Luminescence Spectra of $\beta$-SiAlON/Pr$^{3+}$ Under High Hydrostatic Pressure

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ABSTRACT: In this contribution, steady-state and time-resolved photoluminescence spectra of $\beta$-Si$_{5.9}$Al$_{0.1}$O$_{0.1}$N$_{7.9}$/Pr$^{3+}$$_{0.016}$ obtained at high hydrostatic pressures up to 260 kbar are presented. At ambient pressure, excitation spectra of the $\beta$-SiAlON/Pr$^{3+}$ luminescence consist of sharp lines in the spectral region of 20000–22200 cm$^{-1}$ related to the $^3$H$_4 \rightarrow$ $^3$P$_0$, $^3$P$_0$, $^3$P$_1$, and $^3$P$_2$ transitions and a broad band with two maxima peaking at 30300 and 35700 cm$^{-1}$, which are related to the ionization of Pr$^{3+}$ ions occupying two different crystallographic sites in the $\beta$-SiAlON lattice. In both sites, the luminescence spectra consist of the dominant $^3$D$_2$ red emission and $^3$P$_0$ blue emission of Pr$^{3+}$ ions. The intensity of luminescence related to transitions from the $^3$P$_0$ state and the respective decay time gradually decreases when the pressure increases. The intensity of emission from the $^3$D$_2$ state is independent of the pressure and remains strong over the entire pressure range. Weak dependence of the Pr$^{3+}$ emission on applied pressure can be related to the covalent and strong Pr–N bonds and specific location of Pr$^{3+}$ ions occupying empty lattice points in $\beta$-SiAlON.

INTRODUCTION

Nitridosilicate materials, such as Si$_x$N$_y$ and its solid solutions, have found several applications$^{1−6}$ due to their excellent thermomechanical properties, high chemical stability, high hardness, and so forth. Recently, Si$_x$N$_y$-based derivatives doped with RE ions have been widely investigated as phosphors for white-emitting diodes (W-LEDs).$^{7,−9}$ Silicon nitride has two major crystalline phases, phase α-Si$_3$N$_4$ with a trigonal structure and phase β-Si$_3$N$_4$ with a hexagonal structure. The chemical formula of α-SiAlON is $M_{x}Al_{y}Si_{z}(Si_{1-x}Al_{y}O_{z}N_{16-x})$, where $M$ represents the cation metals Li, Mg, Ca, and Y or rare earth (RE) elements$^9$ and $v$ is the valence of $M$. β-SiAlON is derived from β-Si$_3$N$_4$ by equivalent substitution of the Al–O for the Si–N pairs. The chemical composition of β-SiAlON is described by the formula Si$_{6−z}$Al$_{z}$O$_{z}$N$_{16−z}$, where $z$ represents the number of Al–O pairs being substituted for Si–N pairs ($z$ takes the values from 0 to 4.2).$^{10,11}$ β-SiAlON doped with Eu$^{2+}$ has been extensively investigated as a green phosphor.$^{11−14}$

Luminescence properties of β-SiAlON doped with the RE ions Ce$^{3+}$,$^{15}$ Yb$^{3+}$,$^{16}$ and Pr$^{3+}$,$^{17,20}$ have also been investigated in previous literature.

The radiiuses of four-fold-coordinated Si$^{4+}$ and Al$^{3+}$ are equal to 0.26 and 0.39 Å, respectively, whereas the radius of the Pr$^{3+}$ changes from 0.99 to 1.179 Å for six-fold and nine-fold coordination, respectively.$^{18}$ Therefore, in the case of β-SiAlON/Pr$^{3+}$, Pr$^{3+}$ does not substitute lattice ions. Like other RE ions, Pr$^{3+}$ ions can reside only along the continuous channels parallel to the $c$ direction.$^{11−13,19}$ Steady-state and time-resolved spectroscopy of β-SiAlON/Pr$^{3+}$ obtained at different temperatures (10−293 K) have been presented in previous work.$^{20}$ Luminescence spectra consist of the dominant $^3$D$_2$ red emission and $^3$P$_0$ blue emission of Pr$^{3+}$ ions. It was found that under 330 nm (30300 cm$^{-1}$) excitation, additional luminescence peaks appeared beside those earlier observed in the region of the $^3$P$_0$ and $^1$D$_2$ emission. These additional lines were attributed to the novel site of Pr$^{3+}$.

The main crystallographic site 2b (Wyckoff notation)$^{18}$ corresponds to the Pr$^{3+}$ located at (0,0,0). In this case, the Pr$^{3+}$ ion is coordinated by six nitrogen/oxygen ions at a distance equal to 2.511 Å. In the novel site, Pr$^{3+}$ is located at the (0,0,1/4) position (Wyckoff notation 2a), where it is coordinated by nine nitrogen/oxygen ions, three of them at a distance equal to 2.403 Å and another six at a distance of 2.810 Å. Possible locations of Pr$^{3+}$ in β-SiAlON are presented in Figure 1a and b. The respective lattice points are labeled 2b and 2a, respectively.

Figure 1. Crystal structure of the 2 $\times$ 2 $\times$ 2 unit cell of Si$_{5.9}$Al$_{0.1}$O$_{0.1}$N$_{7.9}$/Pr$_{0.016}$ (a) on the 2b site where the Pr$^{3+}$ ion is located at (0,0,0) surrounded by six N/O ions and (b) on the 2a site where the Pr$^{3+}$ ion is located at (0,0,0.25), surrounded by nine N/O ions.

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In this paper, a detailed study of the luminescence and luminescence kinetics of the β-SiAlON/Pr3+ system under high hydrostatic pressure obtained from the diamond anvil cell (DAC) is presented and discussed. The main motivation to perform a high hydrostatic pressure luminescence study of this material was the fact that Pr3+ ions in β-SiAlON do not occupy its substitutional sites. In the case when lanthanide ions Ln3+ replace the lattice ions, they provide additional localized states to the energetic structure of the system that can be described as belonging to the 4f, 4f2−15d electronic configuration of Ln3+ and the impurity trapped exciton (ITE) described as Ln4+ that binds electrons by means of the Coulomb potential. Pressure causes the increase of the energies of localized states for 4f, 4f2−15d electronic configurations with respect to host bands energies. This effect is seen as pressure-induced diminishing of the energy of the ITE with respect to the energies of the states belonging to the 4f electronic configuration. In such a case, the influence of high hydrostatic pressure on the states of 4f, 4f2−15d electronic configurations can be described using the crystal field approximation. The case when Pr3+ occupies the empty lattice points in β-SiAlON is qualitatively different. Apart from the states of 4f, 4f2−15d electronic configurations, dopants provide the bonding—antibonding states that involve electrons from the 4f5s2 orbital of Pr3+. As a result, Pr3+ occupying the empty lattice point creates more reach structure than Pr3+ in the substitutional site. We expect that high-pressure spectroscopy can show this difference.

■ EXPERIMENT

The β-Si10.8Al3.8O16N7/0.1Pr3+/Pr3+0.016 sample was prepared from α-Si3N4, AlN, Al2O3, and Pr2O3 using the gas pressure sintering (GPS) method. The obtained β-SiAlON/Pr3+ has a hexagonal structure characterized by a P63/m space group. The unit cell parameters are a = b = 7.60953(4) Å and c = 2.91009(6) Å. More details on the preparation and structural investigation are described in the paper by T. C. Liu et al.17

Luminescence excitation spectra were acquired using a FluoroMax-4P TCSPC spectrometer produced by Horiba, containing Czerny–Turner monochromators for excitation and emission. The excitation source in this system was a 150 W ozone-free xenon lamp, which makes it possible to measure luminescence from the 220 to 850 nm range. The fluorescence intensity was measured using a R928 side-on photomultiplier. Steady-state luminescence spectra were excited with the He–Cd and diode lasers with wavelengths of 325 (30770 cm−1) and 473 nm (21140 cm−1), respectively. The photoluminescence signal was dispersed using a PG52 spectrometer working as a monochromator and detected by a Hamamatsu photomultiplier model R943-2 working in the photon counting regime.

The experimental setup for luminescence kinetics and time-resolved emission spectra consists of a PL 2143 A/SS laser as the excitation source and a PG 401/SH parametric optical generator. This system can generate 30 ps laser pulses, with a frequency of 10 Hz with wavelengths ranging from 220 to 2200 nm. The emission signal was analyzed by a Bruker Optics 2501S spectrometer equipped with a 50 grooves/mm grating and the Hamamatsu Streak Camera model C4334-01 with a final spectral resolution 0.47 nm. Time-resolved luminescence spectra were obtained by integration of streak camera images over time intervals, whereas luminescence decays were obtained by the integration of streak camera images over the wavelength intervals. Details of the experimental setup are described in the reference 23. High hydrostatic pressure was applied in a Merrill Bassett type DAC. Polydimethylsiloxane oil was used as the pressure-transmitting medium, and the pressure was measured by the shift of the R1 luminescence line of ruby.

■ RESULTS

The room-temperature excitation spectrum of β-SiAlON/Pr3+ monitored at 15820 cm−1 (D1 → 3H4 transition of Pr3+) is presented in Figure 2 (curve a). The spectrum consists of sharp lines in the spectral region from 20000 to 22220 cm−1 associated with transitions from the ground state to the 3P0, 3P1, and 3P2 excited states of Pr3+ ions and a broad band with two maxima at about 35700 and 30300 cm−1 that can be attributed to the ionization process of Pr3+ ions (transfer of an electron from the Pr3+ ion to the conduction band) in sites 2b and 2a, respectively.

The time-resolved emission spectra of β-SiAlON/Pr3+ measured within the range of 0–2 μs after pulse laser excitation are presented in Figure 2 (curve b and c). The emission spectrum of the system under excitation with energies of 35700 (280 nm) and 21140 cm−1 (473 nm) is presented in Figure 2 (curve b). The lines peaking between 14900 and 16700 cm−1 are related to the 3P0 → 3H4 and the 1I15/2 → 3H4 transitions, and the lines peaking in the regions of 18800–20000 and 14285–14900 cm−1 are related to the 3P0 → 3H4 and 3P2 → 3I11/2 transitions of Pr3+, respectively. Under 280 nm excitation, emission (represented by curve b) that originates from Pr3+ in the 2b site is seen exclusively. The emission spectrum of the system excited in the absorption band with the maximum of 30300 cm−1 that corresponds to the ionization of Pr3+ at the 2a site is presented in Figure 2 (curve c). Under this excitation, additional luminescence peaks appeared beside earlier observed peaks. The new peaks are indicated by arrows in Figure 2c and are related to the luminescence of Pr4+ ions in the 2a site. The energies of the localized states of the Pr4+ ion obtained from the excitation and emission spectra differ from the energies of free ion much more than expected due to the crystal field splitting. Usually, these differences are attributed to the nephelauxetic effect caused by the larger covalency of Pr–N bonds.

The steady-state emission spectra of β-SiAlON/Pr3+ obtained at room temperature under different pressures...
under excitation with \(21140\) (473 nm) and with \(30770\) cm\(^{-1}\) (325 nm) are presented in Figure 3a and b, respectively. In Figure 3a, the emission excited with \(21140\) cm\(^{-1}\) (3H4 \(\rightarrow\) 3P2) is presented. Under this excitation, only luminescence from the 2b site is observed exclusively. In Figure 3b, the emission from both 2b and 2a sites excited with the wavelength \(30770\) cm\(^{-1}\) is presented. The lines in the spectral range of \(18500\)–\(20000\) cm\(^{-1}\) correspond to the emissions from the \(3P_{0}\) state, whereas the lines in the spectral region of \(15380\)–\(16670\) cm\(^{-1}\) are related to emission from the \(1D_{2}\) state. One notices that the emission spectra of 2a and 2b \(Pr^{3+}\) sites are dominated by lines related to the \(1D_{2} \rightarrow 3H_{4}\) transitions.

In Figure 3b, the emission from both 2b and 2a sites excited with the wavelength \(30770\) cm\(^{-1}\) is presented. The lines in the spectral range of \(18500\)–\(20000\) cm\(^{-1}\) correspond to the emissions from the \(3P_{0}\) state, whereas the lines in the spectral region of \(15380\)–\(16670\) cm\(^{-1}\) are related to emission from the \(1D_{2}\) state. One notices that the emission spectra of 2a and 2b \(Pr^{3+}\) sites are dominated by lines related to the \(1D_{2} \rightarrow 3H_{4}\) transitions.

In Figure 3c, energies of the individual lines versus pressure are presented. The pressure increases, all emission lines weakly shift toward the lower energies. The red shift of the emission lines for the \(Pr^{3+}\) ions in 2b and 2a sites are similar. The respective rates range from \(-0.5\) to \(-0.9\) cm\(^{-1}\)/kbar and are small in comparison to the values of \(-1.75\)–\(-4.1\) cm\(^{-1}\)/kbar observed for \(Pr^{3+}\) in oxide matrices.\(^{26–30}\) Furthermore, in oxides doped with \(Pr^{3+}\), the intensity of the luminescence from the \(3P_{0}\) state was strongly quenched with increasing pressure. This effect has been attributed to the decrease of energy of the ITE state with respect to energies of the states of the 4f\(^{2}\) electronic configuration of \(Pr^{3+}\). When the energy of the ITE is between the energies of the \(3P_{0}\) and \(1D_{2}\) states, nonradiative energy transfer from the \(3P_{0}\) to \(1D_{2}\) state of the \(Pr^{3+}\) ITE state quenches the \(3P_{0}\) luminescence.\(^{27–30}\)

A different situation is observed in the case of \(\beta\)-SiAlON/\(Pr^{3+}\), where the \(3P_{0}\) emission intensity weakly decreases with increasing pressure (see Figure 3a and b). The intensity of emission from the \(1D_{2}\) state is independent of pressure and remains strong over the entire pressure range.

In Figure 4a and b, decays of luminescence related to the \(3P_{0} \rightarrow 3H_{4}\) transition of the \(Pr^{3+}\) ion obtained at different pressures are presented. The decays of luminescence of \(Pr^{3+}\) in site 2b excited with 473 nm are presented in Figure 4a. The decays become faster when the pressure increases and remains single-exponential for all pressures. Fitted luminescence lifetimes are presented in Figure 4c. The decays of luminescence of \(Pr^{3+}\) occupying sites 2b and 2a, excited with 30300 cm\(^{-1}\), are presented in Figure 4b. The decays are evidently two-exponential. The 2a site luminescence lifetimes were obtained as the shorter components of the two exponential decays. Obtained lifetimes of the 2b and 2a emission as a function of pressure are presented. The decays of luminescence of \(Pr^{3+}\) in site 2b excited with 473 nm are presented in Figure 4a. The decays become faster when the pressure increases and remains single-exponential for all pressures. Fitted luminescence lifetimes are presented in Figure 4c. The decays of luminescence of \(Pr^{3+}\) occupying sites 2b and 2a, excited with 30300 cm\(^{-1}\), are presented in Figure 4b. The decays are evidently two-exponential. The 2a site luminescence lifetimes were obtained as the shorter components of the two exponential decays. Obtained lifetimes of the 2b and 2a emission as a function of pressure are presented.
pressure are presented in Figure 4c. It is observed that the decay of the luminescence of the 2a site is faster than that of the 2b site. Pressure-induced quenching of the Pr3+ luminescence is accompanied by shortening of luminescence decays with the same rate for both sites.

Luminescence related to emission from the 1D2 state is strong enough that it is possible to spectrally separate the luminescence decay related to the Pr3+ ion in sites 2b and 2a. Decay profiles of the luminescence related to emission from the 1D2 state of Pr3+ ions in sites 2b and 2a monitored at 623 and 632 nm, obtained at different pressures, are presented in Figure 5a and b, respectively. Decays appeared nonexponential, and effective lifetimes were determined using the following relation:

$$\tau = \frac{\int I(t) \cdot t \, dt}{\int I(t) \, dt}$$

(1)

Figure 5. Luminescence decays that correspond to the $^{1}D_{2} \rightarrow ^{3}H_{4}$ transition of Pr3+ for different pressures under pulse excitation: (a) at 21140 cm$^{-1}$ (473 nm) with a monitored luminescence at 16050 cm$^{-1}$ (623 nm) and (b) at 30300 cm$^{-1}$ (330 nm) with a monitored luminescence at 15820 cm$^{-1}$ (632 nm). (c) Average decay time of the luminescence related to the 1D2 emission, only a small shortening of the luminescence decays is observed, and it is accompanied by a small decrease of the intensity of emission. The fact that decay profile of the emission is not single-exponential can be related to nonradiative quenching of the 1D2 emission arising from the cross relaxation process given by the relation ($^{1}D_{2} \rightarrow ^{3}H_{4}$).

The rise of the $^{1}D_{2}$ emission of the Pr3+ ion in site 2b and site 2a is present in Figure 5d. The emission of the Pr3+ ion in site 2a rises faster than that in site 2b. The emission related to site 2a excited with 30300 cm$^{-1}$ appeared almost at once after excitation, while emission related to site 2b excited with 35700 cm$^{-1}$ is delayed by time equal to approximately 200 ns.

### DISCUSSION AND CONCLUSIONS

This high-pressure luminescence study of β-SiAlON/Pr3+ has confirmed the existence of two different Pr3+ sites, one with six-fold and the other with nine-fold coordination of oxygen/nitrogen ions, labeled according to the Wyckoff notation 2b and 2a, respectively. The excitation bands of Pr3+ luminescence in site 2a peaking at 30300 cm$^{-1}$ and site 2b at 35700 cm$^{-1}$ are related to different ionization energies of Pr3+ ions. The emission lines of the Pr3+ ion occupying site 2a appear to have lower energies and are characterized by shorter lifetimes than those in site 2b. Another difference is related to different excitation spectra and different pathways of population of the 1D2 state, which result in different luminescence rise times of the 1D2 emission.

The ionization transition creates the Pr4+ ion and an electron in the conduction band. This process has been observed earlier in various oxide materials doped with Pr3+. After ionization, Coulomb attraction between Pr4+ and e$^{-}$ creates an additional localized state considered as ITE. In both approaches, the Pr4+ ions attract the negative ligands more than those of Pr3+. As a result, the electron–lattice relaxation additionally diminishes the energy of ITE or IVCT states. Such systems can be described by the configuration coordinate diagrams, where electronic energies are given by parabolas where the abscissa axis represents the average distance between the Pr3+ ion and ligands, R. Configuration coordinate diagrams representing Pr3+ ions in 2b and 2a sites at ambient pressure are presented in Figure 6a and b, respectively.

The localized states related to the ground $4f^{2}$ electronic configuration of Pr3+ ions (black and blue parabolas in Figure 6 a and b) have minima at the same value of R. In the case of the ITE state, the minimum energy appears at a shorter distance between Pr3+ and its ligands; therefore, the respective parabolas are shifted to the left. The parabola representing the electronic energy of the ITE in site 2b (Figure 6a) was obtained considering that the broad band in the excitation spectrum of Pr3+ with a maximum at energy 35720 cm$^{-1}$ corresponding to the transition from the ground state of Pr3+ to the ITE state (ionization energy of Pr3+ in site 2b) and lattice relaxation energy $S_{ho}$ is equal to 5400 cm$^{-1}$. To obtain the parabola representing ITE in the case of site 2a (Figure 6b), an ionization energy of 30300 cm$^{-1}$ and electron–lattice coupling (the same as in site 2b) of $S_{ho} = 5400$ cm$^{-1}$ were used. The methodology of estimation of the energy of $S_{ho}$ is seen in Figure 6. The value of $S_{ho}$ was obtained as an energy difference between the energy of the maximum of the excitation band and the zero-phonon transition energy, considered as the energy of the long-wavelength end of the excitation band. The energy of the band maximum can be easily estimated, whereas the energy of the zero-phonon line is not seen in our case.
Therefore, the value of $S_{\text{Hw}}$ is estimated with a rather large error that could be equal to 500 cm$^{-1}$.

The dashed arrows in Figure 6a and b represent the possible relaxation pathways. In site 2b, after excitation to the ITE state, the system relaxes to the minimum energy of the ITE electronic manifold and then to the $^3P_0$ state of Pr$^{3+}$. In this site, the $^1D_2$ state is populated only by nonradiative multiphonon transitions from the $^3P_0$ state. The $^1D_2$ state is not populated by nonradiative transition from the ITE state because crossover of the ITE and $^1D_2$ electronic manifolds has higher energy than the crossover of the ITE and the $^3P_0$ electronic manifolds.

In the case of Pr$^{3+}$ ions in the 2a site, the crossover between the ITE and $^3P_0$ electronic manifolds and the ITE and $^1D_2$ takes place at the same energy, very close to the minimum energy of the ITE electronic manifold. As a result, in the 2a site, it is more likely that the $^1D_2$ state is populated directly by the energy transfer from the ITE state. This different relaxation pathway influences the luminescence processes in Pr$^{3+}$ ions at different sites. Specifically, emission from the $^3P_0$ state in site 2a is much weaker than that in site 2b. For the same reason the rise of the $^1D_2$ emission of Pr$^{3+}$ in site 2a is faster than that in site 2b.

The results of high-pressure spectroscopy of $\beta$-SiAlON/Pr$^{3+}$ should be discussed in the context of other materials doped with Pr$^{3+}$ under high hydrostatic pressure. Typically, at ambient pressure, energies of the $^3P_0$ and $^1D_2$ states are lower than the energy of the ITE state. When the pressure increases, the distance between Pr$^{3+}$ and negatively charged ligand ions decreases. As a result, the energy of the states from the ground electronic configuration 4$f^2$ increases with respect to band states of the host.\textsuperscript{21,22,32–$34$} Therefore, it is expected that under pressure, the energies of the $^3P_0$ and $^1D_2$ states are lower than the energy of the ITE state. When the pressure increases, the distance between Pr$^{3+}$ and negatively charged ligand ions decreases. As a result, the energy of the states from the ground electronic configuration 4$f^2$ increases with respect to band states of the host.\textsuperscript{21,22,32–$34$} Therefore, one would expect that the emission from the $^3P_0$ state of Pr$^{3+}$ in the 2a site should be quenched at lower pressure than the respective emission of the Pr$^{3+}$ in the 2b site. The results show that the nonradiative processes that depopulated the $^3P_0$ state are similar in both sites (Figure 4c). Even at a pressure of 260 kbar, weak emission from the $^3P_0$ in both sites was still observed. An increase of nonradiative transitions from the $^3P_0$ in both sites can be explained due to the fact that high pressure causes an increase of the phonons’ energy, and therefore, the probability of multiphonon relaxation from the $^3P_0$ to $^1D_2$ state also increases.

The reason why the pressure does not change the energy of the ground electronic configuration of the Pr$^{3+}$ ions with respect to the conduction band in $\beta$-SiAlON/Pr$^{3+}$ is still not well understood. At the present stage, one can relate it to the differences between $\beta$-SiAlON/Pr$^{3+}$ and other oxides doped with Pr$^{3+}$. In $\beta$-SiAlON/Pr$^{3+}$, praseodymium ions occupy the lattice points that are empty in undoped lattices, whereas in other oxides, Pr$^{3+}$ ions usually substitute the lattice ions. As a result, Pr$^{3+}$ in the $\beta$-SiAlON/Pr$^{3+}$ introduces additional Pr–N bonding and antibonding states, which do not exist in a pure lattice. Pr–N bonds are probably very covalent and strong and thus responsible for the large nephelauxetic effect in $\beta$-SiAlON/Pr$^{3+}$. As a result, the application of pressure does not change the length of Pr–N bonds and therefore does not change the energies of the states of the 4$f^2$ electronic configuration with respect to the ITE state.

**Figure 6.** Configurational coordinate diagram representing the $\beta$-SiAlON/Pr$^{3+}$ system on (a) $2b$ and (b) $2a$ sites.
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