

Luminescence of O_2^- and $(O^{2-}-F^+)$ color centers in KBr single crystals

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ABSTRACT

The optical properties of KBr single crystals elaborated by the Czochralski method are studied. The excitation of samples with 270 nm shows a series of emission lines between 500-800 nm, which are assigned to the electronic transitions from the lowest vibrational level $\nu' = 0$ of the excited state ${}^2\pi_u$ to vibrational levels ν'' of the ground state ${}^2\pi_g$ of O_2^- centers. However, the emission spectra of samples excited with 360 nm after annealing, present an intense emission band centered at 710 nm and a weak large band between 400-500 nm, formed by three peaks each one situated at 415, 440 and 468 nm. The measure of excitation spectra show that these emission bands are due to $(O^{2-}-F^+)$ centers.

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KEYWORDS

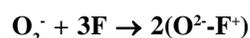
KBr;
 O_2^- color centers;
 $(O^{2-}-F^+)$ color centers;
Photoluminescence.

INTRODUCTION

It is known well that the optical properties of alkali halides are affected by point defects. These materials are characterized by a multitude of point defects: impurity, vacancies and several interstitial positions produced by the displacement of ion from their normal sites. Among all the interesting of point defects, we can enumerate: O_2^- and $(O^{2-}-F^+)$ color centers.

In 1961, John Rolfe^[1] discovered that the yellow luminescence of alkali halide crystals is due to O_2^- centers. In particular, the luminescence of this center has recently received considerable attention since the discovery of its superfluorescence and laser activity^[2]. The O_2^- center consists of an O_2^- molecular ion substituting the negative halide ion^[1].

While, the $(O^{2-}-F^+)$ center or O^{2-} -vacancy defect pairs is center is defined as an oxygen atom doubly ionized next a halide ion vacancy and oriented according to the $\langle 110 \rangle$ directions. This center is studied by F. Fischer^[3], G. Gümmer^[4] and F. Zehani^[5]. The formation of $(O^{2-}-F^+)$ under the crystal of alkali halides can be realized from O_2^- by the formed F centers according to the reaction^[4]:



The purpose of the present study is to dope the KBr crystals with the oxygen of air for formed the $(O^{2-}-F^+)$ centers and also to show the new emission and excitation bands of these centers at 78 K, after annealing characterized by an elevated temperature for a long time. This investigation has not been discussed by G. Gümmer.

EXPERIMENTAL

Single crystals of KBr were grown by Czochralski method in atmosphere air and cleaved to samples of about 1 mm thickness. Some samples have been annealed at 650 °C for 24 hours and then cooled slowly at room temperature.

Photoluminescence spectra (PL) were recorded at 78 K by using a Jobin-Yvon spectrometer HR 460 provided of CCD (Charged Coupled Device) where the source of excitation is a xenon lamp (450 W), which covers a domain spectral of 200-1000 nm. However, the photoluminescence excitation spectra (PLE) were measured at 78 K with a Jobin-Yvon spectrofluorometer Fluorolog-3 using a xenon lamp (450 W), which covers a domain spectral of 240- 850 nm.

RESULTS AND DISCUSSION

To prove the introduction of oxygen under the KBr single crystals, we have excited our samples at 78 K with 270 nm before annealing. The PL spectrum obtained is shown in Figure 1. A series of emission lines between 400-800 nm have been observed where the intense line is located at 608 nm ($\nu'' = 9$). Each line corresponds to a transition from $\nu' = 0$ in the excited state ${}^2\pi_u$ to a vibrational levels with a quantum number ν'' in the ground state ${}^2\pi_g$ of O_2^- molecule ions^[6]. The oxygen is introduced inside the single crystals of KBr because they are elaborated in free atmosphere^[7].

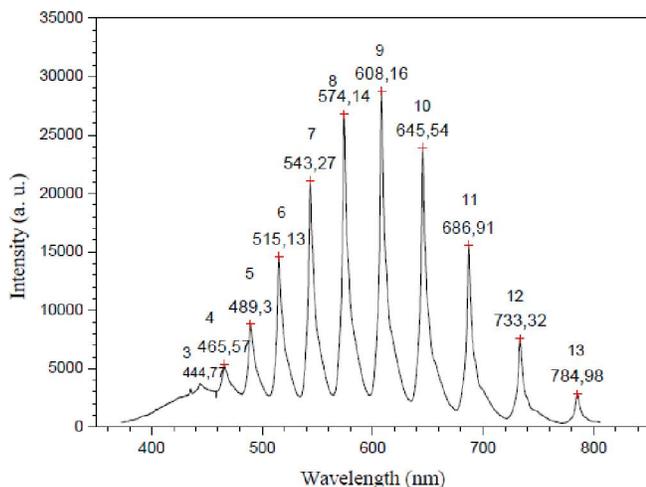


Figure 1 : Emission spectrum of KBr for excitation at 270 nm

The positions and the quantum number ν'' are indicated above of each line emission. These positions were the same as that as those obtained by J. Rolfe^[1, 8]. The measure of the PLE at 608 nm (Figure 2) shows an excitation band situated at 258 nm which can be assigned to O_2^- center in alkali halides^[1].

PL spectrum of samples after annealing at 650 °C during 24 hours and excited with 360 nm at 78 K, are illustrated in Figure 3. We observe an intense emission band at 710 nm and a weak large emission band between 400-500 nm formed by three peaks, situated at 415, 440 and 468 nm (see the inset Figure 3). The excitation spectra measure at 450 nm is represented in Figure 4. An excitation band at 297.5 nm and another weak band about 282 nm have been observed. While the measure of the PLE at 710 nm (Figure 5) presents five excitation bands situated at 270, 283, 301, 311 and 361 nm (see the inset Figure 5). The 415 nm emission band and the 283, 301 and 361 nm excitation bands have been also obtained by Gümmer^[4]. Therefore, the excitation and the emission bands given above are attributed to $(O^{2-} - F^+)$ centers^[4, 9]. The transformation of the O_2^- center to the $(O^{2-} - F^+)$ centers after annealing, is proved by F. Zehani et al^[5].

The excitation bands in UV of $(O^{2-} - F^+)$ centers are interpreted as electron transfer from O^{2-} to the surrounding alkali-ion considering different excited states of the alkali atom. But if the electron in its excited state can return to its ground states of O^{2-} with a direct transition, we obtain the emission bands situated in the UV-visible spectral domain^[3].

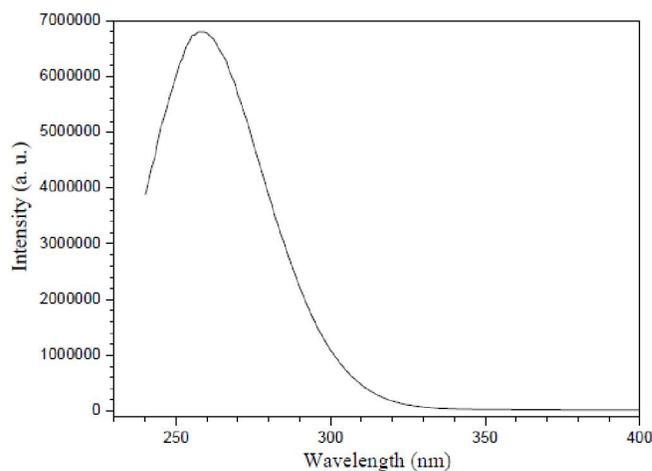


Figure 2 : Excitation spectrum of KBr measured at 608 nm

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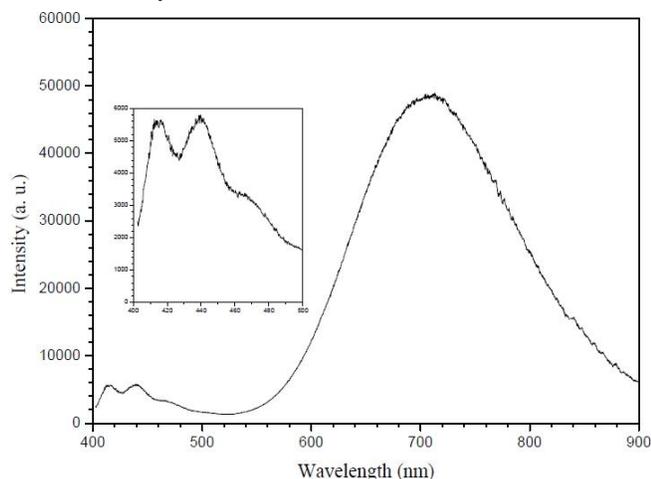


Figure 3 : Emission spectra of KBr corresponding to excitation at 360 nm; The inset shows the emission band between 400-500 nm

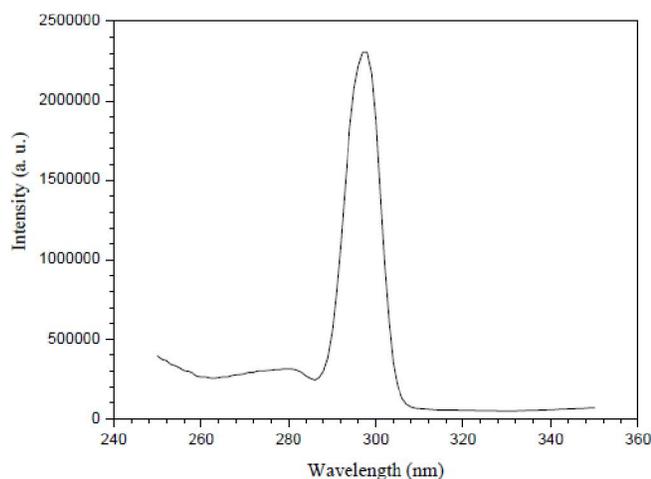


Figure 5 : Excitation spectrum of KBr measured at 710 nm, The inset shows the second derivative method

A comparative study with the results of G. Gümmer has been accomplished which allows to conclude that the annealing at a high temperature for a long time then cooled slowly at room temperature, change again the optical properties of $(O^{2-}-F^+)$ centers. Indeed at 78 K, it was observed the apparition of another excitation spectra formed by six bands located respectively at 270, 283, 297.5, 301, 311 and 361 nm. Whereas, it was noted the appearance of a series of emission bands situated respectively at 415, 440, 468 and 710 nm. G. Gümmer was interested in the change of the absorption spectra of $(O^{2-}-F^+)$ centers during annealing. He showed that this phenomenon is due to the formation of aggregates of these centers. The association of $(O^{2-}-F^+)$ centers is performed randomly in the crystals and may be given

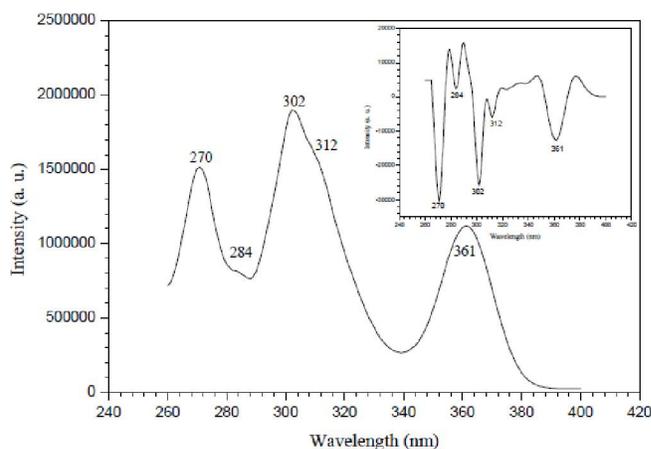
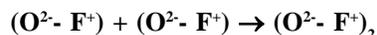


Figure 4 : Excitation spectrum of KBr measured at 450 nm

in the simple case a double center as follows^[4]:



CONCLUSION

In this paper, we have studied at 78 K the emission and the excitation bands of O_2^- and $(O^{2-}-F^+)$ centers in KBr single crystals situated in the UV-visible range. The results above prove the possibility to dope the KBr crystals with the oxygen of air and the formation of $(O^{2-}-F^+)$ centers.

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