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Luminescence of O_2^- and $(Cl^-)^*$ color centers in KCl single crystals grown by Czochralski method

Fouzia Zehani

Laboratoire d'Etude des Matériaux (LEM), Département de physique, Facultés des sciences exactes et Informatique, Université de Jijel, BP 98 Ouled Aissa, Jijel (18000), (ALGERIA)

E-mail: zehanifouzia@yahoo.fr

ABSTRACT

The photoluminescence of O_2^- and $(Cl^-)^*$ color centers in KCl single crystals grown by Czochralski method, are reported. The emission spectra obtained at 78 K presented several emission bands situated between 300-800 nm, whichare attributed to O_2^- and $(Cl^-)^*$ color centers. This study confirmed the introduction of air oxygen and showed the new emission bands of $(Cl^-)^*$ centerssituated in the visible spectral domain.

KEYWORDS

KCl;
O_2^-color centers;
$(Cl^-)^*$ color centers;
Photoluminescence.

INTRODUCTION

Alkali halides are ionic crystals having a large forbidden energy gap between valence and conduction bands (8 eV of KCl)[1]. Pure crystals are optically transparent over a corresponding wide spectral range limited in the halide ions and in the infrared by excitation of lattice vibrations. These materials are characterized by a large number of different defect configurations exist. In general, these seem to be associated with impurity, vacancies, aggregations of vacancies and several interstitial configurations produced by the displacement of ions from their normal sites. Among all the defects formed in alkali halides during the elaboration, O_2^- and $(Cl^-)^*$ are two interesting centers.

The O_2^- molecular ion is an impurity that is very soluble in alkali halide crystals. The incorporation of the O_2^- ions in the lattice of the alkali halides takes place by substitution of halogen ions[2]. These centers have received considerable attention since the discovery of superfluorescence and laser activity[3-6]. While, the $(Cl^-)^*$ color center represents an interstitial position of Cl^- ion in the crystal lattice of alkali halides like KCl. This center is investigated by Jun Gill Kang[7] and it is not studied in detail.

The aim of this work is to elaborate the KCl single crystals in air to dope them with the air oxygen and to show the new emission bands of $(Cl^-)^*$ centers in a KCl crystalline lattice excited in visible range, in order to complete the results of J. G. Kang.

EXPERIMENTAL

Single crystals of KCl weregrown in airfrom the melt by the Czochralski method, using the KCl powder in a porcelain crucible. The starting material of KCl is provided by Panreac Quimica company(Spain). The pulled rate is 7 mm/h at a rotation rate of 1 tr/min. The obtained crystals were

cleaved along the (100) plane in order to prepare 1 mm thick pastilles.

The photoluminescence spectra (PL) and the photoluminescence excitation spectra (PLE) were measured at 78 K with a Jobin-Yvon spectro-fluorometer Fluorolog-3, using a xenon lamp 450 W.

RESULTS AND DISCUSSION

The PL of KCl samples excited with 270 nm and measured at 78 K is illustrated in Figure 1. We observe a fluorescence formed by a series of emission lines, situated between 400 and 800 nm, wherethe great intensity is located at 599 nm. These emission lines are attributed to the electronic transitions from the lowest vibrational levels of the excited state $^2\pi_u$ to vibrational levels of the ground state $^2\pi_g$ of O_2^- molecule ions[8]. The O_2^- center is formed inside the single crystals of KCl because they are elaborated in air. The calculation of emission line positions show that these positions are the same as those obtained by[9]. We note that the emission lines are formed by

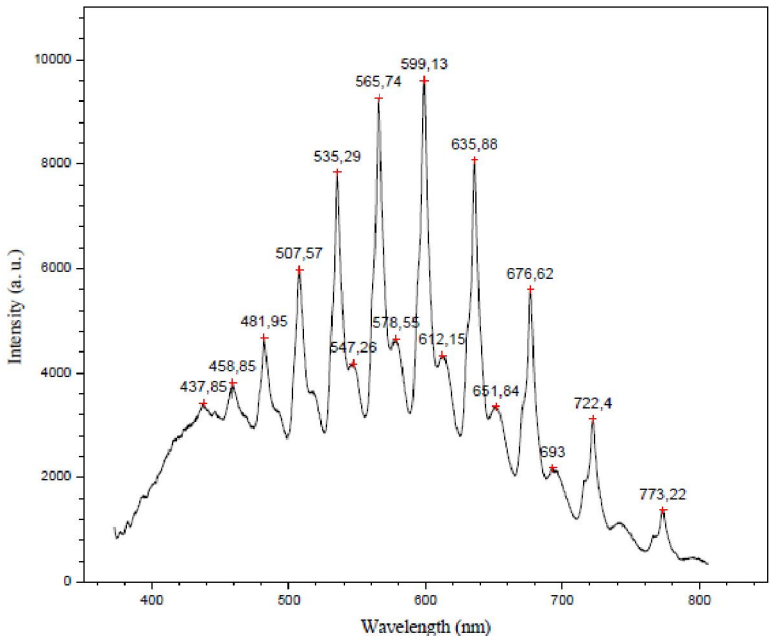

Figure 1 : Emission spectrum of KCl for excitation at 270 nm, The inset shows the band emission 440 nm

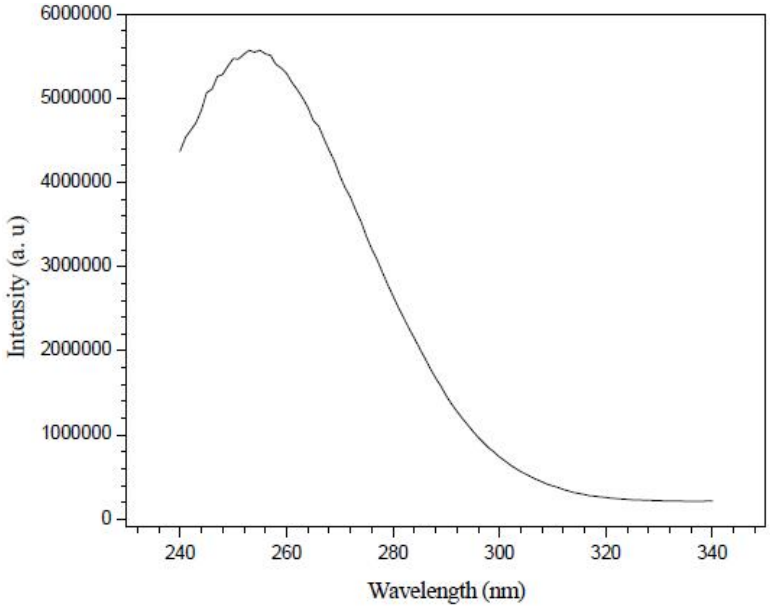

Figure 2 : Excitation spectrum of KCl measured at 599 nm

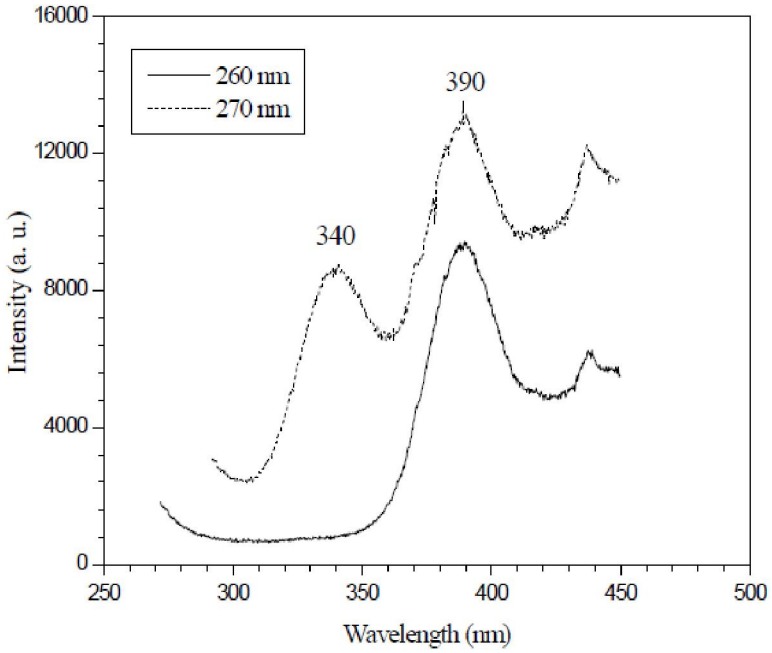

Figure 3 : Emission spectra of KCl corresponding to excitation at 260 and 270 nm

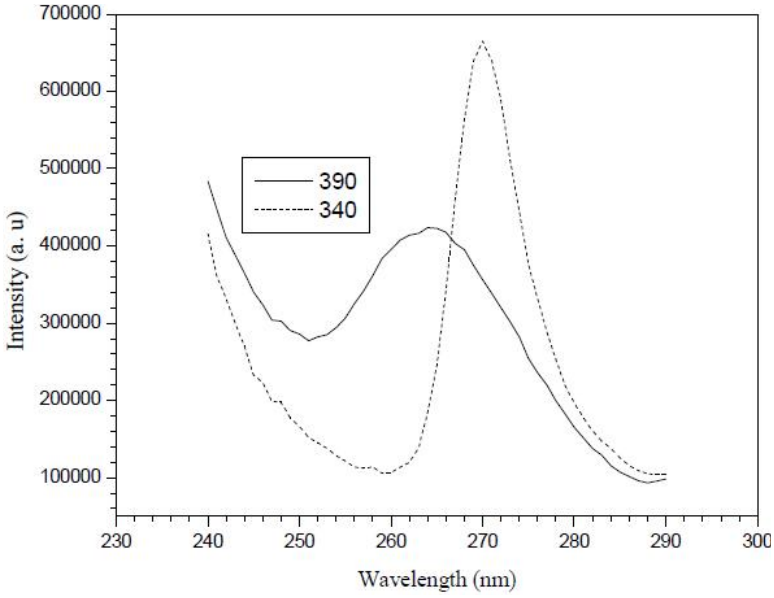

Figure 4 : Excitation spectra of KCl measured at 340 and 390 nm

the double structure. In KCl crystals, each vibrational level of the ground state and the excited state of the O_2^- molecule ions, is degenerate in two levels respectively

($^2B_{2g}$ and $^2B_{3g}$) and ($^2B_{2u}$ and $^2B_{3u}$). The intense emission lines are called ordinary lines and they are due to transition $^2B_{2u} \rightarrow {}^2B_{3g}$. However, the weak lines are attributed to transition $^2B_{2u} \rightarrow {}^2B_{2g}$ and they are called extra lines. The ordinary and extra lines give the double structure[10]. The measure of the PLE at 599 nm (Figure 2) presents an excitation band situated at 254 nm, which is assigned to O_2^- centers in alkali halides[2].

The emission spectra measure between 250-450 nm for two excitations 260 and 270 nm are represented in Figure 3. We note that for excitation 260 nm, it appears an emission band at 340 nm. Whereas for the excitation 270 nm, we see two emission bands at 340 and 390 nm. These emissions were obtained also by Jun Gill Kang. In term of adiabatic potential

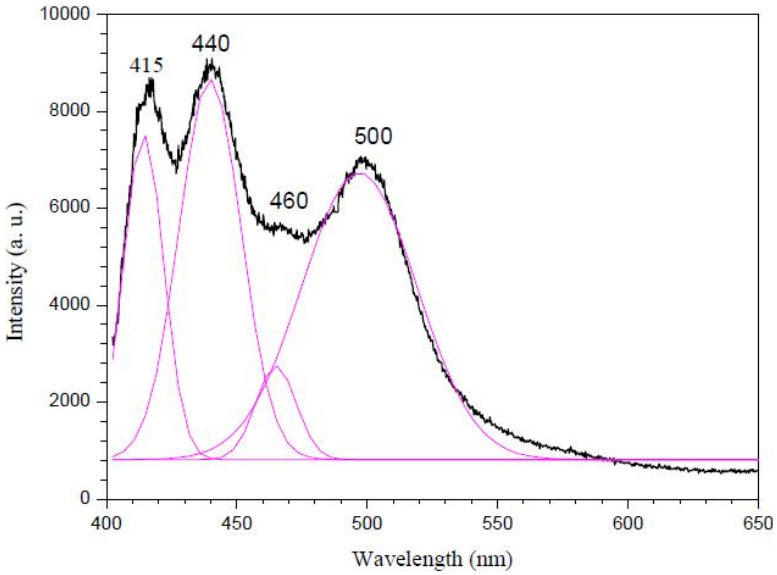

Figure 5 : Emission spectrum of KCl for excitation at 360 nm

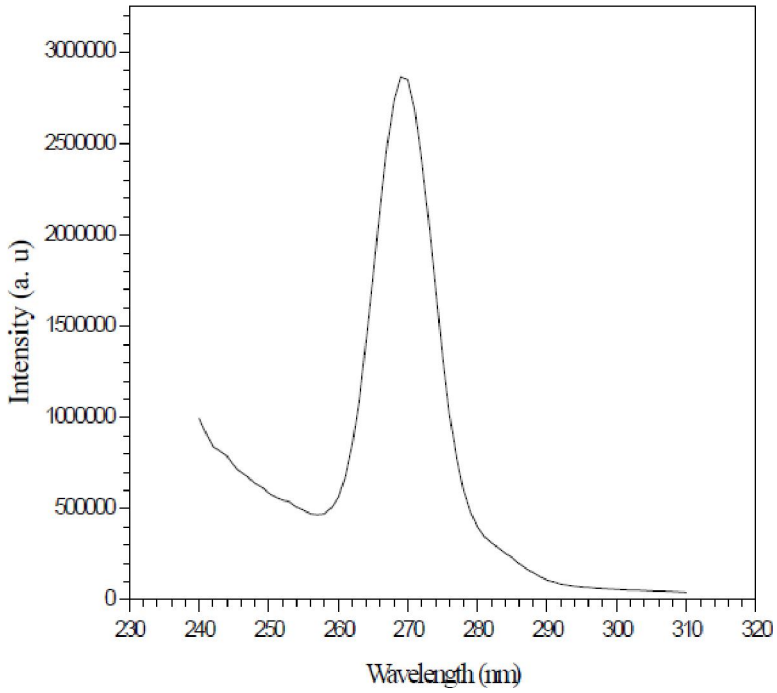

Figure 6 : Excitation spectrum of KCl measured at 440 nm

energy surface and Jahn Teller effect, J. G. Kang has assigned the 340 and 390 nm emissions bands respectively to transitions from the excitedstates $^3A_1$and $^3E$to the ground state $^1A_1$ of $(Cl^-)^*$[7].

Figure 4 shows the excitation spectra measured for two emission bands 340 and 390 nm. For 340 nm, we observe a band excitation at 270 nm. While for 390 nm, we obtained a band excitation at 265 nm. The two excitation bands 270 and 265 nm are attributed respectively to the electronic transitions $^1A_1 \rightarrow {}^3A_1$ and $^1A_1 \rightarrow {}^3E$ of $(Cl^-)^*$ color centers[7].

The PL spectrum of KCl samples exciting with 360 nm and obtained at 78 K is represents Figure 5. This figure shows a wide band emission between 400-550 nm, formed by four peaks situated at 415, 440, 460 and 500 nm. The measure of the excitation spectra at these bands permits to obtain only one excitation band at 270 nm (Figure 6). Therefore, the emission bands 415, 440, 460 and 500 nm are assigned to $(Cl^-)^*$ centers.

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CONCLUSION

In the present experiments, the photoluminescence and the photoluminescence excitation of KCl single crystals are investigated. We have observed the formation of O_2^- and $(Cl^-)^*$ color centers during the growth of crystals.

The results reported above prove the possibility to dope the KCl crystals with the oxygen of air and give a complete picture of the emission bands of $(Cl^-)^*$centers in KCl, where we can make a comparison study between our results and those obtained by J. G. Kang:when the KCl crystals are excited in UV range, the 270 nm excitation band of $(Cl^-)^*$gives one emission situated at 340 nm. But the excitation of these crystals in visible range shows that the 270 nm excitation band has four new emission bands, each one situated at 415, 440, 460 and 500 nm.

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