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Excitation and desexcitation processes of Eu^{3+} luminescence in Eu_2BaZnO_5

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Abstract

Luminescence and Raman crystal field transitions of Eu^{3+} ions in Eu_2BaZnO_5 are investigated in off-resonance conditions for several excitation energies. Luminescence peaks are identified and classified into two groups (transitions from $^5D_0$ and those from $^5D_1$ or $^5D_2$) as a function of their relative intensity versus temperature. Crystal field parameters are found to be very similar for both europium sites. Raman crystal field transitions are studied as a function of temperature. The increase of their intensity when temperature is lowered is explained by the change of the ground state population. The behaviour of the luminescence at several excitation energies has been explained by means of second-order processes. The lattice phonons and thermal population of the lowest excited multiplets have a determining role in the excitation processes of Eu luminescence. © 1998 Elsevier Science S.A.

Keywords: Eu^{3+}; Raman crystal field; Luminescence

1. Introduction

Eu_2BaZnO_5 oxide belongs to the Pnma space group, which is the so-called 'green phase' frequently present in cuprates as an impurity of the superconducting phase ($YBa_2Cu_3O_{6+x}$). This structure is orthorhombic with four formula per primitive cell, and is characterised by isolated oxygen square-based pyramids around the Zn ion [1]. Eu^{3+} ions occupy two different seven-fold oxygen-coordinated sites with the same symmetry site (C_s) but slightly different Eu–O distances.

Crystal field splitting of Eu^{3+} 4f levels has been widely studied when Eu dopes different crystalline matrices (for example, Refs. [2–4]), while optical spectroscopies have been less used when Eu is a constitutional ion of the compound [5]. Nd^{3+} crystal field transitions have been studied in Nd_2BaZnO_5, which has the same composition but a different structure [6].

In a previous work on Eu_2BaZnO_5 compound [7], the determination of the Eu^{3+} crystal field levels was done by comparing the information from luminescence, Raman and reflectance measurements at different excitation energies and temperatures. The energy difference between both Eu ions levels was found to be around 20 cm^{-1}. In the present work, a detailed study about the possible excitation and desexcitation processes of the luminescence is achieved.

2. Experimental details

Eu_2BaZnO_5 compound was prepared as a polycrystalline sample mixing the stoichiometric amounts of the high-purity oxides Eu_2O_3, ZnO and $BaCO_3$. The homogenised mixture suffered different thermal treatments for several hours and, finally, the powder was pressed into a pellet. The X-ray diffraction data show that the sample is single phase and presents the Pnma structure.

A Renishaw 2000 micro-Raman grating spectrometer equipped with holographic notch filters and a Peltier cooled CCD detector was used to perform measurements with a He–Ne laser as excitation source. On the other hand, a double HR-460 Jobin Yvon monochromator with a CCD detector was employed to detect luminescence excited with all lines of an Spectra Physics Ar^+–Kr^+ laser. In both cases, a continuous flow Oxford Instrument cryostat was used to perform low temperature measurements in backscattering geometry. All spectra have been corrected by the spectral response of the experimental set-ups.

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3. Results and discussion

Eu^{3+} ions in Eu_2BaZnO_5 occupy the centre of two trigonal prisms of seven oxygen ions, with C_s local symmetry. The polyhedrons representing both sites are basically identical except for a rotation of 90° respect to the y-axis, and both share a triangular face. As a consequence, the Eu 4f energy levels of both sites are expected to be very similar, as it was experimentally proven in Ref. [7].

The scheme of the electronic levels of the free ion Eu^{3+} consists on six ^7F_J terms well separated from the ^5D excited states [8]. The first three terms of the excited ^5D term (^5D_J, $J=0,1,2$) are also far from any other level, so that the mixing with other multiplets is not very important. The observed transitions to or from the $^5D_0$ singlet are enough to obtain the levels of the ^7F_J multiplets. These levels are the ones used to calculate the crystal field parameters that describe the Eu^{3+} environments.

Typical luminescence spectra measured at room and low temperature are shown in Fig. 1. These spectra correspond to Eu^{3+} luminescence excited with the 488-nm line of an Ar^+ laser. Luminescence experiments have been performed between 14 000 and 21 000 cm^{-1}, covering the ^5D_J ($J=0,1$)$\rightarrow$$^7F_J$ ($J=0$–4) transitions. Luminescence peaks corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J=0$–4) transitions are labelled in the figure. At RT, luminescence peaks are relatively broad and the resolution of the same transition in both environments is, in general, not possible. When temperature decreases, there is a narrowing of the peaks and both sets of levels can be established in most cases. The maximum energy difference between both Eu sets is 20 cm^{-1}, which is observed in the figure as a double peak corresponding to a transition between singlets ($^5D_0 \rightarrow {}^7F_0$).

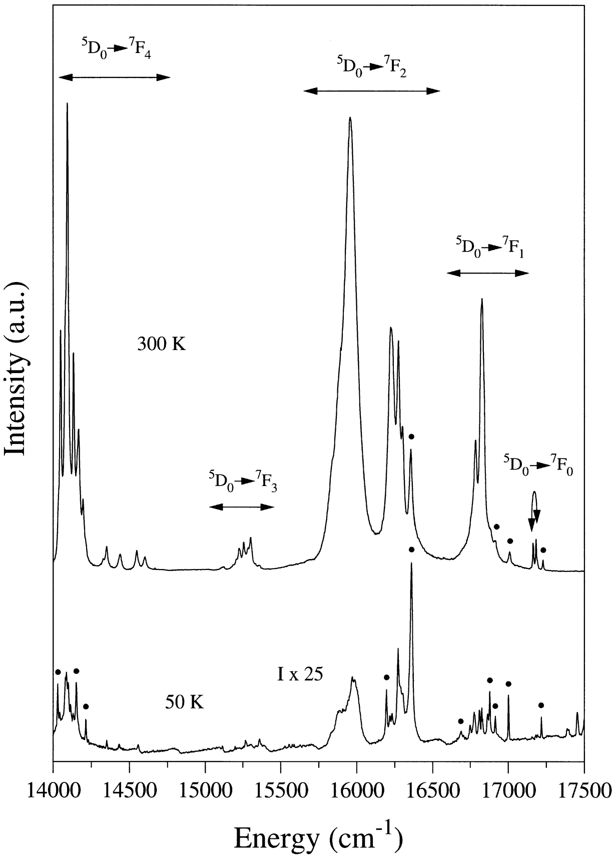

Fig. 1. Luminescence spectra of Eu_2BaZnO_5 oxide, recorded at RT and 50 K with an excitation energy of 488 nm. $^5D_0 \rightarrow {}^7F_J$ ($J=0$–4) transitions are labelled. In order to compare both spectra, that at low temperature is enlarged by a factor 25. Dots mark peaks related to transition from $^5D_1$ and $^5D_2$ multiplets.

When temperature decreases, the relative intensity of the peaks related to transitions from $^5D_1$ and $^5D_2$ multiplets (marked with dots in Fig. 1) is higher than that corresponding to transitions from $^5D_0$ level (opposite to the situation at room temperature). This can be explained assuming the following desexcitation processes: at room temperature, the excited electrons suffer a multiphonon non-radiative decay to the $^5D_0$ level where the emission takes place (the intensities of the peaks corresponding to transitions from this singlet are higher than those from $^5D_1$ and $^5D_2$). At low temperature the non-radiative decay probability is reduced in the same way as the phonon population, so that luminescence processes have their origin mostly in the $^5D_1$ and $^5D_2$ multiplets. This explanation is in agreement with the different excitation processes as a function of temperature given below for this wavelength.

3.1. Crystal field parameters

From the Eu^{3+} energy levels up to 22 000 cm^{-1} [7], the crystal field (CF) parameters for both Eu^{3+} environments are calculated. In Eu_2BaZnO_5 crystals, the local symmetry of Eu^{3+} ions is C_s. For this symmetry, the CF hamiltonian has 15 CF parameters. In order to reduce the large number of parameters, we use the approximate C_{2v} symmetry, where the number of parameters is reduced to nine.

Both europium ions are surrounded by three oxygen ions forming a Y figure and the other four oxygen ions are in a rhombohedral configuration in the perpendicular plane. The distortion of these four ions from a rectangle is higher at the Eu_1 site, so the Eu_2 site is closer to a C_{2v} symmetry.

Crystal field parameters obtained for one Eu site are reported in Table 1. The CF parameters obtained for both sites are very similar. Low values of B_2^0 and B_2^2 parameters are due to the experimentally obtained small $^7F_1$ (and $^5D_1$) splitting. Large values of fourth-rank parameters are characteristic of compounds with O ions as ligands for RE ions and are related to the covalence of oxygen bonds [9].

3.2. Raman crystal field transitions

In order to study the behaviour of the Raman crystal field transitions with temperature, we need to know that a transition between two electronic levels is Raman allowed

Table 1
Crystal field parameters (in cm^{-1}) obtained for one Eu site in Eu_2BaZnO_5 compound

	Site 1
B_2^0	122±15
B_2^2	25±9
B_4^0	1523±35
B_4^2	−73±33
B_4^4	1312±25
B_6^0	−493±41
B_6^2	429±40
B_6^4	−295±29
B_6^6	−27±38

if the direct product of their representations contains some of the irreducible representations of the Raman-active phonons. In our case, all possible intra- and intermultiplets ^7F_J transitions are Raman allowed. The Raman crystal field transitions (RCFT) recorded at high and low temperature when a 488-nm wavelength is used are collected in Fig. 2. In addition to phonons (shown as reference; note the intensity reduction factor of 1/8), these spectra represent transitions from the ground state to the $^7F_2$ multiplet and, therefore, allow the direct determination of the energy values of this multiplet levels. $^7F_0$ to $^7F_3$ and $^7F_4$ RCFT are also detected at low temperature (not shown) but not $^7F_0 \rightarrow ^7F_1$ transition.

Given that the origin of these transitions is the ground state, the increase in the intensity of the Raman crystal field transitions when temperature is lowered is explained by the increase of the population of the ground state when temperature decreases.

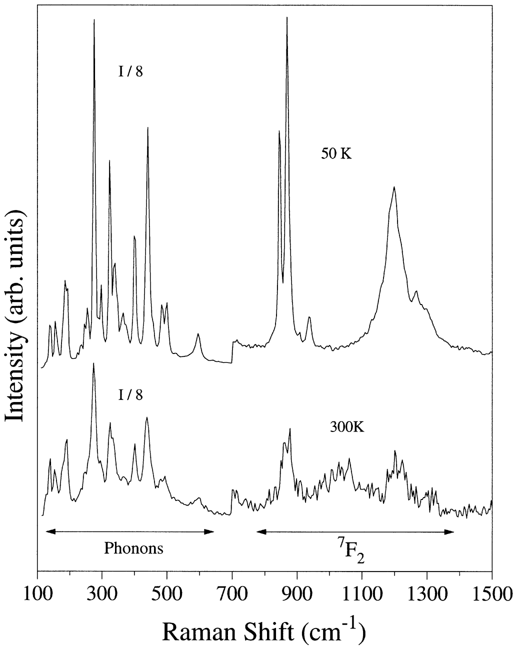

Fig. 2. Raman crystal field transitions recorded at high and low temperature, when the 488 nm wavelength is used. $^7F_0$ to $^7F_3$ and $^7F_4$ transitions have also been observed (not shown). Phonons are shown as a reference (note the intensity reduction factor of 1/8).

As can be seen in Figs. 1 and 2, the peaks corresponding to transitions to the three highest $^7F_2$ levels are specially broad even at low temperature, not only in the Raman crystal field transitions (which are like absorption processes) but also in luminescence, and, therefore, such a broadening has to be associated to the $^7F_2$ multiplet. Furthermore, the broadness appears only in related compounds with Pnma structure, therefore it seems to be associated to this structure. This widening can be due to a hybridisation of this Eu multiplet with other crystal levels or bands (for example, with orbitals of oxygen ions which are very close to the europium ion).

3.3. Excitation of the luminescence

Coming back to the luminescence, this has been studied using 19 different wavelengths, in most cases in off-resonance conditions. The wavelengths used are all the lines of an Ar^+–Kr^+ laser plus the He–Ne laser line (labelled as 3 in Fig. 3). Depending on the situation of the excitation energy, with respect to the electronic levels, the excitation of the ground state electrons is achieved by different paths depending sometimes on the temperature. Fig. 3 shows the luminescence intensity obtained with each wavelength used (labelled from 1 to 19) at room tempera-

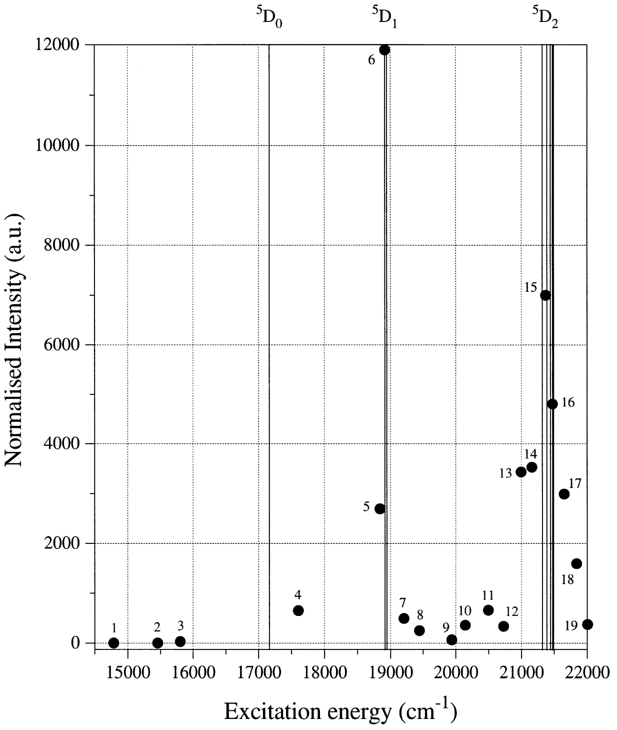

Fig. 3. Behaviour of the luminescence intensity versus the excitation energy. The spectra were recorded at room temperature. Dots labelled from 1 to 19 represent the different wavelengths used. Vertical solid lines symbolise the experimental detected levels of the ^5D_J (J=0,1,2) multiplets.

ture. In order to compare the intensity of the different spectra, a $LiNbO_3$ crystal film was placed over the Eu_2BaZnO_5 sample. The $LiNbO_3$ highest frequency phonon was used to correct the luminescence spectra by the set-up sensibility and, at the same time, to normalise their intensity.

Vertical solid lines in the figure symbolise the experimentally detected levels of the three ^5D_J ($J=0,1,2$) multiplets respect to the ground state ($^7F_0$) of the Eu^{3+} ion. When the excitation energy corresponds to these solid lines (resonance conditions) the luminescence intensity is appreciably high, but even in completely off-resonance conditions the intensity is appreciable. In the case of the wavelengths labelled as 6, 15 and 16, the excitation energy approximately coincides with the energy difference between the ground state and the ^5D_J ($J=1,2$) multiplets, and the luminescence intensity is high. In all other cases, we are in off-resonance conditions but there are several excitation and desexcitation processes, depending basically on the situation of the excitation energy with respect to the nearest electronic levels.

The red lines (1, 2 and 3) are far below the $^5D_0$ level and, therefore, no luminescence is expected. Nevertheless, weak luminescence is detected with lines 2 and 3 at room temperature; its origin can be tentatively assigned to the transitions from the thermally populated $^7F_2$ multiplet which allows the electrons to reach the $^5D_0$ singlet. This thermal population also allows lines 4, 10 and 11 to reach upper multiplets ($^5D_1$ and $^5D_2$) where desexcitation process starts.

For lines very close to the $^5D_1$ and $^5D_2$ multiplets, the absorption or emission of one phonon or the thermal population of the first excited multiplet ($^7F_1$) are enough to reach the nearest electronic level. Luminescence excited with the wavelengths labelled from 7 to 14 has two kinds of behaviours: lines 7, 8 and 9 present a decreasing intensity when the incident wavelength separates from the $^5D_1$ multiplet, indicating that a relaxation to this level is occurring. The other lines (from 10 to 14) reach the $^5D_2$ multiplet via phonon coupling or thermal population of the lowest excited multiplets.

An example of the intensity behaviour with temperature can be explained on the basis of Fig. 1, where luminescence excited with 488 nm and measured at 50 K is very weak (enlarged for clarity). This intensity variation has to be attributed to different excitation processes at high and low temperature: at RT, the incident photons excite electrons from the thermally populated lowest levels of the $^7F_2$ multiplet to the $^5D_2$ state, at 20 476 cm^{-1} above, which corresponds to the incident energy (488 nm=20 492 cm^{-1}). After that, the excited electrons experience a nonradiative decay to the $^5D_1$ and $^5D_0$ levels from which emission occurs. At 50 K, the thermal equilibrium population of the $^7F_2$ multiplet is about 10^{-9} times lower than at RT. The excitation that gives rise to the detected luminescence must have another origin: the excitation of electrons can be achieved by two mechanisms.

(1) The $^7F_2$ multiplet is populated by the Raman-scattering process previously described. In fact, this mechanism populates the $^7F_2$ multiplet increasingly when the temperature decreases and the ground state thermal population increases. Therefore, this non-thermal population of the $^7F_2$ levels can be excited to the $^5D_2$ multiplet.

(2) Another path can be the absorption of a photon which has suffered a Stokes second- or third-order Raman scattering loosing enough energy to coincide with the $^7F_0\rightarrow{}^5D_1$ transition.

Both paths involve two electrons. The first electron suffers one of the Raman processes described above, which is a very rapid one, and afterwards another electron suffers a transition between real electronic states ($^7F_2\rightarrow{}^5D_2$ or $^7F_0\rightarrow{}^5D_1$), and subsequently a relaxation to the $^5D_1$ and $^5D_0$ levels emits the detected photons. The energy diagram

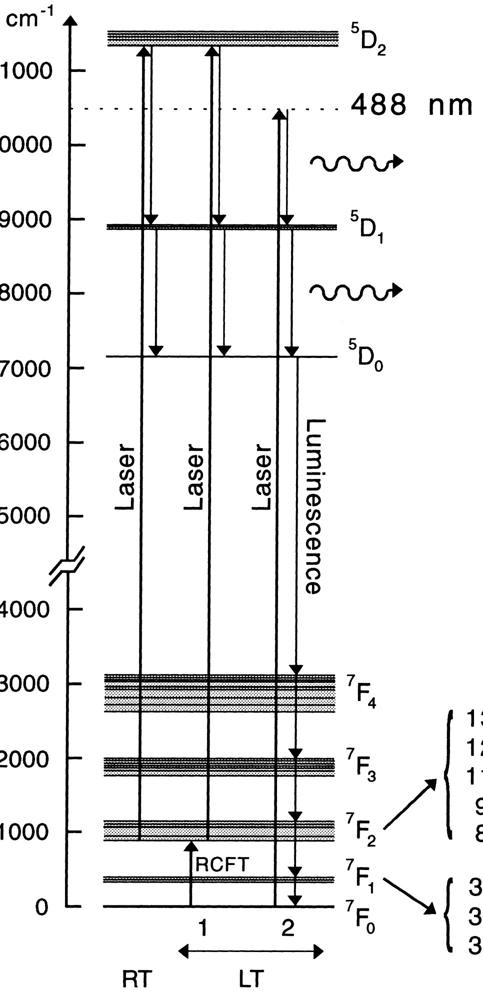

Fig. 4. Excitation and emission processes at high and low temperature when the excitation energy is 488 nm. Dashed line shows the position of the incident wavelength respect to the ground state. Wavy arrows represent the non-radiative decay via phonons. RCFT, Raman crystal field transitions.

of the lowest Eu^{3+} levels and the possible excitation and emission processes at high and low temperature are collected in Fig. 4.

In summary, excitation processes are strongly dependent on the population of levels and on the phonon population. The desexcitation ones depend on the probability of non-radiative decay.

4. Conclusions

Luminescence and Raman experiments have been performed on a Eu_2BaZnO_5 compound. Luminescence spectra have been obtained in the visible region at 19 different excitation energies, in most cases in off-resonance conditions. Spectra show peaks corresponding to transitions from $^5D_0$ and from $^5D_1$ and $^5D_2$ multiplets the behaviour of which with temperature is different for each case. In addition to Raman phonons, Raman transitions between ground state and $^7F_2$, $^7F_3$ and $^7F_4$ multiplets have been observed. It has been found that the intensity of these transitions increases when temperature decreases due to the change in the thermal population of the ground state. Crystal field parameters have been calculated doing an approximation to the C_{2v} symmetry, and have turned out to be very similar for both Eu^{3+} sets.

The behaviour of the luminescence intensity versus the excitation energy indicates excitation and desexcitation processes different for each wavelength, which have been determined. At room temperature, the excitation is achieved by transitions of electrons of the thermally populated $^7F_1$ and $^7F_2$ multiplets. At low temperature, this path is negligible and second-order processes must be invoked: the excitation can be done by electrons which have been promoted to the $^7F_1$ and $^7F_2$ levels by a previous Raman scattering process. Another path is the absorption from the ground state of photons emitted after an inelastic Raman scattering with lattice phonons.

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