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Time-resolved luminescence spectroscopy of Eu^{2+} in $BaFCl:Eu^{2+}$ X-ray storage phosphor

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Photoluminescence (PL) spectra recorded at room temperature (RT) in polycrystalline $BaFCl:Eu^{2+}$ X-ray storage phosphor have shown the europium associated luminescences, a broad luminescence band at 385nm (3.22eV) with a 3.3±0.1μs PL lifetime accompanied by a luminescence line at about 368nm (3.37eV). The energy difference $\Delta E^{B-L}=226cm^{-1}$ between the two excited levels from which the europium associated band and line luminescences took place was computed. An additional broad luminescence band at about 425nm (2.92eV) with 0.7±0.1μs PL lifetime has been attributed to the europium luminescence perturbed by an impurity. Time resolved spectroscopy measurements have shown that no other impurity luminescences (like oxygen-vacancy centres) can be observed at RT except the europium associated ones.

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1. Introduction

X-ray storage phosphors are materials capable to store the energy of incident radiation in the form of stable electron and hole pairs. They are alternatives to conventional silver-based film for industrial and medical radiography [1]. Phosphor covered plates are able to store the X-ray radiation energy in the form of locally trapped electron-hole pairs as a latent image, the stored information being recovered by optical stimulation with laser. During the optical stimulation in the electronic F centres, the electrons are released and recombine with the trapped holes centres, which results in the characteristic activator emission, usually a rare earth (i.e. photostimulated luminescence or PSL). Europium doped barium fluorohalides $BaFX:Eu^{2+}$(X=Br, Cl) have a number of favourable properties that make them suitable for using as phosphors in detection systems developed for two-dimensional X-ray imaging in the fields of radiography and crystallography [1,2].

In the present paper photoluminescence (PL), PL lifetime and time resolved spectroscopy measurements have been used to study the europium excited states in $BaFCl:Eu^{2+}$ X-ray storage phosphor.

2. Experimental details

Europium doped BaFCl polycrystalline powders were prepared by coprecipitation method europium impurity being added as EuF_2 at a concentration of about 200ppm/mol [3]. In order to complete the chemical reactions and to improve the material homogeneity the samples were pressed and then thermally treated in vacuum bellow the melting temperature.

Photoluminescence (PL) spectra have been recorded using lock-in technique with a standard luminescence set-up composed by two monochromators for excitation and emission, respectively, a xenon lamp (100W) as excitation source and a photomultiplier as light detector. Since the samples are opaque, the PL measurements were performed at the surface of the samples at oblique incidence. The spectra have been corrected with he spectral characteristic of the experimental set-up.

For the PL lifetime measurements we have used time domain technique in which a short pulse of light excites the sample and the subsequent luminescence emission is recorded as a function of time. Time resolved PL measurements have been performed at different delay times up to 12.5μs As excitation sources we have used a flash-lamp (nitrogen filled) together with an optical filter in order to select the optical output in the 250-350nm range. The luminescence signal has been detected with a photomultiplier and scanned with an EG&G box-car integrator.

3. Experimental results

Photoluminescence (PL) spectra recorded at RT have shown a strong broad luminescence band at 385nm (3.22eV) accompanied by a shoulder at about 425nm (2.92eV). A very small and narrow luminescence at about 368nm (3.37eV) has also been observed. The PL lifetimes decay curves depicted in the Fig.2 show essentially one exponential decay for both 385nm (3.22eV) and 425nm (2.92eV) bands from which we have been computed PL lifetimes of about 3.3±0.1μs and 0.7 ±0.1μs, respectively.

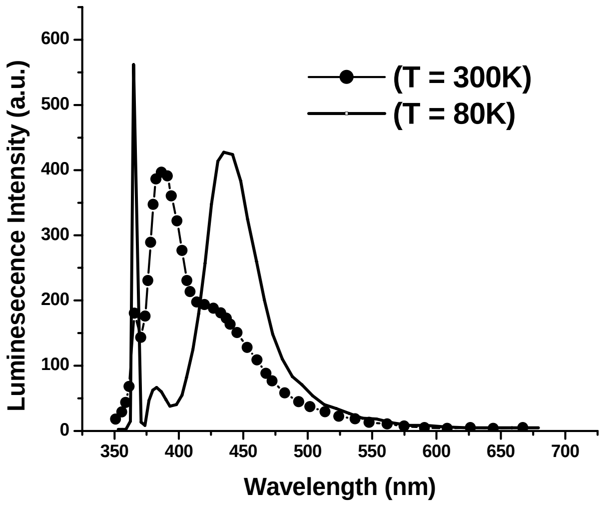

Fig.1. Photoluminescence spectra recorded in BaFCl:Eu^{2+} at RT and 80K. The excitation wavelength was 275nm (4.5eV). For clarity the 365nm line emission (at T=80K) was 20 times decreased in amplitude.

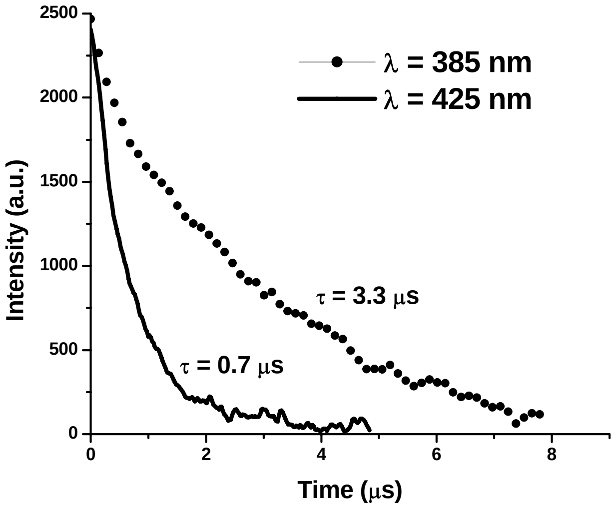

Fig.2. Photoluminescence lifetimes of the 385nm (3.22eV) and 425nm (2.92eV) emission bands recorded at room temperature in BaFCl:Eu^{2+} using excitation in the 250-350nm range.

As can be seen in the Fig. 1 the two luminescences from 385nm (3.22eV) and 368nm (3.37eV) are showing an anti-parallel temperature dependence. After cooling down to T=80K the line emission strongly increase and is shifts to 365nm (3.40eV). In the same time the broad band decrease and is observed at 382 nm (3.25eV). The shoulder is better resolved and is observed at 436nm (2.84eV). In the Fig.3 (dotted curve) is represented the temperature dependence of the logarithm of the ratio R between the integrate intensities of the line and band luminescences.

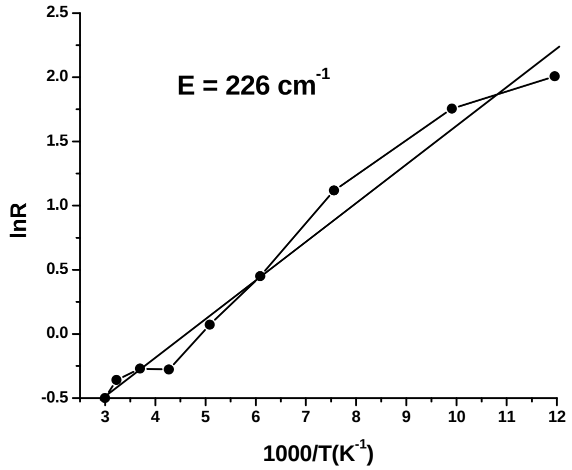

Fig. 3. Temperature dependence of the logarithm of the ratio between the integrate intensities of the luminescence line $^6P_{7/2}\rightarrow{}^8S_{7/2}$ from 365nm (3.40eV) and luminescence band $4f^65d \rightarrow {}^8S_{7/2}$ from 385nm (3.22eV) for λ_{ex}=275nm (4.5eV) (dotted curve) and fitted with an exponential (solid curve).

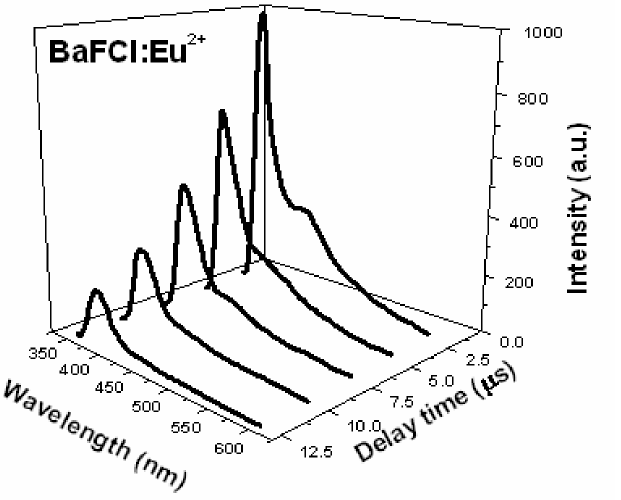

Fig. 4. Time resolved spectroscopy measurements recorded at room temperature in BaFCl:Eu^{2+} using excitation in the 250 - 350 nm range. The time delay between the curves is 2.5µs.

Time resolved luminescence measurements have been recorded in the 350-600nm range at different delay times up to 12.5µs (with 2.5µs step) after the light excitation pulse (Fig.4). These measurements have shown only the 385nm (3.22eV) and 425nm (2.92eV) luminescences.

4. Discussion

The europium ion shows a luminescence that strongly depends on its valence state and the nature of the host lattice [4]. The ground state of the Eu^{2+} ion, $^8S_{7/2}$, belongs to the 4f^7 configuration. Within this configuration the lowest excited state is $^6P_{7/2}$. Transitions from this $^6P_{7/2}$ manifold to $^8S_{7/2}$ are responsible for the line emission. Their transition probability is low (spin and parity-forbidden). Another excited configuration is the $4f^65d$ and generally it is located above the $^6P_{7/2}$ manifold. The luminescence occurs from the lowest crystal-field component to the $^8S_{7/2}$ level (parity-allowed). This emission has a broadband character and is strongly dependent on the host lattice because the position of the crystal-field levels of the $4f^65d$ configuration depends on the surroundings of the Eu^{2+} ions [4].

The 385nm (3.22eV) broad luminescence band recorded at room temperature (Fig.1) is due to the $4f^65d \rightarrow {}^8S_{7/2}$ transition [5]; the PL lifetime 3.3 ±0.1μs is consistent with this attribution. The weak line emission from 365nm (3.40eV) (Fig. 1) is due to $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition [4]. These luminescences are showing an anti-parallel temperature dependence (Fig. 1). Regarding the 425nm (2.92eV) luminescence band it has been tentatively attributed to the Eu^{2+} luminescence perturbed by an impurity [3]. The present PL lifetime data supports this attribution because the PL lifetime 0.7 ± 0.1μs is characteristic for the europium associated broad band lifetime in the host crystals [4].

We have computed the energy difference between the two excited levels from which the europium associated band and line luminescences took place in the frame of a three level model in which the degeneracies of the three levels have been supposed to be equal [5]. According to this model the ratio between the integrate intensities of the line and band luminescences is given by [3]:

$$R= g^f A^f \exp(\Delta E^{B-L}/k_B T) / g_l A_l \qquad (1)$$

where the A_l is the probability average of the radiative transition between the l excited state and the $^8S_{7/2}$ ground state, the g_l is the degeneracy of the l state and ΔE^{B-L} is the difference between the two excited levels. From the temperature dependence of the logarithm of the ratio between the integrate intensities of the line and band luminescences (Fig.3), and using the above formula, we have computed the energy difference between the two excited levels, $\Delta E^{B-L}=226cm^{-1}$, which agrees with the data from literature [4]. However for Eu^{2+} the model is not quite appropriate because there are many ^6P_J and $4f^65d$ levels [6] and therefore the ΔE^{B-L} value is not quite exact [4].

Time resolved spectroscopy measurements have shown that no other impurity luminescences (like oxygen-vacancy centres [2]) can be observed except the europium associated ones (Fig. 4).

5. Conclusions

The energy difference between the two excited levels from which the europium associated luminescences from 385nm (3.22 eV) and 65 nm (3.40 eV) has been computed $\Delta E^{B-L}=226cm^{-1}$.The 425nm (2.92eV) luminescence band with 0.7±0.1μs PL lifetime has been attributed to the Eu^{2+} luminescence perturbed by an impurity. Time resolved spectroscopy measurements have shown that no other impurity associated luminescences are observed at RT except the europium associated ones.

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References

[1] M. Sonoda, M. Takano, J. Miyahara, H. Kato; Radiology **148**, 833 (1983).
[2] S. Schweizer Phys. stat. solidi (a) **187**(2), 335 (2000).
[3] M. Secu, L. Matei, T. Serban, E. Apostol, C. Silion, G. Aldica, Optical Materials **15**, 115 (2000).
[4] G. Blasse, Materials Science of Luminescence p.462, Edited by Baldasare di Bartolo, Plenum Press, (1978)
[5] J. Systma, G. Blasse, A. Meijerink, J. Lum. **51**, 183 (1992).
[6] J. Sugar, N. Spector, J. Opt. Soc. Am. **64**, 1484 (1974).

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