

# Flux Crystal Growth, Crystal Structure, and Optical Properties of New Germanate Garnet $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$

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## Abstract

A new germanate garnet compound,  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , was synthesized via flux crystal growth. Truncated spherical, reddish-orange single crystals with a typical size of 0.1–0.3 mm were grown out of a  $\text{BaCl}_2$ – $\text{CaCl}_2$  melt. The single crystals were characterized by single-crystal X-ray diffraction analysis, which revealed that it adopted a cubic garnet-type structure with  $a = 12.5487(3)$  Å in the space group  $Ia\bar{3}d$ . Its composition is best described as  $A_3B_2C_3O_{12}$ , where Ce/Ca, Mg, and Ge occupied the  $A$ ,  $B$ , and  $C$  sites, respectively. A UV–vis–NIR absorption spectroscopy measurement on the germanate garnet revealed a clear absorption edge corresponding to a band gap of 2.21 eV ( $\lambda = 561$  nm). First-principle calculations indicated that the valence band maximum was composed of Ce  $4f$  bands, whereas the conduction band minimum mainly consisted of Ce  $5d$  bands. These findings explain the observed absorption edge through the Ce  $4f \rightarrow 5d$  absorption. Photoluminescence emission spectra exhibited a very broad peak centered at 600 nm, corresponding to transition from the lowest energy  $d$  level to the  $4f$  levels.

## 1 Introduction

The garnet structure, having the general chemical formula  $\{A\}_3[B]_2(C)_3O_{12}$ , has been widely studied as a host material for various optical applications, such as laser amplifiers, color converters, scintillators, and cathode ray phosphors [1]. In particular, the  $Ce^{3+}$ -doped  $Y_3Al_5O_{12}$  garnet phosphor (YAG:Ce) is one of the most interesting materials in terms of practical application as a blue-to-yellow converter in white-emitting diodes. Although YAG:Ce exhibits good thermal and chemical stability and high luminescence efficiency, improvements to the low thermal quenching temperature and cool correlated color temperature remain significant issues [2] [3] [4]. In principle, the  $5d-4f$  emission bands in  $Ce^{3+}$ -doped phosphors are strongly influenced by the host lattice through crystal field splitting of the  $5d$  levels of the  $Ce^{3+}$  ion. In the garnet host, there are three types of cation sites: the  $\{A\}$  site with 8-fold dodecahedral coordination, the  $[B]$  site with 6-fold octahedral coordination, and the  $(C)$  site with 4-fold tetrahedral coordination (Figure 1). The  $A$  site is typically occupied by rare-earth ( $RE$ ) ions such as  $La^{3+}$ ,  $Gd^{3+}$ , or  $Lu^{3+}$ , as well as by  $Y^{3+}$ , and by alkaline earth ions such as  $Ca^{2+}$ . The  $B$  site is occupied by smaller ions that prefer octahedral coordination environments, such as  $Mg^{2+}$ ,  $Mn^{3+}$ ,  $Fe^{3+}$ ,  $Sc^{3+}$ ,  $Al^{3+}$ , or  $Zr^{4+}$ , while the  $C$  site accommodates ions that take on tetrahedral coordination, including  $Al^{3+}$ ,  $Ga^{3+}$ ,  $Si^{4+}$ , or  $Ge^{4+}$  ions. The dodecahedral site, which the trivalent  $Ce^{3+}$  ion prefers to occupy, connects to the adjacent  $A$ ,  $B$ , and  $C$  sites through common oxygen atoms via corner and edge sharing. Thus, the crystal field impinging on the  $Ce^{3+}$  ions is created not only by the  $A$  site cations but also the  $B$  and  $C$  site cations [5, 6] [7]. Owing to the wide range of cations that can be accommodated by the garnet structure, new compositions of garnet phosphors that compensate for the above-mentioned shortcomings of YAG:Ce have been successfully synthesized.

When considering the crystal chemistry of the garnet family, the ability of the cation sites, especially the  $A$  site, to accommodate different elements, is an important factor [8]. A large number of garnet compounds have been previously reported [1, 9-11] but the variety of  $RE$  ions in the  $A$  site is typically limited to  $RE = Gd-Lu$  and  $Y$ , all smaller than the desirable  $Eu^{3+}$  cation, because incorporation of larger cation causes markedly unfavorable lattice distortions around the dodecahedral sites. To the best of our knowledge, only very few garnet compositions that include early  $RE$  ions larger than  $Gd^{3+}$  have been synthesized (via various techniques such as the sol-gel method and hydrothermal reaction), and include:  $Eu_3Al_5O_{12}$  [12],  $RE_3Te_2Li_3O_{12}$  ( $RE = Pr-Eu$ ) [13],  $RE_3W_2Li_3O_{12}$  ( $RE = Pr, Nd$ ) [13] (Kasper, 1969),  $RE_3Fe_5O_{12}$  ( $RE = Pr-Eu$ ) [14] [15] [16] [17],  $La_3Sc_2Ga_3O_{12}$  [18],  $RE_3Ga_5O_{12}$  ( $RE = Pr-Eu$ ) [19] [20],  $Li_7La_3Zr_2O_{12}$  [21], and  $Li_5La_3Sb_2O_{12}$  [22]. It is notable that even among these, achieving a garnet

composition with  $\text{Ce}^{3+}$  fully occupying the *A* site is challenging; however,  $\text{Ce}^{3+}$  doping as high as 56 at.% with respect to  $\text{Y}^{3+}$  has been achieved in  $\text{YFe}_5\text{O}_{12}$  via the glycothermal process.[23]

In this study, we report the flux crystal growth of the new metastable germanate oxide  $\{\text{Ce}_2\text{Ca}\}[\text{Mg}]_2(\text{Ge})_3\text{O}_{12}$ , which crystallizes in the garnet structure in the space group  $Ia\bar{3}d$  with  $a = 12.5487(3)$  Å. The garnet phase was synthesized via the flux crystal growth method where truncated spherical, reddish-orange single crystals were obtained from a  $\text{BaCl}_2\text{--CaCl}_2$  melt. High-temperature solid state reactions failed to yield the target phase, even as a polycrystalline powder, suggesting that the phase is metastable. Herein we discuss the crystal structure, electronic structure, and optical properties of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ .

## 2 Experimental

### 2.1 Crystal Growth

Single crystals of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  were grown via the flux method using a eutectic  $\text{BaCl}_2\text{--CaCl}_2$  mixture[24]. For  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , a magnesia crucible was loaded with 1 mmol  $\text{CeO}_2$  (Aldrich, 4N), 1 mmol of  $\text{GeO}_2$  (Rare Metallic, 4N), 1 mmol of S (High Purity Materials, 4N), 3.1 mmol of  $\text{BaCl}_2$  (Rare Metallic, 3N), and 3.1 mmol of  $\text{CaCl}_2$  (Rare Metallic, 3N). The top of the tube was closed with a magnesia cap, and the tube was sealed inside a silica tube under vacuum. As described later, the magnesia tube was found to act as a magnesium source. The starting materials were heated in a box furnace to 900 °C at 150 °C/h, held for 25 h, cooled to 500 °C at 5 °C/h, and then allowed to cool naturally to room temperature. The products were washed in distilled water, aided by sonication, before the reddish-orange transparent truncated spherical crystals of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , together with colorless transparent crystals of  $\text{CeOCl}$ , were collected via vacuum filtration. The typical dimensions of the single crystals of the garnet compound were  $0.3 \times 0.3 \times 0.3$  mm<sup>3</sup> (Figure 2). The structure of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  was determined by single-crystal X-ray diffraction.

### 2.2 Single crystal structure determination

X-ray intensity data from an orange polyhedron were collected at 301(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073$  Å) [25]. The data collection covered 100% of the reciprocal space to  $2\theta_{\text{max}} = 75.2^\circ$ , with an average reflection redundancy of 35.3 and  $R_{\text{int}} = 0.064$  after absorption correction. The raw area detector data frames were reduced and corrected for absorption effects using

the SAINT+ and SADABS programs [26] [25]. Final unit cell parameters were determined by least-squares refinement of 3812 reflections taken from the data set. An initial structural model was obtained with SHELXT [27]. Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2018 using the ShelXle interface [28].

### 2.3 Solid state synthesis

The synthesis of polycrystalline powder samples of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  was attempted using  $\text{CeO}_2$ ,  $\text{CaCO}_3$  (or  $\text{CaO}$ ),  $\text{MgO}$ , and  $\text{GeO}_2$  in a stoichiometric ratio. The mixture was ground intimately, pelletized, and heated in a flowing  $\text{N}_2$  or  $\text{H}_2$  (20%)–Ar (80%) mixed gas atmosphere or in an evacuated sealed tube using a tubular furnace at temperatures ranging from 900 to 1500 °C.

### 2.4 XRD, UV-vis, PL, EPL, and magnetic measurements

Single crystals of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  were crushed with an agate mortar and pestle to obtain fine powders used for obtaining synchrotron X-ray powder diffraction (SXRD) patterns, UV–vis diffuse reflectance spectra, and photoluminescence (PL) and photoluminescence excitation (PLE) spectra. The products obtained via solid state reactions were examined at room temperature by powder XRD analysis using a Rigaku MiniFlex X-ray diffractometer ( $\text{Cu } K\alpha$  radiation) in the  $2\theta$  range of 5–65° with a step size of 0.04°. SXRD measurement was performed at room temperature using a one-dimensional detector installed on BL15XU, NIMS beamline at SPring-8 in Japan. The synchrotron radiation X-rays were monochromatized to a wavelength of 0.65298 Å. The  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  powder sample was loaded into a 0.1-mm diameter glass capillary. The diffraction data were recorded in 0.003° increments over the range 2–60° and analyzed by Rietveld refinement using the program RIETAN-FP [29]. Diffuse reflectivity measurements were performed at room temperature using a Shimadzu UV-2600 spectrophotometer equipped with an ISR-2600Plus integration sphere. The diffuse reflectance data were internally converted to absorbance by the instrument using the Kubelka–Munk function. The PLE and emission spectra were recorded using a fluorescence spectrophotometer (Hitachi F-7000). The magnetic susceptibility of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  was measured using a SQUID magnetometer (Quantum Design, MPMS-XL). The crushed single crystals were measured at an applied magnetic field ( $H$ ) of 1 kOe in the range of 10–300 K under both zero-field-cooled (ZFC) and field-cooled (FC) conditions.

### 2.5 First-principles calculations

First-principles total energy calculations of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  were performed using the projector augmented wave method[30][31] as implemented in the Vienna Ab-initio Simulation Package (VASP) [32][33][34]. In the present study, the cut-off energy for the plane wave basis was 550 eV. The exchange-correlation interaction potentials of electrons were handled within a framework of the generalized gradient approximation (GGA) of with the PBEsol type[35]. The configurations of the valence electrons of Ce, Ca, Mg, Ge and O were  $5s^2 5p^6 4f^1 5d^1 6s^2$ ,  $3s^2 3p^6 4s^2$ ,  $2p^6 3s^2$ ,  $3d^{10} 4s^2 4p^2$  and  $2s^2 2p^4$ , respectively. Spin-polarized calculations were carried out. For Ce ions, the effect of the strong correlation interaction of the 4f orbital was treated based on the GGA+ $U$  method. [36] The value of  $U$  was set to be 5.4 eV in this study. [37][38] Structure optimization calculations were carried out until the residual forces were less than 0.02 eV/Å.

### 3 Results and Discussion

#### 3.1 Crystal growth and structure determination

After washing the products inside the magnesia tube with water to remove the solidified flux, we found that reddish-orange single crystals had grown on the inner wall of the tube (Figure 2) alongside with a plate-like pale-purple crystalline CeOCl byproduct. The EDS analysis of the reddish-orange crystals revealed the presence of Ce, Ca, Mg, and Ge in approximate atomic ratios of 1.9:1.0:2.1:2.6. The origin of the magnesium is the magnesia tube that, apparently, was slightly dissolved by the flux during the reaction. Single-crystal X-ray diffraction analysis revealed that the product crystallized in the cubic system with  $a = 12.5479(4)$  Å. The space group  $Ia\bar{3}d$  (space group no. 230) was uniquely determined by the pattern of systematic absences in the intensity data and confirmed by structure solution. The product exhibits a garnet-type structure, wherein the asymmetric unit consists of one mixed Ce/Ca atomic site (Ce1/Ca1, site 24c), one Ge site (Ge1, 24d), one Mg site (Mg1, 16a), and one O site (O1, 96h). The composition of site 24c was determined by trial refinements of several models incorporating cationic elements determined by EDS to be present in the crystals (*i.e.*, only Ce, Ca, Mg, and Ge). Modeling the site with mixed Ce/Ca occupancy resulted in the most reasonable model and is consistent with their similar ionic radii ( $r_{\text{Ce}^{3+}} = 1.143$  Å,  $r_{\text{Ca}^{2+}} = 0.97$  Å) [39] and their observed bond distances to O (2.427(4) and 2.547(4) Å, respectively). To maintain overall charge balance, the Ce and Ca occupancies were fixed at 2/3 Ce and 1/3 Ca. Trial refinements with Ce and Ca occupancies constrained to sum to 1.0 but otherwise free to vary, refined closely to these values, supporting the decision to fix the occupancies at 2/3 Ce and 1/3 Ca. All atoms were refined with anisotropic displacement parameters. The final refined chemical composition was  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ ,

which is consistent with the result of the EDS analysis. The  $R_{\text{int}}$  and  $wR_2$  converged to reasonable values of 3.83 and 5.51%, respectively. The goodness-of-fit value was 1.29. The incorporation of Ce(III) ions into the structure was consistent with the reddish-orange sample color. Details of the structure refinement are listed in Table 1. Atomic coordinates and atomic displacement parameters are listed in Tables 2 and S1, respectively. Selected bond distances and bond angles are compiled in Table 3.

Figure 3 shows the room-temperature synchrotron X-ray diffraction pattern collected from a powder sample obtained by grinding hand-picked single crystals. The model determined by the SCXRD analysis was used for the Rietveld refinement. The calculated pattern well reproduced the observed pattern as the fitting converged smoothly with reasonable reliability factors,  $R_{\text{wp}} = 5.37$ ,  $R_{\text{B}} = 3.45$ , and  $R_{\text{F}} = 2.92$ . The final refined crystallographic data, including the atomic coordinates and isotropic displacement parameters are listed in Table S2. The results are consistent with the results obtained from the SCXRD analysis.

### 3.2 Solid state reaction

Synthesis of a polycrystalline sample of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  was attempted by solid-state reactions using a stoichiometric mixture of  $\text{CeO}_2$ ,  $\text{CaCO}_3$  (or  $\text{CaO}$ ),  $\text{MgO}$ , and  $\text{GeO}_2$ . The reactions were carried out under vacuum, with mixed  $\text{H}_2$ (20%)- $\text{Ar}$ (80%) gas or  $\text{N}_2$  gas atmospheres at temperatures between 900 and 1300 °C. Unfortunately, none of the reaction conditions we examined yielded the target phase; but a substantial amount of unreacted  $\text{CeO}_2$  always remained in the products (see Figure S1). A garnet structure was obtained as a minor phase at 1300 °C in the  $\text{N}_2$  gas atmosphere; however, the lattice parameter of the garnet phase was smaller by 0.5% compared with that for  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  and the product was dark grayish-green. Therefore, if Ce atoms were incorporated into the lattice, the garnet phase obtained by solid state reaction should have a lower Ce concentration than that of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ . Further heating at the same temperature after regrinding and pelletizing resulted in a partial decomposition of the garnet phase and an increase in the amount of  $\text{CeO}_2$ , suggesting that the garnet phase was metastable under these reaction conditions.

### 3.3 Stability of the garnet structure

As described earlier, the garnet structure can accommodate a wide range of elements in the three different cation sites, but the underlying stability of the garnet structure, including its tolerance for RE ions, is not yet well understood. Our present germanate garnet exhibited an unusual occupancy of

two-thirds of the  $A$  sites by  $\text{Ce}^{3+}$  ions, a  $\text{Ce}^{3+}$  concentration substantially higher than the 56 at.%  $\text{Ce}^{3+}$ -doping concentration found in  $\text{Y}_{1-x}\text{Ce}_x\text{Fe}_5\text{O}_{12}$  ( $x = 1.7$ ). [23] Very recently, Song *et al.* have formulated the tolerance factor ( $\tau$ ) of the garnet structure, [40] which is analogous to the Goldschmidt tolerance factor describing the relationship of the chemical compositions and structural stability in perovskites. [41] The  $\tau$  of the garnet structure is expressed as

$$\tau = \frac{3\sqrt{(r_B+r_O)^2 + \frac{4}{9}(r_A+r_O)^2}}{2(r_C+r_O)} \quad (\text{Eq. 1})$$

where  $r_A$ ,  $r_B$ ,  $r_C$ , and  $r_O$  represent the ionic radii of the  $A$ ,  $B$ ,  $C$  site cations and  $\text{O}^{2-}$  ion, respectively. The tolerance factor calculated for more than 100 garnet compounds falls within the range of 0.75 to 1.33. For the formula  $\text{RE}_3\text{B}_2\text{C}_3\text{O}_{12}$ . ( $\text{RE} = \text{La-Lu}$ ,  $\text{Y}$ ;  $\text{B} = \text{C} = \text{Fe, Al, Ga}$ ), the  $\tau$  values systematically increase toward unity with decreasing size of the  $\text{RE}$  ions, e.g., 0.76 to 0.93 from La to Lu for  $\text{RE}_3\text{Al}_5\text{O}_{12}$  and 0.89 to 1.02 for  $\text{RE}_3\text{Fe}_5\text{O}_{12}$ . [40] This is consistent with the general trend observed for their structural stability when containing  $\text{RE}$  ions. The formula  $\text{RE}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  ( $\text{RE} = \text{La-Lu}$ ,  $\text{Y}$ ), including hypothetical compositions, exhibits a similar size dependence of the tolerance factor, but the  $\tau$  values range from 1.06 for La, through 1.07 for Ce, to 1.15 for Lu. The stabilization of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  with a  $\tau$  value close to unity seems to be compatible with the geometric requirements for the garnet structure. However, a favorable tolerance factor does not assure the success of the target phase formation via chemical synthesis. In fact, the solid-state reactions we examined to obtain  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  were not successful. At present, the reason for the large amount of Ce ions incorporated into the garnet lattice is unclear; however, it is likely that the molten salts used in this study play a crucial role in stabilizing the phase under the flux reaction conditions. From the PXRD data of the products obtained by solid state reactions, it is apparent that  $\text{CeO}_2$  was not fully consumed in the reactions, indicating its low reactivity and slow atomic diffusion even at high temperatures. In the flux reaction, the  $\text{BaCl}_2\text{-CaCl}_2$  salt likely dissolves  $\text{CeO}_2$  powder at a relatively low temperature, where the fact that the starting materials are now in solution is expected to decrease considerably the activation energy for reaction between the starting materials and thus yield the target garnet phase. We surmise that the  $\text{Ca-Cl}$  melt at high temperatures under vacuum acts as a reducing agent for Ce ions, likely forming  $\text{Cl}_2$ . The formation of  $\text{Ce}^{3+}$  in the halide melt favors the stabilization of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  as well as of the byproduct  $\text{CeOCl}$ . Sulfur, which was a starting material for the flux reaction, was not found to significantly contribute to either the reduction of Ce



ions nor to the formation of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ . Performing the flux crystal growth in the absence of sulfur results in the same mixed product formation.

### 3.4 Optical and magnetic properties

Figure 4(a) shows the UV–vis absorption spectrum collected for  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , exhibiting a clear absorption edge at around 560 nm. An extrapolation of the linear portion of the absorption curve to the  $x$ -axis indicates an optical band gap of  $E_g = 2.22$  eV. This steep increase in the absorption is followed by two broad sub-bands centered at 458 and 305 nm, also observed in the UV–vis absorption curves of YAG:Ce. These two absorption peaks can be assigned to the optical transitions from the Ce  $4f$  ground state to the lowest and second-lowest excited states of the Ce  $5d$  orbitals ( $5d_1$  and  $5d_2$ , respectively). [2] A third weak peak at around 250 nm is probably due to defects or impurities. The lowest absorption is in the blue spectral region, which results in the reddish orange color of the garnet compound. The photoluminescence emission (PE) and excitation (PLE) spectra of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  are shown in Figure 4(b). The PE spectrum excited at 519 nm contains a broad band centered around 600 nm, which could be assigned to the transition from the  $5d_1$  level to the two  $4f$  levels split by spin-orbit coupling into  $^2F_{5/2}$  and  $^2F_{7/2}$ . The maximum value of the emission band for  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  is red-shifted compared to that of  $\text{Y}_2\text{Mg}_3\text{Ge}_3\text{O}_{12}:\text{Ce}(2\%)$  [42] but comparable to that for  $\text{Gd}_2\text{Mg}_3\text{Ge}_3\text{O}_{12}:\text{Ce}(2\%)$  [43].

Figure 5 shows the temperature evolution of the magnetic susceptibility  $\chi$  ( $= M/H$ ) measured in a magnetic field  $H = 1$  kOe. Both the ZFC and FC data increase smoothly with decreasing temperature, indicative of a paramagnetic state persisting down to low temperatures. No hysteresis was observed in the temperature range between 10 and 300 K. Fitting  $\chi(T)$  to the Curie–Weiss law yields  $C = 1.407(4)$  (emu K/mol) and  $\theta = -59.9(9)$  K, where  $C$  and  $\theta$  stand for the Curie and Weiss constants, respectively. The  $C$  value is somewhat smaller than the theoretical value expected from two mol  $\text{Ce}^{3+}$  ions with  $^2F_{5/2}$  per formula unit. The negative  $\theta$  value suggests that  $\text{Ce}^{3+}$  ions are antiferromagnetically coupled to each other. The absence of a long-range magnetic order is probably due to a random distribution of Ce and Ca atoms on the  $24c$  site

### 3.5 Theoretical calculations

From the experimental crystal structure analysis of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , Ce and Ca ions are found to occupy the  $A$  site of the  $A_3B_2C_3\text{O}_{12}$  garnet structure. In first principles calculations using structure models under periodic boundary conditions, mixed occupancy of atomic sites cannot be directly



computed. Therefore, we initially determined the preferred distribution of Ce and Ca ions on the *A* site with a ratio of 2:1 in a fixed size model having the garnet structure. We chose a primitive unit cell of the garnet structure as a base model. Structure models having symmetrically non-equivalent configurations of Ce and Ca ions were constructed. In total, 20 independent configurations of Ce and Ca ions on the *A*-site were found from the base model using the CLUPAN code. [44] The mesh size of *k*-point sampling was  $3 \times 3 \times 3$  in the Brillouin zone of the input structure models. We compared the total energies of these models obtained by structure optimization calculations.

From the series of total energy calculations of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  models, the most stable configuration that was found is shown in Figure 6. We analyzed the electronic structures of this model. Figure 7 shows total density of states (tDOS) and projected partial density of states (pDOS) of each constituent element. In Figure 7, the energy level of a valence band top is set to be 0 eV on the horizontal axes. Positive and negative values on the vertical axes indicate the DOS of up-spin and down-spin, respectively. The tDOS values show that the calculated band gap is about 2.2 eV, which is in a good agreement with the value estimated from the UV–vis absorption spectrum. It can be clearly seen that very sharp spikes of the DOS exist at the topmost energy levels of the occupied states. Such sharp DOS peaks indicate strong localization states of the electron orbitals. From the pDOS values, we can see that these peaks originate from the occupied 4f orbital of the  $\text{Ce}^{3+}$  ions. The DOS near the conduction band bottom seems to be mainly composed of an unoccupied 5d orbital of  $\text{Ce}^{3+}$  ions and a 4s orbital of the  $\text{Ge}^{4+}$  ions.

## 4 Conclusion

We have successfully synthesized a new metastable germanate garnet,  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , using a flux crystal growth method. Reddish-orange single crystals were grown in a reactive MgO tube; however, the polycrystalline sample could not be prepared via a solid state reaction. Flux reactions are clearly useful for extending the garnet family to compositions that include the early lanthanide metals, especially those larger than Gd, which have been less explored. The PL intensity was so weak that it could not be confirmed visually; this is probably due to  $\text{Ce}^{3+}$ -concentration quenching effects or photoionization involving a charge transfer between  $\text{Ce}^{3+}$  and  $\text{Ge}^{4+}$ . [45, 46] Work to synthesize La or RE ( $< \text{Ce}^{3+}$ )-doped  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  and the substitution of Si for Ge, which would enhance PL properties, is ongoing.

## 5 Conflict of Interest

274 The authors declare that the research was conducted in the absence of any commercial or financial  
275 relationships that could be construed as a potential conflict of interest.

## 276 **6 Author Contributions**

277 The manuscript was written through contributions of all authors. All authors have given approval to  
278 the final version of the manuscript.

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## 286 **9 Reference**

## 287 **10 Supplementary Material**

288 CIF files of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{10}$  based on single crystal XRD data. Anisotropic displacement parameters  
289 for  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{10}$ . Crystallographic data obtained from the Rietveld refinement against the SXRD  
290 data. Powder XRD data collected from the products of the solid state reactions.

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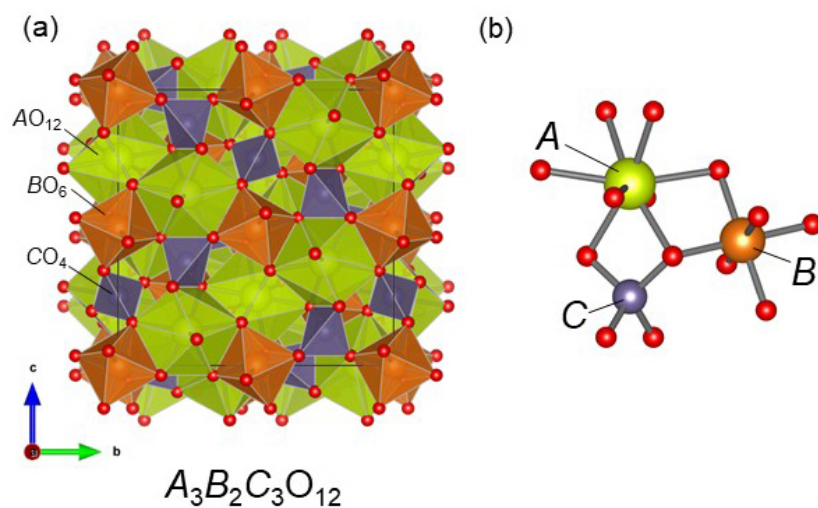


Figure 1. (a) Crystal structure of the garnet compound  $A_3B_2C_3O_{12}$  and (b) the local coordination environment around the metal cations. In  $Ce_2CaMg_2Ge_3O_{12}$ , Ce/Ca, Mg, and Ge atoms occupy the A, B, and C sites, respectively.

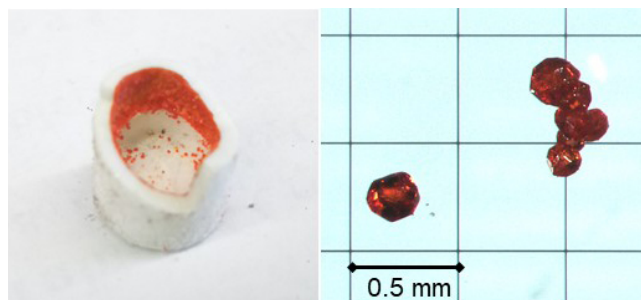


Figure 2. Photographs of single crystals of  $Ce_2CaMg_2Ge_3O_{12}$  grown on the inner wall of a MgO crucible.

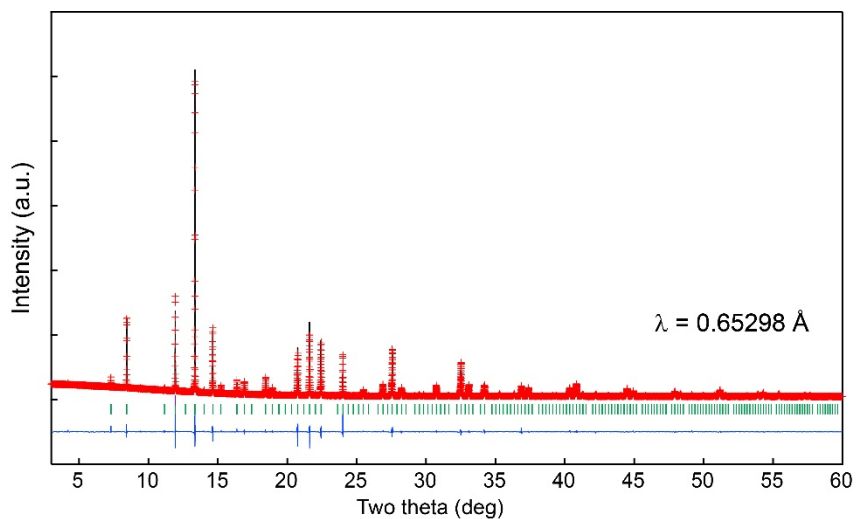


Figure 3. Observed (crosses), calculated (upper solid line), and difference (lower solid line) plots obtained from the Rietveld analysis of the room temperature synchrotron X-ray powder diffraction data collected using ground single crystals of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ . Vertical lines represent expected Bragg peak positions.

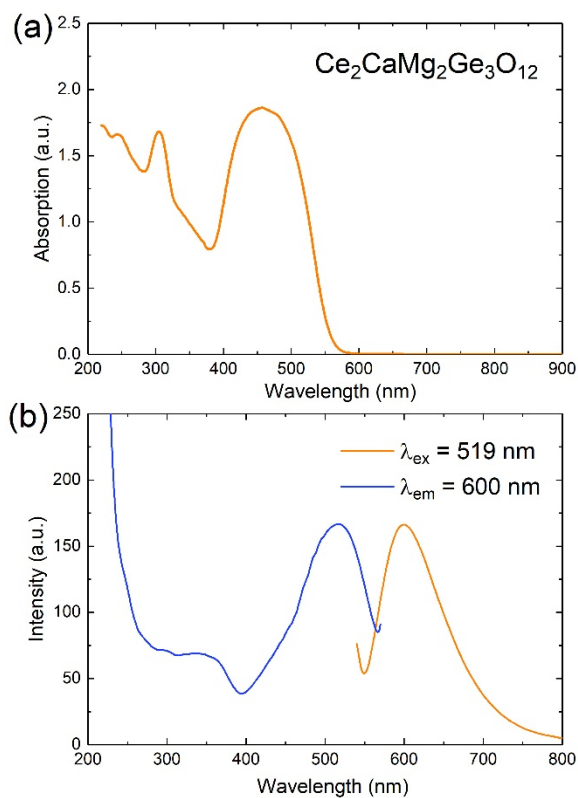


Figure 4. (a) UV-vis absorption spectrum, and (b) photoluminescence emission ( $\lambda_{\text{ex}} = 519 \text{ nm}$ ) and excitation ( $\lambda_{\text{em}} = 600 \text{ nm}$ ) spectra for  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , collected at room temperature.

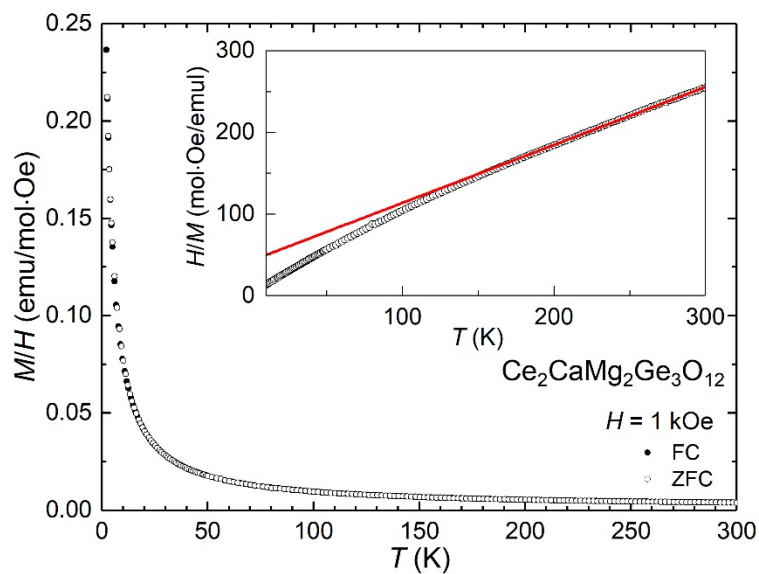


Figure 5. Magnetic susceptibility of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$ , measured in a magnetic field of 1 kOe. The inset shows its inverse  $\chi$  vs  $T$  plot. The red solid line is the fit to the Curie-Weiss law.

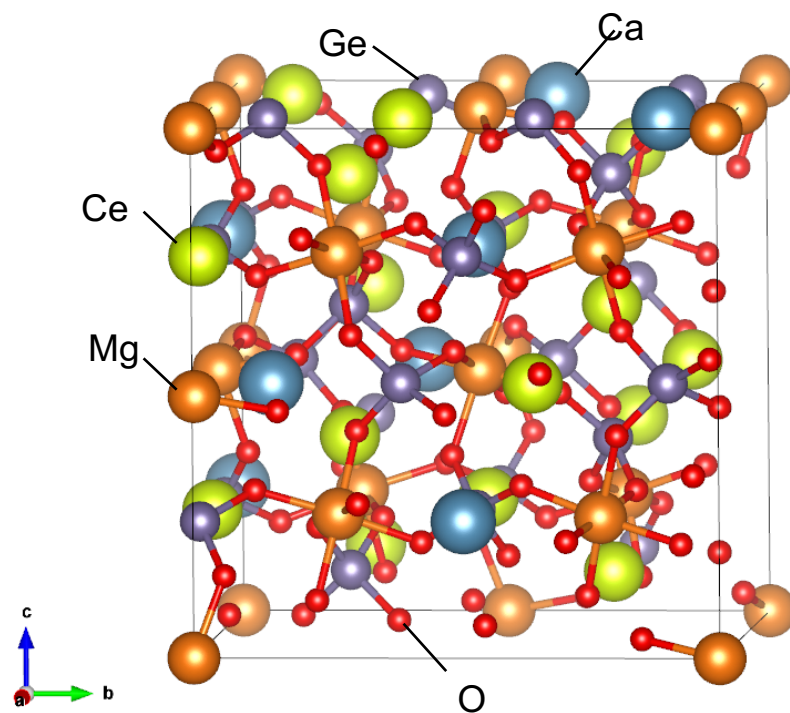


Figure 6. Most stable configurations of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  found by a series of first principles calculations in the present study. Search conditions are described in the main text.

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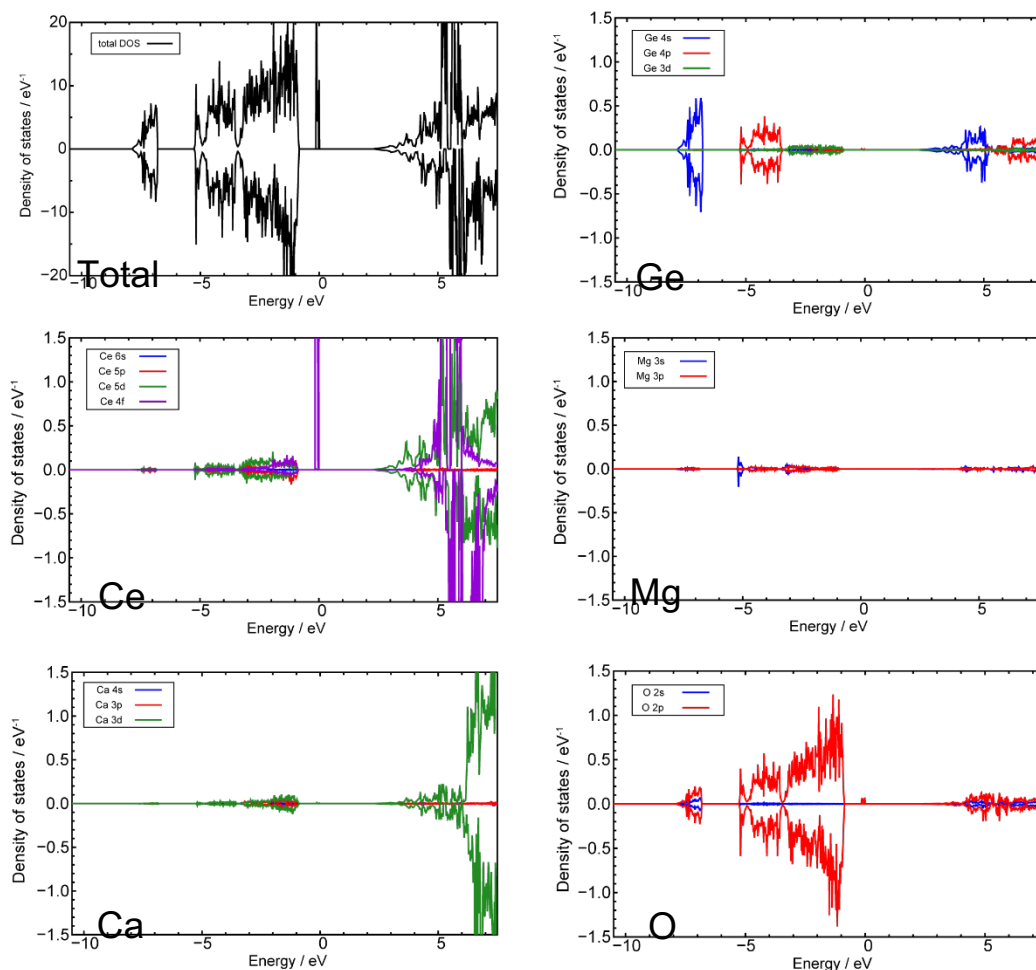


Figure 7. Total and projected partial density of states calculated from the model shown in Fig.6. The energy level of a valence band top is set to be 0 eV on the horizontal axes. Positive and negative values of the vertical axes indicate the DOS of up-spin and down-spin, respectively. Blue, red, green, and purple lines indicate the *s*, *p*, *d*, and *f* orbitals of each element, respectively.

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Table 1. Results of structural refinement of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  using single-crystal XRD data

|                                                                       |                   |
|-----------------------------------------------------------------------|-------------------|
| Space group                                                           | <i>Ia-3d</i>      |
| Crystal system                                                        | Cubic             |
| $a$ (Å)                                                               | 12.5487(3)        |
| $V$ (Å <sup>3</sup> )                                                 | 1976.04(14)       |
| $Z$                                                                   | 8                 |
| Density (g/cm <sup>3</sup> )                                          | 5.235             |
| Temperature (K)                                                       | 301(2)            |
| $\theta$ range (°)                                                    | 3.978–37.590      |
| $\mu$ (mm <sup>-1</sup> )                                             | 18.765            |
| Crystal dimensions (mm <sup>3</sup> )                                 | 0.080×0.050×0.030 |
| Collected reflections                                                 | 17162             |
| Unique reflections                                                    | 445               |
| $R_{\text{int}}$                                                      | 0.0645            |
| GOF                                                                   | 1.286             |
| $R_1(F)$ for $ Fo^2 > 2\sigma(Fo^2) $                                 | 0.0383            |
| $R_w(Fo^2)$                                                           | 0.0551            |
| $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e/Å <sup>3</sup> ) | 0.931/−1.069      |

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Table 2. Atomic coordinates and equivalent isotropic displacement parameters  $U_{\text{eq}}$  for  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  obtained from the structure refinement using single-crystal XRD data

| Atom | Site | $x$       | $y$       | $z$       | $g^a$ | $U_{\text{eq}}$<br>( $\text{\AA}^2 \times 10^2$ ) |
|------|------|-----------|-----------|-----------|-------|---------------------------------------------------|
| Ce1  | 24c  | 1/8       | 0         | 1/4       | 0.667 | 0.737(15)                                         |
| Ca1  | 24c  | 1/8       | 0         | 1/4       | 0.333 | 0.737                                             |
| Mg1  | 16a  | 0         | 0         | 0         | 1     | 0.75(5)                                           |
| Ge1  | 24d  | 3/8       | 0         | 1/4       | 1     | 0.0660(18)                                        |
| O1   | 96h  | 0.0948(2) | 0.1976(3) | 0.2852(3) | 1     | 0.68(5)                                           |

328 <sup>a</sup>  $g$  represents site occupancy.

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Table 3. Selected interatomic distances and bond angles of  $\text{Ce}_2\text{CaMg}_2\text{Ge}_3\text{O}_{12}$  at 301 K

|           | Bond distance ( $\text{\AA}$ ) |                 | Bond angle (deg) |
|-----------|--------------------------------|-----------------|------------------|
| Ce/Ca–O×4 | 2.427(4)                       | Ce/Ca–O–Mg      | 97.48(12)        |
| Ce/Ca–O×4 | 2.547(4)                       | Ce/Ca–O–Mg      | 101.26(15)       |
| Mg–O×6    | 2.102(3)                       | Ce/Ca–O–Ge×2    | 95.60(13)        |
| Ge–O×4    | 1.766(3)                       | Ce/Ca–O–Ce/Ca×2 | 101.13(14)       |

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