Cathodoluminescence and thermoluminescence studies on the three STE π emission bands in KCl:KBr mixed crystals

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Abstract. Three different kinds of $(Br_2^- + e)$ emission band in KCl:KBr mixed crystals have been investigated based on cathodo- and thermoluminescence measurements. The green emission band is considered to be the normal $(Br_2^- + e)$ π emission; the violet and blue bands observed below 120 K are suggested to originate from the $(Br_2^- + e)$ emission perturbed by a Cl^- ion at two different sites. The relationships between the intensities of these three bands and the temperature are also reported.

1. Introduction

Extensive studies have been made on the luminescence originating from self-trapped excitons (STEs) in alkali halide crystals containing heavy halogen impurity ions, i.e. the MX:Y$^-$ system (M is the alkali metal, X the host halogen atom and Y the heavy halogen impurity atom). The emissions from both the one-centre type STE, $(Y^0 + e)$, and the two-centre type STEs, namely $(X_2^- + e)$, $(Y_2^- + e)$ and $((XY)^- + e)$, have been reported [1–3]. For example, the $(I^0 + e)$, $(Cl_2^- + e)$, $(I_2^- + e)$ and $((ClI)^- + e)$ emissions have been observed in KCl:I$^-$ and RbCl:I$^-$, but no $((ClBr)^- + e)$ emission in KCl:Br$^-$ has been firmly identified. It has been concluded from both experimental and theoretical works that the luminescence energy from the one-centre type STE is higher than 5 eV (in the near-edge band) and that from the two-centre type STEs is between 2 and 5 eV. The peak energy of the $(Y_2^- + e)$ impurity dimer STE emission in MX:Y$^-$ is generally higher than that of the $(Y_2^- + e)$ emission in the pure MY crystal. This has been explained by the smaller Stokes shift in MX than in the MY lattices.

Luminescence in the MX:MY binary mixed crystals have been reported in the meantime, e.g. Nakagawa *et al* [4] have reported the study of NaCl:NaBr and Katsuyama *et al* [5] have reported the complex H centre in KCl:KI. The same kinds of emission band as in the MX:Y$^-$ crystals with analogous peak energies (but broader) have been observed in the mixed crystals. It has been reported in systematic studies [4, 6] that most of the emission peaks move in the lower-energy direction when the MY component increases in the mixed crystal.

Systematic measurements of the low-temperature luminescence in KCl:KBr crystals with various compositions have been reported by Tanaka *et al* [6] and Wakita and Hirar [7]. Violet and blue emission bands were observed and discussed. The thermoluminescence

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(TL) above room temperature, the peak energy of the F absorption band and some other studies on the KCl:KBr mixed crystals have also been reported [8, 9].

40–300 K cathodoluminescence (CL) measurements and the 18–290 K TL measurements on KCl:KBr (3:7), KCl:KBr (4:6) and KCl:KBr (7:3) have been performed in this new work. Three emission bands in the violet, blue and green regions, as well as the $(Br_2^- + e)$ σ emission in the UV region, are observed at low temperatures. The violet, blue and green bands are discussed with reference to the CL and TL results of pure KBr and KCl that have been reported previously [11].

2. Experiments

The KCl:KBr undoped mixed crystals are from the Harshaw Company. Before examination, samples were quenched by heating up to 550 °C for 5 min followed by a fast cooling in air.

The CL system has been described by Yang *et al* [11]. The beam energy used in this work was 10 kV, the beam current was 0.1–0.3 μA. The modulation frequency was 90 Hz except for those cases specially mentioned. Emission signals with different wavelengths were recorded in scanning mode to obtain the emission spectra. The monochromator can also be fixed to a certain wavelength for the measurement of the intensity of a certain emission band versus temperature or irradiation time.

The temperature indicated on the thermodetector of the CL system is the temperature of the crystal holder. The electron beam irradiates the upper surface of the sample, from which the photons are emitted, but only the lower surface is in contact with the crystal holder. Therefore, there will be a 5–10 K difference between the indicated temperature and the real emission temperature.

The very sensitive new TL spectra system has been described by Luff and Townsend [12]. For every TL measurement, 40 kV, 15 mA *in situ* x-ray irradiation was used at 18 K for 5 min. This delivers a dose rate of 40 Gy min^{-1}. Spectra were recorded from 200 to 800 nm with time steps for signal integration of 4 s and a heating rate of 6 K min^{-1}. Signals with different wavelength were recorded simultaneously to avoid any uncertainty in wavelength–temperature changes, which could occur with a scanning monochromator system. All spectra are presented after the wavelength dependence of the entire phonon detector system has been corrected by a computer program.

The resolution of the wavelength is $\sim$ 5 nm in both the CL and TL cases.

3. Results

The emission intensity of KCl:KBr (4:6) versus the wavelength and temperature is shown in figures 1 and 2 for the CL and TL measurements, respectively.

A 370 nm violet band and a 425 nm blue band are observed at low temperatures. In the CL case, these two emission bands can be observed below 120 K and their maximum intensities are recorded at 62 K. In the TL case, two glow peaks of these bands are observed: a weak peak at about 25 K and a very strong one at 58 K. No signal from these two emissions can be detected above 100 K in the TL measurements. A small difference in the temperature dependence between these two bands is found in both figure 1 and figure 2. In figure 1, it is seen that at about 60 K the violet emission is stronger than the blue one, but at about 40 K the blue one becomes stronger. In the TL case, the intensities of these two bands are nearly the same for the 25 K glow peak, but the 370 nm emission is obviously stronger in
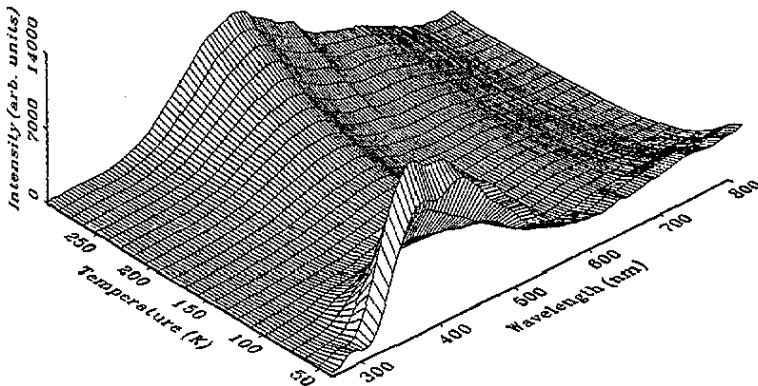
Figure 1. The CL intensity of KCl:KBr (4:6) versus wavelength and temperature; data were recorded during cooling from 300 to 40 K.
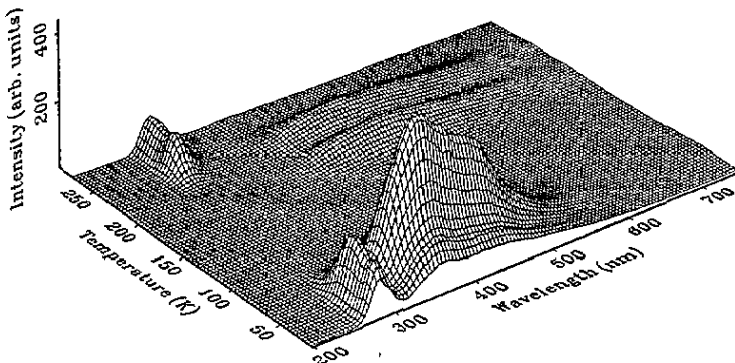

Figure 2. The 18–290 K TL intensity of KCl:KBr (4:6) versus wavelength and temperature, after a 200 Gy x-ray irradiation at 18 K.

the 58 K peak. The relative intensities of these two bands and the peak temperatures vary slightly with the crystal history and the irradiation dose in the TL measurements.

These violet and blue emission bands are also observed at 390 and 440 nm in KCl:KBr (3:7) and at 360 and 415 nm in KCl:KBr (7:3). As in KCl:KBr (4:6), these two bands are observed only at low temperatures. With increasing KCl component in the mixed crystal, the temperature at which the highest emission intensity of these two bands is observed becomes lower. The maximum CL intensity is observed at 65 K in KCl:KBr (3:7) and at 60 K in KCl:KBr (7:3). The strongest TL peaks are at 64 K in KCl:KBr (3:7) and at 48 K in KCl:KBr (7:3).

No such emission bands have been reported in pure KBr or KCl.

Besides the violet and blue bands, another two emission bands are observed in the mixed crystals in both CL and TL measurements. One of them is at 290 nm in KCl:KBr (3:7), at 285 nm in KCl:KBr (4:6) and at 270 nm in KCl:KBr (7:3), detected below 90 K only. This is the well known STE σ emission, i.e. the $(Br_2^- + e)$ σ emission in the mixed crystals [7, 6]. Another is a broad band at 400–650 nm. This is observed at all temperatures in the CL case. In the TL case, this band is very weak at low temperatures, but there are two strong glow peaks of this band above 190 K: the 194 K and 226 K peaks in KCl:KBr (3:7), the 197 K and 235 K peaks in KCl:KBr (4:6) and the 210 K and 238 K peaks in KCl:KBr (7:3).

A guide to trends observed is given in table 1.

The CL spectra of KCl:KBr (4:6) at 45 K with different modulation frequencies are given in figure 3. It is found in this figure that at this temperature the lifetime of the blue emission is shorter than that of the 400–650 nm emission, but longer than those of the violet emission and the STE σ emission; the latter possesses the shortest lifetime in the whole spectrum.
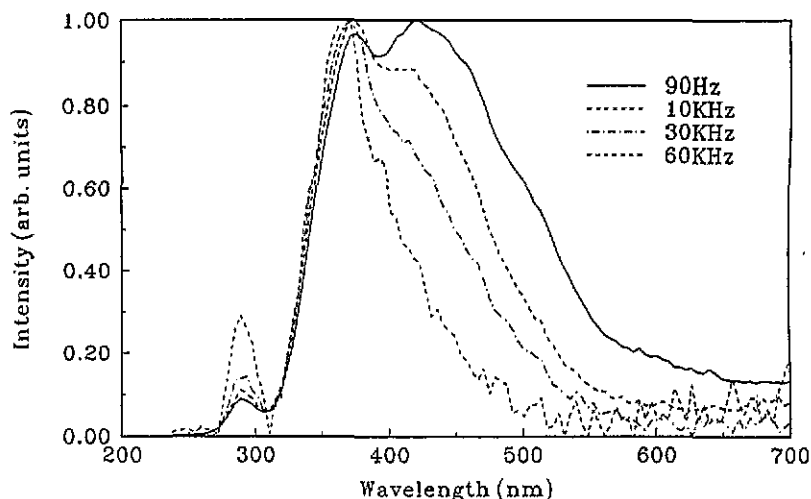

Figure 3. The 45 K CL spectra of KCl:KBr (4:6) with different modulation frequencies.

4. Discussion

The results from KCl:KBr (4:6) are used as examples for the discussion, but all considerations are the same for the results from KCl:KBr (3:7) and KCl:KBr (7:3).

4.1. The 400–650 nm emission band

A related emission band with nearly the same lineshape and similar temperature dependence has been observed in the 40–300 K CL and 18–290 K TL measurements in pure KBr.

The CL spectra at 120 K of pure KBr and KCl:KBr (4:6) are given in figure 4. The intensities of each spectrum are normalized for comparison. A valley at about 600 nm is caused by the F-band self-absorption. The 400–650 nm emission band of pure KBr consists

Table 1. Guide to trends observed. Sample 1 is KCl:KBr (3:7), sample 2 KCl:KBr (4:6) and sample 3 KCl:KBr (7:3). Note that for 'pure' KBr the peaks are a UV band at 295 nm and a broad green band at 400–650 nm. TL peak temperatures for pure KBr and KCl vary with crystal history and radiation dose.

	UV			Violet			Blue			Green		
	1	2	3	1	2	3	1	2	3	1	2	3
Peak wavelength (nm)	290	285	270	390	370	360	440	425	415	a broad band with components at 400–650 nm; peak positions undetermined[a]		
Peak temperature (K) CL	54	53	51	65	62	60	65	62	60	—	—	—
		25 (weak)			25 (weak)			25 (weak)				
TL	50	45	35	64	58	48	64	58	48	194	197	210
										226	235	238
	observed below 90 K			observed below 120 K			observed below 120 K			observed at all temperatures in CL		

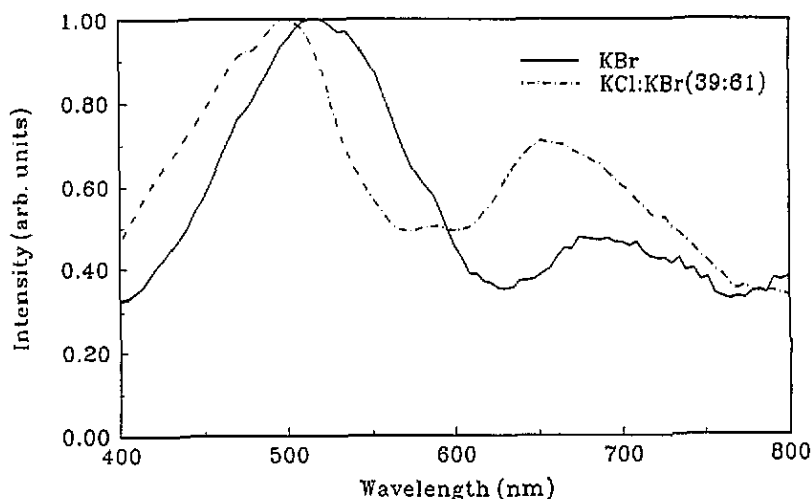[a] Bands shift to shorter wavelength from sample 1 to 3.

Figure 4. The 120 K CL spectra of pure KBr and KCl:KBr (4:6).

of the unperturbed STE π emission and the α centre emission, but there is no ion vacancy perturbed STE emission at 120 K. It is suggested that the emission band of KCl:KBr (4:6) shown in figure 4 consists of the same components, i.e. the unperturbed homonuclear two-centre type STE π emission and the α centre emission, as the line shape of this band is very similar to that in pure KBr and the shift of the emission energy is supposed to be caused by the change in lattice dimensions.

The Br$^-$ should act as a stronger hole trap than the Cl$^-$ in the KCl:KBr mixed crystals since the electronegativity of Br is less than that of Cl. No Cl$_2^-$ has been detected in the Cl$^-$ impurity doped KBr:Cl$^-$ crystal, so it will be unlikely to have a large number of Cl$_2^-$ in the mixed samples in this work, especially in the KBr dominated mixed crystal KCl:KBr (3:7) and KCl:KBr (4:6). However, the observed 120 K CL intensity of the 400–650 nm band in KCl:KBr (4:6) is not weaker than that in pure KBr. Therefore, it is suggested that the core of the STE in this broad emission band in the mixed crystal is mainly Br$_2^-$, i.e. the emission is produced when an electron is recombined with a Br$_2^-$ V$_K$ centre, or an F centre is recombined with a Br$_2^-$ H centre. This emission will hereafter be called the normal (Br$_2^-$+e) π emission in the mixed crystals.

It is difficult to discuss the 400–650 nm TL emission at low temperature as it is too weak (see figure 2). The 197 K thermal peak of this band in figure 2 emerges above 150 K, at which temperature the Br$_2^-$ V$_K$ centres become mobile and no ion vacancy perturbed STE can be produced. Therefore, it is considered that this 197 K glow peak originates from the STE emission, and for the same reason as explained above for the CL case, the core of the STE is also suggested to be a Br$_2^-$ molecular ion.

Because of the F-band self-absorption, the wavelengths of the peak of the normal (Br$_2^-$+e) π emissions in the mixed crystals cannot be determined in this work.

4.2. The violet and blue emission bands

These two bands are considered to be the intrinsic emissions since they have been observed in the undoped KCl:KBr mixed crystals in the previous reports from different authors [7, 6]. According to the emission energy, they may also belong to the two-centre type STE emissions.
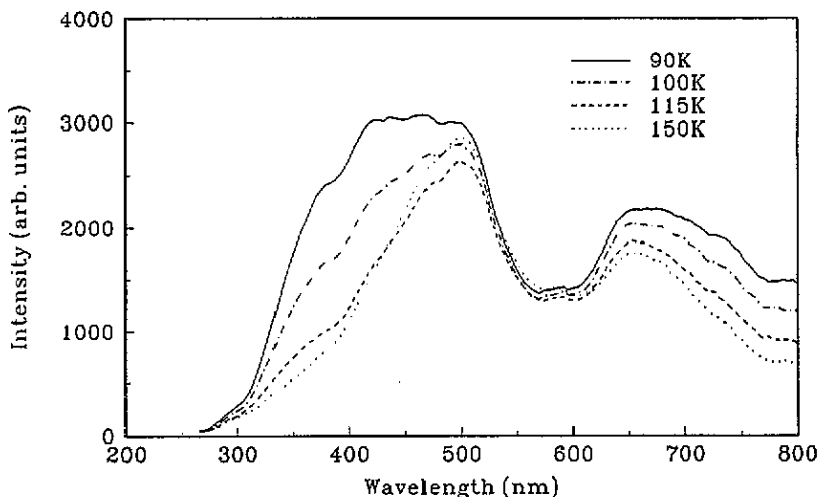
Figure 5. The CL spectra of KCl:KBr (4:6) at different temperatures; data were recorded during cooling.

The CL spectra of KCl:KBr (4:6) at different temperatures from 150–90 K during cooling are shown in figure 5. In the 150 K spectrum, there is no violet or blue emission band observed. These two bands grow up rapidly from 115 K. One can notice from figure 5 and figure 1 that when these two emissions are getting stronger and stronger, the normal $(Br_2^- + e)$ π emission does not decrease at all (in pure KBr, there is an increase of this band from 90 to 50 K). It is likely that the normal $(Br_2^- + e)$ π emission would be ignored if only the spectra at lower than 70 K were studied, because the violet and blue emissions are extremely strong at those temperatures and the F-band self-absorption makes the normal $(Br_2^- + e)$ π emission more difficult to detect, but in fact, the CL signals of this band are detected at 400–650 nm in the KCl:KBr mixed crystals in this work at all temperatures from RT to 40 K as shown in figure 1. Therefore, none of the violet and blue bands will be considered to be the normal $(Br_2^- + e)$ π emission.

This consideration is supported by another experimental result: the highest intensity of these two emissions and that of the well known $(Br_2^- + e)$ σ emission are detected at different temperatures. The intensities of the 285 and 425 nm emission bands in KCl:KBr (4:6) in CL and TL measurements versus temperature are shown in figure 6(*a*) and (*b*), respectively. It is found that the peak of the 285 nm band, i.e. the normal $(Br_2^- + e)$ σ emission in the mixed lattice, is at 53 K, but that of the 425 nm band is at 62 K in figure 6(*a*). These two peaks are at 48 and 58 K, respectively, in figure 6(*b*). This difference is also recorded for the emissions in KCl:KBr (3:7) and KCl:KBr (7:3) as given in table 1. It is difficult to measure the intensity of the normal $(Br_2^- + e)$ π emission changes with temperature in the low-temperature region because of the overlap of the strong blue band and the disturbance of the F-band self-absorption, but in pure KBr, the maximum intensities of the STE σ emission and π emission have been recorded at the same temperature in both CL and TL cases [11].

It is considered that both Br and Cl are involved in these violet and blue emissions as they are only observed in the binary mixed crystals.

These two bands were suggested to be the $((BrCl)^- + e)$ emissions [7], but it has been reported that from the ESR results [13] there are only a few $(BrCl)^-$ V_K centres (the H type $(BrCl)^-$ centre will be discussed in the following paragraphs) in KCl:Br$^-$ when the
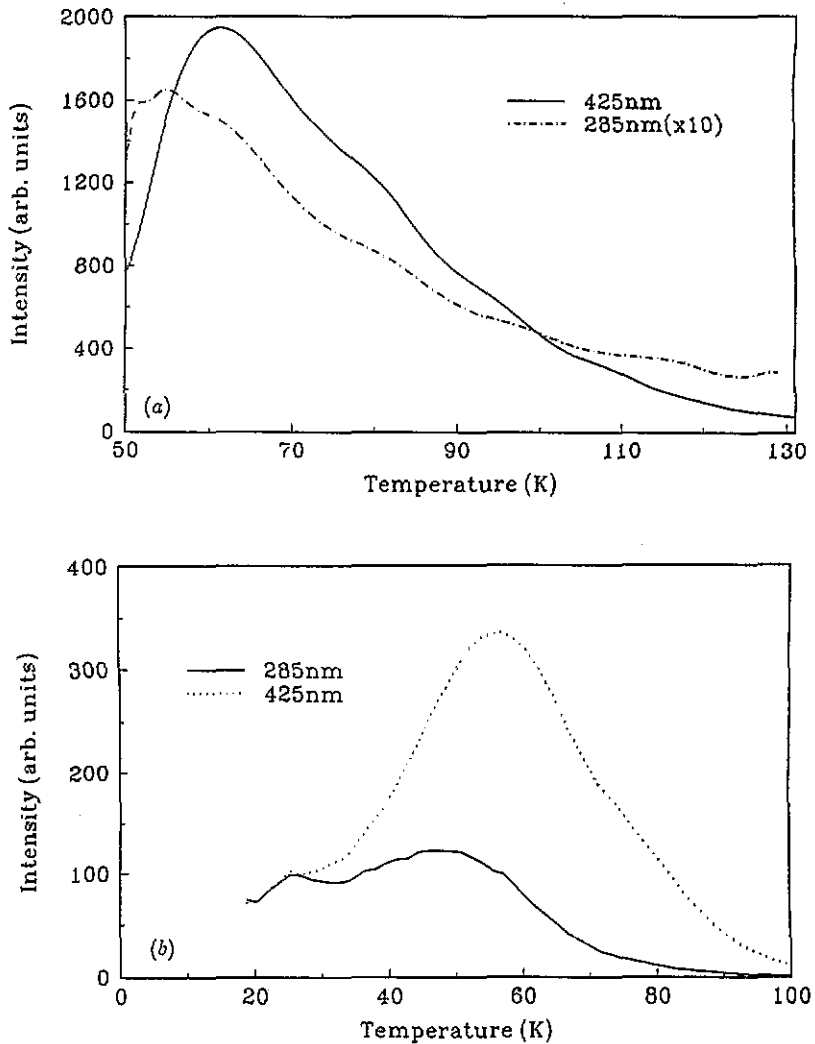
Figure 6. (*a*) CL and (*b*) TL intensities of the 285 nm and 425 nm emissions in KCl:KBr (4:6) versus temperature.

temperature is lower than 170 K. The number of $(BrCl)^-$ V_K centres increases from 170 K when the sample is warmed up. Its maximum concentration has been detected at about 220 K, and then the centres decay at about 240 K, but no violet or blue emission is observed above 120 K in the present work or in the previous reports. Of course, the situation in a mixed crystal could be different from that in KCl:Br$^-$, but the peak temperature of these two bands should become higher and higher through the sequence from KCl:KBr (3:7) to KCl:KBr (4:6) and then to KCl:KBr (7:3) (finally to KCl:Br$^-$) if these two bands are the $((BrCl)^- + e)$ emissions. However, the experimental results are in contradiction to this: as described in section 3, the peak temperature of these two bands becomes lower when more KCl is contained in the mixed crystal.

Tanaka *et al* [6] have reported that the intensity of the violet emission band in KCl:Br$^-$ (3.60 eV) is proportional to the square of the Br concentration, so there are possibly two
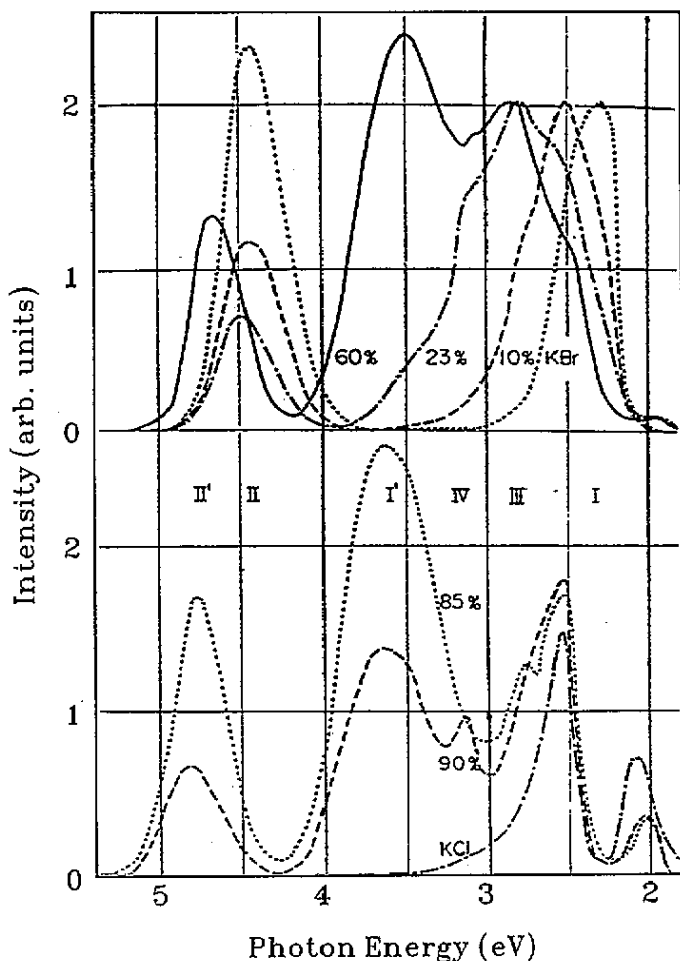
Figure 7. The luminescence spectra of KBr:KCl mixtures at liquid helium temperature. The numbers with % in each curve stand for the mole percentage of KCl in the mixed crystal, quoted from Wakita and Hirai [7].

Br ions involved in the luminescence centre.

The model of an electron recombined with an interstitial Cl$^-$ ion perturbed Br$_2^-$ V$_K$ centre is now suggested. The distances between the Cl$^-$ ion and the two Br$^-$ ions can be equal or unequal. In other words, the recombination centre is in the form of (BrClBr)$^{2-}$ or (BrBrCl)$^{2-}$. These centres can be called the interstitial Cl$^-$ ion perturbed V$_K$ centre or the complex H centre. The first name is preferable, because the hole density on the Br$^-$ ion will be more than that on the Cl$^-$ ion. These three ions may be, but also may not be, on the linear positions, especially for the (BrBrCl)$^{2-}$ model. (The linear (BrBrCl)$^{2-}$ would be a normal Br$_2^-$ H centre in the mixed lattice). Further studies are necessary for the details of these models.

The interstitial ions in KBr and KCl are stable only at very low temperature [14]. In agreement, the violet and blue emission bands can be observed at low temperatures only. These two bands disappear at 120 K in the CL measurement of the mixed crystals. An increase of the normal (Br$_2^-$+e) π emission is observed from 120 K to higher temperature.

But in pure KBr, the CL intensity of the $(Br_2^- + e)$ π emission keeps almost constant from 100 to 200 K. In the TL measurement, the ratio between the intensities of the $(Br_2^- + e)$ π emission in the 197 K glow peak and in the low-temperature peak is nearly 1:1 in pure KBr, but the peak at about 200 K is much stronger than the low-temperature one in the mixed crystals (see figure 2). It is assumed that in the mixtures there is possibly a conversion from some of the interstitial perturbed Br_2^- centres to the normal Br_2^- centres when the interstitial Cl^- ions become unstable.

Unfortunately, in this work, insufficient KCl:Br combinations were available in order to follow the change of the emission energies of these three $(Br_2^- + e)$ type π emission bands, but we would like to quote the experimental results reported by Wakita and Hirai [7]. The quoted spectra are given in figure 7. It is seen in this figure that in the spectrum of KCl:KBr (90% KCl) the violet band is at about 3.6 eV, and in the spectra of the 60%, 23% and 10% KCl samples, on the lower-energy side of the blue band, there is an emission band whose intensity increases with decreasing fraction of the KCl component. This band joins in the normal $(Br_2^- + e)$ π emission for the KCl $\rightarrow$ 0 limit. The feature shown in figure 7 is in agreement with the presumptions given in this work.

5. Conclusions

As the same as in pure KBr, the normal $(Br_2^- + e)$ σ and π emissions are recorded in the UV and green regions, respectively, in KCl:KBr mixed crystals by both CL and TL measurements. Two strong emission bands in the violet and blue regions are observed below 120 K. They are presumed to be the Cl^- perturbed $(Br_2^- + e)$ π emissions.

The wavelengths of all the emission peaks shift in the shorter-wavelength direction when the KCl component in the mixed crystals is increased. There is also a temperature shift for the emission peaks, but the direction of the shift is not the same for different emission bands.

Acknowledgments

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