Luminescence of Ce^{3+} in lanthanum silicon oxynitride*

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The luminescence properties of lanthanum silicon oxynitride (La-Si-O-N) series doped by trivalent Ce ions have been investigated to seek for tunable wavelength-conversion phosphor for white light emitting diode applications. Four compound hosts of $LaSiO_2N$, $La_4Si_2O_7N_2$, $La_5Si_3O_{12}N$, and $La_2Si_6O_3N_8$ were synthesized and examined in this work. Crystallographic examination for the equal amount of Ce^{3+} substitution indicated that the covalency degree decreased in a sequence $LaSiO_2N > La_2Si_6O_3N_8 > La_4Si_2O_7N_2 > La_5Si_3O_{12}N$, not simply in correlation to the ratio of N^3/O^2. Excitation and emission spectrum measurements showed the main features of Ce^{3+} luminescence in the series: the centre of gravity of 5d bands depends on crystal-field splitting more strongly than that on covalency of Ce–N bonding; nephelauxetic effect could not be observed clearly for the investigated series; to some extent Stokes shift was dominated by crystal-field splitting rather than Ce–N covalency degree.

Keywords: photoluminescence, nitrides, oxides, chemical synthesis

PACC: 7855, 0660E, 0765E, 3250

1. Introduction

The 4f ground state of trivalent Ce ion is split into $^2F_{7/2}$ and $^2F_{5/2}$ levels with an energy difference of about 2000 cm^{-1} due to spin–orbit coupling, and its lowest excited state is the 5d band that is easily affected by the crystal field. The crystal-field splitting usually forms 2 to 5 5d configurations with a large separation of ∼15000 cm^{-1}.[1] Ce^{3+} fluorescence is related to an electric dipole 4f–5d transition. The transition is parity- and spin-allowed with a shorter decay time than 100 ns. When Ce^{3+} is placed in a crystal, the emission band covers from ultraviolet to visible band depending on the particular compound or host symmetry, because the 5d state of Ce^{3+} is strongly affected by three interrelated effects: crystal field splitting (crystal-field effect), covalency (nephelauxectic effect) and Stokes shift.[2] Therefore, the luminescence centre is a good candidate as activators in phosphors with the designed excitation and emission wavelengths because luminescence positions can be flexibly adjusted. It is interestingly noted here that the positions of the energy levels of 5d excited states of Ce^{3+} are affected not only by crystal-field splitting but also by nephelauxectic effect, which might shift absorption and emission to long wavelength band.[3] For example, the large crystal-field splitting has been found from the host lattice of cubic $Y_3Al_5O_{12}$,[4] and the strong nephelauxectic effect from halides, oxynitrides, sulfides and oxysulfides,[5−11] and the large Stokes shift from SrY_2O_4.[12]

Rare earth oxynitride systems have attracted considerable interest in the exploration on wavelength-conversion phosphor activated by blue radiation for white light emitting diodes (LED). So far the compound hosts such as SiAlON,[13,14] $MSi_2O_2N_2$ (M = Ca, Sr, Ba)[15] activated by band luminescence centres of Eu^{2+} have been found to be able to meet the optimum requirements of white-light LED phosphors due to their high quantum efficiency and thermal/chemical stability. Under the radiation in the blue range the oxynitrides activated by Eu^{2+} exhibit efficient emissions from green to red region. However, when Ce^{3+} is incorporated into these hosts,[16] only blue or ultraviolet emission could be detected as in the usual oxide system. Therefore we believe that the luminescence properties of Ce^{3+} in the oxynitrides should relate to the Ce–N covalency more possibly rather than the crystal field splitting dominated by the crystal structure.

In this paper, we have compared the Ce^{3+} luminescence hosted in a typical rare-earth oxynitride La-Si-O-N series to understand the crystal field and

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the nephelauxectic effect of Ce^{3+} ion by varying the oxygen/nitride concentration and the crystal symmetry. In this series silicon coordinated with oxygen and nitrogen ions forms a tetrahedral network. Depending on the N^{3-}/O^{2-} ratio and the linkage scenario of the silicon network, four host crystals of $LaSiO_2N$, $La_4Si_2O_7N_2$, $La_5Si_3O_{12}N$, and $La_2Si_6O_3N_8$ were investigated. The N^{3-}/O^{2-} ratio increases in the sequence $La_5Si_3O_{12}N$, $La_4Si_2O_7N_2$, $LaSiO_2N$, and $La_2Si_6O_3N_8$ with the single SiO_4 tetrahedra, dimeric $Si_2O_5N_2$, trimeric $Si_3O_6N_3$ and Si_3N_4 layer, respectively.[17,18] Two crystalline symmetries are involved: hexagonal $La_5Si_3O_{12}N$ and $LaSiO_2N$, and monoclinic $La_4Si_2O_7N_2$ and $La_2Si_6O_3N_8$. The luminescence properties of Ce^{3+} in the hosts were investigated in the work.

2. Experimental

The investigated samples were prepared by a solid-state reaction in an induction furnace using the starting materials La_2O_3, CeO_2, Si_3N_4, and SiO_2 powders with purity > 99.5%. These materials with the desired stoichiometric proportions were first thoroughly mixed in an appropriate amount of ethanol with an agate mortar. The mixtures were pressed into a pellet and placed on a platinum plate. Ce^{3+}-activated $LaSiO_2N$ were prepared at 1475 °C for 4 h, $La_5Si_3O_{12}N$ at 1600 °C, $La_4Si_2O_7N_2$ at 1650 °C and $La_2Si_6O_3N_8$ at 1700 °C in a reducing atmosphere (25% H_2/75%N_2), in order to reduce Ce^{4+} to Ce^{3+}. Crystal purity and structure were examined by x-ray diffraction with Cu Kα radiation (XRD, D/max-RB). Photoluminescence spectra were recorded on a Hitachi-4500 fluorescence spectrophotometer equipped with xenon lamp. Diffusion reflectance spectrum measurement was carried out using a Shimadzu UV-2450 ultraviolet and visible spectrophotometer.

3. Results and discussion

3.1. Crystal structure

The x-ray powder diffraction patterns show that all the Ce^{3+}-doped compounds in the La-Si-O-N series are polycrystalline. The attempt for the preparation of pure $La_2Si_6O_3N_8$ has not been successful. The presence of $La_5Si_3O_{12}N$ and some amorphous glass should be inevitable from our repetitious preparation explorations. The impurity amount should be dependent on the SiO_2 concentration in the starting Si_3N_4 powder. The eventual impurity content of $La_5Si_3O_{12}N$ phase in the work was minimized less than 5 at% estimated by comparing the relative peak intensity of I(204) in $La_2Si_6O_3N_8$ and I(102) in $La_5Si_3O_{12}N$.

Typical XRD patterns for the samples substituted La with 2 wt% Ce are shown in Fig. 1. The detailed analyses of the XRD patterns of samples $LaSiO_2N$ (hexagonal), $La_2Si_6O_3N_8$ (monoclinic), $La_4Si_2O_7N_2$ (monoclinic), and $La_5Si_3O_{12}N$ (hexagonal), by using the Rietveld powder diffraction profile-fitting technique, were carried out and crystalline parameters were also obtained. Due to lower ion radius of Ce^{3+} than that of La^{3+}, the obtained crystalline volumes decrease after the equal amount of Ce^{3+} substitution, in accordance with Vegard's law. However, the constriction degree of crystal volume obtained by the fitting route varies in a sequence 0.057% for $LaSiO_2N$, 0.041% for $La_2Si_6O_3N_8$, 0.033% for $La_4Si_2O_7N_2$, and 0.025% for $La_5Si_3O_{12}N$, respectively. Except for

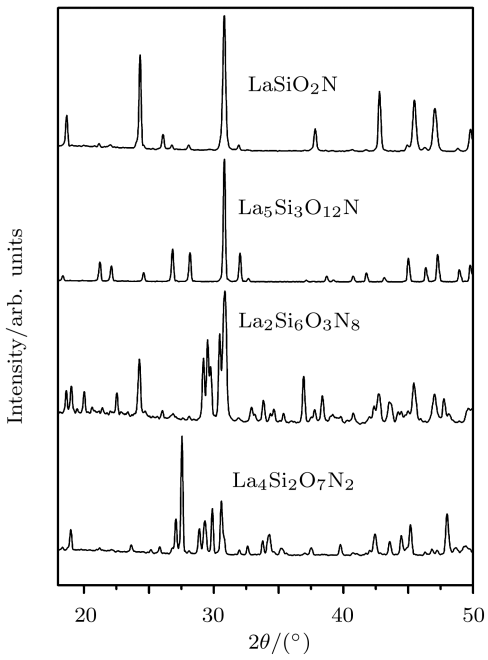


Fig. 1. The XRD patterns of $LaSiO_2N$, $La_4Si_2O_7N_2$, $La_5Si_3O_{12}N$, and $La_2Si_6O_3N_8$ with Ce^{3+} substitution on La^{3+} sites in a fixed molar concentration 2% with respect to the total oxynitrides.

$La_2Si_6O_3N_8$, the degree of lattice constriction after the equal amount of the Ce substitution decreases with the decrease of the N^{3-}/O^{2-} ratio. Considering that the Ce–N bond is more covalent than the Ce–O bond, more N^{3-} versus O^{2-} coordinated to Ce^{3+} decreases

the lattice volume more drastically. The abnormal N^{3-}/O^{2-} ratio in $La_2Si_6O_3N_8$ phase should involve the detailed crystal structure because the phase is actually solid solution structure of $La_2O_3{\cdot}2Si_3N_4$.[18] The covalent saturation of Ce^{3+} is to some extent dominated by oxygen coordination. The varied crystalline volume also indicates that Ce^{3+} ions have indeed substituted for La^{3+} ions in the lattice with an effective covalence with N^{3-}. Furthermore, the involved covalency degree varies in the same sequence $LaSiO_2N$ > $La_2Si_6O_3N_8$ > $La_4Si_2O_7N_2$ > $La_5Si_3O_{12}N$.

3.2. Ground-state splitting

Figure 2 shows emission spectra of Ce^{3+} with the content 2 at% in the investigated four host samples. Except for $La_4Si_2O_7N_2$, Ce^{3+} centres in these hosts exhibit a strong emission. Even so, all emission spectra show a broad band originating from the allowed 4f–5d transition of Ce^{3+} ions. The broad emission spectra display remarkably asymmetric because the inhomogeneous broadening of the spin–orbit splitting of Ce^{3+} ground state ($^2F_{7/2}$ and $^2F^{5/2}$). The doublet peak positions are resolved mathematically by using Gaussian curves. The positions of the two peaks are estimated at 387 nm and 412 nm for $LaSiO_2N$, 411 nm and 444 nm for $La_2Si_6O_3N_8$, 445 nm and 487 nm for $La_4Si_2O_7N_2$, 453 nm and 496 nm for $La_5Si_3O_{12}N$, respectively. The corresponding ground-state splitting energy levels are separated by 1980 cm^{-1} for $LaSiO_2N$, 1810 cm^{-1} for $La_2Si_6O_3N_8$, 1940 cm^{-1} for $La_4Si_2O_7N_2$, 1910 cm^{-1} for $La_5Si_3O_{12}N$, respectively. The obtained splitting ranges from 1800 cm^{-1} to 2000 cm^{-1} that is smaller than ∼2100 cm^{-1} in Y-Si-O-N[2] and 2200 cm^{-1} in free ions of Ce^{3+},[19] indicating that the spin–orbital coupling in La-Si-O-N series is slightly weakened due to the atomic size of host rare earth element.

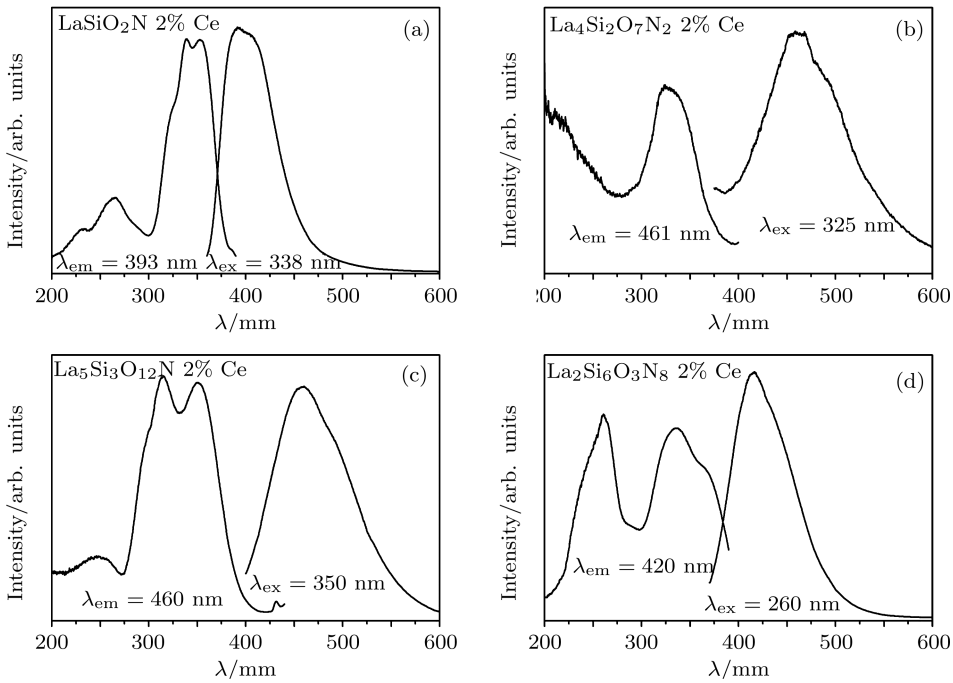


Fig. 2. Excitation and emission spectra of Ce^{3+} hosted in La-Si-O-N series (a) $LaSiO_2N$, (b) $La_4Si_2O_7N_2$, (c) $La_5Si_3O_{12}N$, and (d) $La_2Si_6O_3N_8$. The doped Ce concentration was fixed at 2 at% for all samples. The excitation spectra were monitored at λ_{em}, and the excitation wavelength was marked in λ_{ex}, respectively.

3.3. Emission centre versus covalency

Due to similar ground-state splitting, the emission centre of Ce^{3+} is defined as the average value of doublet peak positions. The emission centre increases from 400 nm in $LaSiO_2N$, to 428 nm in $La_2Si_6O_3N_8$, to 466 nm in $La_4Si_2O_7N_2$, and to 475 nm in $La_5Si_3O_{12}N$. The upwards trend is in good accordance with the degree of crystalline volume constriction mentioned above, indicating that the emission centre monotonously shifts to the long wavelength re-

gion with the decrease of covalency. The phenomenon is unusual compared to the nephelauxetic effect of Ce^{3+} luminescence. According to the nephelauxetic effect, the stronger the covalency is, the smaller the energy difference between the ground state $4f^1$ and activated band 5d of the Ce^{3+} ions is. Consequently, the emission peak should shift to long wavelength band with the increasing covalency. Therefore, the observed variation of emission centre should also result from the position of 5d band which can be shifted by the crystal field.

3.4. Excitation spectra

Excitation spectra are also shown in Fig. 2 measured by monitoring the wavelength at emission maxima. Due to the distortion from S_6 symmetry of rare-earth ions in $LaSiO_2N$, the excitation band of $LaSiO_2N$:Ce should be split into five levels. In agreement with this, five excitation peaks at 222, 266, 320, 338 and 358 nm spectra are indeed observed. For $La_4Si_2O_7N_2$:Ce, only a broad excitation band peaked at ∼325 nm with the larger half-width of ∼50 nm is observed, possibly due to the more rare-earth occupancy sites (4 sites) and low point symmetry (C_1) in $La_4Si_2O_7N_2$ that cause a strong overlapping. For $La_5Si_3O_{12}N$:Ce, due to close crystal symmetry, the excitation spectrum exhibits a similar profile as that of $LaSiO_2N$:Ce, but there are only four peaks located at 252, 294, 314 and 354 nm can be clearly determined. However, the band near 248 nm is relatively broad. Gaussian fitting results in two maxima at 242 nm and 256 nm. From the excitation spectrum of $La_2Si_6O_3N_8$:Ce, three excitation levels at 255, 331 and 367 nm. Although the detailed point symmetry of rare-earth ions in the compound still keeps uncertain, there are strong resemblance between the excitation peak appearances of $La_2Si_6O_3N_8$:Ce and La_2O_3:Ce, indicating that the excitation of Ce^{3+} is dominated by hexagonal crystal ligands as in La_2O_3 case.

3.5. Crystal-field splitting and stokes shift

The gravity centre of 5d bands is defined by averaging the observed excitation maxima. The obtained values are 34900 cm^{-1} in $La_5Si_3O_{12}N$, 34300 cm^{-1} in $LaSiO_2N$, 32200 cm^{-1} in $La_2Si_6O_3N_8$ and 30800 cm^{-1} in $La_4Si_2O_7N_2$. The variation trend is not obviously correlative to N^{3-}/O^{2-} ratio but to the detailed crystal symmetry. In the La-Si-O-N series, the centre of gravity of the 5d bands in the hexagonal crystal symmetry ($La_5Si_3O_{12}N$ and $LaSiO_2N$) stands at 34000–35000 cm^{-1}, while the monoclinic symmetry comes down in energy to 30000–32000 cm^{-1}.

Due to the strong dependence of crystal-field splitting of Ce^{3+} 5d bands on coordination symmetry and strength, the determination of the crystal-field splitting should present all components of full-scale 5d bands. Unfortunately in the investigated series, the site symmetries are quite complicated and some detailed crystal structures have also been unavailable. Moreover, the assignment of different 5d bands still keeps uncertain. Therefore, here we define the crystalline splitting approximately as the energy difference of the lowest and highest 5d band, as done by Krevel in the research of Ce^{3+} luminescence in Y-Si-O-N series.[2] Even so, the splitting in $La_4Si_2O_7N_2$ still could not be determined because only a broad unresolved peak is detected.

The splitting values of Ce^{3+} ion are estimated 17100 cm^{-1} in $LaSiO_2N$, 12000 cm^{-1} in $La_2Si_6O_3N_8$, 13100 cm^{-1} in $La_5Si_3O_{12}N$. Again the splitting variation shows non-correlation with the N^{3-}/O^{2-} or covalency. The results are somewhat different with that in Y-Si-O-N series, in which Krevel[2] proposed the crystal-field splitting shows an upwards tendency for higher nitrogen contents. More efforts should be made because the covalency or crystal symmetry in the investigated compounds cannot be used solely to explain the observed splitting characteristics.

The energy separation of excitation peak with the longest wavelength and the emission peak with the shortest wavelength is defined as the Stokes shift of Ce^{3+} in the current investigation. Of course, the definition can introduce error due to the possible temperature quenching or re-absorption of the highest energy emission.[20] The estimated Stokes shifts based on the excitation and emission spectra are 2100 cm^{-1} in $LaSiO_2N$, 2900 cm^{-1} in $La_2Si_6O_3N_8$, ∼5900 cm^{-1} for $La_4Si_2O_7N_2$ and 6200 cm^{-1} in $La_5Si_3O_{12}N$. The Stokes shift in $La_4O_2O_7N_2$ and $La_5Si_3O_{12}N$ shows an relatively large value, which is slightly smaller than 8000 cm^{-1} of SrY_2O_4:Ce[12] but is near 5800 cm^{-1} of the iso-structural $Y_4Si_2O_7N_2$:Ce[2] and even larger than ∼4000 cm^{-1} of the well-known efficient phosphor $Y_3Al_5O_{12}$:Ce.[4] The large Stokes shift can be used to explain the low emission efficiency in $La_4Si_2O_7N_2$:Ce, because the large Stokes shift usually results in the relatively low quenching temperature.

The Stokes shift increases in a sequence $LaSiO_2N$

$< La_2Si_6O_3N_8 < La_4Si_2O_7N_2 \sim La_5Si_3O_{12}N$, in agreement with the decrease trend of the covalency. It should be realized that the Stokes shift actually involves the spin–orbit coupling degree of 4f electron of ground state Ce^{3+}, the excitation gravity centre position, and the crystal-field splitting degree of 5d bands. The spin–orbit coupling in the investigated La-Si-O-N hosts is relatively lower in comparison with Y-Si-O-N series and the nephelauxectic effect has not been observed obviously in this series (if occurs, the centre of gravity will shift to lower energy band). Therefore, the variation trend of Stokes shift is considered mainly as the crystal-field splitting of the 5d bands. The corresponding energy diagram is schematically shown in Fig. 3. The exploration on the blue-activated Ce^{3+} luminescence should pay more attention to crystal symmetry rather than Ce–N covalency effect.

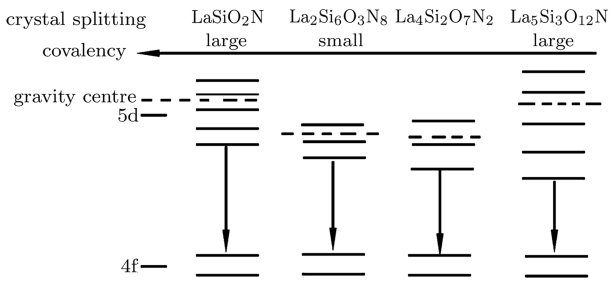


Fig. 3. Schematic luminescence diagram of Ce^{3+} ions in La-Si-O-N series. The increase of covalency moves the Stokes shift to shorter wavelength. The nephelauxetic effect that shifts the centre of gravity of 5d bands to lower energy has not been observed in this series. The longer emission wavelength observed in $La_5Si_3O_{12}N$ should be ascribed to the crystal splitting which reduces the lowest activated state energy.

4. Conclusions

Crystalline and luminescent properties of Ce^{3+} in oxynitride La-Si-O-N series are reported. The covalency and crystal-field effects are specifically evaluated for understanding Ce^{3+} luminescence. The following concluding remarks can be made.

(i) After the substitution of an equal amount of Ce^{3+} substitution for Y^{3+} in the La-Si-O-N series, the crystal volume constriction degree varies in a sequence $LaSiO_2N > La_2Si_6O_3N_8 > La_4Si_2O_7N_2 > La_5Si_3O_{12}N$, not simply in correlation to N^{3-}/O^{2-} ratio rather than to Ce–N covalent bonding nature.

(ii) The centre of 5d bands gravity depends on crystal-field splitting more possibly than that on the covalency of Ce–N bonding. Crystal symmetry with the increasing lattice rigidity in $LaSiO_2N$ and $La_5Si_3O_{12}N$ hosts can explain the relatively larger centre of gravity. Nephelauxetic effect has not been observed unambiguously in the series.

(iii) To some extent Stokes shift is dominated by crystal-field splitting rather than Ce–N covalency degree.

In summary, the luminescence of Ce^{3+} in La-Si-O-N covers the band from ultraviolet to blue, and the excitation bands range from 250 nm to 400 nm which still locate in ultraviolet region. The effort for the exploration using Ce^{3+} luminescence centre in blue-activated phosphors should be made to focus on the crystal field effect. The introduction of Ce–N in the current series or other oxynitrides should not be large enough to shift the ultraviolet excitation and blue emission to longer wavelengths.

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