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Photoluminescence Spectra Correlations with Structural Distortion in Eu^{3+} - and Ce^{3+} -Doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg},\text{Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) Garnet Phosphors

Heonji Ha ¹, Sungjun Yang ² and Sangmoon Park ^{1,3,*} 
¹ Department of Engineering in Energy Materials, Graduate School, Silla University, Busan 46958, Republic of Korea

² UNIST Central Research Facilities, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea

³ Department of Environmental Energy & Chemistry, College of Engineering and Department of Fire Protection and Safety Management, College of Health and Welfare, Silla University, Busan 46958, Republic of Korea

* Correspondence: spark@silla.ac.kr; Tel.: +82-51-999-5891

Abstract: Garnet-type materials consisting of $\text{Y}_3\text{Al}_{5-2x}(\text{Mg},\text{Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$), combined with Eu^{3+} or Ce^{3+} activator ions, were prepared by a solid-state method to determine the structural and optical correlations. The structure of $\text{Y}_3\text{Al}_{5-2x}(\text{Mg},\text{Ge})_x\text{O}_{12}$ ($x = 1, 2$) was determined to be a cubic unit cell (Ia-3d), which contains an 8-coordinated Y^{3+} site with octahedral $(\text{Mg},\text{Al})\text{O}_6$ and tetrahedral $(\text{Al},\text{Ge})\text{O}_4$ polyhedra, using synchrotron powder X-ray diffraction. When Eu^{3+} or Ce^{3+} ions were substituted for the Y^{3+} site in the $\text{Y}_3\text{Al}_{5-2x}(\text{Mg},\text{Ge})_x\text{O}_{12}$ host lattices, the emission spectra showed a decrease in the magnetic dipole f - f Eu^{3+} transition and a redshift of the d - f Ce^{3+} transition, related to centrosymmetry and crystal field splitting, respectively. These changes were monitored according to the increase in Mg^{2+} and Ge^{4+} contents. The dodecahedral and octahedral edge sharing was identified as a key distortion factor for the structure-correlated luminescence in the $\text{Eu}^{3+}/\text{Ce}^{3+}$ -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg},\text{Ge})_x\text{O}_{12}$ garnet phosphors.

Keywords: garnet; X-ray diffraction; phosphor; distortion



Citation: Ha, H.; Yang, S.; Park, S. Photoluminescence Spectra Correlations with Structural Distortion in Eu^{3+} - and Ce^{3+} -Doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg},\text{Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) Garnet Phosphors. *Materials* **2024**, *17*, 2445. <https://doi.org/10.3390/ma17102445>

Academic Editor: Alexander N. Obraztsov

Received: 30 April 2024

Revised: 14 May 2024

Accepted: 17 May 2024

Published: 19 May 2024



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1. Introduction

Ce^{3+} -doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) phosphor has been widely utilized as a smart light source in conjunction with blue LED chips [1–3]. Initially developed in 1967 by G. Blasse and A. Bril, the yellow Ce^{3+} -activated YAG phosphor was prepared for use in flying-spot cathode-ray tubes for color television, emitting intense yellow light via the $5d$ - $4f$ transition of Ce^{3+} ions within the cubic garnet YAG structure [4]. The garnet mineral belongs to the nesosilicate subclass, characterized by isolated tetragonal polyhedra [5]. The YAG garnet structure, a cubic crystal system (Ia-3d), consists of dodecahedral YO_8 , octahedral AlO_6 , and tetrahedral AlO_4 units. The local dodecahedral YO_8 polyhedra within the garnet structure exhibit edge-sharing with YO_8 and AlO_6 polyhedra, as well as vertex-sharing with isolated AlO_4 tetrahedra [6–9]. In garnet host lattices, Ce^{3+} activator ions can occupy the dodecahedral site, influencing crystal field splitting and resulting in a shift of the d - f transition [10–12]. Researchers J. Ueda and S. Tanabe have explored the effects of crystal and electronic structures on Ce^{3+} -doped YAG, particularly regarding the crystal field splitting of the lowest $5d$ levels and a new distortion parameter estimated by the ratio of dodecahedral edges [6]. Similarly, Eu^{3+} activator ions provide insight into site-resolved luminescence, distinguishing between centrosymmetric and non-centrosymmetric sites in garnet-type phosphors using the magnetic dipole and electric dipole transitions observed in emission spectra [13–15]. In this study, the structure of single-phase $\text{Y}_3\text{Al}_{5-2x}(\text{Mg},\text{Ge})_x\text{O}_{12}$ ($x = 1, 2$) garnet materials was determined using synchrotron X-ray analysis, revealing a cubic unit

cell with $Ia\bar{3}d$ symmetry. The cell parameters, volume, and distances within the host lattices were discussed. By substituting Ce^{3+} or Eu^{3+} activator ions into $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 0, 1, 2$), correlations between emission spectra, dipole transitions, and crystal field splitting were investigated in relation to structural distortion parameters.

2. Materials and Methods

Garnet materials doped with Eu^{3+} - or Ce^{3+} -doped $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 0, 1, 2$) compounds were synthesized by mixing appropriate stoichiometric amounts of powdered Y_2O_3 (Alfa, 99.9%), MgO (Alfa, 99.95%), Al_2O_3 (Alfa, 99.95%), GeO_2 (Alfa, 99.999%), Eu_2O_3 (Alfa, 99.9%), and CeO_2 (Aldrich, 99.9%), along with 5 wt% LiF (Alfa, 99.98%) or Li_2CO_3 (Alfa, 99%) flux. The powdered precursors were mixed in an agate mortar and pestle and then heated at 950 °C and 1400 °C for 6 h in air in a box furnace. The obtained powder samples containing the CeO_2 precursor underwent additional reheating at 1000 °C for 12 h in a 5% H_2 /95% N_2 atmosphere. Phase identification was conducted using a powder diffractometer (Cu $K\alpha$ radiation; Shimadzu XRD-6000, Kyoto, Japan), and structural analysis of the obtained garnet materials was performed using synchrotron powder X-ray diffraction ($\lambda = 0.65303$ Å). The new structural data were collected at the PLS-II 6D UNIST-PAL beamline of the Pohang Accelerator Laboratory (PAL) [16]. The garnet $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 1$ and 2) structures were refined using the Rietveld refinement program FullProf Suite [17,18]. Excitation and emission photoluminescence spectra of the powdered phosphors were obtained via UV spectroscopy using spectrofluorometers (FluoroMate FS-2, Scinco, Seoul, Korea).

3. Results and Discussion

Figure 1a,b illustrate the Rietveld refinement fitting of the powdered X-ray diffraction (XRD) data for $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 1$ and 2). The summarized structural data are provided in Tables 1–3. A single phase of the garnet structure, determined to be a cubic unit cell ($Ia\bar{3}d$), was obtained through a solid-state reaction method. This cubic phase of garnet, including $Y_3Al_5O_{12}$ (YAG, ICSD 170157) and $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 1$ and 2) structures, comprises 8-, 6-, and 4-coordinated Y^{3+} , $Al^{3+}(1)-Mg^{2+}$, and $Al^{3+}(2)-Ge^{4+}$ ions, respectively, occupying 24c, 16a, and 24d Wyckoff sites. The 6-coordinated Mg^{2+} (with a radius of 0.72 Å for 6 coordination number (CN)), $Al^{3+}(1)$ (with a radius of 0.535 Å for 6 CN), and 4-coordinated Al^{3+} (with a radius of 0.39 Å for 4 CN) and Ge^{4+} (with a radius of 0.39 Å for 4 CN) sites are suitable for substitutions in the garnet structure [19]. Therefore, the formula for the garnet-structured $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 0, 1, 2$) can be expressed as $Y_3Al(1)_{2-x}Mg_xAl(2)_{3-x}Ge_xO_{12}$ based on the ionic radii of the cations in the unit cell, as depicted in Figure 1c. Similar to the isolated AlO_4 tetrahedra in the YAG structure, the tetrahedral $(Al,Ge)O_4$ polyhedron in the $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ structures is also isolated, with no sharing of O atoms. There are two different bond distances between Y^{3+} and O^{2-} ions in the YO_8 polyhedron, whereas a single bond distance is observed in the $(Mg,Al)O_6$ and $(Al,Ge)O_4$ polyhedra within the host lattices. The YO_8 polyhedron shares edges with nearby YO_8 polyhedra and $(Mg,Al)O_6$ octahedra. YAG exhibits lattice parameters and volume, such as $a = 11.9900(14)$ Å and $V = 1723.68$ Å³ (as shown in Table 1). The cell parameters and volumes of $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 1$ and 2) are larger than those of YAG compounds, such as $Y_3MgAl_3GeO_{12}$ ($a = 12.1479(2)$ Å and $V = 1796.82(17)$ Å³) and $Y_3Mg_2AlGe_2O_{12}$ ($a = 12.2628(1)$ Å and $V = 1844.027(14)$ Å³). The Y–O bond distances of an 8-coordinated Y (with a radius of 1.019 Å) comprise four long distances (2.433 Å) and four short distances (2.303 Å) in the YAG structure. The Y–O bond distances in $Y_3MgAl_3GeO_{12}$ and $Y_3Mg_2AlGe_2O_{12}$ host lattices remain consistent with those of the YAG structure, as shown in Figure 1c. However, the bond distances of a 6-coordinated $(Mg,Al)-O_6$ and $Mg-O_6$ exhibit distinct increases from 1.921 Å (for Al–O in YAG) to 1.997 Å and 2.094 Å, respectively, representing 4% and 9% differences. Conversely, the bond distances of $Al-O_4$ and $(Al,Ge)-O_4$ tetrahedra in the garnet structures remain similar, ranging from 1.766 to 1.785 Å and 1.760 Å. Interestingly, with the increase in the cell parameter and volume, the bond distance

increase is observed primarily in the octahedral polyhedron in the $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ structure when $x = 0, 1$, and 2 .

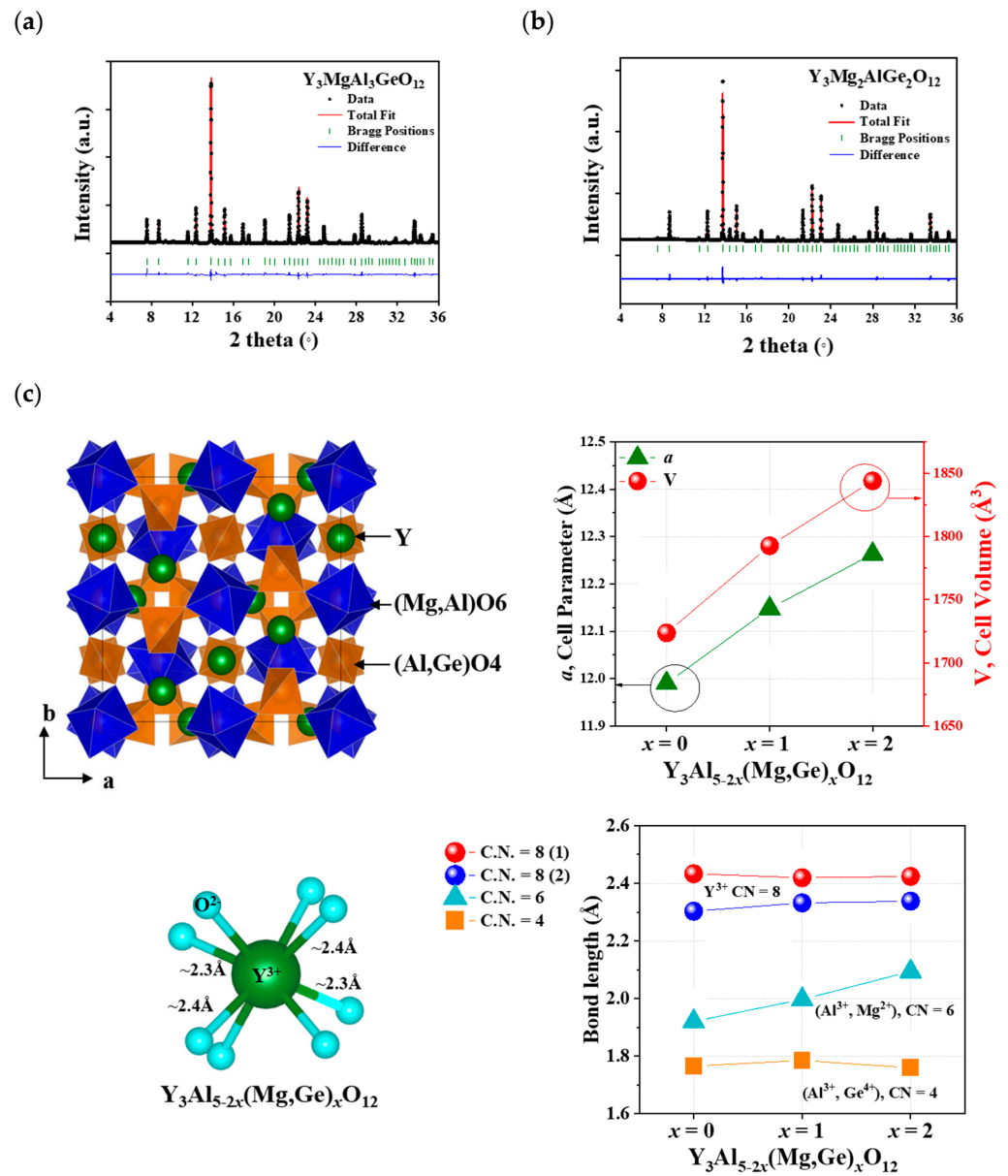


Figure 1. Synchrotron XRD patterns of $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ (a) $x = 1$ and (b) $x = 2$ and (c) the garnet $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 0, 1, 2$) structure with cell parameters and cell volumes.

Table 1. Rietveld refinement and crystal data for $Y_3Al_{5-2x}(Mg,Ge)_xO_{12}$ ($x = 0, 1, 2$).

Chemical Formula	$Y_3Al_5O_{12}$ (ICSD 170157)	$Y_3MgAl_3GeO_{12}$	$Y_3Mg_2AlGe_2O_{12}$
Radiation type, λ (Å)		Synchrotron (6D-BM), 0.65303	
2θ range (deg)		4–36	
Crystal system	Cubic	Cubic	
Space group	Ia-3d	Ia-3d	
Lattice parameter (Å)	$a = 11.9900$ (14)	$a = 12.1479$ (2)	$a = 12.2628$ (1)
Volume (Å ³)	$V = 1723.68$	$V = 1792.682$ (17)	$V = 1844.027$ (14)
Density (g/cm ³)	4.57	4.888	4.816

Table 1. Cont.

Chemical Formula	Y ₃ Al ₅ O ₁₂ (ICSD 170157)	Y ₃ MgAl ₃ GeO ₁₂	Y ₃ Mg ₂ AlGe ₂ O ₁₂
R _p (%)		0.717	0.728
R _{wp} (%)		1.22	1.47
R _{exp} (%)		1.26	1.88
S		0.96	0.78
χ ²		0.931	0.608

Table 2. Refined atomic coordinates of Y₃Al_{5-2x}(Mg,Ge)_xO₁₂ (x = 0, 1, 2).

Y ₃ Al ₅ O ₁₂ (ICSD 170157)						
Atom	Wyckoff position	x	y	z	B _{iso}	SOF
Y	24c	0.125	0	0.25	0.00365 (12)	1
Al(1)	16a	0	0	0	0.0030 (3)	1
Al(2)	24d	0.375	0	0.25	0.0011 (3)	1
O	96h	0.28023 (17)	0.10110 (16)	0.19922 (17)	0.0036 (4)	1
Y ₃ MgAl ₃ GeO ₁₂						
Atom	Wyckoff position	x	y	z	B _{iso}	SOF
Y	24c	0	0.25	0.125	0.33 (8)	1
Mg	16a	0	0	0	0.49	0.5
Al(1)	16a	0	0	0	0.49	0.5
Al(2)	24d	0	0.25	0.375	0.57	0.6667
Ge	24d	0	0.25	0.375	0.57	0.3333
O	96h	−0.0305 (5)	0.0551 (6)	0.1518 (6)	0.4 (2)	1
Y ₃ Mg ₂ AlGe ₂ O ₁₂						
Atom	Wyckoff position	x	y	z	B _{iso}	SOF
Y	24c	0	0.25	0.125	0.2 (2)	1
Mg	16a	0	0	0	1.0 (2)	1
Al(2)	24d	0	0.25	0.375	0.1 (2)	0.3333
Ge	24d	0	0.25	0.375	0.1 (2)	0.6667
O	96h	−0.0315 (7)	0.0576 (6)	0.1576 (6)	0.2 (2)	1

Table 3. Selected interatomic distances for Y₃Al_{5-2x}(Mg,Ge)_xO₁₂ (x = 0, 1, 2).

Y ₃ Al ₅ O ₁₂ (ICSD 170157)		Y ₃ MgAl ₃ GeO ₁₂		Y ₃ Mg ₂ AlGe ₂ O ₁₂	
Atom	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)
Y-O (×4)	2.433	Y-O (×4)	2.419 (2)	Y-O (×4)	2.424 (4)
Y-O (×4)	2.303	Y-O (×4)	2.332 (2)	Y-O (×4)	2.338 (4)
Al-O (×6)	1.921	(Mg/Al1)-O (×6)	1.997 (2)	Mg-O (×6)	2.094 (4)
Al-O (×4)	1.766	(Al2/Ge)-O (×4)	1.785 (2)	Ge/Al-O (×4)	1.760 (4)

In Figure 2a,b, a distinct shift in the apparent peaks to lower angles, particularly those at $2\theta = 32\text{--}34^\circ$, was observed as Al³⁺ ions were gradually replaced by Mg²⁺ and Ge⁴⁺ ions in the Eu³⁺- and Ce³⁺-doped Y₃Al_{5-2x}(Mg,Ge)_xO₁₂ (x = 0, 1, 2) phosphors, respectively. A single phase of the garnet structure with a cubic crystal system (Ia $\bar{3}$ d) was obtained, free from any apparent impurities. The cell volumes of both Y_{2.5}Eu_{0.5}Al_{5-2x}(Mg,Ge)_xO₁₂ and Y_{2.95}Ce_{0.05}Al_{5-2x}(Mg,Ge)_xO₁₂ (x = 0, 1, 2) phosphors increased as the content of Mg²⁺ and Ge⁴⁺ increased. Figure 3a displays the emission photoluminescence (PL) spectra of Y_{2.5}Eu_{0.5}Al_{5-2x}(Mg,Ge)_xO₁₂ (x = 0, 1, 2) phosphors. The electronic *f-f* transitions of Eu³⁺ ions in the host lattices are assigned as ⁵D₀–⁷F₁, ⁵D₀–⁷F₂, ⁵D₀–⁷F₃, and ⁵D₀–⁷F₄ within the range of 550 and 750 nm [13–15]. It is known that when Eu³⁺ ions are located at the centrosymmetric site in a crystal structure, the magnetic dipole transition (⁵D₀–⁷F₁) dominates, whereas, in the absence of inversion Eu³⁺ ions in the host lattice, the electric dipole transition

(5D_0 – 7F_2) dominates [13–15]. The centrosymmetric symmetry of the local-environment-center Eu^{3+} ions in the $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ structure was inferred from the normalized intensity ratio of the magnetic dipole transition, as depicted in Figures 3a, S1 and S2. All intensity values in the emission spectra were normalized by dividing them by the maximum intensity value of the electric dipole transition peak. As Eu^{3+} ions occupy the 8-coordinated Y^{3+} site in the $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) structures, the dominant magnetic dipole transition around 590 nm was noticeably decreased up to $x = 0, 1$, and 2. This indicates that the ideal cubic field, characterized by a centrosymmetric Y^{3+} center (D_{4h} point group), was gradually distorted to a dodecahedral field with the substitution of Mg^{2+} and Ge^{4+} ions. Figure 3b presents the emission spectra of $\text{Y}_{2.95}\text{Ce}_{0.05}\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) phosphors (S1 and 2) and relative energy diagrams of cubic and distorted cubic polyhedrons, showcasing the 8-coordinated site geometry for the $5d$ Ce^{3+} orbital energy levels in the host materials. Upon substituting Mg^{2+} and Ge^{4+} ions for Al^{3+} ions in the structure, the distorted 8-coordinated Ce^{3+} ions in the YAG exhibit a significant redshift of the e_g orbital splitting from a normal cubic polyhedron, resulting in emissions from the red-shifted $5d$ energy level caused by the high-crystal-field effect [10–12].

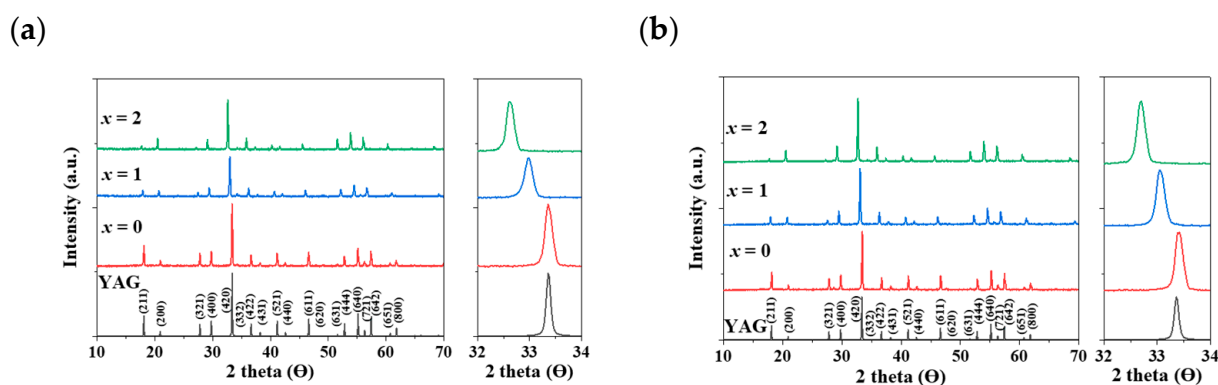
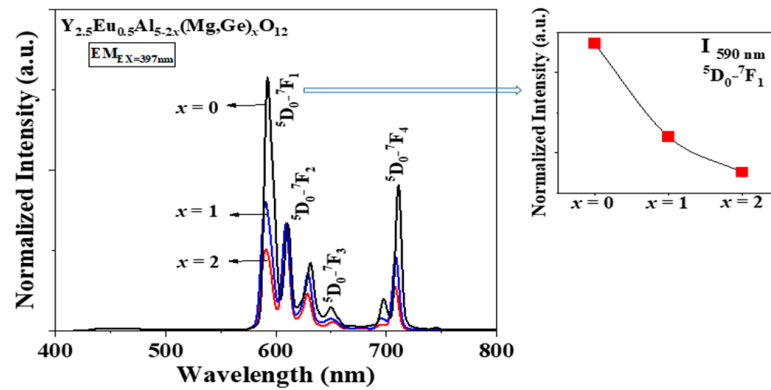


Figure 2. The calculated XRD pattern of YAG with Miller indices and obtained XRD patterns: (a) Eu^{3+} -doped and (b) Ce^{3+} -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) phosphors.

In Figure 4a, the unit cell and local structure of the dodecahedral site in $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ are depicted. Ce^{3+} ions engaged in the Y^{3+} site of garnet structures can emit light due to the distortion factor expressed by the ratio of dodecahedral edges. The four short and long $\text{Y}(\text{Ce})\text{-O}$ bond distances in the garnet structures can be influenced by the deviation of O-O bonds shared with adjacent dodecahedra (d_{88}) and two non-shared tetrahedra (d_{81}) [6]. This deviation in the local structural arrangement around the Ce^{3+} ions within the garnet lattice can have an impact on the energy levels of the Ce^{3+} ions [6]. As distortion increases due to the compression on the cube, the maximum emission shifts to longer wavelengths according to the lower excited state of energy level in the cubic crystal field splitting. Figure 4b summarizes distortion parameters including d_{88} , d_{68} , d_{81} , d_{88}/d_{81} , and d_{68}/d_{81} for Ce^{3+} -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) phosphors. The edge-sharing distance of d_{88} and distortion parameter of d_{88}/d_{81} gradually decreased by substituting Mg-Ge ions in the structures, indicating that the compression of the cube was released by the decrease in distortion. However, the maximum emission wavelength of the Ce^{3+} d - f transition shifts to longer wavelengths, as shown in Figure 3. Furthermore, the centrosymmetric Eu^{3+} emission decreased when $x = 0$ to 1 and 2 in Eu^{3+} -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ garnet phosphors. When Mg^{2+} - Ge^{4+} ions were doped into the $\text{Y}_3\text{Al}_5\text{O}_{12}$ structure, the bond length of Mg-O among Y-O , Al-O , and Ge-O bonds from the structure analysis solely increased with increasing cell volumes, as shown in Figure 1c. For the distorted Eu^{3+} and Ce^{3+} cubic sites in the $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ garnet structures, the parameter of dodecahedral and octahedral edge-sharing should be estimated as a distortion factor. Figure 4b illustrates the steady increase in edge-sharing distance d_{68} and distortion ratio of d_{68}/d_{81} in terms of key

distortion parameters, resulting in the non-centrosymmetric manners and the redshift of the maximum emission wavelength.

(a)



(b)

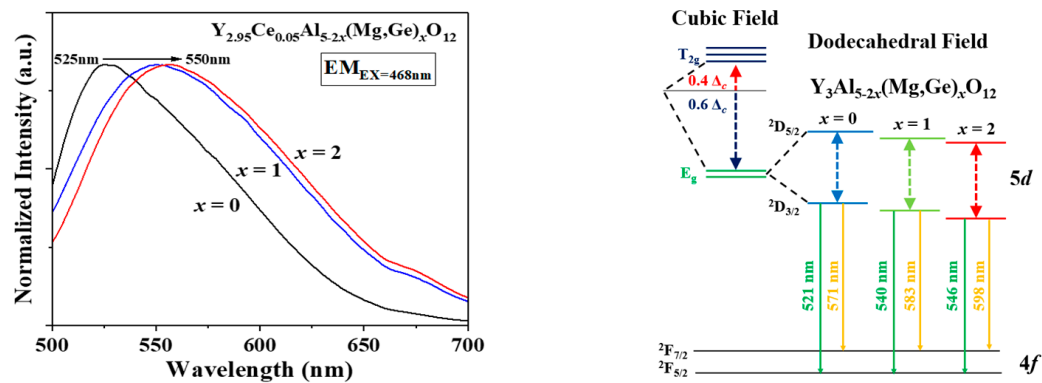


Figure 3. The emission spectra of (a) Eu^{3+} -doped and (b) Ce^{3+} -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) phosphors with relative centrosymmetric intensity and energy-level diagram.

(a)

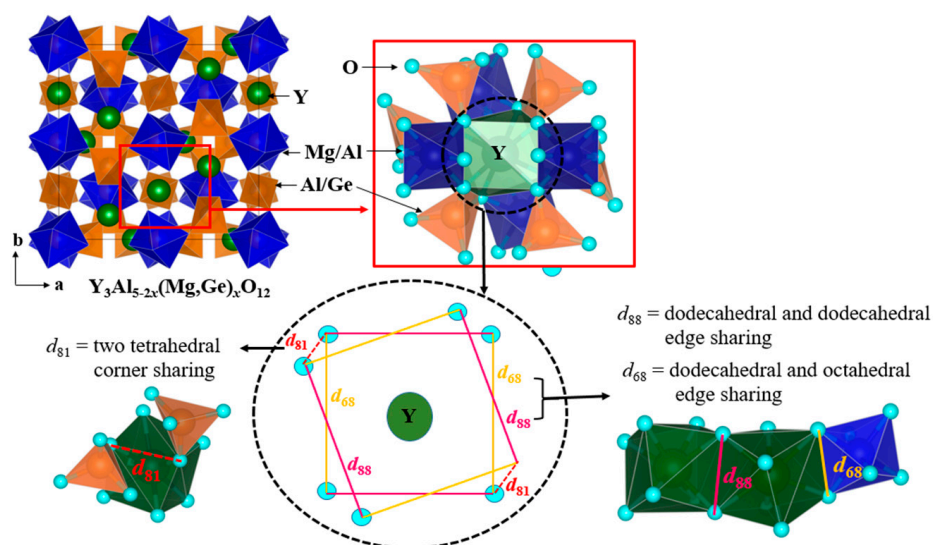
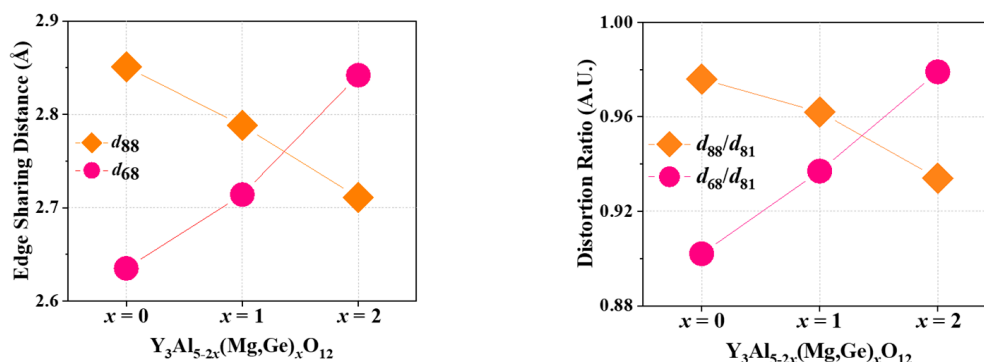


Figure 4. Cont.

(b)



$\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$	d_{88}	d_{68}	d_{81}	d_{88}/d_{81}	d_{68}/d_{81}
$x = 0$	2.851	2.635	2.922	0.976	0.902
$x = 1$	2.788	2.714	2.898	0.962	0.937
$x = 2$	2.711	2.842	2.903	0.934	0.979

Figure 4. (a) Unit cell and local structure of the dodecahedral site in $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ (b) distortion parameters of d_{88} , d_{68} , d_{81} , d_{88}/d_{81} , and d_{68}/d_{81} for Ce^{3+} -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) phosphors.

4. Conclusions

$\text{Eu}^{3+}/\text{Ce}^{3+}$ -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) phosphors were synthesized using a solid-state reaction method assisted by excess LiF or Li_2CO_3 flux at high temperature. Synchrotron powder X-ray diffraction analysis confirmed that the single-phase of $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 1$ and 2) garnet materials possessed a cubic unit cell ($\text{Ia}\bar{3}\text{d}$) with lattice parameters of $a = 12.1479(2)$ Å and $a = 12.2628(1)$ Å, respectively. These garnet structures consisted of an 8-coordination environment for Y^{3+} with $(\text{Mg}^{2+}, \text{Al}^{3+}(1))\text{O}_6$ octahedra and $(\text{Al}^{3+}(2), \text{Ge}^{4+})\text{O}_4$ tetrahedra. Interestingly, the distance value of the $\text{Mg,Al}(1)\text{O}_6$ octahedra only increased with the doping of Mg^{2+} and Ge^{4+} ions into the YAG host lattice. Upon doping Eu^{3+} or Ce^{3+} ions into the $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) garnet structure, the resulting phosphors exhibited increases in non-centrosymmetric and strong crystal field splitting manners with increasing contents of Mg^{2+} and Ge^{4+} ions. This indicated that the cubic polyhedra were compressed by the increase in distortion. The distortion factor of dodecahedral–dodecahedral edge sharing/non-edge sharing (d_{88}/d_{81}) decreased with the substitution of Mg^{2+} – Ge^{4+} ions, while the distortion factor of dodecahedral–octahedral edge sharing/non-edge sharing (d_{68}/d_{81}) gradually increased. In $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ($x = 0, 1, 2$) garnet structures, when substituting ions in octahedral and tetrahedral sites, the dodecahedral–octahedral edge sharing/non-edge sharing (d_{68}/d_{81}) should be considered as the most crucial distortion parameter.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma17102445/s1>, Figure S1: The X-ray diffraction patterns and excitation and emission spectra of Eu^{3+} - and Ce^{3+} -doped $\text{Y}_3\text{Al}_{5-2x}(\text{Mg,Ge})_x\text{O}_{12}$ ((A) $x = 0$, (B) $x = 1$, (C) $x = 2$) phosphors.; Figure S2: The excitation and emission spectra of (A) $\text{Y}_{2.5}\text{Eu}_{0.5}\text{Mg}_x\text{Al}_{5-2x}\text{Ge}_x\text{O}_{12}$ and (B) $\text{Y}_{2.95}\text{Ce}_{0.05}\text{Mg}_x\text{Al}_{5-2x}\text{Ge}_x\text{O}_{12}$ ($x = 0$ –2).

Author Contributions: S.P.: Supervision, Conceptualization, Methodology, Writing—review and editing. H.H.: Synthesis, Data curation, Software, Writing—original draft. S.Y.: Data curation, Software, Writing—original draft. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the “Regional Innovation Strategy (RIS)” through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (MOE) (2023RIS-007).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The authors state that data supporting the study in the manuscript are available on reasonable request. Informed consent was obtained from all subjects involved in the study.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Naira, G.B.; Swarta, H.C.; Dhoble, S.J. A review on the advancements in phosphor-converted light emitting diodes (pc-LEDs): Phosphor synthesis, device fabrication and characterization. *Prog. Mater. Sci.* **2020**, *109*, 100622. [\[CrossRef\]](#)
2. Ye, S.; Xiao, F.; Parn, Y.X.; Ma, Y.Y.; Zhang, Q.Y. Phosphors in phosphor-converted white light-emitting diodes: Recent advances in materials, techniques and properties. *Mater. Sci. Eng. R* **2010**, *71*, 1–34. [\[CrossRef\]](#)
3. Schubert, E.F.; Kim, J.K. Solid-state light sources getting smart. *Science* **2005**, *308*, 1274–1278. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Blasse, G.; Bril, A. A new phosphor for flying-spot cathode-ray tube for color television: Yellow-emitting $\text{Y}_3\text{Al}_5\text{O}_{12}\text{-Ce}^{3+}$. *Appl. Phys. Lett.* **1967**, *11*, 53–55. [\[CrossRef\]](#)
5. Kim, Y.; Park, S. Eu^{2+} , Mn^{2+} co-doped $\text{Ba}_9\text{Y}_2\text{Si}_6\text{O}_{24}$ phosphors based on near-UV-excitable LED lights. *Mater. Res. Bull.* **2014**, *49*, 469–474. [\[CrossRef\]](#)
6. Ueda, J.; Tanabe, S. Review of luminescent properties of Ce^{3+} -doped garnet phosphors: New insight into the effect of crystal and electronic structure. *Opt. Mater. X* **2019**, *1*, 100018. [\[CrossRef\]](#)
7. Xia, Z.; Meijerink, A. Ce^{3+} -Doped garnet phosphors: Composition modification, luminescence properties and applications. *Chem. Soc. Rev.* **2017**, *46*, 275–299. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Berends, A.C.; van de Haar, M.A.; Krames, M.R. YAG: Ce^{3+} Phosphor: From Micron-Sized Workhorse for General Lighting to a Bright Future on the Nanoscale. *Chem. Rev.* **2020**, *120*, 13461–13479. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Dobrzycki, L.; Bulska, E.; Pawlak, D.A.; Frukacz, Z.; Woźniak, K. Structure of YAG Crystals Doped/Substituted with Erbium and Ytterbium. *Inorg. Chem.* **2004**, *43*, 7656–7664. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Shang, M.; Fan, J.; Lian, H.; Zhang, Y.; Geng, D.; Lin, J. A Double Substitution of $\text{Mg}^{2+}\text{-Si}^{4+}/\text{Ge}^{4+}$ for $\text{Al}(1)^{3+}\text{-Al}(2)^{3+}$ in Ce^{3+} -Doped Garnet Phosphor for White LEDs. *Inorg. Chem.* **2014**, *53*, 7748–7755. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Pan, Z.; Li, W.; Xu, Y.; Hu, Q.; Zheng, Y. Structure and redshift of Ce^{3+} emission in anisotropically expanded garnet phosphor $\text{MgY}_2\text{Al}_4\text{SiO}_{12}\text{:Ce}^{3+}$. *RSC Adv.* **2016**, *6*, 20458–20466. [\[CrossRef\]](#)
12. He, C.; Ji, H.; Huang, Z.; Wang, T.; Zhang, X.; Liu, Y.; Fang, M.; Wu, X.; Zhang, J.; Min, X. Red-shifted emission in $\text{Y}_3\text{MgSiAl}_3\text{O}_{12}\text{:Ce}^{3+}$ garnet phosphor for blue light-pumped white light-emitting diodes. *J. Phys. Chem. C* **2018**, *122*, 15659–15665. [\[CrossRef\]](#)
13. Yen, W.M.; Shionoya, S. *Phosphor Handbook*; CRC Press: Boca Raton, FL, USA, 1999.
14. Park, C.; Park, S. Centrosymmetric and non-centrosymmetric structural and optical study of Eu^{3+} ions in $(\text{Ba,Ca,Na})_9(\text{Al,Y})_2\text{Si}_6\text{O}_{24}$ orthosilicate phosphors. *Opt. Mater.* **2022**, *123*, 111863. [\[CrossRef\]](#)
15. Pater, D.K.; Vishwanadh, B.; Sudarsan, V.; Kulshreshtha, S.K. Difference in the Nature of Eu^{3+} Environment in Eu^{3+} -Doped BaTiO_3 and BaSnO_3 . *J. Am. Ceram. Soc.* **2013**, *96*, 3857–3861.
16. Shin, S.; Yang, S.; Lee, S.-H.; Shin, T.J.; Park, S. Distinctive occurrences of green-yellow luminescence from orthogermanate-type $\text{Ba}_9\text{Y}_2(\text{GeO}_4)_6\text{:Ce}^{3+}$, Na^+ phosphors under blue excitation and white-light performance with light-emitting diodes. *J. Alloys Compd.* **2022**, *897*, 163213. [\[CrossRef\]](#)
17. Rodríguez-Carvajal, J.; Roisnel, T. FullProf.98 and WinPLOTR New Windows Applications for Diffraction. *Commission on Powder Diffraction, IUCr, Newsletter*, 20 May–August 1998.
18. Rodríguez-Carvajal, J. Recent developments of the program FullProf. *Commission on Powder Diffraction, IUCr, Newsletter*, 26 December 2001.
19. Shannon, R.D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst.* **1976**, *A32*, 751–767. [\[CrossRef\]](#)

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