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Luminescence of $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]:\text{Ce}^{3+}$

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Abstract

The luminescence properties of Ce^{3+} in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ are reported. Excitation and emission bands corresponding to $4f^1 \rightarrow 5d^1$ transitions of Ce^{3+} were identified. The center of gravity of the 5d states lies at remarkable high energy ($43.2 \times 10^3 \text{ cm}^{-1}$) for Ce^{3+} in a silicate compound. This high value is attributed to the combined oxygen/fluoride coordination of the Ce^{3+} ion. Emission from the lowest 4f5d level to the $^2F_{5/2}$ and $^2F_{7/2}$ levels was found at 32.4×10^3 and $30.4 \times 10^3 \text{ cm}^{-1}$. These results are compared with literature data on silicates and fluorides. From the values found for Ce^{3+} , predictions are made for the positions of the 4f5d bands of Pr^{3+} and Er^{3+} in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$. For both ions, it is concluded that in this host lattice emission is expected from high lying 4fⁿ energy levels. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transitions on rare-earth ions in which an electron from one of the 4f orbitals is excited to a 5d orbital are parity allowed and are usually situated in the UV or vacuum UV ($\lambda < 200 \text{ nm}$). These transitions play an important role in phosphors that are applied in mercury-based fluorescent tubes. For example, in two of the most widely used phosphors the absorption properties of the phosphors are determined by fd transitions: in $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ the 4f5d band of Eu^{2+} absorbs UV radiation and in $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}$ the 4f5d bands of Ce^{3+} are responsible for the efficient absorption of the mercury discharge

emission (see e.g. Refs. [1,2]). Also in the development of new phosphors for VUV excitation (needed in Xe-based fluorescent tubes and plasma display panels) [2] 4f5d transitions of rare-earth ions most probably will be of considerable importance for the VUV absorption properties. Therefore, it is useful to understand the factors determining the positions of $4f^{n-1}5d^1$ states. Although the 4f5d levels of many of the rare-earth ions have been determined in a lot of different host lattices (see e.g. Ref. [3]), it is still difficult to predict the position of these levels and, if present, the position of the corresponding emission bands. This is due to the fact that various factors contribute to the position of 4f5d states, like the nature of the coordinating anions, the coordination number, site symmetry and the nature of the next nearest cation neighbors [1–8].

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For a few years now, research is being done in our group on the energy levels of rare-earth ions in the VUV region. Many new $4f^n$ levels have been discovered in this region and also spin allowed and spin forbidden $4f5d$ transitions were observed for all heavy lanthanides [9,10]. Up to now, mainly rare-earth-doped fluoride host lattices have been used to study the VUV spectroscopy of these ions. The band gap of fluorides is large, giving a large optical window to study VUV excitations and emissions. However, in phosphor industry mainly oxidic host lattices are used [2]. Therefore, it is interesting to extend our research on VUV spectroscopy of rare-earth ions to other host lattices. In this respect, our attention was drawn to the recently discovered class of the lanthanide fluoride silicates [11–13]. In these compounds, both oxygen and fluoride ions coordinate the lanthanide ions. It was hoped that this would lead to positions of the $4f5d$ levels between what is usually found for oxide and fluoride host lattices. High positions of the fd bands are desired, because they allow absorption of VUV radiation. Further, different compounds with varying silicate to fluoride ratios can be synthesized [13], allowing the possibility to influence the positions of the $4f5d$ levels of the lanthanides. This article reports on our investigations on a Ce^{3+} -doped sample of $La_3F_3[Si_3O_9]$. In the past the $5d$ levels of Ce^{3+} have been investigated in many different host lattices, partly because they are positioned in the easy accessible UV region and not in the VUV region as many other lanthanides. Among the different host lattices, various silicate lattices doped with Ce^{3+} were studied [14–21]. In these lattices the onset of the $5d$ levels is found between 26×10^3 and $35 \times 10^3 \text{ cm}^{-1}$. The Stokes shift is usually a few thousand wave numbers, up to $10,700 \text{ cm}^{-1}$ for Ce^{3+} on a 6h site of $Gd_{0.33}\square_{0.67}[SiO_4]_6O_2$ [14]. Also, many fluoride host lattices doped with Ce^{3+} have been studied. The center of gravity of the $5d$ bands of Ce^{3+} is usually found at about $48,000 \text{ cm}^{-1}$. The highest energies for both excitation and emission are reported for LaF_3 . The excitation onset in this host is found at ca. $40,000 \text{ cm}^{-1}$ and emission to the ground state has a maximum at $35,090 \text{ cm}^{-1}$ [22,23].

2. Experimental

Powder sample of $La_3F_3[Si_3O_9]$ can be prepared as reported in Ref. [11]. Doping with Ce^{3+} is done by replacing 3% of the LaF_3 in the educt mixture by CeF_3 (molar ratio $LaF_3:CeF_3:La_2O_3:SiO_2$ is 0.97:0.03:1:3). The crystal structure is hexagonal and belongs to the space group P62c [6]. It consists of discrete cyclic $[Si_3O_9]^{6-}$ anions forming layers alternating with graphite-like LaF -networks. The lattice offers only one La-site (point symmetry C_2). The coordination number of the La^{3+} ions is best described as $9+2$. Six oxygen ions form a distorted trigonal prism (four ions at about 2.5 \AA , two at 2.9 \AA), three fluoride ions form a plane which intersects the prism at a right angle and are at a distance of about 2.5 \AA from the La^{3+} ion. Two other oxygen ions are at a distance of about 3.2 \AA and are in the same plane as the fluoride ions. All oxygen ions are part of the $[Si_3O_9]^{6-}$ anions.

Optical measurements were performed on a Spex 1680 spectrofluorometer with 0.22 m double monochromators. This apparatus was adapted for VUV measurements. The excitation source was a D_2 -lamp (Hamamatsu L1835, 150 W) fitted with a MgF_2 window. The gratings of the monochromators were blazed at 150 nm (excitation) and at 500 nm (emission). Lamp housing, excitation monochromator and sample chamber were flushed with nitrogen to avoid absorption of VUV radiation by oxygen. Spectra were recorded at liquid helium temperature (4 K) by using an Oxford Instruments Optistat^{CF-V} liquid helium cold finger cryostat equipped with MgF_2 windows. Excitation spectra were corrected for lamp intensity by recording sodiumsalicylate excitation spectra, emission spectra were corrected for the monochromator and the detector response using a typical response curve provided by the manufacturer.

3. Results and discussion

In Fig. 1, an excitation spectrum and an emission spectrum of $La_3F_3[Si_3O_9]$ doped with Ce^{3+} are presented, both recorded at 5 K. The excitation spectrum shows five intense bands and

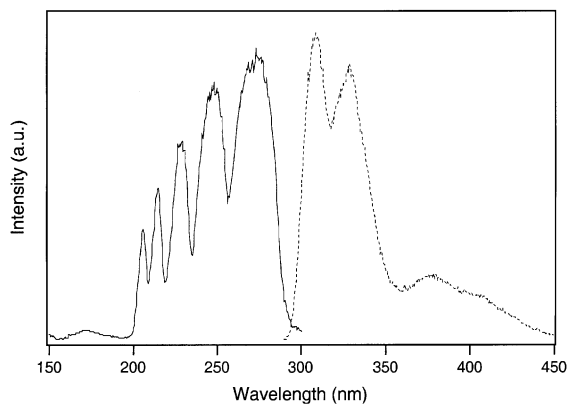


Fig. 1. Excitation spectrum (—) and emission spectrum (----) of $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]:\text{Ce}^{3+}$ at 5 K. The excitation spectrum is recorded monitoring the $4f^05d^1 \rightarrow {}^2F_{5/2}$ transition (309 nm), the emission spectrum is recorded upon excitation in the $4f5d$ bands at 280 nm.

one broad band at higher energy. The latter band with its maximum at about 170 nm (Fig. 1), is assigned to a host lattice related excitation band. Upon excitation in this band, only broad band emission in the UV/visible range was observed (also visible in Fig. 1). This indicates that energy transfer to Ce^{3+} is inefficient which is in agreement with the observation that the host lattice emission band does not overlap with the Ce^{3+} excitation bands. The nature of the host lattice emission band is not clear. Often in fluorides and oxides a broad host lattice emission band is observed and assigned to a defect related trapped exciton emission. The host lattice emission band can also be excited upon excitation in Ce^{3+} at 280 nm, as is evident in Fig. 1. The five intense excitation bands in Fig. 1 are attributed to the crystal field levels of the $4f5d$ state. In C_2 symmetry (the site symmetry of Ce^{3+} in this lattice), it is expected that the $4f5d$ state splits into five crystal field components. However, the splitting is not often observed as nicely as for Ce^{3+} in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ with five clearly separated bands at regular intervals of about 3000 cm^{-1} . The positions of the maxima of the bands are given in Table 1. The mean value of the positions of the peaks is at $43.2 \times 10^3\text{ cm}^{-1}$, which is taken as the center of gravity of the $4f5d$ levels. It lies in between values for the centers of gravity

Table 1

Positions of peak maxima of crystal field split $4f^1 \rightarrow 4f^05d^1$ transitions of Ce^{3+} in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ measured at 5 K

Peak positions ($\times 10^3\text{ cm}^{-1}$)
48.5
46.5
43.8
40.4
36.7

normally found for Ce^{3+} in fluorides (around $48 \times 10^3\text{ cm}^{-1}$) and oxides (around $35 \times 10^3\text{ cm}^{-1}$). This can be understood from the structure of the compound, as the Ce^{3+} ion is coordinated by both fluoride and oxygen atoms. Moreover, all oxygen ions are bound to Si^{4+} ions. This lowers the covalency of rare-earth oxygen bonds. Thus, the nephelauxetic effect is reduced and the positions of the $4f5d$ levels shift upwards in energy in comparison to Ce^{3+} in some other oxides. The same effect for example is observed in silicate apatites like $\text{La}_{9.33}\square_{0.67}[\text{SiO}_4]_6\text{O}_2$ [14]. These lattices offer different sites for the La^{3+} ion. One site has a coordination number of 7 and one of the oxygen ions does not belong to a SiO_4 tetrahedron and is at a relatively short distance from the central La^{3+} ion. The other site has a coordination number of 9. On this site, all coordinating O^{2-} ions are part of $[\text{SiO}_4]$ tetrahedra. The covalency is larger for the sevenfold coordinated site, which leads to the lower positions of the $4f5d$ levels of Ce^{3+} : the maximum of the first $4f5d$ peak is observed at $31.3 \times 10^3\text{ cm}^{-1}$ whereas for the other site it is observed at $34.5 \times 10^3\text{ cm}^{-1}$. A comparable example is provided by $\text{Gd}_2\text{O}[\text{SiO}_4]$ doped with Ce^{3+} (see Ref. [15]). Here also the nature of the oxygen ions has a significant influence on the energy of the $4f5d$ transitions of Ce^{3+} .

Recently, Srivastava et al. have reported on the position of the $4f^15d^1$ levels of Pr^{3+} in oxidic host lattices [6–8]. It was shown that the onset of these levels in $\text{SrAl}_{12}\text{O}_{19}$, $\text{LaMgB}_5\text{O}_{10}$ and LaB_3O_6 is at high energy, comparable to values found in fluorides. The authors argued that the position of the $4f5d$ bands in these lattices is high due to the large coordination number of Pr^{3+} on the lanthanide sites. This causes a small crystal field

splitting and as a result the lowest 4f5d level is situated above the 1S_0 level and 1S_0 emission, previously only found in fluorides, could be observed. In $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ also a small crystal field splitting is expected since this compound offers a large site for the La^{3+} ion (high coordination number: 11, or rather 9+2, see Ref. [11]). From the energy difference between the lowest and the highest crystal field level the crystal field splitting is calculated to be $12,000\text{ cm}^{-1}$. A crystal field splitting of $12,000\text{ cm}^{-1}$ is relatively small for Ce^{3+} . Typically, values between $10,000$ and $20,000\text{ cm}^{-1}$ are found. Note that sometimes smaller crystal field splittings are reported in the literature, but often not all 4f5d crystal field levels of Ce^{3+} are observed, due to instrumental limitations or to overlapping bands and the reported crystal field splitting is not the energy difference between lowest and highest energy 5d level.

The coordination of Ce^{3+} in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ is comparable to the coordination of the Ce^{3+} ion in LaF_3 . The coordination number of La^{3+} in this lattice is also best described by 9+2 [11], i.e. 9 fluoride ions are at approximately the same distance to the central cation and 2 are positioned further away. The site symmetry is also C_2 [22]. A comparison of the luminescence spectra of Ce^{3+} in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ and Ce^{3+} in LaF_3 shows that the spectra are similar. As expected for a coordination by F^- only, the five fd excitation bands are at slightly higher energy for Ce^{3+} in LaF_3 (center of gravity ca. $45,000\text{ cm}^{-1}$) and the crystal field splitting is slightly smaller (ca. $10,000\text{ cm}^{-1}$) than for Ce^{3+} in a mixed O^{2-}/F^- coordination as is found in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$.

The emission spectrum of $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]:\text{Ce}^{3+}$ shows two stronger and one weaker band. The bands peaking at 329 nm ($30.4 \times 10^3\text{ cm}^{-1}$) and 308.5 nm ($32.4 \times 10^3\text{ cm}^{-1}$) are attributed to transitions from the lowest crystal field levels of the 4f5d band to the $^2F_{7/2}$ and the $^2F_{5/2}$ level, respectively. The energy difference between the peaks (2000 cm^{-1}) is in accordance with the spin orbit splitting of the 2F ground state of Ce^{3+} . Compared to other silicates, the emission bands are found at high energies. This is due to the high-energy position of the 4f5d bands. The Stokes shift is 4300 cm^{-1} . This value is rather large for Ce^{3+} . A

few thousand wave numbers is usually found for the Stokes shift of the Ce^{3+} emission in lanthanide silicates (see e.g. Refs. [14–21]). The La^{3+} site in this lattice has a high coordination number, which allows the excited Ce^{3+} atom to relax significantly, leading to a large Stokes shift [1]. A very similar value for the Stokes shift is found for Ce^{3+} in LaF_3 , namely 4100 cm^{-1} . This is expected, as the coordination of the lanthanide ions in the two compounds is very similar. In LaF_3 the Ce^{3+} emission is still efficient at room temperature. In the present study thermal quenching of the luminescence has not been investigated, but efficient Ce^{3+} emission at room temperature can be expected.

As demonstrated by Dorenbos in an extensive review on the position of 4f5d transitions of lanthanides [3], it is possible to use the position of the 4f5d levels of Ce^{3+} to predict the positions of the 4f5d levels of all other rare-earth ions quite accurately (typically within 600 cm^{-1}). This can be done because the influence of the crystal field and covalency of the host lattice on the 4f5d levels is approximately equal for all rare-earth ions. From the presently observed energy of the lowest fd state for Ce^{3+} in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$, the lowest $4f^2 \rightarrow 4f^15d^1$ transition for Pr^{3+} in this host lattice can be predicted to be at about $48,900\text{ cm}^{-1}$, which is just above the 1S_0 level. As a result quantum cutting from the 1S_0 level can be expected [24–26]. Another interesting ion in this respect is Er^{3+} . Recently, high-energy levels within the 4f configuration were calculated and experimentally observed [27]. At around $55,000\text{ cm}^{-1}$ the $^2F(2)_{7/2}$ level is situated. As shown in Ref. [27], in a number of host lattices emission is observed from this level. The 4f5d states are predicted to be located above this level in $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ (estimated value for its onset is about $62,000\text{ cm}^{-1}$) and thus also in this lattice emission is expected from the $^2F(2)_{7/2}$ level. High emitting energy levels are interesting in view of quantum cutting (see e.g. Ref. [28]).

4. Conclusions

The 4f5d transitions of Ce^{3+} in the novel lanthanum fluoride silicate $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ have been

studied. It was found that the onset of the 4f5d levels lies at high energy in this compound (the position of the first crystal field level is at $36.7 \times 10^3 \text{ cm}^{-1}$). The excitation spectrum shows very nicely the five expected 4f5d bands at regular intervals of about 3000 cm^{-1} . The high energy of the 5d state is explained by the low covalency of the coordinating ligands. The mixed coordination (oxide and fluoride) put the energy of the center of gravity of the 5d state ($43.2 \times 10^3 \text{ cm}^{-1}$) in between values typically observed for Ce^{3+} in fluorides ($48 \times 10^3 \text{ cm}^{-1}$) and oxides ($35 \times 10^3 \text{ cm}^{-1}$). The crystal field splitting is smaller than what is usually observed for Ce^{3+} in pure silicate lattices. From the high energy of the lowest 5d level it can be expected that also other lanthanide ions will show interesting luminescence properties in this host lattice (e.g. Pr^{3+} and Er^{3+}).

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