Appendix A : Supplementary materials

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

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S1. Eu detection by variable-angle HAADF imaging

Variable-angle HAADF imaging's ability to detect Eu in Ca-α-SiAlON is confirmed using an image simulation with a thickness of 5.7 nm and 10 dopant sites. Firstly, we calculated the four cases without Eu doping, wherein Ca atoms were (1) uniformly doped with an occupancy of 0.3, (2) uniformly doped with the occupancy of 0.6, (3) were segregated at the top, and (4) segregated at the bottom, as shown in Fig. S1-1. Then, the Eu atoms were doped into cases of (1-4) at different positions. The column intensity as a function of the annular detector angle is summarized in Fig. S1-2. The Ca arrangement was found to significantly affect the column intensities. In the cases of Fig. S1-3 and Fig. S1-4, detecting the number and position of Eu was especially difficult owing to their similar contrast profiles at different detection angles.

		○	●	□	▲		○	●	□	▲		○	●	□	▲		○	●	□	▲
	Ca	0.3	0.6	0.3	0.3		0.3	0.6	0.3	0.3		0.3	0.6	0.3	0.3		0.3	0.6	0.3	0.3
		Uni	Uni	Up	Dw		Uni	Uni	Up	Dw		Uni	Uni	Up	Dw		Uni	Uni	Up	Dw
	Eu	No					Middle					Top					Bottom			
1	0.5708	×	×	Ca	×		×	×	Ca	×		Eu	Eu	Eu	Eu		×	×	Ca	×
2	1.1415	Ca	Ca	×	×		Ca	Ca	×	×		Ca	Ca	×	×		Ca	Ca	×	×
3	1.7123	×	Ca	Ca	×		×	Ca	Ca	×		×	Ca	Ca	×		×	Ca	Ca	×
4	2.283	×	×	×	×		×	×	×	×		×	×	×	×		×	×	×	×
5	2.8538	Ca	Ca	Ca	Ca		Eu	Eu	Eu	Eu		Ca	Ca	Ca	Ca		Ca	Ca	Ca	Ca
6	3.4245	×	×	×	×		×	×	×	×		×	×	×	×		×	×	×	×
7	3.9953	×	Ca	×	×		×	Ca	×	×		×	Ca	×	×		×	Ca	×	×
8	4.566	×	Ca	×	Ca		×	Ca	×	Ca		×	Ca	×	Ca		×	Ca	×	Ca
9	5.1368	Ca	×	×	×		Ca	×	×	×		Ca	×	×	×		Ca	×	×	×
10	5.7075	×	Ca	×	Ca		×	Ca	×	Ca		×	Ca	×	Ca		Eu	Eu	Eu	Eu

Fig. S1-1 calculated arrangement of Ca and Eu atoms.

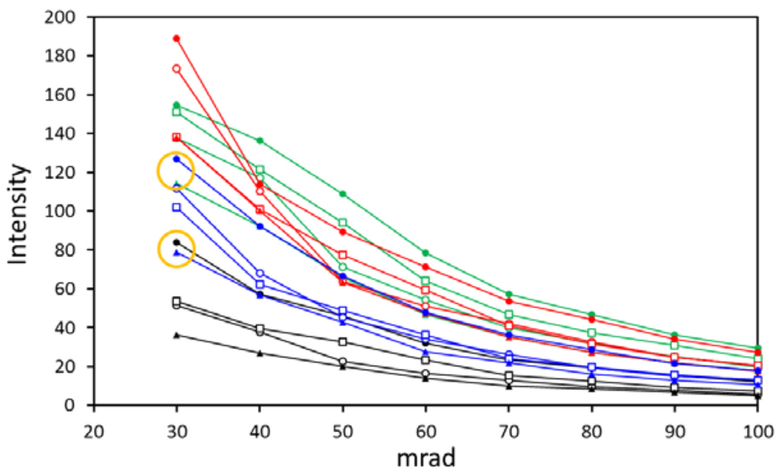

Fig. S1-2 the column intensity with the different arrangements of Ca and Eu atoms shown in Fig. S1-1 as a function of the annular detector angle (300 kV, the convergence semi-angle: 22 mrad, outer angle of the HAADF detector: 200 mrad).

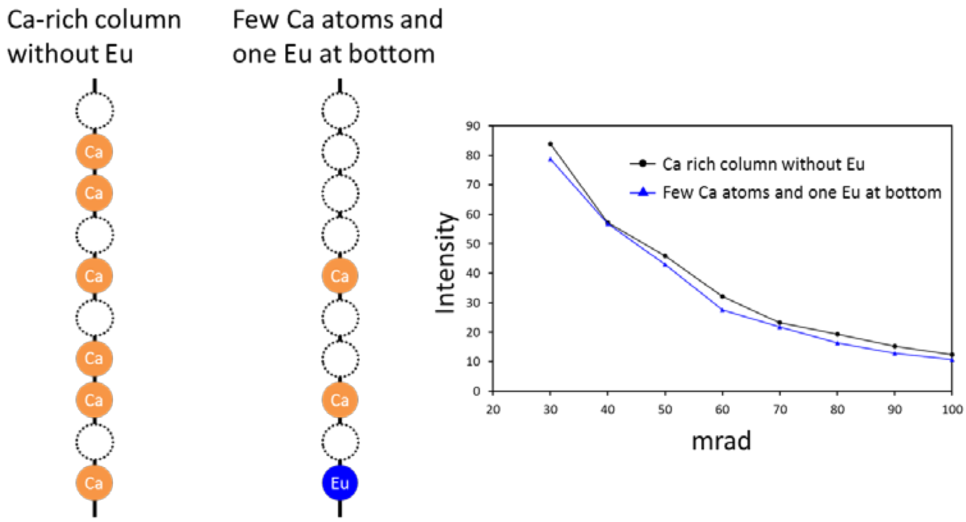

Fig. S1-3 Comparison of ‘Ca-rich column without Eu’ and ‘Few Ca atoms and one Eu at bottom’

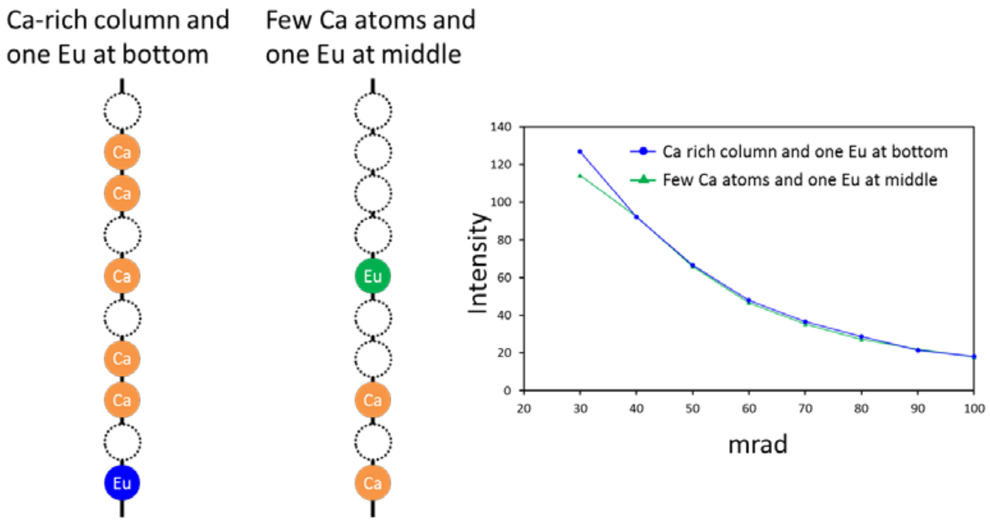

Fig. S1-4 comparison of ‘Ca-rich column and one Eu at bottom’ and ‘Few Ca atoms and one Eu at middle’

S2. Eu detection by through-focus HAADF imaging

As in Section S1, we also confirmed through-focus HAADF imaging's ability to detect Eu. The calculated thickness was 20 nm (36 atomic columns). Fig. S2-1 shows the calculated arrangements of Ca and Eu atoms, in which the convergence semi-angle was set to be 30 mrad with 300 kV. Fig. S2-2 shows the results during through-focus HAADF imaging. When the Ca concentration and arrangement were varied without the Eu addition, the contrast profiles changed, as shown in Fig. S2-2(a). After the Eu addition, sharper peaks with higher intensities clearly appeared, and the peak positions matched the Eu positions well. In summary, although Ca segregation generates broad peaks in the contrast profile, we can distinguish the presence of Eu atoms from Ca segregation because of the sharper, higher-intensity peaks from the presence of Eu.

	ID	○	●	□	▲	○	●	□	▲	○	●	□	▲	○	●	□	▲	○	●	□	▲	○	●	□	▲
	Ca	0.3	0.6	0.3	0.3	0.3	0.6	0.3	0.3	0.3	0.6	0.3	0.3	0.3	0.6	0.3	0.3	0.3	0.6	0.3	0.3	0.3	0.6	0.3	0.3
		Uni	Uni	Up	Dw	Uni	Uni	Up	Dw	Uni	Uni	Up	Dw	Uni	Uni	Up	Dw	Uni	Uni	Up	Dw	Uni	Uni	Up	Dw
	Eu	No				0 nm				5 nm				10 nm				15 nm				20 nm			
1	0.5708	×	×	×	×	Eu	Eu	Eu	Eu	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
2	1.1415	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×
3	1.7123	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca
4	2.283	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
5	2.8538	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×
6	3.4245	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×
7	3.9953	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
8	4.566	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×
9	5.1368	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca
10	5.7075	×	Ca	×	×	×	Ca	×	×	Eu	Eu	Eu	Eu	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
11	6.2783	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
12	6.849	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×
13	7.4198	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
14	7.9905	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
15	8.5613	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca
16	9.132	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×
17	9.7028	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
18	10.274	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	Ca	Ca	×	×	×	Ca	×	×	×	Ca	×	×
19	10.844	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Eu	Eu	Eu	Eu	Ca	×	×	×	Ca	×	×	×
20	11.415	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
21	11.986	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca
22	12.557	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×
23	13.127	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
24	13.698	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
25	14.269	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca
26	14.84	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
27	15.41	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	Eu	Eu	Eu	Eu	×	Ca	×	×
28	15.981	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca
29	16.552	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca
30	17.123	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
31	17.693	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca
32	18.264	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca
33	18.835	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×	×	Ca	×	×
34	19.406	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca	×	×	Ca	Ca
35	19.976	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca	Ca	Ca	×	Ca
36	20.547	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	Eu	Eu	Eu	Eu

Fig. S2-1 calculated arrangements of Ca and Eu atoms.

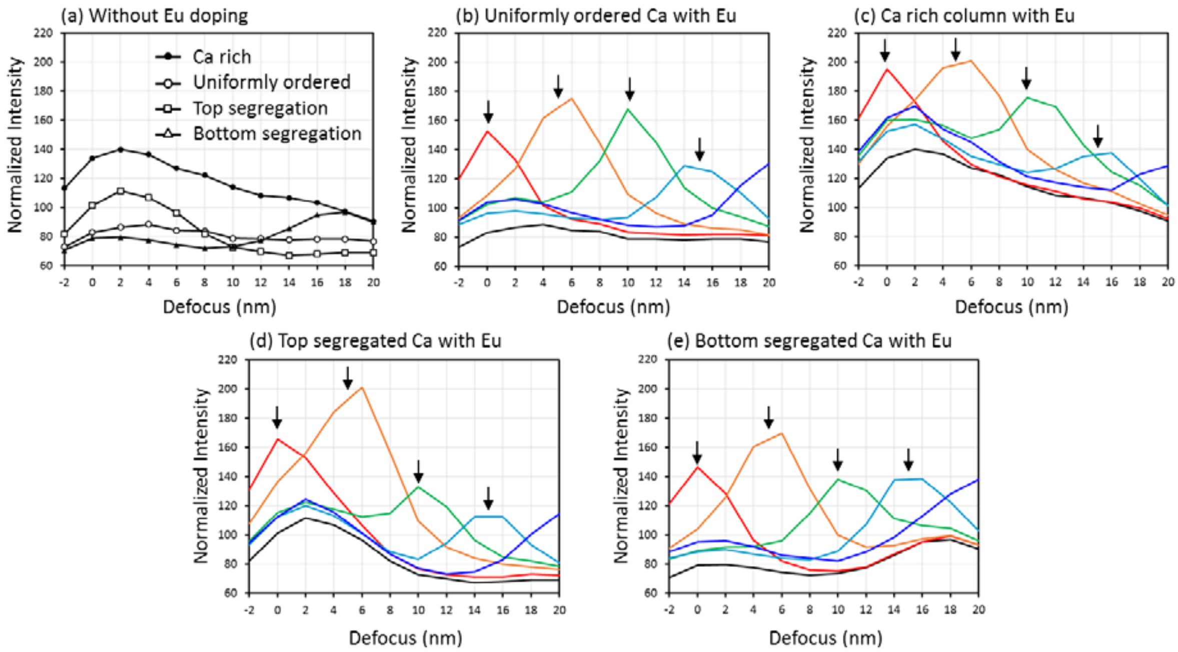

Fig. S2-2 relationships between the normalized intensity and defocus for various arrangements of Ca and Eu atoms. The line colors correspond to the colors in the top row of Fig. S2-1.

S3. Estimation of the sample thickness using the column intensity

The sample thickness was estimated from the intensity of two different Si columns. Fig. S3-1 shows the structural model, in which we focus on the intensity of Si3 and Si4. Fig. S3-2 shows the relative intensity of Si3 and Si4 as a function of the sample thickness when the intensity of column 'N' is 1.0. The changes in the intensities of Si3 and Si4 were found to show different trends (Fig. S3-2, left). By subtracting these two signals, (Fig. S3-2, right), the sample thickness was estimated to be approximately 30 nm.

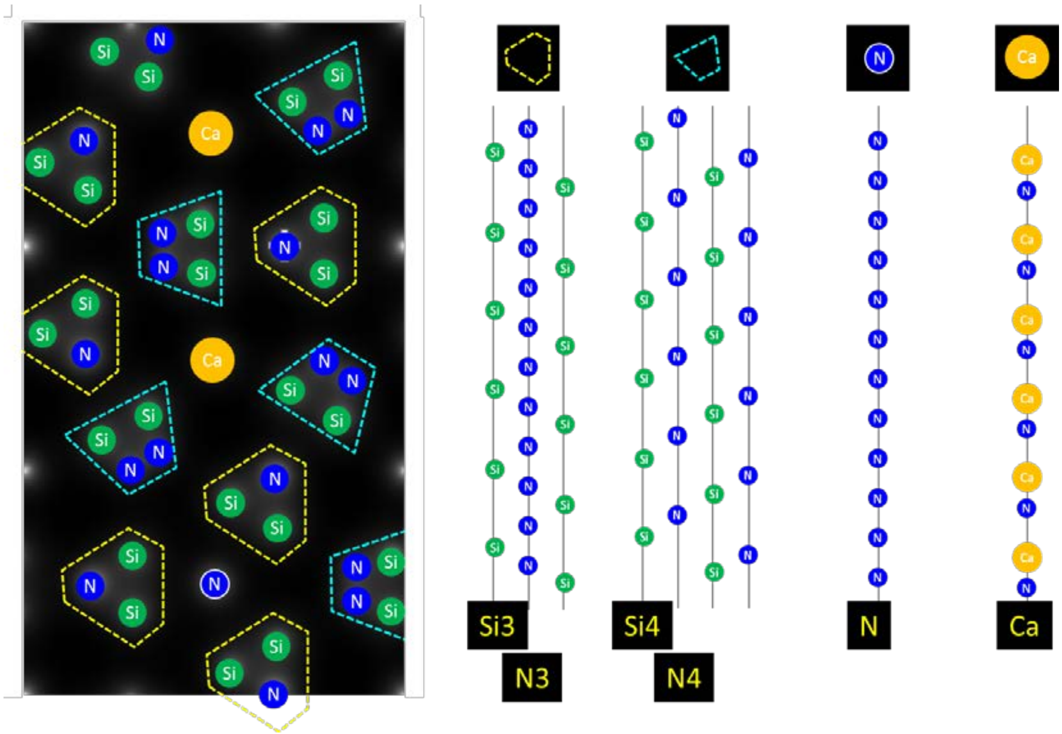

Fig. S3-1 Structural model of Ca-α-SiAlON and the corresponding atomic columns.

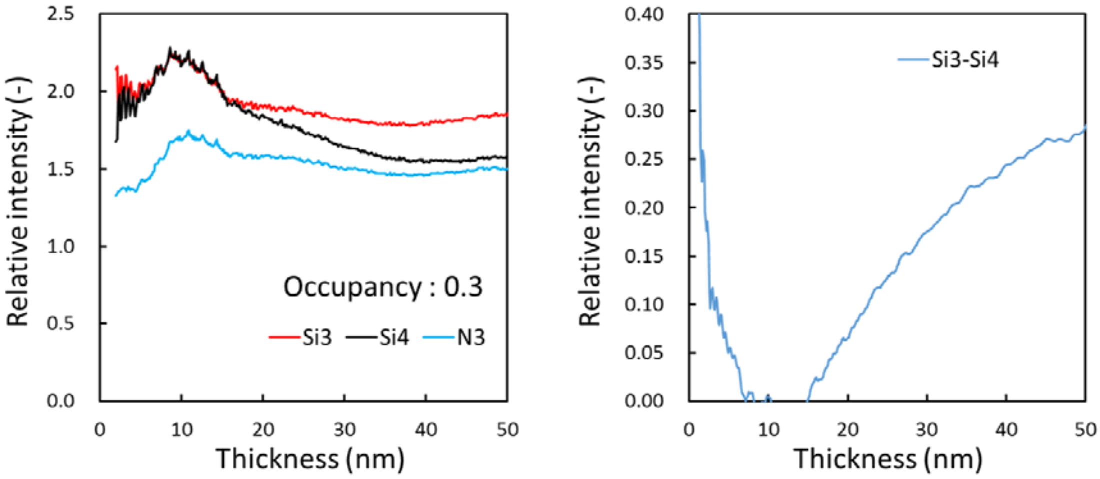

Fig. S3-2 Intensity of atomic columns as a function of the sample thickness (left). The difference between the intensities of Si3 and Si4 (right).

S4. Effect of the sample thickness on the contrast profile

The effect of the sample thickness on the contrast profile evaluated by the through-focus method is summarized in Fig. S4, with the Eu atom located at -5.48 nm and the Ca atoms uniformly distributed. The column intensity increased with the increasing sample thickness. However, the peak position did not change. These results indicate that the sample thickness does not significantly affect the detected Eu position.

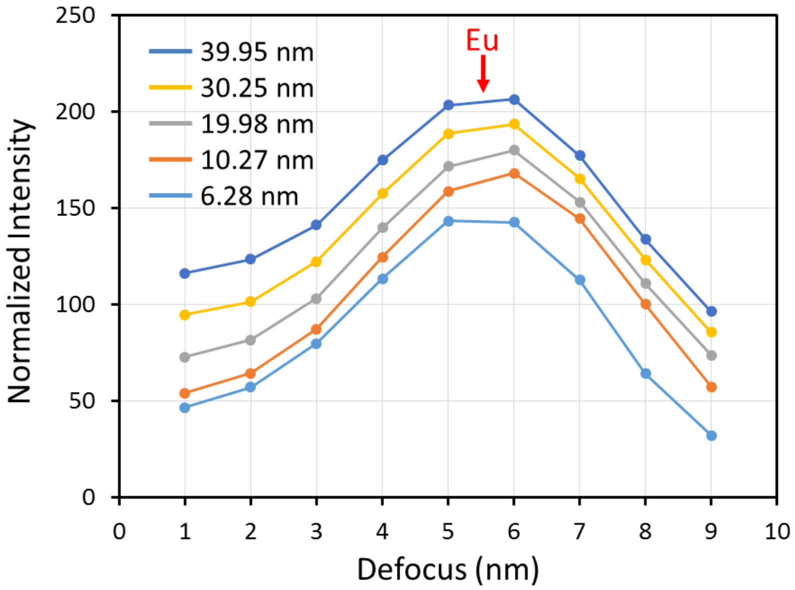

Fig. S4 Contrast profile at different sample thicknesses.

S5. Calibration for the defocus steps

Table S5 Calibration for defocus steps

	z displacement [um]	Defocus [um]
1 MAG 225kX	−10	−6.46
	−5	−2.56
	0	0
	5	3.83
	10	7.15
2 MAG 40000x	−10	−6.58
	−5	−3.15
	0	0
	5	3.63
	10	7.24

※convergence semi-angle : 21.4mrad

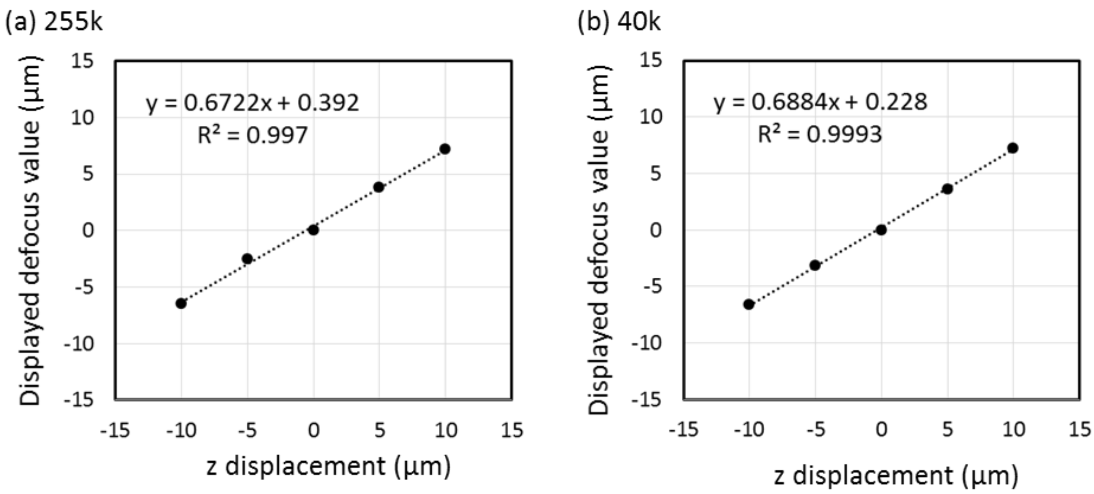

Fig. S5 Results of the calibration for defocus steps

S6. Conversion of the coordination system

The difference in the coordination system is caused by the difference between the Eu distance and the width of the defocus steps. When two Eu atoms located at 0.57 nm distance were separated by the width of 0.68 nm, two different separations can be considered. We calculated the fraction of the distance for the conversion under such a consideration.

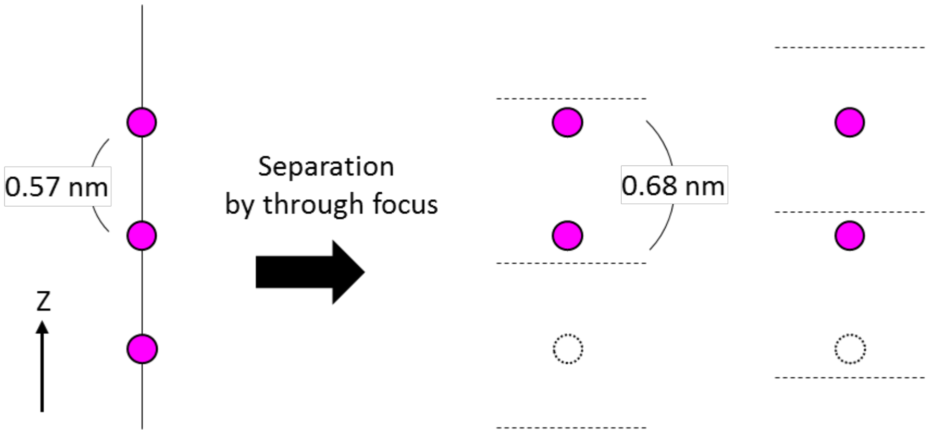

Fig. S6 illustration of the coordination system conversion

S7. Eu detection from the contrast profile

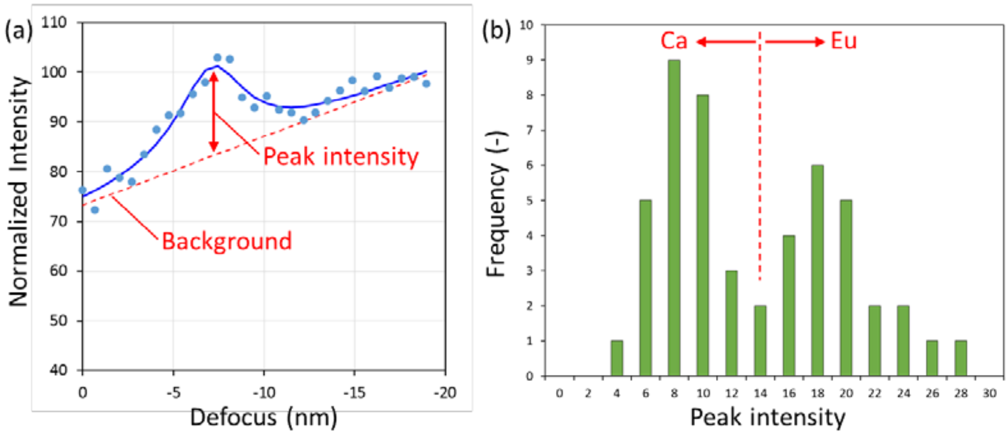

Fig.S7 (a) Background model of contrast profile, (b) distribution of these peak intensities.