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Charge transfer transitions and location of the rare earth ion energy levels in Ca-α-SiAlON

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ABSTRACT

The broad bands in the room-temperature excitation spectra of Sm^{3+}-, Dy^{3+}- and Tm^{3+}-activated Ca-α-SiAlON phosphors are interpreted as the N^{3-}-to-rare earth charge transfer transition (CTT). From the energies of the charge transfer transitions and from the optical data presented for the Eu^{2+} ion, the location of the divalent rare earth ion energy levels relative to the valence and the conduction band of Ca-α-SiAlON is derived. The salient features of the energy-level diagram are shown to be practical in explaining the temperature-dependent variations of the Eu^{2+} and Yb^{2+} luminescence efficiency in Ca-α-SiAlON. A comparative study pertaining to the nature of the Yb^{2+} and Eu^{2+} ion luminescence in Ca-α-SiAlON and in $SrSi_2O_2N_2$ is presented. A tentative energy-level diagram of the trivalent rare earth ions in Ca-α-SiAlON is also constructed.

1. Introduction

The archival literature contains a large amount of information on the charge transfer transition (CTT) of trivalent rare earth ions (RE^{3+}) that are relatively easily reduced to their respective divalent states (such as Eu^{3+}, Sm^{3+} and Yb^{3+}). However, there is a paucity of data on the charge transfer transitions of rare earth ions that are not easily reduced. Thus, for example, in Ref. [1] where systematic variations between the energies of ligand-to-RE^{3+} charge transfer transition were examined, there was only one compound in which the ligand-to-Pr^{3+} CTT was identified. Since then, the ligand-to-Pr^{3+} CTT has been identified in the excitation spectra of $LaBr_3$ [2], LuI_3 [3], $PrCl_3$ [4], $LuCl_3$ [5], $Cs_2NaPrCl_6$ [6] and $CaGa_2S_4$ [7]. With the exception of (La,Pr)Cl_3 [4], the CTT bands in these materials are separated from the host lattice and the Pr^{3+} $4f^2 \rightarrow 4f^1 5d^1$ interconfigurational excitation transition so that there identification is relatively easily accomplished. In $LaBr_3$ [2], LuI_3 [3] and $CaGa_2S_4$ [7], the ligand-to-Pr^{3+} CTT band dominates the excitation spectrum.

The CTT band in the excitation spectrum of Sm^{3+} is frequently observed and easily identified [1]. On the other hand, the only clear-cut case of a solid in which the ligand-to-Dy^{3+} CTT band has been observed is $CaGa_2S_4$, where this band is located near 3.85 eV [8]. The CTT band of the Dy^{3+} ion has also been identified in the excitation spectrum $REPO_4$ (RE = La, Y) [9,10].

Broadly speaking, the identification of the CTT band in the excitation spectrum of trivalent rare earth ions that are not easily reduced to their respective divalent states will contribute to our knowledge of the factors which control the energy of the ligand-to-RE^{3+} charge transfer transition in solids. Such studies increases the experimental data on these transitions and further assist in understanding the systematic differences between the energy of the charge transfer transitions of rare earth ions in solids.

In this paper we will demonstrate that members of the oxynitride family of materials are suitable host lattices for studying the ligand-to-RE^{3+} charge transfer transitions. The specific case of Ca-α-SiAlON is considered and the data presented in the archival literature is further analyzed. The work starts with the identification of the CTT bands in the excitation spectra of Sm^{3+}- and Dy^{3+}-activated Ca-α-SiAlON. When this is combined with the literature data presented on the optical properties of the Eu^{2+} ion in Ca-α-SiAlON, the absolute energy levels of the divalent rare earth ions relative to the top of the valence band of the host lattice can be derived following the model proposed by Dorenbos [1]. The absolute energy location of the divalent and the trivalent rare earth ion levels relative to the valence and the conduction bands of the host lattice provides a quantitative understanding of the factors that controls the luminescence properties of the rare earth ions in solids.

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The Ca-α-SiAlON structure can be derived from the α-Si_3N_4 structure by partially replacing Si–N with Al–O and Al–N charge compensated by Ca^{2+}. The composition is represented as $Ca_{m/2}Si_{12-m-n}Al_{m+n}O_nN_{16-n}$ where usually $0.5<m<3$ and m is approximately $2n$. In the crystal structure of Ca-α-SiAlON, the Ca^{2+} ion is seven coordinated by (N^{3-}, O^{2-}) anions [11]. The results of EXAFS measurements on Er and Yb-α-SiAlON show that out of the seven anionic sites, two are preferentially occupied by the O^{2-} anion while the rest are occupied by the N^{3-} anion [12,13]. The crystal structure of $SrSi_2O_2N_2$, which is also a subject of our discussion, is closely related to that of $CaSi_2O_2N_2$ [14]. The coordination polyhedra around the Ca^{2+} ion consist of six O^{2-} anions forming a distorted trigonal prism, which is capped by a single N^{3-} anion.

2. Experimental

For reason that will be made clear in Section 4.2, a sample with the composition $(Ca_{1-3x/2}Tm_x)_{m/2}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ where $x=0.03$, $m=2$ and $n=1$ was synthesized by heating to 1500 C a mixture of the starting materials in the required proportions for five hours under an atmosphere of 99%N_2–1%H_2 gas mixture. The sample, when analyzed by X-ray diffraction had the same diffraction pattern as obtained for the $m=2$ phase of the Ca-α-SiAlON formulation, in reference [15]. However, a careful examination of the diffraction pattern did reveal the presence of a small amount of Si_3N_4.

The room-temperature excitation and emission spectra were measured as previously described [16].

3. Results

The diffuse reflectance spectrum of the undoped Ca-α-SiAlON has been reported in Ref. [15,17]. From the spectrum we can derive the onset of the fundamental absorption edge at 230 nm (5.4 eV). The host lattice absorption band at ~210 nm (5.9 eV) is assigned to the first exciton absorption (E^{ex}).

The room-temperature excitation spectrum of Ca-α-SiAlON:Sm^{3+} consists of a broad band centered at 308 nm (4.03 eV) [15]. The full-width at half-maximum (FWHM) is approximately 75 nm (1 eV). The room-temperature excitation spectrum of Ca-α-SiAlON:Dy^{3+} consists of a 1.3 eV broad band peaking near 245 nm (5.06 eV). The excitation spectrum corresponds to an absorption band near 250 nm in the diffuse reflectance spectrum of the sample [15].

4. Discussions

4.1. Identification of the broad bands in the excitation spectra of Sm^{3+}- and Dy^{3+}- doped Ca-α-SiAlON

The excitation spectrum of Ca-α-SiAlON:Sm^{3+} consists of a broad band peaking at 308 nm (4.03 eV). No explanation for this band is provided in Ref. [15]. The large FWHM of this band (~1 eV) is suggestive of a ligand-to-Sm^{3+} charge transfer transition. Since the rare earth site is surrounded by O^{2-}/N^{3-} anions, the charge transfer transition can involve either the O^{2-} or the N^{3-} anions. Since the energy of the $O^{2-}\rightarrow Sm^{3+}$ CTT in solids usually exceeds ~5 eV [1], the 308 nm band (4.03 eV), which dominates the excitation spectrum of Ca-α-SiAlON:Sm^{3+} is assigned to the $N^{3-}\rightarrow Sm^{3+}$ charge transfer transition.

The ligand-to-Eu^{3+} CTT is always located at about 1.21 eV below the corresponding ligand-to-Sm^{3+} charge transfer transition in solids [1]. Hence, the $N^{3-}\rightarrow Eu^{3+}$ charge transfer transition in Ca-α-SiAlON can be anticipated at 2.84 eV. In Fig. 2 of Ref. [18] a prediction, based on the Jorgensen optical electronegativity model, where to expect the $N^{3-}\rightarrow Eu^{3+}$ charge transfer energy was made. The predicted range 2.5–4.5 eV provides further confirmation for the assignment of the broad band in the excitation spectrum of Ca-α-SiAlON:Sm^{3+} to the $N^{3-}\rightarrow Sm^{3+}$ charge transfer transition.

The excitation spectrum of Ca-α-SiAlON:Dy^{3+} consists of a broad band centered near 245 nm (5.06 eV). From the compilation of the systematic differences between the energies of the charge transfer transitions of rare earth ions [1], the $N^{3-}\rightarrow Dy^{3+}$ CTT in Ca-α-SiAlON is predicted at about 1 eV higher energy than the $N^{3-}\rightarrow Sm^{3+}$ CT and this agrees very nicely with the observed band at 5.06 eV. In view of the agreement between the experimental and the predicted values, the broad band in the excitation spectra of Dy^{3+} in Ca-α-SiAlON is assigned to the ligand (N^{3-})-to-Dy^{3+} charge transfer transition.

We wish to point out that, in principle, the excitation spectra may also contain contribution from a charge transfer transition, which originates from the oxygen valence band. However, in these materials, the oxygen to nitrogen ratio is 1–15 and if present the CTT originating from the O^{2-} valence band will be about 15 times weaker than the corresponding N^{3-} related CTT band. Furthermore, the O^{2-}-based CTT band is expected at energies higher than the N^{3-} CTT band and at energies close to the host excitation band. Hence, any CTT band related with the oxygen ligands will be weak and fully masked by the more intense N^{3-} centered CTT band and host excitation bands.

4.2. Absolute energy location of the divalent rare earth ions ground and $4f^{N-1}5d^1$ states in Ca-α-SiAlON

Having established the energies of the charge transfer transitions in Sm^{3+}- and Dy^{3+}-activated Ca-α-SiAlON, the absolute energy level of the divalent rare earth ions in this host lattice can be located with the method described in Ref. [1]. First, the mobility edge (bottom of the conduction band) of undoped Ca-α-SiAlON is estimated at about 6.4 eV from the maximum of the host lattice excitation band at ~210 nm (5.9 eV), which is assigned to the first exciton absorption (E^{ex}). We assume that the mobility edge is roughly $1.08\times E^{ex}$. Second, the energies of the charge transfer transition define the energy difference between the top of the valence band and the respective ground states of the Sm^{2+} and Dy^{2+} ions (E_{vf}). The top of the valence band is defined as the zero of energy. The ground state of the other rare earth ions within the band gap of Ca-α-SiAlON can be located from the reported ΔE_{vf} values [1].

Since the optical properties of the Eu^{2+} ion in Ca-α-SiAlON has been reported [19], the lowest energy $4f^{N-1}5d^1$ level of the divalent rare earth ions relative to the top of the valence band can be positioned provided that the energy of the Eu^{2+} $4f^7\rightarrow 4f^6[^7F_0]5d^1$ transition in the excitation spectrum of Ca-α-SiAlON:Eu^{2+} is identified. This identification is not straightforward because of the absence of the "staircase" spectrum in the room-temperature excitation spectrum of Ca-α-SiAlON:Eu^{2+} [19]. However, the energy of this transition can be determined in a relatively straightforward manner provided an estimate of the Stokes shift is made. The Stokes shift can be determined from the energy of the zero phonon line (E_{ZPL}), which is taken as the point of intersection between the normalized excitation and emission bands. In Ca-α-SiAlON:Eu^{2+}, the overlap of the excitation and emission spectra occurs at about 525 nm (2.36 eV) [19]. The Stokes shift is twice the energy difference between E_{ZPL} and the emission energy [20].