The F_A center in $KCl_{(1-x)}Br_x$ doped with sodium

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ABSTRACT. In the present work, the optical absorption of the F_A center in $KCl_{(1-x)}Br_x$:Na mixed crystals has been studied experimentally; as in KCl and KBr, F_{A1} and F_{A2} absorption bands has been obtained finding a nonlinear energy shift with the molar composition.

RESUMEN. En el presente trabajo se estudia experimentalmente la absorción óptica del centro F_A en cristales mixtos $KCl_{(1-x)}Br_x$:Na; como en cristales KCl, KBr, se han obtenido las bandas F_{A1} y F_{A2}, encontrándose que ellas presentan un corrimiento no lineal en energía con la composición molar.

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1. INTRODUCTION

The F_A center is produced on $KCl_{(1-x)}Br_x$ mixed crystals doped with sodium, in order to characterize the F_A centers on these crystals [1–3]. As we know an experimental study about F_A center has been realized by Asami *et al.* [4] in these mixed crystals doped with Li. This work reports only experimental results, exploring the possibility the mixed crystal can be used for laser application [5,6], it is known that in KCl:Li this effect is produced through the F_A center [7]. On the other hand, in Na doped crystals F_A centers can be produced, but have no laser effect, although they are able to store information [8].

Theoretically, the F_A center in alkali halides has been studied by several authors. Kojima [9,10] approximated the wave function from its ground and first excited states through a linear combination of atomic orbitals located over the near neighbors, Alig [11] utilized the Bartram's ion size [12] in order to calculate the F_{A1} and F_{A2} optical absorption energies of the F_A center. Also Vázquez and Ruiz-Mejía [13] calculated the energies of F_{A1} and F_{A2} optical absorption bands by using the perturbation theory with F center wave functions. On the experimental part, an excellent revision has been done by Lüty [14].

In the present work experimental results are reported about the F_A center in mixed $KCl_{(1-x)}Br_x$ alkali halide crystals doped with 1 Wt% of Na.

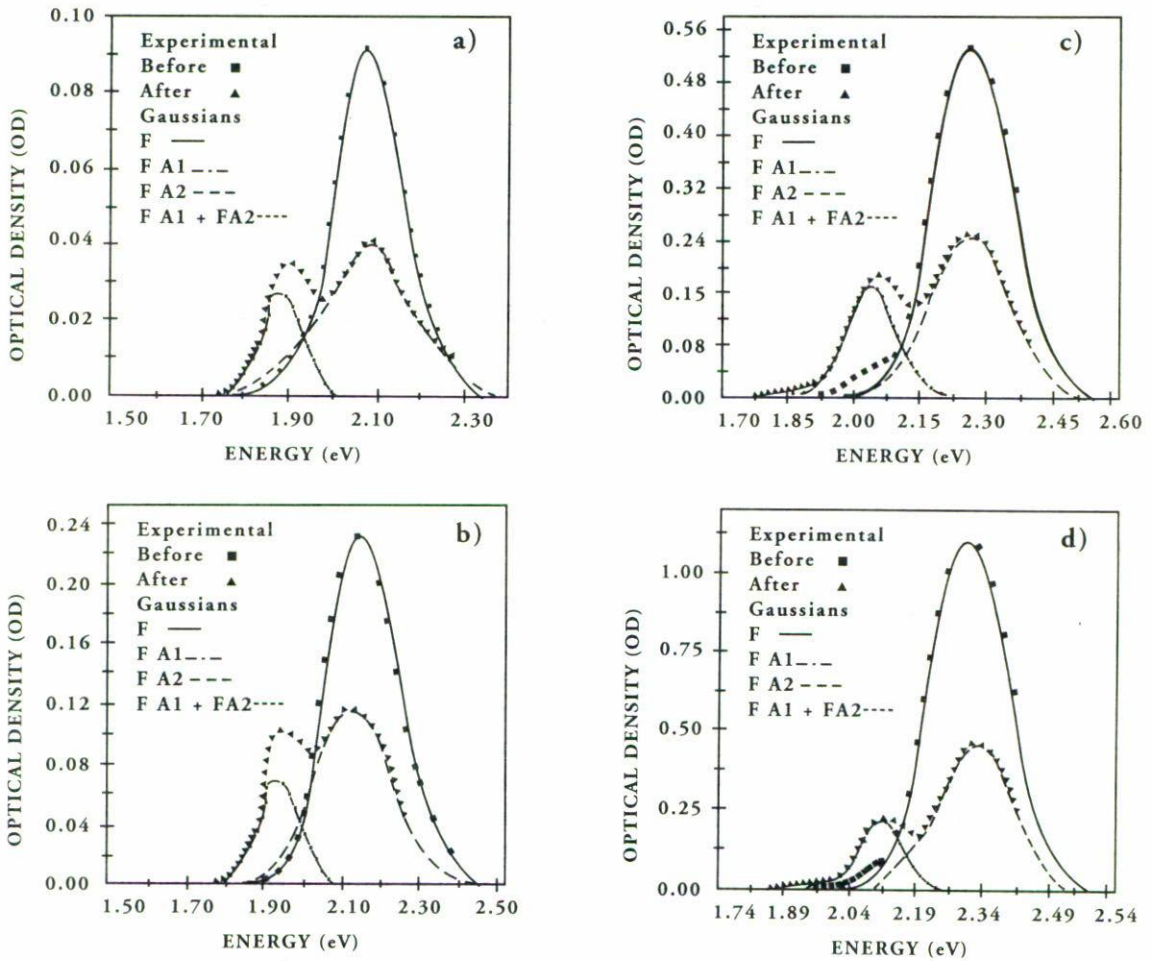* Instituto de Física "Manuel Sandoval Vallarta", UASLP, San Luis Potosí, 78000 México.

FIGURE 1. Absorption spectra in different concentrations x of the $KCl_{(1-x)}Br_x$ of the F band before the photo-thermal process and the F_{A1} and F_{A2} bands after the photo-thermal procedure a) $x = 1$, b) $x = 0.4845$, c) $x = 0.1355$ and d) $x = 0$.

2. EXPERIMENTAL WORK

The crystals were grown by the Czochralski technique in the Crystal Growth Laboratory of IFUNAM. Six mixtures were grown, $x = 0$, 0.1355, 0.2947, 0.4548, 0.7148 and 1. The dopant was added in the melt as NaCl in 0.1% concentration. The samples of $6 \times 6 \times 5$ mm^3 were colored by exposuring the crystal to x-rays. For the coloring, an apparatus Siemens of x-rays was used with a current of 30 mA and voltage of 40 kV finding 10^{15} and 10^{17} centers/cm^3. The optical absorption measurements were made with a spectrophotometer λ 9 of Perkin Elmer. For the $F \rightarrow F_A$ centers conversion, the technique proposed by Lüty [14] was used by irradiating the crystals with F light at 220 K. The photo-thermal process to convert to F_A centers were carried out with a 150 watt tungsten lamp and wide band filters [15].

TABLE I. Values of the maximum energy peaks of the absorption bands for the following cases: E (pure) F band in a $KCl_{(1-x)}Br_x$:Na crystal, E_{A1}, energy of the F_{A1} band in the same crystal and E_{A2}, energy of the F_{A2} band in the same crystal $KCl_{(1-x)}Br_x$. All measurements to $T = 12$ K.

Molar fraction	Peaks Energy Bands (eV)			
x	E (pure)	E (1% Na)	E_{A1}	E_{A2}
1.0000	2.0761	2.0792	1.8850	2.0818
0.7148	2.1082	2.1138	1.8964	2.0874
0.4845	2.1570	2.1549	1.9236	2.1173
0.2947	2.2125	2.2109	1.9847	2.1860
0.1355	2.2644	2.2697	2.0429	2.2625
0.0000	2.3208	2.3211	2.1169	2.3356

3. RESULTS AND DISCUSSION

Figure 1 shows the optical absorption spectrum of four values of x. The solid curve corresponds to just colored crystals. After photo-conversion the absorption spectrum present a strong component of the F absorption centers and small aggregates absorption bands (continuous curve in Fig. 1). After several exposures to F light, the absorption spectrum presents the characteristic F_{A1} and F_{A2} absorption bands of the F_A centers. By cooling the samples to 12 K, these bands could be well resolved.

The absorption energies of the F, F_{A1} and F_{A2}, denoted by E, E_{A1} and E_{A2} respectively, are listed on Table I for each of the KBr concentration x in the mixed crystal. The F_A absorption band is shifted to the red as x increases. The shift of the component F_{A1} is different from that F_{A2}. As it is well known, for an impurity set in (100) with respect to the vacancy, the component F_{A1} corresponds to direction (010) and the component F_{A2} to (100).

Table II shows the separations of the energy peaks between the F_{A1} and F_{A2} bands and between the F band and the energy peaks of the F_{A1} and F_{A2} bands. The size of the unfold E (bigger for KCl than KBr) in mixed crystals ($0 < x < 1$) increases as the chlorine ions participation is higher; also for this ($0 < x < 1$) the shift respect the F band, such as for the parallel transition in direction to Na^+ ion, as well as for the perpendicular (ΔE_1, ΔE_2 in Table II) is positive, having a maximum value for $x = 0.4845$ (approximately the same as for the concentration of different component of mixed crystals). Taking into account these results it is possible to conclude that the participation of the near nearest neighbors of the F center (the halogen ions) reduce the value of the transition energies of the F_A center. For the energy of the F_{A2} band ΔE_2 was about 0.04 eV and 0.23 eV for ΔE_1, in the case of the molar fraction $x = 0.5$ of KBr in KCl.

The positions of the F_{A1} and F_{A2} band peaks are shifted to longer wavelengths until they reach a maximum, as the KBr content decreases in the mixed crystals values (Fig. 2). In the Fig. 2 the peaks of maximum energy of the F, F_{A1} and F_{A2} bands are sketched as the concentration x of the $KCl_{(1-x)}Br^-$ varies. The receding from linearity of the F_{A1} and F_{A2} band energies of the F_A center is higher than in the case of the F band [16].

TABLE II. Values of the separation between the energy peaks of the absorption band in the following cases: ΔE_A between the F$_{A2}$ band peak and the F$_{A1}$ band; ΔE_{A1} between the peak of F band and the F$_{A1}$ band; ΔE_{A2} between the F band peak and F$_{A2}$ band.

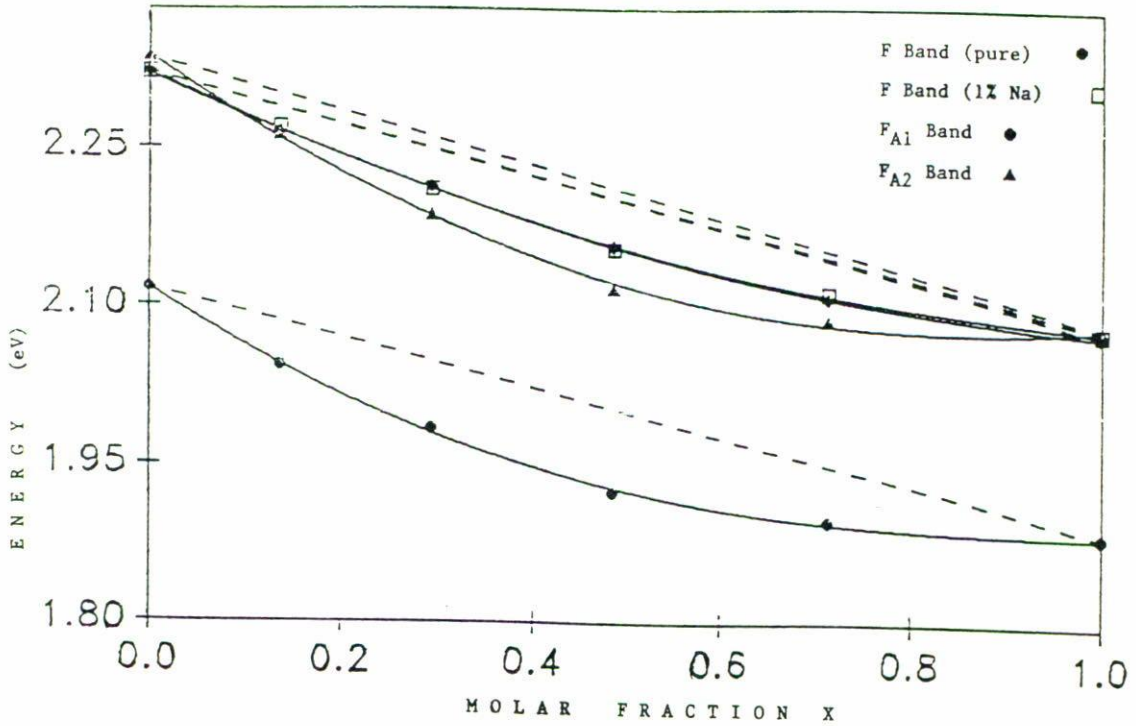| Molar Fraction	Separation of the peaks of the energy bands (eV)		
x	ΔE_A $(E_{A2} - E_{A1})$	ΔE_{A2} $(E - E_{A2})$	ΔE_{A1} $(E - E_{A1})$
1.0000	0.1968	−0.0057	0.1911
0.7148	0.1905	0.0208	0.2113
0.4845	0.1937	0.0397	0.2334
0.2947	0.2013	0.0265	0.2278
0.1355	0.2196	0.0019	0.2215
0.0000	0.2187	−0.0148	0.2039

FIGURE 2. Graph of the maximum energy peak of the F, F$_{A1}$ and F$_{A2}$ bands as function of the concentration x of the KCl$_{(1-x)}$Br$_x$ crystals.

The presence of the Br$^-$ ion in the surroundings of the F center affects in a high proportion the dimensions of the vacancy in the perpendicular directions to the symmetry axis. Halogen ion in the vicinity of the F$_A$ center (the same as in the case of the F center) increases the size of the vacancy, producing electronic levels, which remains themselves closer and are of lower energy. In the case of F$_{A2}$ band which energy value is small, it seems this band is less affected by the Br$^-$ ions.

In the future, it would be important to investigate which is the configuration of the F_A center in the mixed crystals, taking into consideration the near nearest neighbors effects. Is the Br^- set in (100) or the (011) direction as the concentration x is increased?. It is necessary to perform more work about the F_A center in mixed ionic crystals.

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