	33.50
40 kbars	Ex	35.7	35.30	34.89	34.42	34.30	34.22	34.00
8 kbars	Em	23.4	23.06	22.77	22.55	22.75	22.90	23.10
40 kbars	Em	27.7	27.11	26.35	26.06	26.35	26.50	26.60
KCl _{1-x} Br _x :Tl								
18 kbars	Ex	39.98	39.39	39.18	38.58	38.30	38.14	37.94
40 kbars	Ex	41.01	40.24	40.06	39.21	38.81	38.57	38.40
18 kbars	Em	33.12	31.86	31.56	31.13	31.25	31.67	32.16
40 kbars	Em	37.45	35.20	35.10	34.62	34.78	35.25	35.58
NaCl _{1-x} Br _x :Tl								
10 kbars	Ex	38.70	38.25	37.90	37.60	37.15	36.95	36.04
	Em	34.36	33.20	32.30	31.70	31.90	32.20	32.59
Half-widths ^b								
KCl _{1-x} Br _x :In								
8 kbars	Em	3.70	3.99	3.86	3.90	3.92	3.89	3.80
40 kbars	Em	4.25	4.21	4.15	4.10	4.17		3.95
KCl _{1-x} Br _x :Tl								
18 kbars	Ex	2.23	2.93	2.65	2.88	2.48	2.02	2.07
40 kbars	Ex	2.01	2.88	2.58	2.87	2.42	1.91	1.97
18 kbars	Em	4.20	4.26	4.29	4.35	4.24	4.32	4.19
40 kbars	Em	3.37	4.13	4.17	3.97	3.85	3.52	3.14

^aEx, excitation; Em, emission.^bIn kilokaysers (10³ cm⁻¹).

done for KCl_{1-x}Br_x:Tl and NaCl_{1-x}Br_x:Tl, using $\delta_S(x)$ measured in this laboratory and $\epsilon(x)$ from Kamiyoshi and Nigara.⁶ The results, given in Table II, point out that *A* is not a constant, since $\delta_S(x)$ and

$$L(x) = \frac{1}{\alpha^3(x)} \left(\frac{\epsilon(x) - 1}{\epsilon(x) + 2} - \frac{n^2(x) - 1}{n^2(x) + 2} \right) \quad (4)$$

do not give a constant ratio, as predicted by (1). In short, the Stokes shift is not described quanti-

TABLE II. Composition dependence of Stokes shift and mixed-crystal parameters.

<i>x</i>	NaCl _{1-x} Br _x :Tl			KCl _{1-x} Br _x :Tl		
	$\delta_S(x)$ (cm ⁻¹)	<i>L</i> (<i>x</i>) (×10 ¹⁹ cm ⁻³)	<i>A</i> ^a	$\delta_S(x)$ (cm ⁻¹)	<i>L</i> (<i>x</i>) (×10 ¹⁹ cm ⁻³)	<i>A</i> ^a
0	4340	183	23.7	6860	115	59.7
0.1		179		7530	113	66.6
0.2	5690	174	32.7		112	
0.25				7620	110	69.3
0.3		170			109	
0.4	5930	165	35.9		107	
0.5		160		7450	105	71.0
0.6	5830	156	37.4		102	
0.7		151			99	
0.75				7050	97	72.7
0.8	4970	146	34.0		96	
0.9		141		6470	93	69.6
1.0	4240	135	31.4	5790	90	64.3

^a*A* = $\delta_S(x)/L(x)$, units 10⁻¹⁹ cm².

TABLE III. Crystal parameters for some doped alkali halides.

	δ_s (cm ⁻¹)		ϵ^d	R^{2d}	a (Å) ^d
	:Tl	:In			
NaCl	4340 ^a		5.93	2.25	5.64
NaBr	4240 ^a		6.34	2.62	5.98
KCl	6860 ^b	11 330 ^c	4.80	2.13	6.28
KBr	5790 ^b	10 400 ^c	4.87	2.338	6.58

^a10 kbars.^c8 kbars.^b18 kbars.^dFrom Ref. 6.

tatively by the composition dependence of the static dielectric constant ϵ and the refraction index n . The pure-crystal parameters used in calculating $L(x)$ are given by Table III.

In spite of the lack of correlation between $L(x)$ and the Stokes shift $\delta_s(x)$, it is interesting that $\delta_s(x)$ and $\epsilon(x)$ show similar behavior with mixture. We show in Fig. 2 the deviation from linearity in Stokes shift ($\Delta\delta_s$) with composition for the Tl⁺-doped systems studied. On a separate scale in the same figure, we have plotted the deviation from linearity in the dielectric constant ($\Delta\epsilon$) due to mixing, from Kamiyoshi and Nigara's⁶ fits to experimental data. We have adjusted the two vertical scales to display a good correlation. Only a single scaling factor, dependent on the impurity, is needed to show excellent agreement between $\Delta\delta_s$ and $\Delta\epsilon$ for both systems. Figure 2 shows the Stokes-shift data for the low-pressure NaCl phase of the KCl-KBr system, since the dielectric data are for this crystal structure.

For $\text{KCl}_{1-x}\text{Br}_x$: In, the deviation $\Delta\delta_s$ maximizes with a value near 300 cm⁻¹ as opposed to approximately 1650 cm⁻¹ for $\text{KCl}_{1-x}\text{Br}_x$: Tl. One expects the heavier Tl⁺ impurity to have a larger electronic polarizability than the In⁺ ion,¹² which might explain why $\Delta\delta_s$ is larger for Tl⁺ than for In⁺.

Another motivation for correlating the optical transitions to the dielectric constant is that in both $\text{KCl}_{1-x}\text{Br}_x$ and $\text{K}_{1-x}\text{Rb}_x\text{I}$, the F bands show low-energy composition deviations¹¹; Kamiyoshi and Nigara⁶ show that, for both these systems,

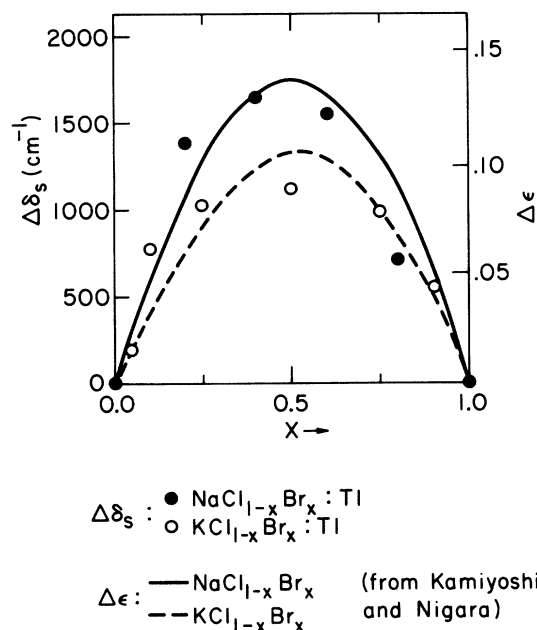


FIG. 2. Deviation of Stokes shift and dielectric constant from linearity with composition— $\text{NaCl}_{1-x}\text{Br}_x$: Tl and $\text{KCl}_{1-x}\text{Br}_x$: Tl.

the dielectric constant maximizes with composition. That the nonlinear effects of composition on F -band location are similar for changing nearest-neighbor cations or second-nearest-neighbor anions is surprising. Because of the diffuse nature of the F center, a change in a bulk property, such as the dielectric constant, can be quite useful in describing the effect of mixture on the optical properties of the localized center.

In summary, while no analytical explanation was found for the composition dependence of the optical parameters in doped mixed alkali halides, it was found that the observed composition dependence of the Stokes shift empirically correlates quite well to known dielectric-constant deviations with mixture, using a single scaling factor dependent on the impurity ion. Such a correlation might also apply for other types of centers (e. g., F centers).

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