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Optical vibronic spectra of aggregates in Eu^{2+} -doped KCl and KBr crystals

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The vibronic structure on the optical absorption, emission, and excitation spectra of aggregates in Eu^{2+}-doped KCl and KBr crystals has been obtained. The crystals were annealed at 435K. During the aggregation process, four groups of narrow bands were found in KCl:Eu^{2+} and two, in KBr:Eu^{2+}, which were considered as the signature of different Eu^{2+}-ion aggregated phases. The vibration frequency for each group is very similar.

Keywords: Luminiscence in solids; alkali halides with europium

La estructura vibrónica de los espectros de emisión, absorción y excitación de cristales de KCl y KBr impurificados con europio divalente, se ha obtenido experimentalmente. Los cristales fueron envejecidos a 435K. Durante el proceso de agregación, se encontraron cuatro grupos KCl: $Eu^{+}2$ y dos en KBr: $Eu^{+}2$, las cuales se consideraron como la firma de diferentes fases agregadas de iones $Eu^{+}2$. La frecuencia de vibración para cada grupo es muy similar.

Descriptores: Luminiscencia en sólidos; halogenuros alcalinos con europio

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1. Introduction

As is well known, annealing of Eu^{2+}-doped alkali halides induce the formation of Eu^{2+}-ion aggregates with settings of distinct symmetry, which modify the electron transition energies of the Eu^{2+}-ion. In the particular case of annealed KCl:Eu and KBr:Eu with low concentration of Eu^{2+}-ion, it has been reported that the emission spectra obtained with low resolution photoluminescence (LRPL) shows only a band related with the formation of one aggregated phase. One of the characteristical effects of these phases is to modify the symmetry of the crystalline field around the impurity giving rise to a splitting of the Eu^{2+}-ion $4f^65d$ excited state in e_g and t_{2g} components. Absorption and excitation spectra corresponding to the aggregates presents a greater separation of the bands e_g and t_{2g} proportional to the strength of the crystalline field. In this respect, it allows to differentiate the Eu^{2+}-ion aggregates by its relation with the emission bands of the $4f^6\,5d \rightarrow 4f^7$ transition in the Eu^{2+}-ion. The differences between these emission bands are due to the interaction of the $4f^6$5d state with the crystalline field which depends on each type of aggregate. By using LRPL, López *et al.* [1] have found in the emission spectra of freshly quenched KCl:Eu^{2+} crystals a band peaked at 419 nm and in samples annealed at temperatures lower than 373 K, an additional band at 427 nm. Analyzing the kinetic behavior of these bands and the strength of the crystalline field on the impurity, they associated the 419 nm emission band with the free Eu^{2+}-V_C dipole, and the 427 nm band with a Suzuki phase. Two additional emission bands located at 439 nm and 478 nm, reported for the same crystals annealed at 473 K were associated with different $EuCl_2$-type aggregates nucleated along the $\{111\}$ and $\{310\}$ directions, respectively [2]. A similar study carried out in KBr:Eu^{2+} crystals shows two broad emission bands located at 419 and 430 nm corresponding to free dipoles and a Suzuki phase, respectively [3]. On the other hand, Nunes *et al*. [4] and Matinaga *et al*. [5] used two-photon absorption (TPA) spectroscopy to determine Eu^{2+}-ion aggregates in KCl:Eu^{2+} crystals. Each type of aggregate was associated with a group of lines corresponding to the $4f^7 \rightarrow 4f^7$ transitions of the Eu^{2+} ion. Although the $4f^7$ states are less affected than the $4f^6\,5d$ multiplet by changes in the crystalline field, the sharpness of the spectral bands of these transitions does the TPA more sensitive than the LRPL to detect different types of Eu^{2+}-ion complexes. By using TPA, Matinaga *et al*. [5] have detected two Eu^{2+} -V_C dipole aggregates in freshly quenched samples and two more in well aged samples. Taking into account the order in which the line groups were appearing and how its intensity increased, they considered that the Suzuki phase in room temperature annealed KCl: Eu^{2+} crystals appears as a second step after a long annealing time.

Kovalev [6] used the vibronic lines in the emission spectra associated with the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+}-ions to study the aggregation process in KCl: Eu^{2+} crystals. This technique utilizes the interaction of the $4f^65d$ state with the crystalline field, as well as the sharpness of the vibronic lines. This author found a large group of vibronic lines over the 419 and 430 nm bands (410.33, 416.8, 418.87, 422.02, 423.23, 424.72, 425.61, 425.86, 426.62, and 427.6 nm) with changes of intensity during the aggregation process. Based on the evolution of the intensity of the emission bands he associates it with different Eu^{2+}-ion aggregates. The line at 410.33 nm was associated with free Eu^{2+}-V_C dipoles, the lines at 416.8, 418.87, 422.02, 423.23, and 424.72 nm with dimmers, and that lines at 425.61, 425.86, 426.62, and 427.6 with different configurations of trimmers.

In this work, the vibronic lines are analyzed in emission, excitation and absorption spectra of quenched and well-aged samples to differentiate aggregates in europium doped KCl and KBr crystals. The analysis is based on the zero-phonon line (ZPL) and its associated vibronic lines series to determine a type of aggregate. Our method differs from that used by Kovalev in the sense that we have localized a ZPL for each aggregate.

2. Experimental

KCl:Eu^{2+} and KBr:Eu^{2+}single crystals were grown by the Czochralski method in the Crystal Growth Laboratory of IFUNAM, under a controlled atmosphere of dry Argon. $EuCl_2$ was added to the melt, resulting in a concentration of approximately 200 ppm in the crystal as detected with the method developed by Hernández *et al.* [7] From these crystals, samples of about 1 x 5 x 5 mm^3 were obtained. Some of them were annealed at 773 K for one hour followed by a fast cooling down to RT by contact with a copper plate (quenched samples). Other samples were stored at RT for more than two years (well-aged samples). Optical absorption and fluorescence measurements were carried out in a λ9 Perkin-Elmer spectrophotometer and a Spex Fluoromax spectrofluorometer, respectively. The low temperature measurements were carried out on samples fixed to the cold finger of a closed cycle APD helium cryostat.

3. Results

Optical absorption and excitation spectra obtained in this work are similar to that previously reported [2]. These spectra are composed by two broad bands e_g and t_{2g} located in the 220-300 and 300-425 nm spectral ranges, respectively. The e_g and t_{2g} bands are associated with the e_g and t_{2g} components of the splitting of the $4f^65d$ state induced by the crystalline-field. In all the cases, the low-energy side of the t_{2g}-band shows a well-formed vibronic structure.

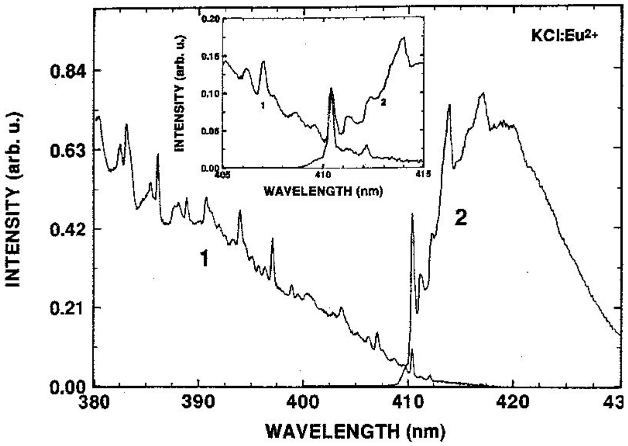

FIGURE 1. Low energy side of the absorption (curve 1) and emission (curve 2) spectra of a quenched KCl:Eu^{2+} crystal. The emission spectrum has been obtained with 325 nm excitation light. Inset shows an amplification of curves 1 and 2.

3.1. KCl:Eu^{2+}

Figure 1 shows the low-energy side of the optical absorption (curve 1) and emission (curve 2) spectra of a quenched sample at 15 K. The emission spectrum consists of a broad band with maximum around 417 nm, which appears in the early stage of the aggregation process. It appears also at RT and according to Rubio *et al.* [2], it is associated with free dipoles and also to first aggregation products since it does not change during this early stage of the process altough their measurementes of ionic thermocurrents (ITC) in the same crystals indicated the loss of free dipoles.

The vibronic structure in the absorption spectrum is very complex but it seems to be composed by several groups of lines. At the low-energy end of this spectrum (curve 1) the higher intensity line is recognized as the zero phonon line which is the lowest energy of absorption. Around the ZPL of 410.4 nm appear three sidebands at 409.5, 411.1, and 412.1 nm. In previous reports [8], the 411.1 and 409.5 nm sidebands have been considered as the Stokes and anti-Stokes components. However, the fact that a similar structure appears in both absorption and emission spectra at the same spectral position (inset of Fig. 1) led us to explore a posible relation of these lines with some type of Eu^{2+}- complex. A detailed spectroscopic analysis by scanning the excitation light of this region from 400 to 413 nm has been carried out. Figure 2 shows emission spectra corresponding to the excitation lines at 400 (1), 410.3 (2), 411 (3), and 412 nm (4). For the 400 nm excitation line, the emission band presents the maximum around the 417 nm (curve 1) with the vibronic lines at 410.4, 411.0, 412.1, 413.8, 415.6, 417.1, and 419 nm. This is the typical spectrum for almost all the excitation lines of wavelength lower than 410.4 nm although small changes in the intensity of the vibronic lines appear. If the crystal is exposed to 410.3 nm, the most intense vibronic lines are the lines at 413.8 and 417.1 nm and the relation of intensity of these peaks are the same than for 400 nm excitation light.

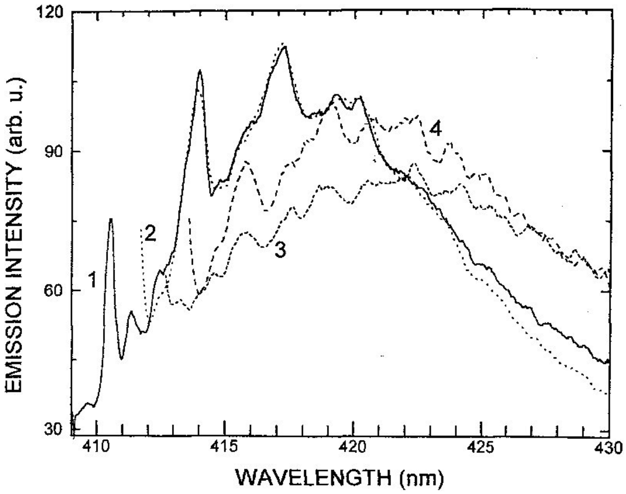

FIGURE 2. Emission spectra of a quenched crystal for excitation light at 400 (1), 410.4 (2), 411 (3), and 412 nm (4).

For 411 and 412 nm excitation lines, the intensity of the lines at 413.8 and 417.1 nm substantially decrease, while the lines at 415.6 and 419 nm remain present in the emission band producing a band shift to 420 nm. Excitation line at 413 nm produce an emission band shifted to 423 nm (as can be seen in Fig. 3). For this emission spectrum, the first lines are at 415.6, 417.1, 419, 420.4, 422.1, 423.4, and 425, where the lines at 422.1, 423.4, and 425 are the most intense but the most important lines are the lines at 417.1 and 420.4 nm, because their excitation spectra are different to those obtained for the vibronic lines previously discussed. The excitation spectrum of the 420.0 emission line taken in the range from 412.5-418 nm (curve 1 of Fig. 3) shows a vibronic line at 417 nm as the last line of the side of lower energy, suggesting that this excitation spectrum must correspond to another emission band beginning at 417 nm which is not detected in previous experiments due to its lower intensity. These important results indicate the existence of several component bands identified by the higher energy line in its excitation spectra. They are at 410.4, 411, 412 and 417 nm approximately. On the other hand, each line is part of a group. These groups are 410.4, 413.8, and 416.9; 411, 414.6, and 418.2 nm; 412.1, 415.8, and 419 nm. The mean frequency of these three groups were 197, 207, 202 cm^{-1} in absorption and 192, 210, 202 cm^{-1} in emission.

Figure 4 shows the excitation spectra for the 1) 410.4, 2) 411.1, 3) 412.1, 4) 422.3, and 5) 423.5 nm fixed emissions. As is expected, the excitation spectra show series of lines associated with each emission line. Unfortunately, these series could not be so isolated due to the limitations in the resolution of our experimental setup.

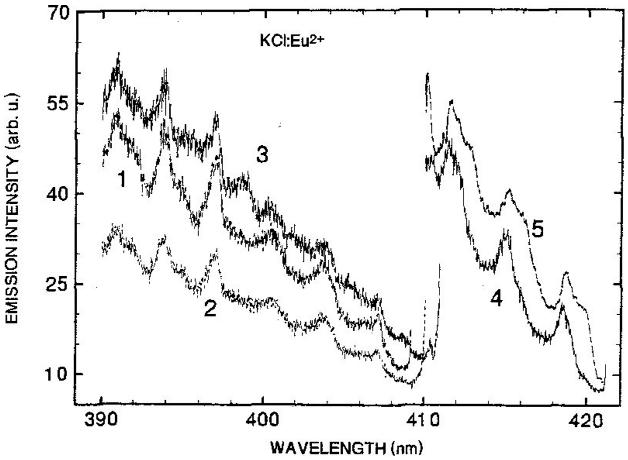

FIGURE 4. Vibronic excitation spectra of a well-aged KCl:Eu^{2+} crystal for the vibronic emission lines fixed at 1) 410.4, 2) 411.1, 3) 412.1, 4) 422.2, 5) 423.4 nm.

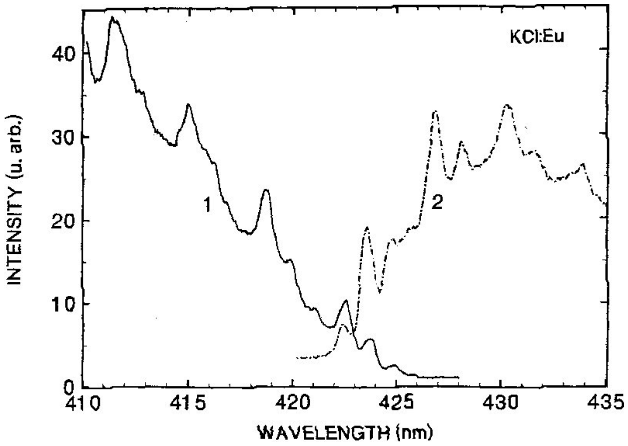

FIGURE 5. Excitation and emission spectra of a well-aged KCl:Eu^{2+} crystal. (1) Excitation spectrum for emission at 429 nm. (2) Emission spectrum for excitation at 350 nm.

Figure 5 shows the absorption and emission spectra of a well-aged crystal. the emission spectrum obtained with 400 nm excitation light (curve 2) shows a broad band centered on 430 nm. In a previous report [9], this band is ascribed to a larger aggregate or precipitated phase with fcc structure called Suzuki phase due to its higher effect in the 10*Dq* splitting. The vibronic structure of this band present lines at 422.2, 423.7, 424.8, 425.6, 427, 428.3, 429.2, 430.32, 431.5, and 433.9 nm. A comparison of the emission spectrum with the absorption spectrum shows that the 422.2, 423.7 and 424.8 nm are common lines although its intensity ratios are very different. In the emission spectrum, the intensity ratio between these lines is a function of the excitation wavelength as Fig. 4 shows for the emission lines at 422 and 423 nm. Figure 6 displays three emission spectra corresponding to excitation lines at 418.6 (1), 420 (2), and 421nm (3). They are normalized to the intensity of the 427 nm line. These results led us to distinguish three series on the 430 nm band: 422.2, 425.6, and 429.2; 423.7, 427, and 430.3; and 424.8, 428.3, and 431.5. Also series of lines are associated with the 422.3, 423.5 and 424.7 nm in the absorption spectrum. In the absorption spectrum, the series of the 422.3, 423.5 and 424.7 nm lines are separated at mean intervals of 209, 209 and 213 cm^{-1}, while in the emission spectrum, they are at 185, 187 and 194 cm^{-1}, respectively.

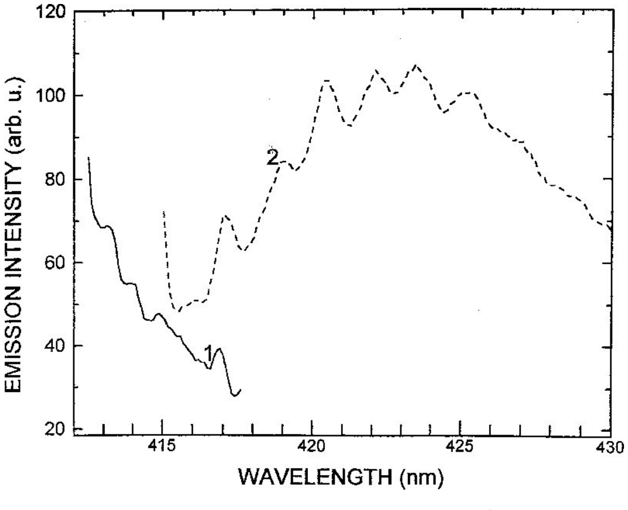

FIGURE 3. Optical spectra of a quenched KCl:Eu^{2+} crystal. (1) Excitation spectrum for emission at 420 nm. (2) Emission spectrum for excitation at 412.8 nm.

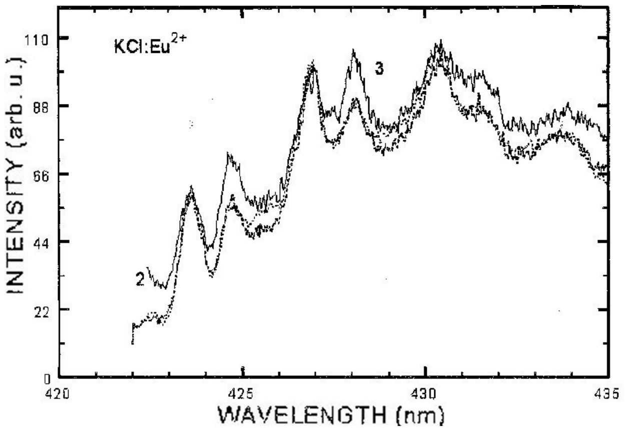

FIGURE 6. Emission spectra of a well-aged KCl:Eu^{2+} crystal for excitations at 418.6, 420 and 421 nm.

3.2. KBr:Eu^{2+}

Emission, absorption and excitation measurements were also carried out in both quenched and RT annealed KBr:Eu^{2+} crystals. The emission spectrum in quenched samples shows a broad band located around 418 nm, while in RT annealed crystals present an additional band at 430 nm when the wavelength of excitation light is in the range of the absorption spectrum (Fig. 7). These bands measured at RT by Aguilar *et al.* [3] were ascribed to the first aggregation products and a Suzuki precipitated phase, respectively. Both the 418 and 430 nm bands show vibronic structure. In the 418 nm band the vibronic lines form a unique series. The mean values of the frequency difference between these lines are 111 cm^{-1} in the emission and 106 cm^{-1} in the absorption spectra which are very similar to that reported by Bron and Wagner [10] for this material. The vibronic structure in the 430 nm band shows replays of two lines which begin at 422.1 and 423.1 nm. The independence of these two groups was also investigated. Figure 8 shows excitation spectra of consecutive vibronic emission lines at (1) 424.85 and (2) 425.85 nm, and emission spectra for consecutive excitation lines at 421.1 (curve 3) and 422.1 nm (curve 4). They present periodic differences indicating that in these spectra there are two independent groups of lines associated with the 422.1 and 423.1 nm, respectively. These lines are considered as ZPL's of different emission centers.

4. Discussion

As is well known, the vibronic lines of the optical spectra correspond to transitions between two vibrational levels m and n of the initial and final electronic states, respectively, where m and n are integers greater than or equal to zero. The vibrational series for m to n transitions appears over a broad electronic transition band and may experimentally define it. The higher energy line of the emission spectrum and the lower energy line of the absorption or excitation spectrum of the same crystal is a pure electronic transition known as the zero-phonon line (ZPL). In the case of KCl:Eu^{2+} the 410.4 nm has been considered as the ZPL of absorption and emission of the $4f^7$ – $4f^6 5d$ in freshly quenched crystals. From the narrow bands of the band it is the most resolved and shows the higher intensity, however, we assume that in other

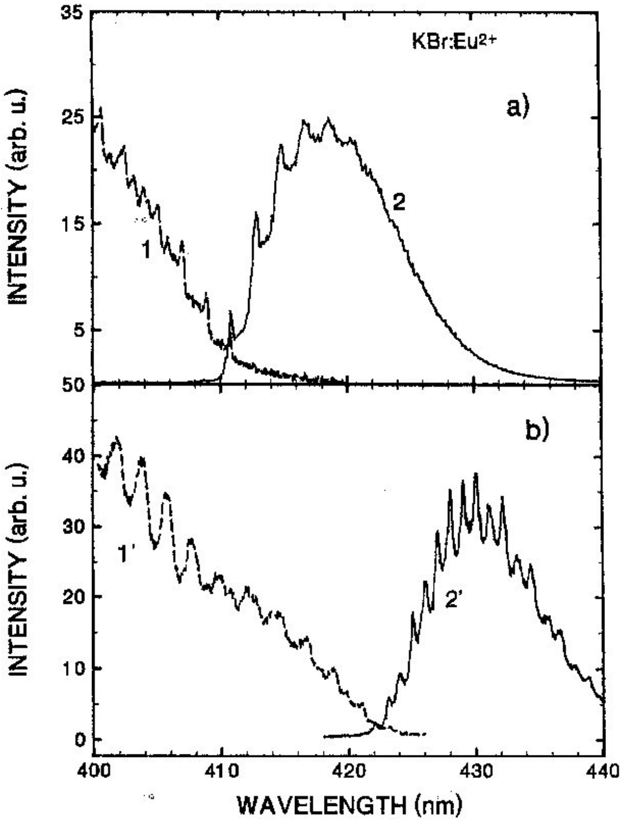

FIGURE 7. Low energy absorption (1) and emission (2) spectra of quenched (a) and annealed (b) KBr:Eu^{2+} crystals. The emission spectrum was obtained with excitations at (a) 350 nm and (b) 417 nm.

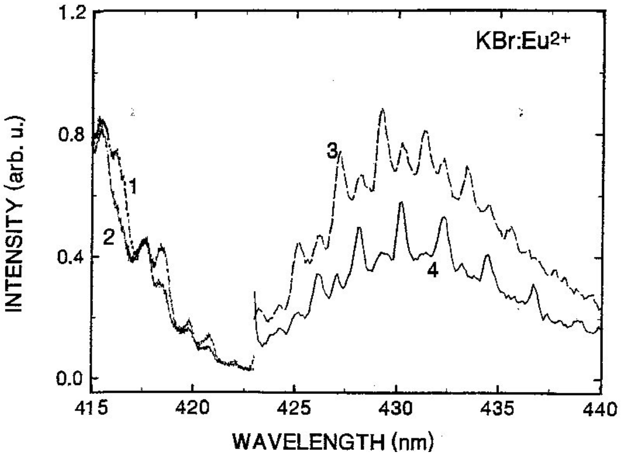

FIGURE 8. Vibronic excitation (1, 2) and emission (3, 4) spectra of a well aged crystal KBr:Eu^{2+} crystal. Excitation spectra correspond to emission wavelengths fixed at 424.85 (1) and 425.85 nm (2). Emission spectra were obtained with excitation light at 419.8 (3) and 418.6 nm (4).

bands the ZPL may presents lower intensity than the other peaks on the corresponding series. So, if there are several independent series on an emission spectrum then they may be associated with different electronic levels of the same impurity or with different complexes containing the impurity. This is the case of the emission spectra observed in this work. The $4f^6 5d$ level of the Eu^{2+}-ion changes due to the crystalline field interaction induced by the ions configuration in the aggregation state producing different emission and absorption bands shifting the corresponding ZPL on the spectrum. Thus by identifying the ZPL's, different types of aggregates can be determined. In the spectra of quenched KCl:Eu^{2+} crystals we have identified the coincidence of four narrow peaks at 410.4, 411.1, 412.1, and 417 nm with ZPL characteristics. Our results indicate a better resolution of its related series in the emission spectrum when the crystal is excited with one line of the corresponding excitation series as can be seen in the Figs. 3 and 4. These results suggest that in KCl:Eu^{2+} the broad emission band at 417 nm is the overlapping of four independent bands each associated with a different form of small Eu^{2+}-V$_C$ aggregate nucleated in the very early stage of the aggregation process. The 410.4 nm ZPL has been associated with isolated Eu^{2+}-V$_C$ dipoles oriented in the $\{110\}$ direction [10]. The 412.1 nm line may be due to a coupling between the impurity electronic transition and the longitudinal acoustic modes [8] in the aggregates or to Eu^{2+}-V$_C$ dimmers, which may have formed during the cooling stage of the annealing procedure. These aggregates could be those detected by two-photon absorption [5]. In the 430 nm band of well aged crystals, the 422.3, 423.7, and 424.7 nm vibronic lines are considered as ZPL of different aggregates. The 423.7 line which is the most intense, could be originated in the Suzuki phase, while the 422.3 and 424.7 nm lines may be associated with two metastable phases since both aggregates have similar broad excitation spectra. This result is in partial agreement with the observation of Matinaga *et al.* [5] who also found a small aggregate formed in well aged samples at 323 K previously to the Suzuki phase formation.

Similar results have been found on KBr:Eu^{2+} crystals for which one center is detected in the higher energy band and two more in the lower energy band. In this case, the band of 418 nm is ascribed to free dipoles and the 429 nm band is associated with two types of aggregates with the same characteristics of the Suzuki phase as it was assigned by Aguilar *et al.* [3].

5. Conclusion

In summary, we have identified several ZPL which has been used as a new method to detect old and new aggregated phases of Eu^{2+}-ions associated with the $4f^6 5d$ – 4f7 electronic transition of the Eu^{2+}-ion due to the sharpness of the vibronic lines in the optical absorption and emission spectra. Furthermore, the method has been independent of any knowledge of the size of the aggregates. But it is a very promising method which could be used for monitoring of changes of size in different aggregates during the thermal treatments.

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