Combined Rietveld refinement of $CaMgSi_2O_6:Eu^{2+}$ using X-ray and neutron powder diffraction data

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Recently, much attention has been paid to finding new or advanced phosphors to improve the performance of plasma display panels (PDPs) because color-emitting phosphors are directly associated with luminous efficiency and life time of PDPs [1–2]. Eu doped $CaMgSi_2O_6$ ($CMS:Eu^{2+}$) as a blue phosphor of PDPs has been proposed to overcome the drawback of $BaMgAl_{10}O_{17}:Eu^{2+}$($BAM:Eu^{2+}$), which is sensitive to the manufacturing process variables such as the thermal treatment and irradiation by vacuum ultra-violet (VUV) photons [3–6].

To completely understand and improve luminescent properties of $CaMgSi_2O_6:Eu^{2+}$ ($CMS:Eu^{2+}$), the crystal structural information is fundamentally necessary. In particular, to determine the quantitative amount of Eu^{2+} in the crystal lattice as a luminescent center, which may be partially replaced any constituent atoms in the $CaMgSi_2O_6$ compound, is very important because the amount of Eu^{2+} doped into the crystal lattice is directly dependent on the emission intensity of $CMS:Eu^{2+}$.

This paper is focused on the combined Rietveld refinement using X-ray and neutron powder diffraction data to determine the crystal structural parameters of $CMS:Eu^{2+}$.

The neutron powder diffraction is valuable for the information of oxygen atoms in oxide compounds, and for compounds which consist of similar atomic numbers in the unit cell due to their inherent scattering lengths which are not depend on scattering angles. On the other hand, the X-ray experiment might be applicable to get structural information for compounds having a large absorption element for neutron radiations. Therefore, the combined Rietveld refinement using X-ray and neutron diffraction data is worth getting structural parameters of $CMS:Eu^{2+}$ because there are Eu atoms showing a large absorption effect for neutron radiation (absorption cross-section: 4.530×10^{-19} cm^{-2}), a number of oxygen atoms and adjacent atoms, Mg and Si. The individual characteristics of the two scattering experiments provide clear reasons why the combined Rietveld refinement using both the X-ray and the neutron powder diffraction data is used in this study.

$CMS:Eu^{2+}$ samples were prepared by a conventional solid-state reaction using $CaCO_3$, MgO, SiO_2, and EuF_3 as starting materials. The starting materials were mixed and heated at 1150 and 1200 °C under a reducing atmosphere of a mixture of H_2 (5%) and N_2 (95%) for 3 hr. The PL spectra were measured at room temperature under an excitation of 147 nm radiation from a D_2 lamp. The excitation spectrum in the VUV region was corrected using sodium salicylate. The X-ray diffraction data were measured over the scattering angle range $15^\circ \leq 2\theta \leq 130^\circ$ at a 2θ step of 0.02° using CuK_α radiation with a graphite monochromator in the reflection geometry at room temperature (Rigaku Dmax 2200V). The Neutron powder diffraction data were collected over scattering angles range $15^\circ \leq 2\theta \leq 145^\circ$ at a 2θ step of 0.05° a using 1.8348 Å on High Resolution Powder Diffractometer (HRPD) of the Korea Atomic Energy Research Institute. The structural refinement was made with the general structure analysis system (GSAS) program [7]. The experimental diffraction profiles were modeled by a pseudo-Voigt function within GSAS [8].

Fig. 1 shows the PL excitation and emission spectra of the $CMS:Eu^{2+}$ sample under 147 nm excitation at room temperature, respectively. The emission spectrum shows a broad emission with its maximum at about 447 nm due to the transition of Eu^{2+} from the $4f^65d$ excited state to the $4f^7$ ground state. The emission spectrum indicates that the valence state of Eu atom in $CMS:Eu^{2+}$ is divalent due to the presence of only one broad line at approximately 447 nm.

The initial structural model which has an approximation for the actual structure for $CMS:Eu^{2+}$ was constructed with crystallographic data based on monoclinic

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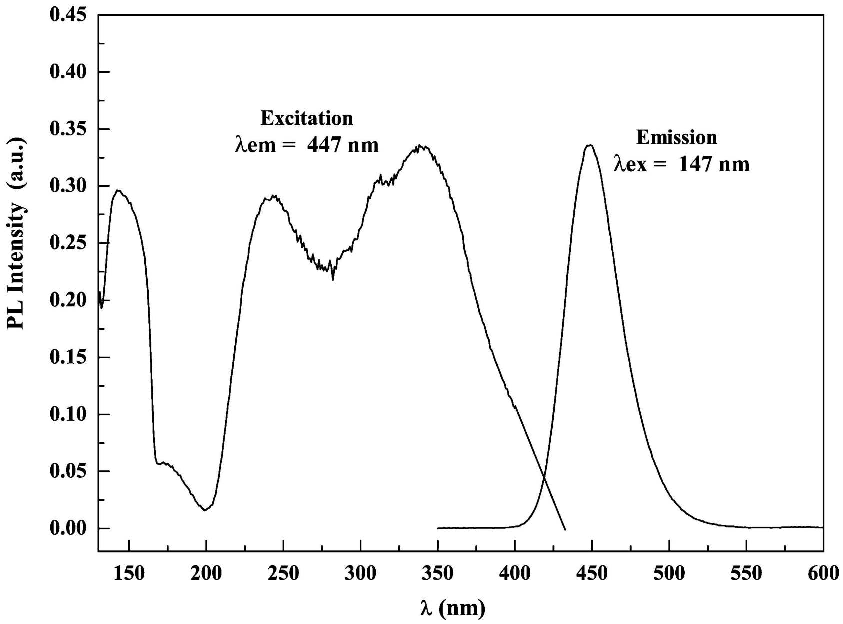

Figure 1 Excitation and emission spectra of $CaMgSi_2O_6:Eu^{2+}$ phosphor.

space group C2/c [9]. The Rietveld refinement of this study begins with the neutron powder diffraction data of the two data because $CMS:Eu^{2+}$ is composed of a number of oxygen atoms and adjacent atoms, Mg and Si, in the unit cell and the neutron powder diffraction is valuable for compounds which consist of similar atomic numbers and a number of oxygen atoms due to their inherent scattering lengths.

The initial structural refinement cycles included the zero-point shift, the lattice parameters, the scale factor and background parameters as variables. Following satisfactory matching of peak positions, the atomic positions, the thermal parameters and the peak profile parameters including the peak asymmetry were refined. α-Al_2O_3 and Si (NIST 640c) powders were used as external standards to correct the zero-point shift for the measured neutron and X-ray diffraction data, respectively.

In spite of satisfactory convergence of the refinement against neutron powder diffraction data, some unknown diffraction peaks remained unaccounted for within the experimental profiles. Considering the starting materials and experimental variables such as pressure, temperature, and

TABLE I Refined structural parameters for $CaMgSi_2O_6:Eu^{2+}$ obtained from the combined Rietveld refinement using X-ray and neutron powder diffraction data at room temperature. The symbols, g and U_{iso}, represent the occupation and isotropic thermal parameters, respectively. The numbers in parentheses are the estimated standard deviations of the last significant figure

Atom	Site	x	y	z	g	$100\times U_{iso}/Å^2$
			$CaMgSi_2O_6:Eu^{2+}$			
Ca	4*e*	0.0	0.3004 (2)	0.25	0.988 (1)[a]	1.27 (2)[b]
Eu	4*e*	0.0	0.3004 (2)	0.25	0.012 (1)	1.27 (2)
Mg	4*e*	0.0	0.9086 (1)	0.25	1.0	0.91 (2)
Si	8*f*	0.2863 (2)	0.0937 (1)	0.2296 (2)	1.0	0.61 (3)
O	8*f*	0.1155 (1)	0.0873 (2)	0.1420 (2)	1.0	0.55 (2)
O	8*f*	0.3623 (2)	0.2486 (2)	0.3190 (2)	1.0	0.92 (2)
O	8*f*	0.3512 (2)	0.0169 (2)	0.9957 (2)	1.0	0.65 (3)
Space group : *C12/c1* (No. 15) and Z = 4						
$a = 9.7478(2)$, $b = 8.9390(1)$ Å and $c = 5.2490(1)$ Å. $\beta = 105.87(1)$ °						
			SiO_2			
Si	4*a*	0.2914 (21)[b]	0.2914 (21)	0.0	1.0	1.25 (29)
O	8*b*	0.2515 (22)	0.0888 (20)	0.1749 (27)	1.0	1.88 (25)
Space group: $P4_1\ 2_1\ 2$ (No. 92) and Z = 2						
$a = b = 4.9848(23)$ Å and $c = 6.9592(62)$ Å						
			Weight fraction			
		$CaMgSi_2O_6:Eu^{2+}$			SiO_2	
		97.09 (2)%			2.91 (2)%	

[a] Constraint on occupancy: $g(Ca) + g(Eu) = 1.0$.

[b] Constraint on isotropic thermal factor: $U_{iso}(Ca) = U_{iso}(Eu)$.

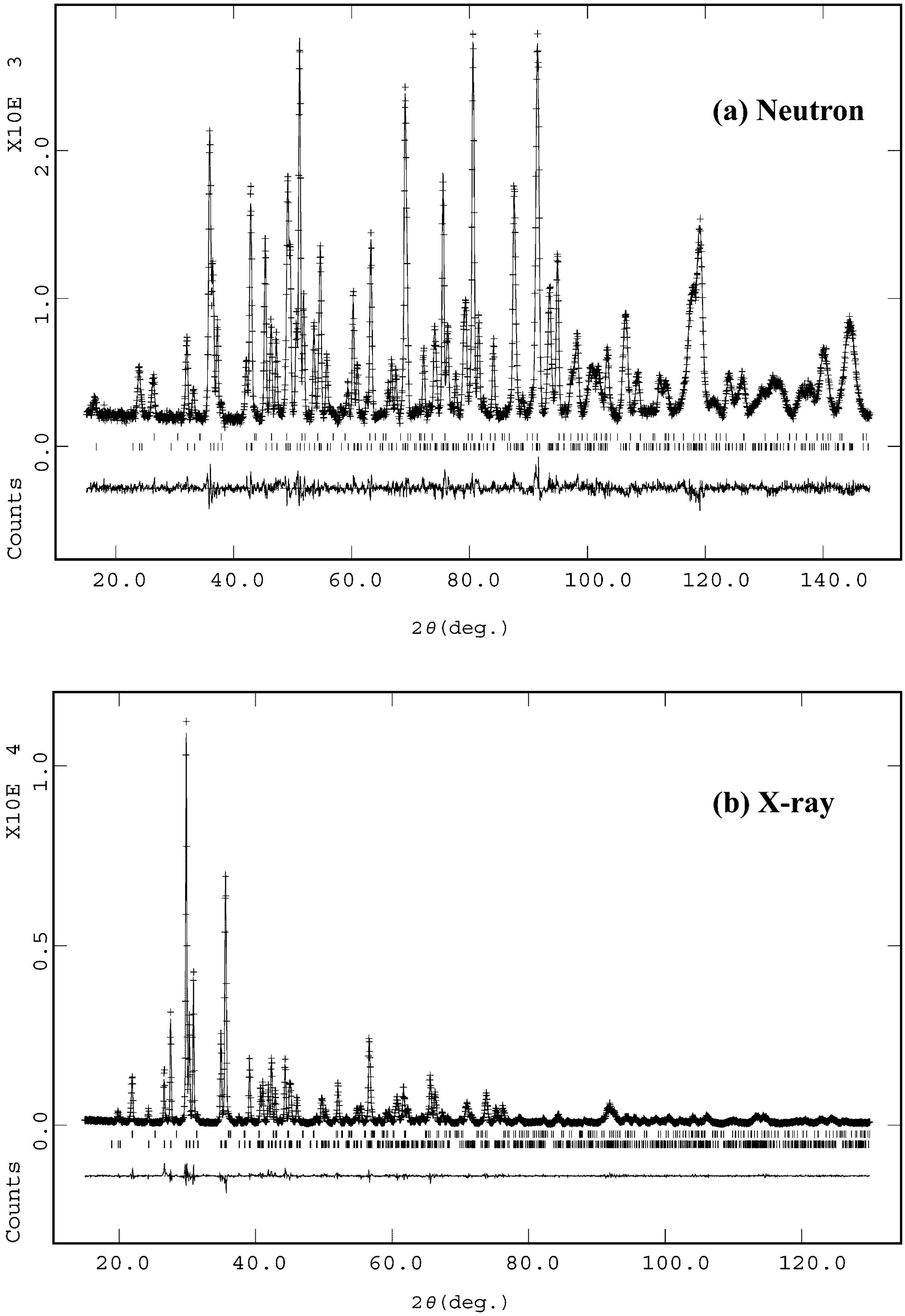

Figure 2 Combined Rietveld refinement patterns of a mixture $CaMgSi_2O_6:Eu^{2+}$ and SiO_2 phases using (a) neutron and (b) X-ray powder diffraction data. Plus (+) marks represent the observed intensities, and the solid line defines calculated ones. A difference (obs. − cal.) plot is shown beneath. Tick marks above the difference indicate the reflection positions. The upper and lower tick marks indicate the reflection positions for SiO_2 and $CaMgSi_2O_6:Eu^{2+}$ phases, respectively.

environment atmosphere, some oxide compounds such as CaO, SiO_2, MgO, EuO, $CaSiO_3$, etc., can exist within the CMS:Eu^{2+} sample as a secondary phase. Of them, the remaining reflection peaks could be indexed successfully to SiO_2 with the space group of $P4_12_12$ and $Z = 2$ [10]. Therefore the Rietveld refinement proceeded based on a mixture of CMS:Eu^{2+} and SiO_2 phases.

When Eu^{2+} ions are incorporated into the crystal structure of CMS, Eu^{2+} ions may partially substitute for one or more of cationic sites, Ca^{2+} (4e), Mg^{2+} (4e) and Si^{4+} (8f). However, considering their relative ionic radii allowed oxygen-coordination number (n), Mg^{2+} (0.72 Å, $n = 6$), Si^{4+} (0.26 Å, $n = 4$), Ca^{2+} (1.12 Å, $n = 8$), and Eu^{2+} (1.25 Å, $n = 8$) [11], it seems difficult for Eu^{2+}

TABLE II Selected interatomic distances and bond angles for $CaMgSi_2O_6$:Eu^{2+} obtained from the combined Rietveld refinement using X-ray and neutron powder diffraction data at room temperature

	Number of bond	distance (Å)		Number of bond	distance (Å)
Interatomic Distances (Å)					
	Four-coordinated polyhedron			Six-coordinated polyhedron	
Si–O (1)	1	1.6036 (1)	Mg–O (1)	2	2.11804 (1)
Si–O (2)	1	1.5797 (1)	Mg–O (1)	2	2.0580 (1)
Si–O (3)	1	1.6738 (1)	Mg–O (2)	2	2.0608 (1)
Si–O (3)	1	1.6867 (1)			
	Eight-coordinated polyhedron				
M(1)[a]–O (1)	2	2.3594 (1)	M(1)–O (3)	2	2.5640 (1)
M(1)–O (2)	2	2.3347 (1)	M(1)–O (3)	2	2.7306 (1)
Bond Angles (°)					
Bond type		angle (°)	Bond type		angle(°)
	Four-coordinated polyhedron			Six-coordinated polyhedron	
O(1)–Si–O (2)		118.82 (1)	O(1)–Mg–O (1)		82.16 (1)
O(1)–Si–O (3)		110.24 (1)	O(1)–Mg–O (1)		84.51 (3)
O(1)–Si–O (3)		109.94 (1)	O(1)–Mg–O (1)		93.95 (1)
O(2)–Si–O (3)		109.72 (1)	O(1)–Mg–O (1)		171.81 (1)
O(2)–Si–O (3)		103.22 (1)	O(1)–Mg–O (2)		93.26 (1)
O(3)–Si–O (3)		103.66 (1)	O(1)–Mg–O (2)		177.96 (1)
			O(1)–Mg–O (2)		89.07 (1)
			O(1)–Mg–O (2)		92.35 (1)
			O(2)–Mg–O (2)		92.07 (1)
	Eight-coordinated polyhedron				
O(1)–M(1)–O (1)		72.29 (1)	O(2)–M(1)–O (3)		137.71 (1)
O(1)–M(1)–O (2)		84.01 (1)	O(2)–M(1)–O (3)		62.84 (1)
O(1)–M(1)–O (2)		78.55 (1)	O(2)–M(1)–O (3)		109.31 (1)
O(1)–M(1)–O (3)		136.36 (1)	O(2)–M(1)–O (3)		83.90 (1)
O(1)–M(1)–O (3)		119.71 (1)	O(3)–M(1)–O (3)		81.97 (1)
O(1)–M(1)–O (3)		91.12 (1)	O(3)–M(1)–O (3)		66.46 (1)
O(1)–M(1)–O (3)		161.13 (1)	O(3)–M(1)–O (3)		59.76 (1)
O(2)–M(1)–O (2)		158.38 (1)	O(3)–M(1)–O (3)		106.54 (1)

[a] M(1):Ca or Eu

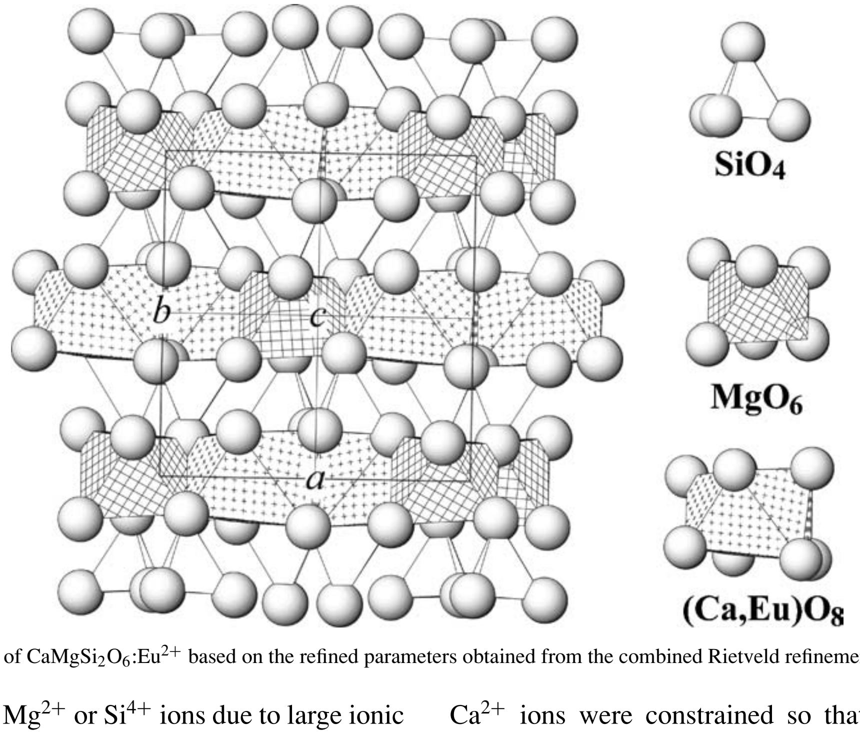

Figure 3 Crystal structure of $CaMgSi_2O_6$:Eu^{2+} based on the refined parameters obtained from the combined Rietveld refinement.

ions to substitute for Mg^{2+} or Si^{4+} ions due to large ionic radius difference between Eu^{2+} ions and them.

Consequently, the combined Rietveld refinement proceeded under the assumption that Eu^{2+} ions substituted only for Ca^{2+} ions. The occupancies for Eu^{2+} and Ca^{2+} ions were constrained so that the site, 4e (0, *y*, 1/4), was fully occupied and the total occupancy of Eu^{2+} and Ca^{2+} ions was maintained to be unity. The isotropic temperature parameters of both ions were constrained to be equal. After the previous refinement cycles had converged, the occupation and thermal factors were refined with the mentioned above two constraints.

Fig. 2 shows the combined Rietveld refinement patterns using both X-ray and neutron powder diffraction data for a mixture model of CMS:Eu^{2+} and SiO_2 phases. The final weighted and profile R-factor, R_{wp} and R_p, on all data was 8.43 and 6.28% ($R_{wp} = 9.73\%$ and $R_p = 7.31\%$ for X-ray, $R_{wp} = 6.46\%$ and $R_p = 4.99\%$ for neutron data, respectively) and the goodness-of-fit indicator, S (=R_{wp}/R_e), was 1.48. Table I and Table II listed the refined structural parameters and the selected bond distances of CMS:Eu^{2+} obtained from the combined Rietveld refinement, respectively. The site occupation of Eu^{2+} ions occupying the Ca site (4e) (0, y, 1/4) was 0.012 and totally substituted for 1.2% of the Ca ions. The weight fraction of CMS:Eu^{2+} and SiO_2 based on the refined scale factor was 97.09(1)% and 2.89(2)%, respectively. The refined lattice parameters of CMS:Eu^{2+} were $a = 9.7478(2)$, $b = 8.9390(1)$ Å, $c = 5.2490(1)$ Å and $\beta = 105.87(1)$ °. Fig. 3 shows the crystal structure of $CaMgSi_2O_6$:Eu^{2+} based on the refined parameters obtained from the combined Rietveld refinement.

The structural parameters for the blue-emitting phosphor, $CaMgSi_2O_6$:Eu^{2+}, synthesized by a conventional solid-state reaction, such as lattice parameters, mass fractions, the occupancy of Eu^{2+} ions, atomic coordinates, isotropic thermal parameters were determined by means of the combined Rietveld refinement with the crystal structure model, which describes a structure in monoclinic space group C12/c1 with $Z = 4$ and Eu atoms occupying the Ca sites (4e) (0, y, 1/4). These refined structural parameters might be applied to calculate the critical distance for energy transfer between sensitizer and activator, which is necessary to understand the energy transfer mechanism of CMS:Eu^{2+}.

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