Red-emissive Mn-doped Li$_2$Ge$_4$O$_9$ phase synthesized via glass-ceramic route

Jun KUNITOMO, Rie SUZUKI, Yoshihiro TAKAHASHI,[†] Takamichi MIYAZAKI,[*] Nobuaki TERAKADO and Takumi FUJIWARA

Department of Applied Physics, Tohoku University, 6–6–05 Aoba, Aoba-ku, Sendai 980–8579, Japan
[*]Department of Instrumental Analysis, Tohoku University, 6–6–11 Aoba, Aoba-ku, Sendai 980–8579, Japan

We synthesized the lithium-tetragermanate (Li$_2$Ge$_4$O$_9$) phase doped with Mn^{4+} by glass-ceramics technique using the stoichiometric glass-precursor with different MnO$_2$ concentrations, i.e., 20Li$_2$O–80GeO$_2$–xMnO$_2$ (x = 0.1–0.7), and examined their photoluminescent property. The doped phase showed clear red-emission at room temperature, and the internal quantum-yield was found to be approximately 40% in the samples with x = 0.1–0.3.
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Europium ion has been used to develop the red-emitting materials because of an efficient luminescent center due to the f–f (Eu^{3+}) and/or f–d (Eu^{2+}) transition.[1),2)] On the other hand, recently it is of particular interest to fabricate photoluminescent (PL) material free from rare-earth (RE) ions, the so-called RE-free phosphor.[3)–5)] Although efficient PL and long-lasting PL have been found in the phosphors, which are activated with d^0-system ion of transition-metal with high Clarke number, i.e., titanium ion (order of the number; #10),[6)] the Ti^{4+}-including phosphors generally show the PL band in the range of ~400–520 nm, i.e., blue–green color region.[7)] To synthesize the red-emitting phosphor, the crystalline phases doped with the d^3-system ions, i.e., chromium (#20) and manganese (#12) ions (Cr^{3+} and Mn^{4+}), have been examined.[8)–10)] In octahedral site, ionic radius of the Mn^{4+} is very close to that of germanium ion (Ge^{4+}: 0.53 Å) so that germanate compound consisting of the octahedral GeO$_6$ unit has a potential to be nice host for the red-emissive phosphor due to the d–d transition of Mn^{4+}.

Lithium tetragermanate, Li$_2$Ge$_4$O$_9$, is reported to be ferroelectric, and crystallizes from the stoichiometric glass.[11),12)] Li$_2$Ge$_4$O$_9$ phase belongs to an orthorhombic system and consists of slightly-distorted GeO$_6$ octahedron connected with [GeO$_3$]$_n$-chains to form a three-dimensional framework (Fig. 1).[13)] In previous study, present authors' group has examined the structural phase transition at $T_0 \sim 100°$C in Li$_2$Ge$_4$O$_9$ doped with Mn^{4+} as an emissive probe by means of spectroscopic technique.[14)] Interestingly, the Li$_2$Ge$_4$O$_9$ phase with Mn^{4+}-probe possessed the visible red-emission at room temperature. However, no detailed investigation of the red-emission has been performed so far. Therefore, in this note, we synthesized Li$_2$Ge$_4$O$_9$ phase with different Mn^{4+}-concentrations by glass-ceramic technique and assessed the concentration dependence on the PL properties.

Li$_2$Ge$_4$O$_9$ phase can be obtained by heat-treatment in the corresponding glass, i.e., 20Li$_2$O–80GeO$_2$, because the glassy phase totally converts into the nano-sized Li$_2$Ge$_4$O$_9$ crystals by crystallization.[15)] Therefore, we synthesized the Mn^{4+}-doped

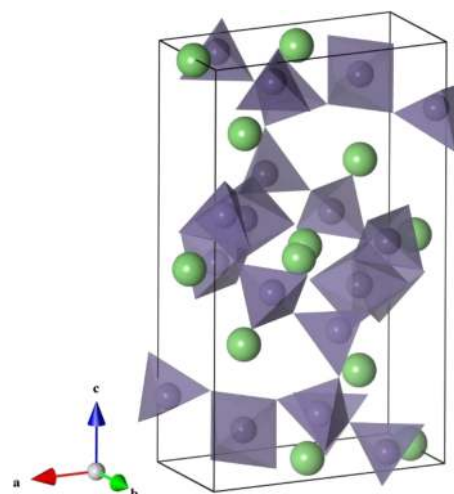Fig. 1. Crystal structure of Li$_2$Ge$_4$O$_9$. Purple polyhedral units, and green sphere correspond to the GeO$_4$/GeO$_6$ unit and lithium ion, respectively.

Li$_2$Ge$_4$O$_9$ phase from the corresponding glassy precursors: Glass compositions in this study is 20Li$_2$O–80GeO$_2$–xMnO$_2$ (mol%; x = 0.1–0.7). Way to prepare the glass is described elsewhere.[15)] The obtained glassy samples were examined by means of a differential thermal analysis (DTA) to evaluate the thermal parameter, glass-transition (T_g), crystallization-onset (T_x), and crystallization peak (T_p) temperatures, and were subjected to isothermal heat-treatment at first crystallization-peak temperature (T_{p1}) for 1 h to synthesize the crystalline phase. The crystalline samples were characterized by means of an X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). In terms of the PL property, the crystalline samples were characterized by a spectrofluorometer with a xenon lamp as an excitation source and PL spectrometer with an integrating sphere (Hamamatsu Photonics: Absolute PL Quantum Yield Measurement System C9920-20). All of experimental measurements in this study were done at room temperature.

[†] Corresponding author: Y. Takahashi; E-mail: takahashi@laser.apph.tohoku.ac.jp
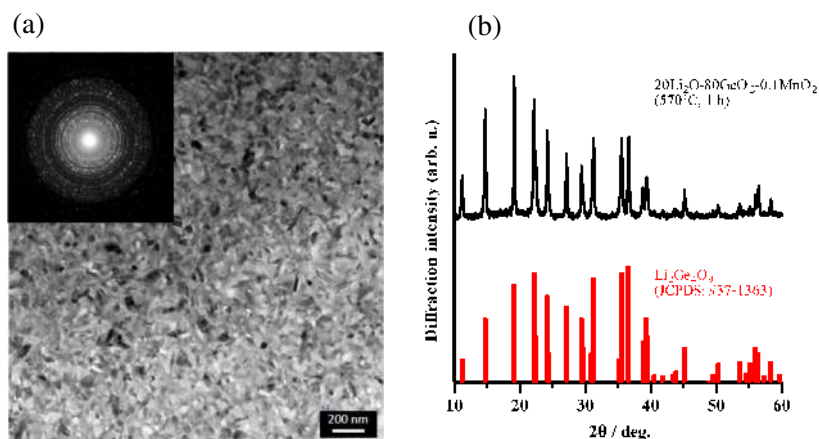
Fig. 2.   Texture and crystallized phase in the Li₂Ge₄O₉ glass with $x = 0.1$ subjected to isothermal heat treatment at $\sim T_{p1}$ for 1 h: (a) TEM image and a typical ED pattern, and (b) powder XRD pattern, together with JCPDS data (#37-1363).

According to the DTA measurement, the glassy precursors doped with different MnO₂-concentrations indicated the thermal parameters; $T_g = 510$–513°C, $T_{x1} = 565$–569°C, $T_{p1} = 565$–569°C, $T_{p2} = 586$–590°C, and the parameters were almost identical to that of the pure (non-doped) glass.[15] We also confirmed the single formation of stoichiometric Li₂Ge₄O₉ phase in all of the heat-treated samples by the powder XRD measurement. For example, in the Li₂Ge₄O₉ phase with $x = 0.1$, the TEM observation revealed that the glassy phase totally convert into crystalline phase, and its particle size was ~ 20 nm [Fig. 2(a)]. In addition, the electron diffraction (ED) indicated a pattern corresponding to polycrystalline phase, and the powder XRD pattern showed the single formation of Li₂Ge₄O₉ phase [Fig. 2(b)]. Taking the DTA result into account, it is strongly suggests that the addition of small amount of MnO₂ to the Li₂Ge₄O₉ glass gives no significant effect on the crystallization trend.

The Li₂Ge₄O₉ glass-ceramic samples generally indicated a reddish-PL under the UV light: For example, the glass-ceramics with $x = 0.1$ showed a sharp PL peak at ~ 1.85 eV (670 nm) and broad PL excitation peaks at ~ 3.75 and ~ 2.66 eV (330 and 465 nm), which are attributed to the $^2E \rightarrow {}^4A_2$ transition, and the $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ transitions, respectively (Fig. 3). On the other hand, the pure sample indicated the blue-emission
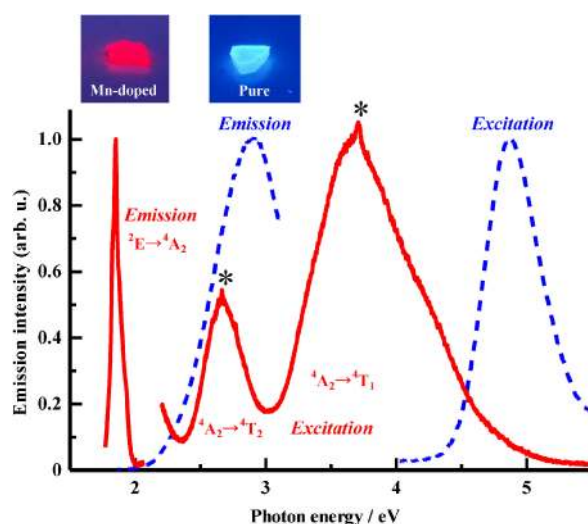

Fig. 3.   PL and PLE spectra in the non-doped and Mn⁴⁺-doped ($x = 0.1$) glass-ceramic samples obtained at 570°C for 1 h. Peaks indicated by asterisk are artifact. Red (solid line) and blue (bashed line) spectra correspond to Mn⁴⁺-doped and pure samples, respectively. Photos indicate the doped (red) and pure (blue) samples irradiated with ultraviolet lamp with wavelength of 365 and 254 nm, respectively.
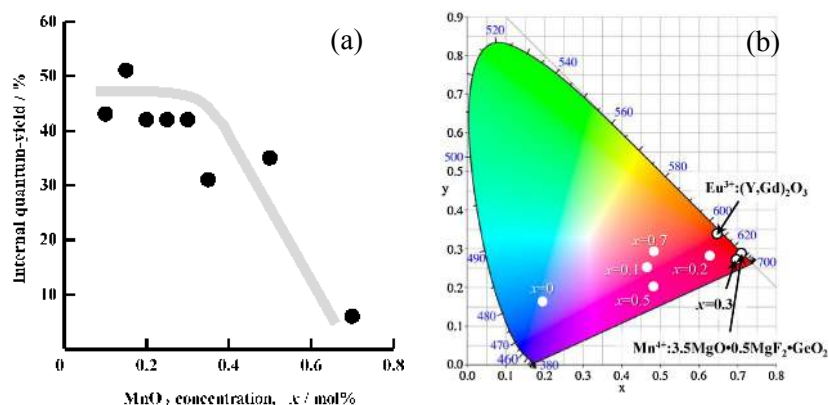

Fig. 4.   (a) Internal QY as a function of MnO₂-concentration (x) in the Li₂Ge₄O₉ phase crystallized from 20Li₂O–80GeO₂–xMnO₂ glass-precursor. Excitation wavelength is 330 nm. Gray curve is guided by my eyes. (b) Chromaticity coordinates of the studied samples in CIE diagram, together with data of Eu³⁺-doped Y₂O₃ and Mn⁴⁺-doped 3.5MgO·0.5MgF₂·GeO₂ (Refs. 8 and 17).

instead (inset of Fig. 3). Chromaticity coordinates of the pure sample was estimated to be (0.188, 0.168). Although at present the origin of blue-emission is not fully understood yet, this also indicates that the sharp PL peak in red-color region is actually due to the d–d transition of doped Mn^{4+} in $Li_2Ge_4O_9$ phase.

In regard to the internal quantum-yield (QY), the value was evaluated to be approximately 40% in the samples with $x = 0.1$–0.3, and tends to decrease as increasing the x, which is attributed to the so-called concentration quenching [Fig. 4(a)]. In addition, the sample with $x = 0.3$ possessed a high red-color purity, which is comparable to that of Mn^{4+}-doped $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2$ phase for fluorescent lamp [Fig. 4(b)]. On the other hand, chromaticity coordinates of the Mn^{4+}-doped samples other than the $x = 0.3$ possessed the intermediate position between the red and blue color positions. This is possibly due to the color-mixing of the red-emission due to the doped $Li_2Ge_4O_9$ phase and blue-emission due to the pure phase. In order to obtain the required red-emission property, investigations of the doping-amount into the phase and of crystallization condition are necessary.

In summary, the $Li_2Ge_4O_9$ phases with different MnO_2 concentrations were synthesized by glass-ceramics technique and their PL property was studied. The red-emission ability was demonstrated in the $Li_2Ge_4O_9$ phase (host crystal) doped with Mn^{4+} (the emissive center) at room temperature, and the internal QY was estimated to be ~40% when the concentration is $x = 0.1$–0.3. Our study leads us to expect that the other tetragermate phases with octahedral GeO_6 unit, e.g., RGe_4O_9 (R: Sr and Ba) with benitoite-like structure,[16] are also potential candidate for red-emitting RE-free phosphor. However, temperature-quenching of the PL around 100°C in the doped $Li_2Ge_4O_9$ phase is a fatal problem for the practical application.[14] Indeed, study for the increment of quenching temperature is now in progress.

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