

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

Compound	Mode ^a	Fraction Br (x)						
		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.

x	NaCl _{1-x} Br _x :Tl			KCl _{1-x} Br _x :Tl		
	$\delta_S(x)$ (cm ⁻¹)	$L(x)$ ($\times 10^{19}$ cm ⁻³)	A^a	$\delta_S(x)$ (cm ⁻¹)	$L(x)$ ($\times 10^{19}$ cm ⁻³)	A^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	$R^2 d$	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

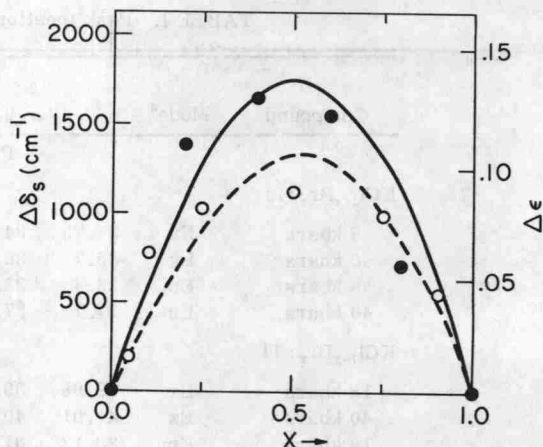
^a10 kbars.^c8 kbars.^b18 kbars.^dFrom Ref. 6.

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,



$\Delta\delta_s$: ● $\text{NaCl}_{1-x}\text{Br}_x$: Tl
○ $\text{KCl}_{1-x}\text{Br}_x$: Tl

$\Delta\epsilon$: — $\text{NaCl}_{1-x}\text{Br}_x$ (from Kamiyoshi and Nigara)
-- $\text{KCl}_{1-x}\text{Br}_x$

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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