Luminescence and photoconversion processes of $(F_2^+)_H$ centres in doped KCl crystals under F-light excitation

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Abstract. The luminescence of $(F_2^+)_H$ centres in additively doped $KCl:CO_3^{2-}$ crystals excited using light in the F-band is reported. The emission spectrum consists of two bands peaking at 610 and 750 nm which are strongly dependent on prior photo- and thermal-treatments. The two bands are associated with different configurations of the $(F_2^+)_H$ centres. The temperature dependences of the luminescence spectra indicate the existence of several stable configurations of the $(F_2^+)_H$ centres which are distinguished through the zero phonon lines observed in the absorption spectrum measured at low temperature.

Laser action of F_2^+-like colour centres in alkali halides has been much studied in recent years [1]. Doping with anionic impurities modifies the ionic structure of these centres and stabilizes them relative to 'pure' F_2^+ centres. $(F_2^+)_H$ centres are stabilized centres consisting of $F_2^+-O^{2-}$ complexes with several similar configurations each having different stability [2, 3]. Transformations between configurations involving short-range reorientations of components are enhanced by excitation to levels higher in energy than the $2p\sigma_u$ laser level. The sequence of events following excitation to higher levels is not fully understood: apparently, matrix-dependent processes take place including thermally activated non-radiative decay to the $2p\sigma_u$ level, which is accompanied by defect reorientation [3, 4]. Only for NaCl crystals have detailed studies been reported [3, 5]. 'Pure' coloured KCl crystals excited by F-band light below $T = 60$ K emit in a broad band with a peak at 610 nm attributed to radiative $2p\pi_u \rightarrow 1s\sigma_g$ transitions from unperturbed F_2^+ centres. At higher temperatures non-radiative decay to the lowest excited $2p\sigma_u$ level leads to emission in the laser transition centred at $\lambda = 1.34\ \mu$m [4]. In doped KCl after low temperature excitation (15 K) with F-band light the 610 nm band is inhibited: luminescence with a peak at 750 nm is then observed. This band was tentatively assigned to the $2p\pi_u \rightarrow 1s\sigma_g$ transitions of perturbed $(F_2^+)_H$ centres [2]. The present paper discusses the origins of the 750 nm emission band in terms of the excitation spectra and temperature dependences of the luminescence of additively coloured KCl crystals containing $(F_2^+)_H$ centres excited via the $1s\sigma_g \rightarrow 2p\pi_u$ transition.

$KCl:CO_3^{2-}$ crystals were grown by the Czochralski method in the Crystal Growth Laboratory of the Universidad Autónoma de Madrid using suprapure grade KCl from Merck laboratories as starting material. K_2CO_3 was added to the melt in concentrations
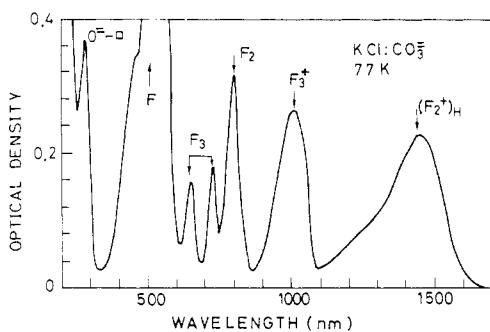
Figure 1. Optical absorption of an additively coloured KCl:$CO_3^=$ crystal after quenching from 600 °C, taken at 77 K.
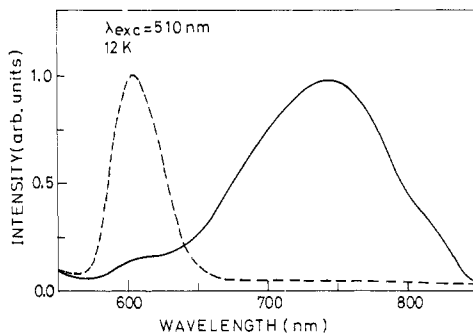
Figure 2. Emission spectrum of a freshly quenched crystal (full curve), and after 5 min exposure to F-band light at 50 K. Both spectra were taken at 12 K with $\lambda_{exc} = 510$ nm.

up to 250 PPM. The CO_3^{2-} concentration after growth, typically 10–50 PPM, was determined from the absorption coefficient in the vibrational band at 1400 cm^{-1} [6]. Crystals 4–5 mm thick were additively coloured in a Van Doorn heat pipe at 650 °C for 1 h using potassium vapour pressures in the range 5–20 Torr. The CO_3^{2-} anions decompose during colouration giving oxygen-vacancy dipoles (O^{2-}–□) needed for the production of $(F_2^+)_H$ centres [7]. Spectroscopic samples cleaved from additively coloured crystals of about 2 mm thickness, were annealed in air at 600 °C and quenched on a Cu block to room temperature (RT). Absorption spectra were measured at temperatures in the range 12–300 K using crystals mounted in a cryo-refrigerator coupled to a CARY-17 spectrophotometer. This cryostat with a Jobin-Yvon spectrofluorimeter was used for excitation and luminescence measurements in the range 200–850 nm. F-band light used to transform centres was provided by a 150 W arc-xenon lamp filtered through a Jobin-Yvon monochromator ($\Delta\lambda = 2$ nm).

The optical absorption spectrum of an additively coloured KCl:CO_3^{2-} crystal quenched from 600 °C to room temperature (RT) is shown in figure 1. The (O^{2-}–□) pairs produced by dissociation of CO_3^{2-} impurities absorb in a broad band centred at 280 nm. In the visible region the F band is dominant although bands from F-aggregate centres are also observed. A broad band in the infrared with peak at $\lambda = 1.45$ μm due to the F_2^+-like centres is observed at LNT. This absorption band is coincident with that of $(F_2^+)_H$ centres, the stable defect in KCl at RT. Illumination with F-band light at low temperature (77 K) shifts this infrared peak to 1.40 μm, coincident with that of F_2^+ centres in pure KCl [2, 4]. In NaCl and KBr, $(F_2^+)_H$ centres are stable only below 200 K [2, 3].

The emission between 550–850 nm excited by F-band light is shown in figure 2. There are two bands with peaks at 610 and 750 nm, the relative intensity of which depend on previous photo- and thermal-treatments. The full curve represents the emission from a sample quenched to RT from 600 °C and then cooled to 12 K in the dark. The broken curve indicates the emission observed after 5 min F-band illumination at 50 K, where the 610 nm band has increased dramatically and the 750 nm band has almost disappeared. The 610 nm band is the only one observed in pure KCl: it is assigned to $2p\pi_u \rightarrow 1s\sigma_g$ transitions of unperturbed F_2^+ centres [4]. The 750 nm band is coincident with that reported in additively coloured KCl:O_2^- crystals due to the $2p\pi_u \rightarrow 1s\sigma_g$ transition of
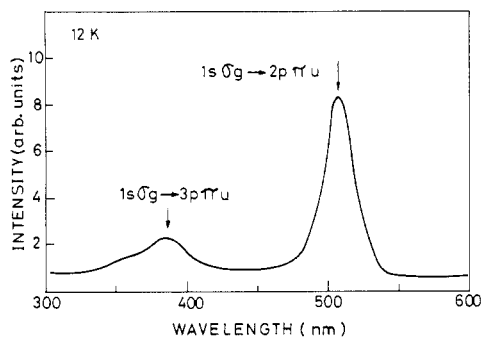
Figure 3. Excitation spectra of the 750 nm band in the range 300–600 nm taken at 12 K.
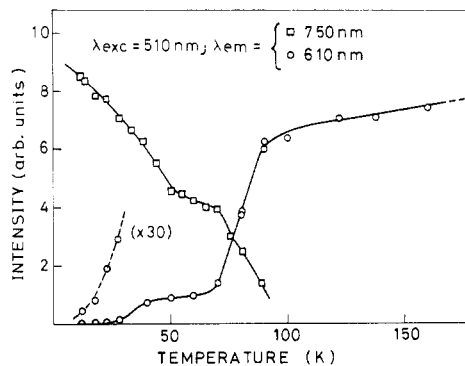

Figure 4. Evolution of the peak intensity of the 750 (squares) and 610 (circles) nm bands after 5 min F-light illumination at different temperatures. All measurements are taken at 12 K.

perturbed $(F_2^+)_H$ centres [2]. Figure 3 shows that the excitation spectrum of the 750 nm band at 12 K consists of several bands in the visible and near UV region, the dominant one being located at 505 nm. This band is accompanied by a weaker excitation band at 390 nm with a weak tail at higher energies. The main transitions are indicated. The observed bands, in accord with the excitation spectrum of the 610 nm band, correspond to the reported absorptions of F_2^+ centres in pure KCl [4], confirming that the 750 nm band is related to (F_2^+)-like centres. That similar excitation spectra result in substantially different emission bands, indicates that the different relaxed excited states are very sensitive to the defect environment and can reveal slight differences in the ionic configurations.

The temperature dependence of the photoconversion kinetics involving the 610 nm and 750 nm bands has been studied using freshly quenched samples cooled to liquid helium temperature (LHeT) in the dark, after which only the 750 nm band is observed (figure 2). The samples are then illuminated with F-light for 5 min at different temperatures, cooled again to 12 K, and the luminescence is re-measured. In this way, luminescence quenching which sets in above 50 K [4], is avoided. As the temperature is increased the decreasing intensity in the 750 nm band is accompanied by enhancement of the 610 nm band. The relative intensities of the 610 nm and 750 nm after bleaching at different temperatures are plotted in figure 4. Evidently the intensity of the 610 nm band increases up to 40 K, is constant between 40 K and 60 K, and then increases further at higher temperatures. There are concomitant trends in the decreasing intensity of the 750 nm band. These correlations suggest a transformation between the centres, emitting in the two luminescence bands. Note that photoconversion between the 610 and 750 nm bands operates even at very low temperatures, as illustrated by the broken curve in figure 4 below $T = 30$ K. The efficiency of the process increases strongly with increasing temperature. The appearance of the different stages in figure 4 may be related to several stable configurations of the $(F_2^+)_H$ centre. In accord with previous observations [2], zero phonon lines (ZPL) at 1.6136 and 1.6205 μm are observed on the low-energy side of the broad $(F_2^+)_H$ absorption band (figure 5). The thermal evolution of these ZPL in the range 12–40 K is shown in figure 5; clearly the 1.6136 μm ZPL disappears at 40 K, in coincidence with the first stage decrease in the 750 nm emission band in figure 4. The ZPL at 1.6205 μm increases in intensity by some 30%. The intensity of this ZPL is constant up to 60 K above
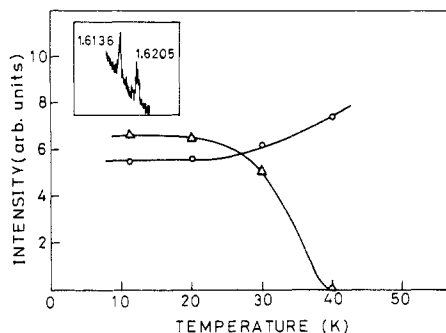
Figure 5. Variation intensity of the 1.6136 (triangles) and 1.6205 (circles) ZPL after F-light illumination during 5 min at different temperatures in the range 10–50 K.
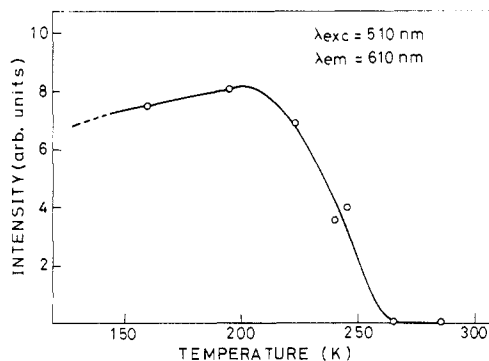
Figure 6. Variation of the 610 nm emission band after 5 min of F-light exposure at different temperatures.

which temperature it disappears. The ZPL at 1.526 μm, due to unperturbed F_2^+ centres, then appears.

The former results confirm the existence of two differently perturbed configurations, which have different thermal stability. The accepted model of the $(F_2^+)_H$ centres in the alkali halides, involves F_2^+ centres perturbed by neighbouring oxygen ions. Depending on the relative position of impurity and defect, four $(F_2^+)_H$ configurations are possible [2, 3] having different optical transition energies. Only two different absorption and luminescence bands are observed. One coincident with that from pure F_2^+ centres is due to a weakly perturbed configuration and the other, shifted to higher energies, is associated with strongly perturbed configurations. The broad band character of the $1s\sigma_g \rightarrow 2p\sigma_u$ transition, makes it difficult to resolve spectra from similarly perturbed ionic configurations. The two stages observed for the $(F_2^+)_H \rightarrow F_2^+$ transformation (figure 4) and the two ZPL (figure 5) indicate that in additively coloured KCl:CO_3^{2-} samples at least two different $(F_2^+)_H$ configurations are stable at low temperature.

The mechanism of $(F_2^+)_H \rightarrow F_2^+$ involves short range reorientations of defect components, leading to transformations between the different configurations [3, 6]. Mechanisms of the ionic movements at these low temperatures involve the role played by the excitation to higher excited states, facilitating these movements in conjunction with non-radiative transitions to the $2p\sigma_u$ laser level. The two photoconversion stages observed at low temperature indicate that non-radiative energy transfer takes place in two stages, the low temperature stage being particularly striking since the photoconversion is observed even at 10 K. Note that in NaCl where the transformation is dominant at 77 K, photoconversion has also been observed at low temperatures ($\sim$12 K) under high intensity excitation [8]. When crystals displaying the 610 nm luminescent band are warmed up to even higher temperatures (200–300 K) the intensity of the 610 nm luminescence band (measured at 12 K), which remains roughly constant up to 210 K, decreases and disappears completely at 270 K (figure 6). In similar measurements it is observed that the 750 nm luminescence recovers completely. Since the same result is obtained when the experiment is performed in the dark, it must be related to a thermal process. This thermal conversion is analogous to that in NaCl which takes place at temperatures above which anion vacancies become mobile ($>$200 K) [5]. The difference

between sodium and potassium chlorides is that in NaCl the stable centre at high temperature is the weakly perturbed F_2^+ centre whereas in KCl the stable configuration is the perturbed $(F_2^+)_H$ centre.

We conclude that in additively coloured $KCl:CO_3^{2-}$ the photoconversion $(F_2^+)_H + h\nu \rightarrow F_2^+$ proceeds via two different stages at ~ 40 K and ~ 70 K. Since these two stages are correlated with the disappearance of ZPL at 1.6136 and 1.6205 μm they indicate the existence of two perturbed $(F_2^+)_H$ configurations. At higher temperatures still (>200 K) a thermally activated conversion $F_2^+ \rightarrow (F_2^+)_H$ is operative.

Acknowledgments

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