

# Garnet-based complex substituted glass ceramic materials

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## ABSTRACT

The Ce-doped  $\text{Y}_2\text{CaAl}_4\text{GeO}_{12}$  and  $\text{Y}_2\text{MgAl}_4\text{GeO}_{12}$  garnets were fabricated as powders using co-precipitation, and as glass ceramics using the solid-state technique. The structural and photoluminescence properties of these materials were studied. The reflections of the garnet phase for powders and glass ceramics were registered in X-ray diffraction patterns. The shift of the reflections for powders and glass ceramics compared to the YAG reference was caused by the formation of substituted garnets. The photoluminescence properties of the garnet crystallites in the glass ceramics were studied. The localization of  $\text{Ce}^{3+}$  ions in positions with different crystal fields was due to spatial variation in the composition of the garnet crystallites in glass ceramics. The formation of crystallites with a composition gradient was related to the fluctuations in the glass composition in the vicinity of garnet nuclei during their formation.

## 1. Introduction

Garnets doped with Ce are widely used as phosphors in solid-state lighting and other applications, and as scintillation detectors. The  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (YAG:Ce) phosphors are predominantly used, but a wide variety of other garnet-type phosphors offer new options. Garnets are convenient for engineering of their properties by exchanging cations in the garnet structure. Flexibility of the garnet crystalline lattice allows for easier isovalent substitutions of cations. This leads to a change in metal–oxygen bond length and, consequently, affects the luminescence properties of rare-earth dopants due to the distortion of their crystalline surrounding. For example, a spectacular improvement in scintillation light yield was demonstrated by partial substitution of  $\text{Al}^{3+}$  by  $\text{Ga}^{3+}$  in garnet MAG:Ce ( $M = \text{Y, Gd, Lu}$ ) (Kamada et al., 2011), and fast timing was demonstrated for a complex substituted garnet scintillator based on  $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}:\text{Ce}$ , where a part of  $\text{Al}^{3+}$  was substituted by  $\text{Ga}^{3+}$  (Auffray et al., 2016).

Heterovalent substitution is another approach to obtain new compounds with garnet structure. Unlike the isovalently substituted compounds, a charge balance should be considered in the heterovalently substituted garnets. Partial substitution of  $\text{Y}^{3+}$  and  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}/\text{Ca}^{2+}$  and  $\text{Si}^{4+}$  or  $\text{Ge}^{4+}$ , respectively, in YAG:Ce is interesting due to the possibility of obtaining garnets with glass-forming elements, e.g.  $\text{Si}^{4+}$  or  $\text{Ge}^{4+}$ . Glass ceramics are promising types of materials due to the

combination of the transparency of glass and efficiency of the crystalline phase. Furthermore, compared with single crystals, glass ceramics can be obtained in larger volumes in substantially shorter times. A relatively low production price may make glass ceramic materials inexpensive alternatives to single crystals or ceramics in different applications. Therefore, development of new glass ceramics based on garnets has potential.

This study aimed at obtaining  $\text{Y}_2\text{CaAl}_4\text{GeO}_{12}:\text{Ce}$  and  $\text{Y}_2\text{MgAl}_4\text{GeO}_{12}:\text{Ce}$  garnets in the forms of powder and glass ceramics and investigating their structural and luminescence properties. Glasses with composition close to the powders were used. It was assumed that such an approach would result in garnet crystallites in glass ceramics with compositions similar to those of the powders. It should be noted, that YAG based garnets with partial substitution of only  $\text{Al}^{3+}$  ions onto  $\text{Mg}^{2+}$  and  $\text{Ge}^{4+}/\text{Si}^{4+}$  are known and described in literature (Shang et al., 2014), while the substituted garnets in this research have other composition, where part of  $\text{Y}^{3+}$  and  $\text{Al}^{3+}$  ions were substituted onto  $\text{Mg}^{2+}/\text{Ca}^{2+}$  and  $\text{Ge}^{4+}$ , respectively.

## 2. Experimental

### 2.1. Synthesis of powder samples

Initially, the mix of  $\text{Y}(\text{NO}_3)_3$ ,  $\text{GeO}_2$ ,  $\text{Ce}(\text{NO}_3)_3$ , and  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Mg}$

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(NO<sub>3</sub>)<sub>2</sub> was prepared and added under vigorous stirring to the precipitant solution (NH<sub>4</sub>HCO<sub>3</sub> of 200 g/l H<sub>2</sub>O). Then the precipitate was isolated and dried in air at 80 °C. Finally, the material was thermally treated in air in two steps: for 2 h at 600 °C and for 2 h at 1500 °C.

## 2.2. Synthesis of glass ceramic samples

Mixtures of CaCO<sub>3</sub> (or MgCO<sub>3</sub>), SiO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> (or Gd<sub>2</sub>O<sub>3</sub>), Al<sub>2</sub>O<sub>3</sub>, GeO<sub>2</sub>, CeO<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub> were used as the initial reactants. Quantities of initial reactants corresponded to the element ratios in Y<sub>2</sub>CaAl<sub>4</sub>GeO<sub>12</sub>:Ce and Y<sub>2</sub>MgAl<sub>4</sub>GeO<sub>12</sub>:Ce garnets, while the excess of Al<sub>2</sub>O<sub>3</sub> (3% excess), SiO<sub>2</sub> (three times more than GeO<sub>2</sub>) and Li<sub>2</sub>CO<sub>3</sub> (4.5 times less than GeO<sub>2</sub>) were used to form the glass matrix. The mixture was homogenized and then melted at 1550 °C for 2 h in a gas furnace with an atmosphere rich in CO gas. The melt was cast on a steel plate at room temperature, after which the glasses were annealed at 500 °C for 4 h. The annealed glasses were transparent and colorless. To transform the glasses into ceramic material, they were annealed in air at 1500 °C. The glasses containing Ca<sup>2+</sup> and Mg<sup>2+</sup> ions were labeled as Glass 1 and 2, respectively, and the corresponding glass ceramics obtained by their annealing at 1500 °C were labeled GC1 and GC2.

## 2.3. Sample characterization

Devices DRON 3 using CoK $\alpha$  irradiation, or Empyrean using CuK $\alpha$  irradiation, were used for X-ray diffraction (XRD) measurements. The DICVOL06 software from the FULLPROF package was used for the calculations of cell parameters.

Photoluminescence (PL) measurements were performed using the microscopic system WITec Alpha 300S operated in confocal mode and coupled with a spectrometer equipped with a thermoelectrically-cooled CCD camera. An objective with numerical aperture 0.6 was used for excitation and collection of the PL signal, ensuring in-plane spatial resolution of ~250 nm and axial resolution of ~1.6  $\mu$ m. A CW laser diode (ALPHALAS) emitting at 405 nm was exploited for excitation.

Spatially-integrated PL spectra were measured using a xenon lamp as the excitation source, double monochromator (Jobin-Yvon Gemini 180 with 150 or 600 grooves/mm gratings), and nitrogen-cooled CCD detector coupled to a monochromator (Jobin-Yvon Micro HR).

## 3. Results and discussion

The XRD patterns and luminescence spectra of Y<sub>2</sub>CaAl<sub>4</sub>GeO<sub>12</sub>:Ce and Y<sub>2</sub>MgAl<sub>4</sub>GeO<sub>12</sub>:Ce garnet powders are presented in Fig. 1.

In the XRD patterns of both samples, intense reflections corresponding to the garnet phase (space group Ia3d, PDF [33–0040]) were observed. The Y<sub>2</sub>CaAl<sub>4</sub>GeO<sub>12</sub>:Ce had a larger cell parameter compared with Y<sub>2</sub>MgAl<sub>4</sub>GeO<sub>12</sub>:Ce: 12.0531(2) and 12.0014(5) Å, respectively. This is a result predominantly from replacement of Y<sup>3+</sup> ions by larger

**Table 1**

Ionic radii for Y<sup>3+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ge<sup>4+</sup> and Si<sup>4+</sup> at definite coordination numbers (c.n.) (Shannon, 1976).

| Ion              | Ionic radii (Å) |       |      |
|------------------|-----------------|-------|------|
| c.n.             | 8               | 6     | 4    |
| Mg <sup>2+</sup> | 0.89            | 0.72  | 0.57 |
| Ca <sup>2+</sup> | 1.12            | 1     | –    |
| Y <sup>3+</sup>  | 1.019           | 0.9   | –    |
| Al <sup>3+</sup> | –               | 0.535 | 0.39 |
| Ge <sup>4+</sup> | –               | 0.53  | 0.39 |
| Si <sup>4+</sup> | –               | 0.4   | 0.26 |

Ca<sup>2+</sup> (localized in dodecahedral sites), while Al<sup>3+</sup> and Ge<sup>4+</sup> had close values of ionic radii in both octahedral and tetrahedral sites. The Mg<sup>2+</sup> ions had a smaller radius than Y<sup>3+</sup> ions, which explains its smaller cell parameter value. Typical values of ionic radii for Y<sup>3+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Ge<sup>4+</sup> are shown in Table 1.

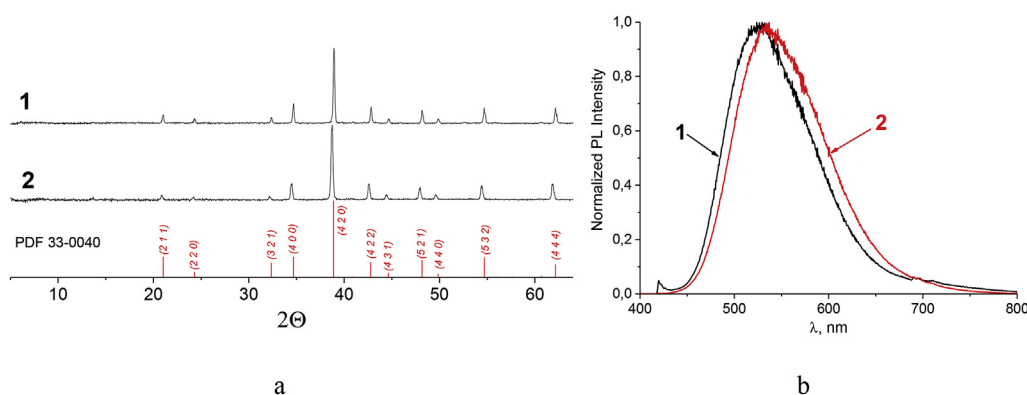
The PL spectra of the samples studied showed wide bands corresponding to the Ce<sup>3+</sup> ion emission (Fig. 1b). They consisted of two strongly overlapping bands corresponding to the 5d  $\rightarrow$  <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> transitions of the Ce<sup>3+</sup> (Tratsiak et al., 2017). A blue shift of the band was observed in the Y<sub>2</sub>CaAl<sub>4</sub>GeO<sub>12</sub>:Ce sample, possibly caused by a partial substitution of Y<sup>3+</sup> by Ca<sup>2+</sup> ions. The substitution resulted in an increase of the length of the bond between Ca<sup>2+</sup> and O<sup>2–</sup> and, as a result, in decreases in the crystal field. The increased bond length between Ce<sup>3+</sup> and O<sup>2–</sup> ions resulted in a blue shift of the emission spectrum. In the case of substitution of Y<sup>3+</sup> by Mg<sup>2+</sup> ions, a decrease of the Ce–O bond occurred, the crystal field increased with a resulting red shift in the emission band.

The XRD patterns of the glass ceramics obtained by heat treatment of Glass 1 and 2 at 1500 °C are presented in Fig. 2.

Only the reflections of the garnet phase were observed in XRD patterns (Fig. 2). The shift of the reflections in relation to their positions in YAG indicated the formation of substituted garnets. A smaller cell parameter value for GC2 than GC1 is consistent with the substitution of Y<sup>3+</sup> by Ca<sup>2+</sup> and Mg<sup>2+</sup>, respectively. For glass ceramics GC1 and GC2 the cell parameters were smaller (11.9823 and 11.9429 Å, respectively) than those for Y<sub>2</sub>CaAl<sub>4</sub>GeO<sub>12</sub>:Ce and Y<sub>2</sub>MgAl<sub>4</sub>GeO<sub>12</sub>:Ce powders. This difference might be explained by partial substitution of Al<sup>3+</sup> by Si<sup>4+</sup>, which was present in excess in the glass matrix. In contrast to Ge<sup>4+</sup>, Si<sup>4+</sup> had smaller ionic radii in both lattice positions (Table 1).

The dependence of the PL properties on the garnet composition in the vicinity of the emitting Ce<sup>3+</sup> ions was studied using confocal microscopy. Typical mapping images of PL band peak position are presented for GC1 and GC2 in Fig. 3 a and b.

A blue shift of the PL peak position from the crystallite center to its border was observed. This feature might be explained by localization of Ce<sup>3+</sup> ions in positions with different crystal fields due to the spatial variation in composition of the garnet crystallite. The formation of



**Fig. 1.** The XRD patterns (a) and luminescence spectra at 450-nm excitation (b) of Y<sub>2</sub>CaAl<sub>4</sub>GeO<sub>12</sub>:Ce (1) and Y<sub>2</sub>MgAl<sub>4</sub>GeO<sub>12</sub>:Ce (2) garnet powders.

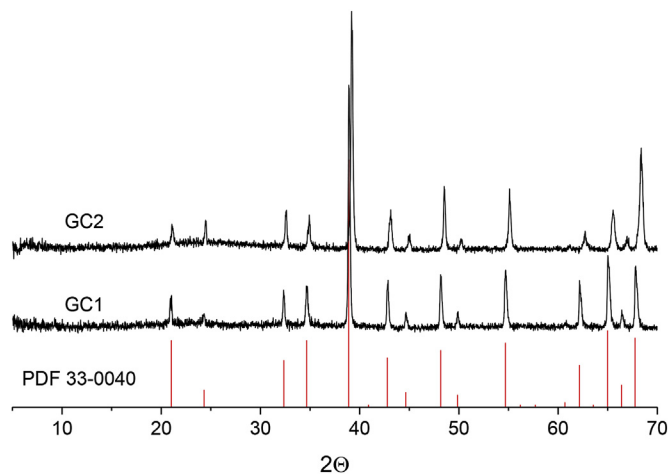


Fig. 2. The XRD patterns of GC1 and GC2 obtained by heat treatment of Glass 1 and 2 at 1500 °C. Vertical lines correspond to the reference reflection [33-0040] of YAG single crystal.

crystallites with composition gradient may be related to fluctuations in glass composition in the vicinity of garnet nuclei during their formation. The composition fluctuations might be caused by a small discrepancy between the ratios of elements in the garnet structure and in the glass matrix. Thus, incorporation of excessive elements into new nuclei or during their subsequent growth is quite probable and should lead to continuous variation in garnet composition. The proposed mechanism of crystallite formation is similar to the epitaxial growth of films, in which each subsequent layer inherits the structure of the previous one but with a slightly different composition.

The bands in PL spectra for GC1 and GC2 had the same nature as described for powders (Fig. 3c). The red shift of emission band for GC2

with respect to its position in GC1 was the effect of cation substitution similar to that described for  $\text{Y}_2\text{CaAl}_4\text{GeO}_{12}:\text{Ce}$  and  $\text{Y}_2\text{MgAl}_4\text{GeO}_{12}:\text{Ce}$  garnets. It should be noted that emission bands of GC1 and GC2 were red shifted compared with corresponding powders – the partial composition modification of garnet crystallites in glass ceramics, as previously described, may be responsible.

#### 4. Conclusions

We attempted to produce  $\text{Y}_2\text{CaAl}_4\text{GeO}_{12}:\text{Ce}$  and  $\text{Y}_2\text{MgAl}_4\text{GeO}_{12}:\text{Ce}$  garnets in the forms of powders and glass ceramics. The powders were obtained using co-precipitation, and the solid-state technique was used for synthesis of glass ceramics. The reflections of the garnet phase for powders and glass ceramics were registered in XRD patterns. The main difference in XRD patterns between the powders and corresponding glass ceramics was interpreted to result from capturing  $\text{Si}^{4+}$  ions in the garnet lattice during formation of crystallites in the glass matrix. Structural inhomogeneity of the crystallites in glass ceramics was revealed by confocal PL spectroscopy as a blue shift of the PL peak position of  $\text{Ce}^{3+}$  from the crystallite center to its border.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.radmeas.2019.02.005>.

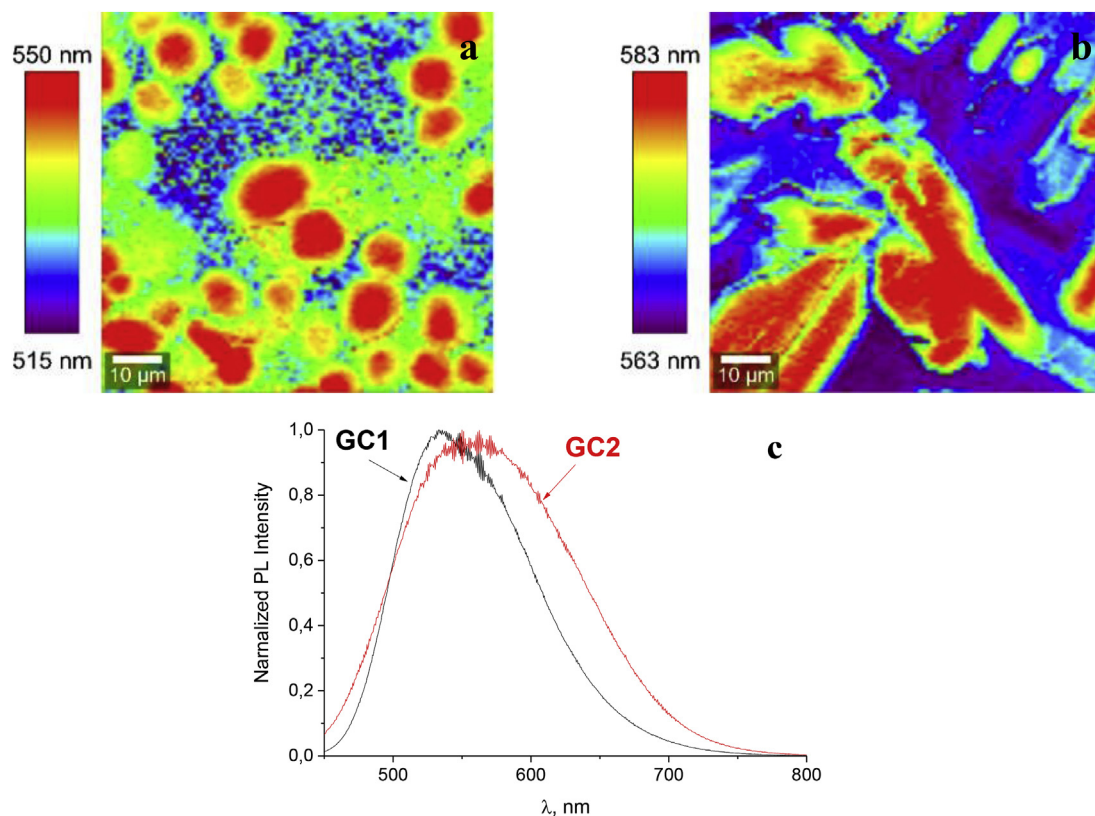


Fig. 3. Mapping images of band peak position (a, b) recorded on areas of  $20\ \mu\text{m} \times 20\ \mu\text{m}$  in size and PL spectra (c) from whole area for GC1 (a, black line) and GC2 (b, red line). Excitation was at 442 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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