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Evidence of Eu^{3+}-O^{2-} associates by luminescence study of some silicates and aluminosilicates

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Abstract

Unusual luminescence spectra with a strong $^5D_0 \rightarrow {}^7F_0$ line, a high position of the $^5D_0$ level and the occurrence of two lines close to 16550 cm^{-1}, i.e. in a frequency domain at the border between $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, have been evidenced in the case of cordierite, $Mg_2Al_4Si_5O_{18}$:Eu, mullite, $2Al_2O_3.SiO_2$:Eu and lanthanum disilicate, $La_2Si_2O_7$:Eu. By comparison with results on apatites and some fluorides, these unusual spectra have been attributed to the presence of a strong and anisotropic crystal field due to an Eu-O bonding. © 1997 Elsevier Science S.A.

Keywords: Eu-doped silicates; Aluminosilicates; Luminescence; Eu^{3+}-O^{2-} associates

1. Introduction

Due to a peculiar environment, rare-earth ion doped-apatite structures exhibit highly favourable spectroscopic properties for use in lasers [1]. When such structures were locally investigated with Eu^{3+}, unusual spectra were observed. In an early paper it was suggested that a covalent Eu-O bonding should be responsible for this behaviour [2]. This assumption seems to be confirmed by the occurrence of the same spectra in fluorides, like CaF_2 and $RbCaF_3$, strongly influenced by the presence of oxygen ions on F^- sites in the lattice [3].

During the use of Eu^{3+} as a local probe in silicates and aluminosilicates prepared by the sol-gel route, such exceptional spectra were also observed and attributed to the same cause. Investigations were performed by using both site-selective excitation (or observation) and time-resolved spectroscopy. The aim of this paper concerns the possible presence of such Eu^{3+}-O^{2-} associates in the structure of Eu-doped cordierite, $Mg_2Al_4Si_5O_{18}$:Eu and mullite, $2Al_2O_3.SiO_2$:Eu. Moreover, such peculiar spectra were also evidenced in the case of lanthanum disilicate, $La_2Si_2O_7$:Eu. This work is one part of our research concerning the influence of site environment on the corresponding luminescence spectra of Eu^{3+} in silicate and aluminosilicate matrices.

2. Experimental

2.1. Synthesis

All samples have been obtained using sol-gel routes involving in all cases $Si(OC_2H_5)_4$ (TEOS) and $Eu(NO_3)_3.5H_2O$ as Si and Eu precursors, respectively. For the other elements, Mg, Al, La, different compounds have been chosen. Whereas in the case of cordierite, $Mg_2Al_4Si_5O_{18}$:Eu, an all-alkoxide route

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has been used [4], in the case of mullite and La disilicate, the second cation (Al and La, respectively) was introduced as nitrate. After hydrolysis and condensation reactions, the resulting gels have been progressively dried up to a 200°C temperature under air and subsequently calcined at higher temperatures, depending on the crystallization scheme of the corresponding samples, to promote the reaction between the components.

2.2. *Characterizations*

The resulting powders have been characterized by X-ray diffraction using a Siemens D500 diffractometer (CoKα1 monochromatized radiation) before spectroscopic measurements. A pulsed nitrogen laser (Jobin Yvon) or the third harmonic of a Q-switched neodymium YAG laser (Spectra Physics) was used as a non-selective excitation source. These lasers were also used to pump a tunable dye laser (Jobin Yvon, LA04/E1T model) for the site-selective excitation. The spectral analysis of the luminescence was achieved by an 80-cm double grating monochromator (PHO Coderg) spectrometer driven by a computer that collected and processed the data. The time-resolved spectroscopy was performed by means of a digital oscilloscope (Tektronix 2430) coupled with the computer by using home-made programs [5]. The samples were cemented with a non-fluorescent glue on the inner wall of a dewar. Although some measurements were carried out at room temperature, most of them were done at 77 K by immersion in liquid N_2 or in a helium close-cycle refrigerator (Cryophysics, CP62-STS).

3. Results

3.1. *Lanthanum disilicate, $La_2Si_2O_7$:Eu*

X-ray diffraction patterns after different annealing experiments reveal that La disilicate crystallizes at around 1200°C with the presence of residual La_2O_3. Increasing the annealing temperature promotes an evolution of the sample with disappearance of La_2O_3 and transformation of the disilicate from α-$La_2Si_2O_7$ to $La_2Si_2O_7$. Whereas the structure of the latter is known [6,7], it is not the case for the former whose composition is uncertain. Therefore, only samples calcined at 1350°C for 12 h have been considered.

From the spectrum under non-selective excitation, three $^5D_0 \rightarrow {}^7F_0$ transitions are clearly evidenced at 17268, 17290 and 17368 cm^{-1}, respectively and can be attributed to three non-equivalent sites for Eu^{3+} ions. Whereas the first two previous transitions appear in the frequency domain, 17200 to 17300 cm^{-1}, usually observed for Eu^{3+} emission, the $^5D_0$ level is quite high for the third one, 17368 cm^{-1}. Results concerning the last site will only be considered in the present paper.

The spectrum under selective excitations in the $^5D_0$ level at 17368 cm^{-1} excitation (Fig. 1) shows the presence of two lines (17038 and 17193 cm^{-1}) and three lines (15936, 15989 and 16176 cm^{-1}) that can be clearly assigned to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively. Two extra lines at around 16550 cm^{-1} are at the junction between these two spectral domains.

3.2. *Cordierite, $Mg_2Al_4Si_5O_{18}$:Eu*

In Eu-doped cordierite samples, $Mg_2Al_4Si_5O_{18}$:Eu, according to structural and luminescence studies, it has been shown [4] that Eu^{3+} ions share between two different positions, one, B, in substitution for Mg in an octahedral coordination, the other one, A, inside the structure channels. The A site family was evidenced only at low temperature. Using a fluorescence line narrowing (FLN) technique by excitation in the $^5D_0$ level, both site families have been characterized. If the first one (B) exhibits features usually observed for Eu^{3+} ions, this will not be the case for the A family with abnormally strong $^5D_0 \rightarrow {}^7F_0$ transition and a high value of the $^5D_0$ level. Moreover, in the frequency domain where $^5D_0 \rightarrow {}^7F_1$ transitions are expected (Fig. 1), only very weak lines were observed, including a doublet close to 16550 cm^{-1}.

3.3. *Mullite, $2Al_2O_3.SiO_2$:Eu*

The composition of synthetic mullite ranges between $3Al_2O_3.2SiO_2$ and $2Al_2O_3.SiO_2$. Its orthorhombic structure is related to the sillimanite structure (Al_2SiO_5) with oxygen vacancies that are more or less ordered. By using sol-gel routes, it is possible to get metastable solid solutions with higher alumina contents. Eu-doped samples have been prepared corresponding to different alumina/silica ratios. The corresponding spectra reveal the presence of broad lines characteristic of a site distribution in the samples. A peculiar behaviour has been observed in the case of the $2Al_2O_3.1SiO_2$ composition and we will focus our attention on this sample.

Under non-selective excitation (337 nm, 29674 cm^{-1}), three different sites seem evidenced according to the presence of three $^5D_0 \rightarrow {}^7F_0$ transitions at 17290, 17400 and 17540 cm^{-1} (Fig. 1). Four other lines (* on Fig. 1) exhibit the same time behaviour as the 17400 cm^{-1} line.

Excitation around 17540 cm^{-1} does not lead to any interesting selectivity. When the excitation is performed in the vicinity of 17290 cm^{-1}, the emission spectra show three $^5D_0 \rightarrow {}^7F_1$ bands and one broad

$^5D_0 \rightarrow {}^7F_2$ band as it is usually observed by fluorescence line narrowing (FLN) in glasses. Around the third site, when the excitation ranges between 17380 and 17460 cm^{-1}, peculiar emission spectra are observed. The most typical, under 17390 cm^{-1} excitation, is shown in Fig. 1. With respect to the previous non-selective spectrum, six rather narrow lines are enhanced. Some of them were already distinguished by their same time evolution. As for the spectrum encountered in $La_2Si_2O_7$, a doublet in the 16550 cm^{-1} region also occurs.

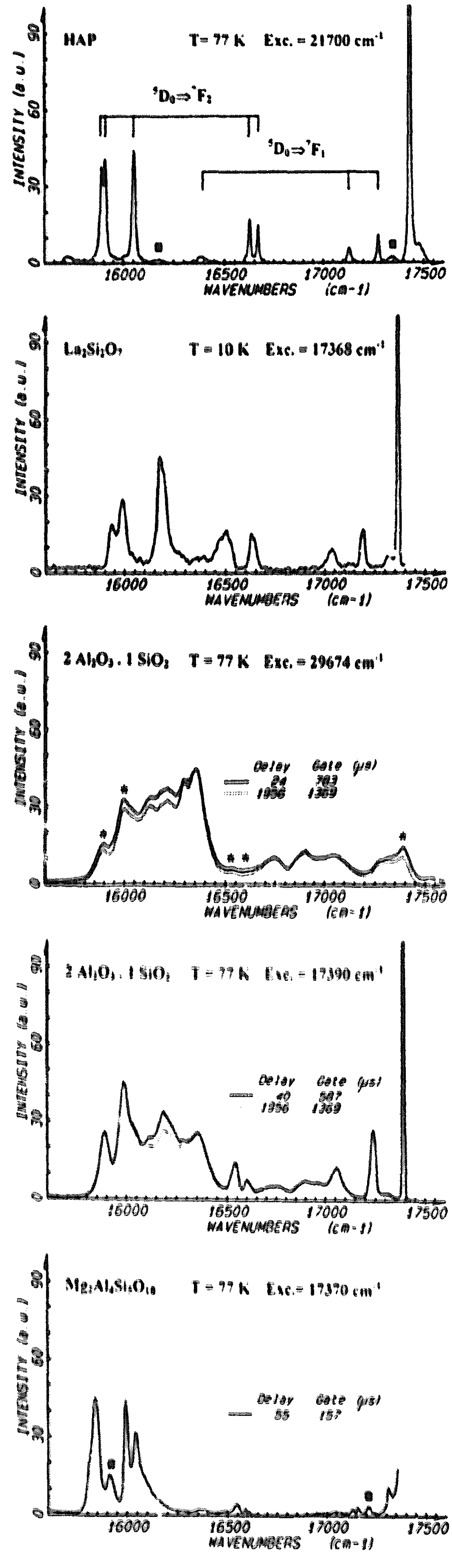
4. Discussion

The peculiar spectra obtained in all cases ($La_2Si_2O_7$, cordierite, mullite) must be related to those of Eu-doped apatite as shown in Fig. 1. The unusual features are mainly:

- a strong $^5D_0 \rightarrow {}^7F_0$ line,
- a high position of the $^5D_0$ level,
- the occurrence of two lines close to 16550 cm^{-1} at about 800 cm^{-1} above the ground level (see Table 1).

After a study on $Ca_5(PO_4)_3F$:Eu single crystal [8], the assignments reported on top of Fig. 1 were given. Such features are due to a strong anisotropic crystal field which induces a large splitting of the $^7F_1$ and $^7F_2$ manifolds to imbricate their components. In a similar way, the odd parameters of the crystal field lead to the considerable oscillator strength of the $^5D_0 \rightarrow {}^7F_0$ transition. In an early paper [2], it was suggested that with an oxygen in the channel a privileged Eu-O bond should be responsible for such effects. More recently, this assumption seems confirmed in the case of some fluorides [3] in which similar spectra attributed to Eu^{3+}-O^{2-} associates were reported. Despite a rigorous C_s local symmetry in apatite structures a pseudo-$C_{\infty v}$ symmetry along the Eu-O bonding agrees well with the data indicating that the double degeneracy of three components is slightly lifted in doublets.

In the case of cordierite, some part of Eu^{3+} ions have been located along the *c* axis inside the structure channels from room temperature structure refinement. However, their position at low temperature is not known. From the spectroscopic measurements,



$^5D_0 \Rightarrow {}^7F_{0,1,2}$ emission spectra. From top to bottom: Ca hydroxyapatite under selective excitation in $^5D_2$ level, La disilicate under selective excitation in $^5D_0$ level, mullite 2/1 under U.V. non-selective excitation, mullite 2/1 and cordierite under selective excitation. Lines marked ■ reveal a different time behaviour and must not be taken into account.

Table 1
Energy levels (in cm^{-1}) of the different sites studied

Level	$La_2Si_2O_7$	Mullite	Cordierite	Hydroxyapatite
$^5D_0$	17368	17390	17350	17437
$^7F_1$	175	151	215	164
	330	333	318	307
	—	—	939	1051
$^7F_2$	731	789	787	768
	865	849	829	811
	1192	1030	—	1382
	1379	1398	1326	1531
	1432	1499	1495	1547

it could be concluded that they are located off-axis close to one oxygen ion. This Eu-O bonding presents a more covalent character than the interaction of Eu^{3+} with the other O^{2-} ions in their neighbourhood.

In the case of mullite, due to the presence of similar features on the luminescence spectra, the same conclusion can be proposed. However, Eu^{3+} ions cannot substitute for Al^{3+} ions in an octahedral environment due to the strong difference between corresponding Eu-O and Al-O bond lengths. In the mullite structure, the presence of oxygen vacancies yield the formation of voids where Eu^{3+} ions could be located. As the number of vacancies increases with alumina content, it could explain why only the sample containing more alumina exhibits this peculiar site.

In the case of $La_2Si_2O_7$, if the first two sites can be clearly related to the two unequivalent La positions in the structure [6,7], any explanation cannot yet be proposed for the presence of the last site. As the presence of interstitial sites appears difficult to consider according to the structure compacticity, the presence of a parasitic phase could be considered even if it is not detected from X-ray diffraction. In the same way, Eu^{3+} ions could also be located in an amorphous phase.

The observation of such peculiar sites seems to be related to the possibility for one ion to move according to its location or its degree of freedom. So, in the case of cordierite and mullite, Eu^{3+} moves inside the channel or the cavity toward oxygen ions whereas in the case of apatite oxygen is shifted toward Eu^{3+} ions.

5. Conclusion

The use of Eu^{3+} as a local probe in cordierite, $Mg_2Al_4Si_5O_{18}$:Eu, mullite, $2Al_2O_3.SiO_2$:Eu and La disilicate, $La_2Si_2O_7$:Eu has revealed the presence of unusual spectra characterized by a strong $^5D_0 \rightarrow {}^7F_0$ line, a high position of the $^5D_0$ level and the presence of two lines close to 16550 cm^{-1}. In the case of cordierite, $Mg_2Al_4Si_5O_{18}$:Eu, the corresponding manifolds in the 16550 cm^{-1} region were less intense. By comparison with apatite samples, such features have been related to a strong anisotropic crystal field which induces a large splitting of the $^7F_1$ and $^7F_2$ manifolds to imbricate their components. The origin of this peculiar crystal field could be found in the presence of a privileged Eu-O bond. Whereas in $La_2Si_2O_7$, the presence of a parasitic or amorphous phase, not evidenced from X-ray diffraction measurements could be invoked, in the case of cordierite, a channel structure exists as in apatites. For mullite, Eu^{3+} ions could be located inside the cavities related to the presence of oxygen vacancies.

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