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Three-dimensional analysis of Eu dopant atoms in Ca-α-SiAlON via through-focus HAADF-STEM imaging

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ABSTRACT

Three-dimensional (3D) distributional analysis of individual dopant atoms in materials is important to development of optical, electronic, and magnetic materials. In this study, we adopted through-focus high-angle annular dark-field (HAADF) imaging for 3D distributional analysis of Eu dopant atoms in Ca-α-SiAlON phosphors. In this context, the effects of convergence semi-angle and Eu z-position on the HAADF image contrast were investigated. Multi-slice image simulation revealed that the contrast of the dopant site was sensitive to change of the defocus level. When the defocus level matched the depth position of a Eu atom, the contrast intensity was significantly increased. The large convergence semi-angle greatly increased the depth resolution because the electron beam tends spread instead of channeling along the atomic columns. Through-focus HAADF-STEM imaging was used to analyze the Eu atom distribution surrounding 10 nm cubes with defocus steps of 0.68 nm each. The contrast depth profile recorded with a narrow step width clearly analyzed the possible depth positions of Eu atoms. The radial distribution function obtained for the Eu dopants was analyzed using an atomic distribution model that was based on the assumption of random distribution. The result suggested that the Ca concentration did not affect the Eu distribution. The decreased fraction of neighboring Eu atoms along z-direction might be caused by the enhanced short-range Coulomb-like repulsive forces along the z-direction.

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1. Introduction

It is well known that dopant atoms in host materials can affect their optical, electrical, and magnetic properties. In the field of white light-emitting diodes (LEDs), rare earth doped phosphors including Ce- or Eu-doped YAG [1], SiAlON [2], $CaAlSiN_3$ [3], and Ca_2SiO_4 [4] have been used to adjust complex LED white light. In this context, analysis of dopant concentration, doping site, and three-dimensional (3D) distribution is very important to understanding and controlling luminescence properties. Of the phosphors currently available, Eu-doped Ca-α-SiAlON is attractive because of its excellent properties including small thermal quenching and high quantum efficiency. The basic structure of α-SiAlON follows that of α-Si_3N_4, but Al and O atoms substitute for Si and N atoms respectively, resulting in solid solution crystals. Because of Al^{3+} and O^{2-} ions, dopant atoms such as Y, Ca, Sr, and Eu can insert into the interstitial sites in α-SiAlON [5, 6]. Eu-doped Ca-α-SiAlON can be described as $Ca_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$: Eu_y ($m = 2x + 2y$, $m = 2n$). In following with this equation, the concentrations of Al and O were increased alongside the dopant concentration to maintain charge neutrality. According to the literature [2, 7, 8], the optimum Eu (y) content for higher luminescence ranges from 0.05 to 0.075. Ca content (x) also affects the luminescence intensity and wavelength. In particular, a high m value leads to increases in intensity and a red shift in the emission wavelength [9]. However, the reason for increased luminescence is still not clear.

Investigation of the 3D distributions of doped rare earth atoms is crucial for a deeper understanding of their luminescence properties because energy transfer can occur between two nearby dopant atoms, which results in a decrease in light emission efficiency [10]. Conventionally, X-ray and neutron diffractometry have been used to identify doping sites [11, 12]. However, it has been difficult to determine the 3D distribution of dopant atoms using these methods. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) is very useful for direct imaging of single, heavy dopants within a host material. The image contrast of HAADF-STEM is proportional to the atomic number ($\propto Z^{1.6-2.0}$) because thermal diffuse scattering (TDS) is dominant in high angle electron scattering. Therefore, HAADF-STEM has been used for analyzing column-by-column atomic structures such as Si and InGaN semiconductors [13–16], oxides [17–19], nitrides [20–24], and so on. Recently, electron tomography [25–29] and slight tilting

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[30] have been proposed to determine 3D single-atom spatial distributions. These methods are effective for analysis of thin materials such as nanoparticles and nanowires. However, they are not suitable when electron channeling behavior changes drastically depending on incident direction. For thorough analysis of the observed STEM image, image simulation, in which scattering and channeling behaviors of the electron probe are predicted quantitatively, is essential. HAADF-STEM imaging by counting electrons with an accurately calibrated ADF detector using frozen phonon calculations has also been proposed [31, 32] and has perfectly clarified the 3D distribution of Ce dopants in wurtzite-type AlN [33]. The quantitative STEM was also applied for 3D imaging of Gd dopant atoms in $SrTiO_3$ [34, 35]. However, these quantitative methods are considered unsuitable for analyzing Eu dopant atoms in Ca-α-SiAlON because when Eu dopant atoms are doped into the Ca column, in which the occupancy of Ca atoms is approximately 0.3–0.6, the Ca concentrations and arrangements vary in each dopant column. These different arrangements of Ca atoms strongly affect the column intensity [36], causing difficulty in the quantitative analysis of Eu atoms in Ca columns (detailed calculation results are supplied in S1 in the Supplementary materials). To solve this problem, we focused on depth sectioning via through-focus or focal-series imaging [37-40]. The advantages of this method are its simple procedure and the lack of need for special customization or complete calibration. Spherical aberration-corrected electron probes improve not only the transverse resolution, but also the depth resolution [41]. Therefore, contrast enhancement is expected for elements around the focal position. Through-focus imaging enables the analysis of individual Eu atoms present within the dopant column at different Ca concentrations and in different arrangements. However, the depth resolution is not still high, and is insufficient for the atomic scale analysis.

In the present study, we propose through-focus HAADF-STEM imaging for 3D distributional analysis of Eu dopant atoms in Ca-α-SiAlON phosphors. To achieve high depth resolution, the defocus was changed by narrow steps. The contrast profile obtained for various depths at each dopant column was compared to simulation results to determine the depth position. Although the depth resolution is limited, the contrast depth profile recorded by through-focus imaging with narrow step widths can determine the possible depth positions of Eu atoms. From the 3D distribution of Eu atoms, the radial distribution function is analyzed with different concentrations of Ca. Finally, we discuss the atomic distribution model of Eu atoms in Ca-α-SiAlON.

2. Experimental

$Ca_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$: Eu_y ($x = 0.6$ and 1.2, $y = 0.06$; $m = 2x + 2y$, $m = 2n$) was prepared via combustion synthesis [42, 43]. The raw materials included Si (> 99.9% purity, 5 µm), Al (99.9% purity, 3 µm), CaO (99.9% purity), Eu_2O_3 (99.9% purity), and α-Si_3N_4 (99.9% purity, 0.5 µm) powders. The mixture was loaded into a porous alumina crucible. The combustion reaction was conducted under nitrogen (99.99% purity), at a pressure of 0.8 MPa by passing current through a carbon foil. To prepare the TEM samples, the synthesized powder was mixed with fine copper powder (99.99%, 1 µm) and hot-pressed at 300 °C for 1 h The composite disk of α-SiAlON and copper was sliced and mechanically polished down to a thickness of less than 20 µm, and then ion-milled with 5 ~ 1 kV Ar ions (PIPS model 691, Gatan Inc.). HAADF-STEM (Titan^3 G2 60–300, FEI Company) was performed at 300 kV. The inner collection semi-angle of the HAADF detector and the convergence semi-angle of the electron probe were 64 and 30 mrad, respectively. Through-focus HAADF-STEM imaging was performed near 10 nm cubes with a defocus step of 0.68 nm, where the defocus steps were calibrated using high-precision z-displacement (detailed results are supplied in S5 of the Supplementary materials). When the STEM images were acquired, the image contrast was maintained to be linear for the detector signal without an automatic contrast or brightness adjustment. A non-saturation brightness level was selected. The drift of the through-focus images was corrected, and the column intensities of both experimentally obtained and calculated images were determined from the integrated intensity, where the diameter of the selected area was approximately 0.15 nm. The number of Eu atoms was determined from the shape and absolute intensity of the contrast profile. The Eu depth position was analyzed using the peak position of the profile. The HAADF-STEM images were also calculated with the Dr. Probe multi-slice image simulator [44], which uses the frozen phonon approximation to incorporate the influence of TDS. A parameterized scattering factor, which was reported by Weickenmeier and Kohl [45], was used as an atomic scattering factor because of its high accuracy at high angles. A frozen phonon calculation was performed by including random atom displacements to represent thermal atom vibrations. Based on the calculated number of pixels, approximately ten variants of frozen phonons were considered for one column, in which the atomic scattering factor was fixed to be 0.5 $Å^{-2}$ for every atom. According to the reciprocal of the number of supercells used, the resolution in reciprocal space was found to be 0.07 $Å^{-1}$. In these image simulations, we used a Gaussian function with a full width at half maximum of 0.04 nm for the electron probe intensity distribution. The defocus spread was set to 3 nm.

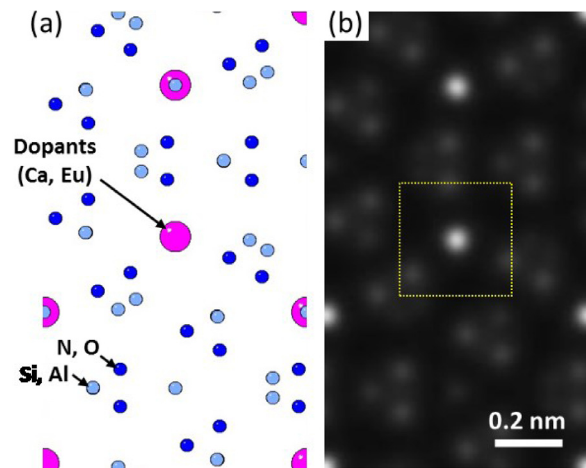

Fig. 1. (a) Atomic structure model of Eu-doped Ca-α-SiAlON, in the [0001] direction. (b) Multi-slice simulated image of Eu-doped Ca-α-SiAlON, in which one Eu atom is located at −5.48 nm along the z-direction and defocus is −5.52 nm (sample thickness: 20 nm, convergence semi-angle: 30 mrad).

3. Results and discussion

Fig. 1(a) shows the atomic structure model of Eu-doped Ca-α-SiAlON along the [0001] direction. Ca and Eu atoms are located in the same column. When Ca content $x = 0.6$ and Eu content $y = 0.06$, the occupancies of Ca and Eu in one dopant column are 0.3 and 0.03, respectively. With an increase in x from 0.6 to 1.2, the amounts of Ca, Al and O increase and the crystal lattice expands due to an increase in long Al-O bonds. The x value also affects the luminescence properties [8]. In this study, samples were synthesized with $x = 0.6$ and 1.2. X-ray diffractometry showed a lattice expansion with an increase in x, and an increase in luminescence properties at $x = 1.2$.

For multi-slice image calculations, a supercell of Ca-α-SiAlON ($x = 0.6$) with a thickness of 20 nm was prepared. When the sample thickness was 20 nm, 36 atomic sites were present in one dopant column. The average numbers of Ca and Eu atoms expected

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