Optical absorption bands due to the s^2 to sp transition in KCl:Sb^{3+} crystals

Optical absorption bands due to the $s^2 \rightarrow$ sp transition in KCl:Sb^{3+} crystals

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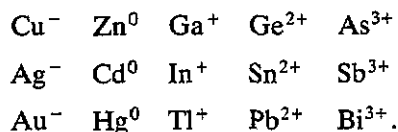‡ Department of Chemistry, Chungnam National University, Daejeon, 305-764, Korea

Abstract. UV absorption spectra of KCl:Sb^{3+} crystals have been studied in detail. Six absorption bands are observed at 271.0, 210.8, 201.7, 199.4, 195.5 and 191.4 nm, the first five bands of which are attributable to the A, B, C$_1$, C$_2$ and C$_3$ bands due to an $s^2 \rightarrow$ sp transition in the Sb^{3+} ion, while the last is due to the charge-transfer-type D′ band.

1. Introduction

Alkali halide crystals containing a small amount of s^2 ground-state-configuration ions like Sn^{2+}, In$^+$ and Tl$^+$ exhibit four absorption bands, called A, B, C and D (or D′) in order of increasing energy, on the low-energy side of absorption due to the bulk crystal (Sakoda and Tsuboi 1980, Tsuboi and Sakoda 1980). The A, B and C bands are due to the electronic transition associated with the change in configuration $s^2 \rightarrow$ sp. The A band is due to the spin–orbit-allowed transition $^1S_0 \rightarrow {}^3P_1$, the C band is the biggest of the three bands because it is due to the dipole-allowed transition $^1S_0 \rightarrow {}^1P_1$, while the smallest B band is temperature dependent because it is caused by the dipole-forbidden but vibration-assisted transition $^1S_0 \rightarrow {}^3P_2$. Unlike the A, B and C bands, the D and D′ bands are caused by the charge transfer from halide ions to s^2 ions. The D′ band has been observed in Pb^{2+}-doped crystals (Tsuboi 1979).

The following is a list of s^2 ions:

$$\begin{array}{ccccc} Cu^- & Zn^0 & Ga^+ & Ge^{2+} & As^{3+} \\ Ag^- & Cd^0 & In^+ & Sn^{2+} & Sb^{3+} \\ Au^- & Hg^0 & Tl^+ & Pb^{2+} & Bi^{3+}. \end{array}$$

Many papers have been published on the optical properties of alkali halide crystals containing various s^2 ions (see review articles e.g. by Ranfagni *et al* 1983, Hizhnyakov and Kristoffel 1984, Jacobs 1991). Few studies, however, have been undertaken on the Sb^{3+} ion. Radhakrishna and Karguppikar (1973) examined the optical absorption spectra of NaCl:Sb^{3+}, while Choi *et al* (1991) measured the luminescence spectra of KCl:Sb^{3+} and KI:Sb^{3+} crystals. Radhakrishna and Karguppikar observed two absorption bands with peaks at 268 and 212 nm. They assigned the 268 nm band to the A band and the large 212 nm band not to the C band but to an absorption due to Sb^{2+} since they
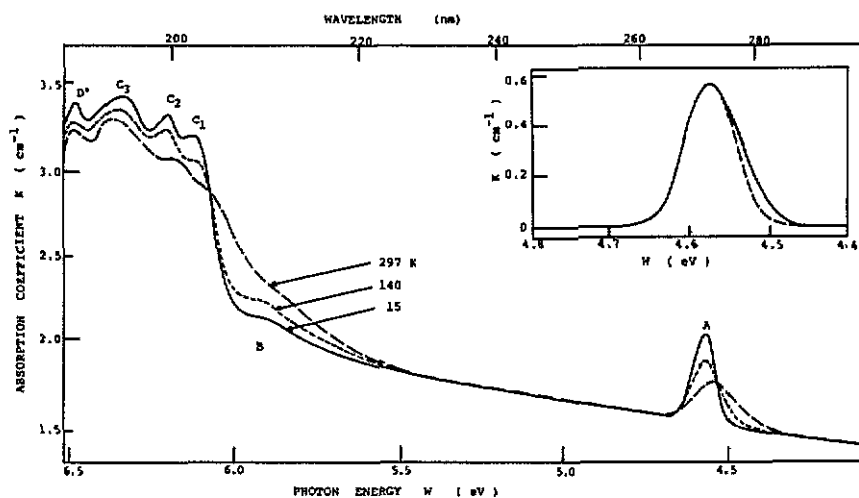
Figue 1. Absorption spectra of a KCl:Sb^{3+} crystal at 15, 140 and 297 K. The line shape of the 271 nm absorption band at 15 K, after subtracting the background, is shown in the inset. A symmetric line shape is shown as a broken curve.

did not observe a triplet structure. Choi and co-workers observed two emission bands by the excitation in the A band. To date, no work has been performed on the B and C bands.

The following question arises: does the Sb^{3+} ion in alkali halides give rise to absorption bands due to the $^1S_0 \rightarrow {}^3P_2$ and $^1P_1$ transitions or not? The present work was undertaken to answer this question. Sb^{3+} ions that are substitutionally incorporated into alkali halide lattices have charge-compensating cation vacancies. It is interesting to investigate whether the vacancies induce optical properties that are different from those displayed by other s^2-doped crystals. Here we examine the absorption spectra of Sb^{3+} ion centres in KCl crystals.

2. Experimental procedure and results

Single crystals of KCl:Sb^{3+} (the Sb concentration is 6 ppm, which was determined by the ICP mass spectrometer) were grown by the vertical Bridgman method at Chungnam National University. The crystals were heated at 450 °C for 30 min and quenched to room temperature on a copper plate immediately before the measurement to avoid the formation of aggregate Sb^{3+} centres. Absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer in a temperature region of 15–300 K.

Figure 1 shows the absorption spectra of a KCl:Sb^{3+} crystal at 15, 140 and 297 K. Three absorption bands are observed at 271.0, 210.8 and 190–204 nm. The line shape of lowest-energy band is slightly asymmetric, without any structure, as shown in the inset to figure 1. As the temperature is increased, its peak height becomes small but the half-width becomes large. The integrated area of the 271.0 nm band is almost temperature-independent below 100 K, but above 100 K it decreases with increasing temperature. The 210.8 nm band is the smallest of the three bands, and grows with increasing temperature as seen in figure 1. The high-energy band appearing around 190–204 nm is the
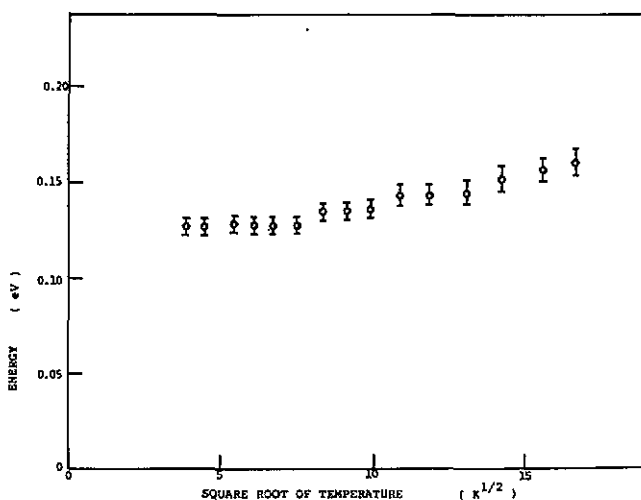
Figure 2. Separation of the C_2 and C_3 components plotted against the square root of temperature.

biggest of the three bands. It consists of four components peaking at 201.7, 199.4, 195.5 and 191.4 nm at 15 K. The position of the 191.4 nm band does not move with increasing temperature, but the 201.7, 199.4 and 195.5 nm bands shift towards low energy.

Onaka *et al* (1965) and Schmitt (1982) measured the absorption spectra of KCl containing a low concentration of Pb^{2+} ions. The A, B, C_1, C_2, C_3 and D' bands are located at 271.5 (270.5), 211 (211), 202.5, 199 (199), 195.5 and 191.5 (189.3) nm at 77 K (4.2 K). The whole absorption spectrum of KCl: Sb^{3+}, and its temperature dependence, is quite similar to the absorption spectrum of a KCl: Pb^{2+} crystal, considering the peak positions of the observed bands and their relative intensities. Indeed, the lowest-energy band (the 271.0 nm band) decreases slightly with increasing temperature as does the A band in KCl: Pb^{2+} (Schmitt 1982). Additionally the weak 201.8 nm band of KCl: Sb^{3+} grows with increasing temperature as in the case of the B band of KCl: Pb^{2+}.

3. Discussion

From the similarity between the spectra of KCl: Sb^{3+} and KCl: Pb^{2+}, we can assign the 271.0, 210.8 and triplet-structured 192–204 nm bands to the A, B and triplet-structured C bands, respectively, and the 191.4 nm band to the D' band. Thus, the 201.7, 199.4 and 195.5 nm bands are attributable to the C_1, C_2 and C_3 components of the C band, respectively. As seen in figure 2, the C_2–C_3 separation of KCl: Sb^{3+} is almost constant at low temperatures but increases in proportion to $T^{1/2}$, suggesting that it obeys the $\coth^{1/2}(h\nu/2kT)$ law just as in the case of the dynamical Jahn–Teller splitting of the C bands in Sn^{2+}-, Pb^{2+}-, Ga^{+}- and In^{+}-doped crystals (Fukuda 1972, Schmitt 1982).

We evaluate the ratio R_{th} of the dipole strength of the C band to that of the A band using the Sugano formula (Fukuda 1964) and compare its value with the experimental

one R_{obs} (equal to $f_C W_A / f_A W_C$, where f_A and W_A represent the oscillator strength and energy of the A band, respectively). The Sugano formula is given by

$$R_{th} = \{2 - x + [1 + 2x(1 - x)]^{1/2}\} / \{1 + x - [1 + 2x(1 - x)]^{1/2}\}$$

where $x = (W_B - W_A)/(W_C - W_A)$.

R_{th} is 3.68 which was evaluated for $x = 0.793$, while R_{obs} is about 3.9; the two values are close to each other. The R_{obs} value is near the value $R_{obs} = 4.1$ (Schmitt 1982) obtained for $KCl: Pb^{2+}$. Therefore it is concluded that the above assignment for the three bands is quite reasonable.

The presence of charge-compensating vacancies near the Sb^{3+} ion reduces the symmetry around the Sb^{3+} ion in the cubic alkali-halide lattice. This gives rise to the splitting of the excited $^3P_1$, $^3P_2$ and $^1P_1$ states (Kang *et al* 1985). As mentioned above, the absorption spectra are similar to those of $KCl: Pb^{2+}$. No splitting was observed in the A band of $KCl: Sb^{3+}$. The C band has a triplet structure, but this arises from the Jahn–Teller effect as in the cases of In^+, Sn^{2+} and Pb^{2+} centres. These facts are surprising because the vacancy effect was expected to be considerably stronger in the trivalent Sb^{3+} centre than in the divalent Pb^{2+} centre. Therefore, taking into account the previous studies of various monovalent, divalent and trivalent s^2 ions doped in alkali halide crystals, we suggest that the s^2-ion centres have a Jahn–Teller effect which is stronger than the vacancy effect.

Acknowledgments

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