Mn-doped $\text{LiNaGe}_4\text{O}_9$ as a rare-earth free phosphor: impact of Na-substitution on emission in tetragermanate phase

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We have synthesized Mn^{4+} -doped mixed tetragermanate phases in the $\text{Li}_2\text{Ge}_4\text{O}_9$ – $\text{LiNaGe}_4\text{O}_9$ system, i.e., $\text{Li}(\text{Li},\text{Na})\text{Ge}_4\text{O}_9$, by a glass-ceramic technique using stoichiometric precursor glasses, and have examined the effect of substitution of Na on their photoluminescence properties. The tetragermanate phases indicated clear red emission based on a ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition, and the entire substitution resulting in an $\text{LiNaGe}_4\text{O}_9$ phase provided an improvement of quenching temperature for the emission. Furthermore, the $\text{LiNaGe}_4\text{O}_9$ phase synthesized by solid-state reaction showed a high internal quantum yield and red color purity, demonstrating it to be a possible candidate as a rare-earth-free red phosphor.

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1. Introduction

The importance of red-emitting phosphors has recently increased because such phosphors not only contribute to improving the color rendering of white LEDs but can also assist photovoltaic generation (i.e., in a spectral converter) and allow the fabrication of growth lights for plant factory. To date, the Eu ion has been almost exclusively used as a dopant in red phosphors because of its efficient luminescent center based on $f-f$ (Eu^{3+}) and/or $f-d$ (Eu^{2+}) transitions.^{1,2)} However, the rare earth (RE) resource has a latent instability of supply since the Clarke numbers of the RE elements are considerably smaller than those of other more common elements. Therefore, it is of particular interest to explore and develop phosphor materials in which the use of RE is minimized, e.g., RE-free phosphors.^{3–5)}

Transition-metal ions with relatively large Clarke numbers, i.e., Cr^{3+} and Mn^{4+} , have the potential to serve as luminescent centers of red phosphors based on their $d-d$ transitions.^{5–8)} Recently, our research group has performed spectroscopic and microscopy studies on a metastable tetragermanate phase, $\text{Li}_2\text{Ge}_4\text{O}_9$, which crystallizes only from the glassy state,^{9,10)} and we have demonstrated strong photoluminescence (PL) with a peak at ~ 670 nm for the Mn^{4+} -doped $\text{Li}_2\text{Ge}_4\text{O}_9$ phase.^{11,12)} Although the Mn^{4+} -doped phase seemed as a possible candidate for application as a red phosphor, the relative intensity of its red emission dramatically decreased in the temperature range of ~ 50 – 100°C .¹¹⁾ An isostructural tetragermanate phase, in which the half of the Li is substituted by Na, i.e., an $\text{LiNaGe}_4\text{O}_9$ phase, produces mixed crystals composed of orthorhombic $\text{Li}(\text{Li},\text{Na})\text{Ge}_4\text{O}_9$ in combination with the $\text{Li}_2\text{Ge}_4\text{O}_9$ phase.^{13,14)} This mixed system shows a drastic change in physical properties,¹⁵⁾ which leads us to expect that the substitution might also have a significant effect on the PL properties of the doped tetragermanate phase.

In this study, we have synthesized Mn^{4+} -doped $\text{Li}(\text{Li},\text{Na})\text{Ge}_4\text{O}_9$ phases through crystallization in the stoichiometric glasses and have examined the impact of Na substitution on the red-emission properties through spectroscopic measurements. Furthermore, we have found that the doped $\text{LiNaGe}_4\text{O}_9$ phase synthesized by a conventional sintering process possesses superior properties to the doped metastable $\text{Li}_2\text{Ge}_4\text{O}_9$ phase.

2. Experimental

Mn^{4+} -doped $\text{Li}(\text{Li},\text{Na})\text{Ge}_4\text{O}_9$ phases were synthesized by a glass-ceramic technique using the stoichiometric precursor glasses, i.e., $(20 - x)\text{Li}_2\text{O} - x\text{Na}_2\text{O} - 80\text{GeO}_2$ ($x = 0$ – 10 ; in mol %), doped with 0.1 mol % MnO_2 . Commercial powders of reagent-grade Li_2CO_3 , Na_2CO_3 , GeO_2 , and MnO_2 (Kojundo Chemical Laboratory Co., Ltd., Japan) were mixed and melted at 1200°C for 30 min in air in a platinum crucible covered with a lid. The melt was poured onto a steel plate and quickly pressed with another steel plate. The obtained glassy samples were subjected to isothermal heat-treatment at their first crystallization-peak temperatures (T_{p1}), as determined by differential thermal analysis (heating rate: 10 K/min), for 1 h in an electric furnace in air to obtain the crystallized samples.

The crystallized samples were characterized by powder X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Visual confirmation of PL was checked by irradiation with an ultraviolet (UV) lamp with light of wavelength of 312 nm. PL and PL excitation (PLE) spectra of the samples were measured by means of a spectrofluorometer with a xenon lamp as excitation source. The internal quantum yield (QY) and the chromaticity coordinate of the PL were evaluated by means of a PL spectrometer with an integrating sphere (Hamamatsu Photonics, Absolute PL Quantum Yield Measurement System C9920-20). Unless otherwise stated, all of the experimental measurements in this study were performed at room temperature. In terms of the temperature dependence of the PL intensity, a piece of the sample was placed in a heating stage to adjust the temperature environ-

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ment, and the light emitted under excitation by an Ar^+ -gas laser operating at 457.9 nm was observed. The red emission arising from the middle of the PLE band corresponding to the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transition was also observed at this wavelength [see the inset in Fig. 3(b)].¹¹⁾ The emission signal was detected using a system consisting of a triple-grating monochromator and a liquid-nitrogen-cooled charge-coupled device detector (HORIBA-Jobin Yvon, T64000).

3. Results and discussion

3.1 Synthesis of mixed phase in the $\text{Li}_2\text{Ge}_4\text{O}_9$ – $\text{LiNaGe}_4\text{O}_9$ system

Figure 1 shows the results of XRD analyses of the heat-treated precursor glasses. The heat-treated samples all exhibited sharp diffraction peaks, and the patterns were identical to that of ICDD data for the $\text{Li}_2\text{Ge}_4\text{O}_9$ / $\text{LiNaGe}_4\text{O}_9$ phase, indicating discrete formation of the tetragermanate phases [Fig. 1(a)]. In addition, the lattice constants of the crystallized phases in the orthorhombic system, which were evaluated on the basis of diffraction patterns, were linearly proportional to the amount of Na substitution, x [Fig. 1(b)]. Furthermore, the lattice constants could be plotted on the lines based on reported values for the $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{LiNaGe}_4\text{O}_9$ phases as end members, i.e., in accordance with the Vegard rule. If a precursor glass with the composition of the intended phase (i.e., stoichiometric glass) singly crystallized to the corresponding phase in the resulting glass-ceramics, then there was a good agreement in the crystallographic parameters between the intended and crystallized phases because the glassy phase was entirely transformed into the crystalline phase.^{16),17)} In order to check the crystallized texture in the glass-ceramics, SEM observation was carried out on the samples with $x = 0$ and 10

Fig. 1. (a) Typical powder XRD patterns of heat-treated precursor glasses of compositions $(20-x)\text{Li}_2\text{O}-x\text{Na}_2\text{O}-80\text{GeO}_2-0.1\text{MnO}_2$, together with the ICDD data for $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{LiNaGe}_4\text{O}_9$ phases. The values of T_{pl} are 568, 551, and 560°C for $x = 0, 4$, and 10, respectively; (b) lattice constants of the crystallized tetragermanate phase as a function of Na-substitution amount, x ; (c, d) SEM images of microstructure in the samples with $x = 0$ and 10.

(i.e., the end members) as the representatives. The microscopy study revealed densely packed structures consisting of nano-sized crystallites (~ 50 – 100 nm) without any glassy phase [Figs. 1(c) and 1(d)]. This suggested complete transformation of the glassy phase into the corresponding mixed tetragermanate phases, implying that a mixed phase suitable for investigation of the effect of Na substitution could be obtained.

3.2 Red-emission property in mixed tetragermanate phase

Figure 2 shows the results of spectroscopic study of the $\text{Li}(\text{Li},\text{Na})\text{Ge}_4\text{O}_9$ phases. In a previous study, we found that the Mn^{4+} -doped $\text{Li}_2\text{Ge}_4\text{O}_9$ phase, in which the Mn^{4+} occupied the octahedral site in GeO_6 units, showed broad PLE peaks in the near-UV and blue regions based on the $^4\text{A}_2 \rightarrow ^4\text{T}_1$ and $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transitions, respectively, and a red-emission with a sharp PL peak based on the $^2\text{E} \rightarrow ^4\text{A}_2$ transition.¹²⁾ The mixed phases also displayed PLE bands at ~ 320 – 330 and 465 nm, and a PL peak similar to that of the doped sample with $x = 0$ [Fig. 2(a)]. It was also confirmed that there was no significant variation in the internal QY as a function of x ; 41–44% [Fig. 2(b)].

Figure 3 shows the temperature dependence of the PL properties. Clear red emission was visually confirmed from pieces of doped $\text{Li}(\text{Li},\text{Na})\text{Ge}_4\text{O}_9$ phases at room temperature under UV irradiation. When the pieces were placed on a stage heated to $\sim 180^\circ\text{C}$, the red emission was quenched in the samples with lower Na content ($x = 0$ – 6), whereas the emission still remained in the samples with $x = 8$ and 10 [Fig. 3(a)]. In terms of the integrated red-emission intensity as a function of temperature (i.e., quenching curve), the sample with $x = 2$ showed similar behavior to that of the doped $\text{Li}_2\text{Ge}_4\text{O}_9$ phase ($x = 0$; cited from Ref. 11), whereas the sample with $x = 10$ showed a large shift of the quenching curve at higher temperature [Fig. 3(b)]. The quenching temperature of the PL, T_q , is defined as the point of intersection of the abscissa and a straight line drawn through the points at which the PL intensity has fallen to 80 and 20% of the maximum value.¹⁸⁾ The values of T_q for the samples with $x = 0, 2$, and 10 were roughly estimated to be $\sim 120, 115$, and 160°C , respectively. Thus, the $\text{LiNaGe}_4\text{O}_9$ phase seemingly showed

Fig. 2. (a) Typical PL and PLE spectra of the tetragermanate phases, samples with $x = 0$ (i.e., $\text{Li}_2\text{Ge}_4\text{O}_9$), 2 ($\text{Li}_{1.6}\text{Na}_{0.4}\text{Ge}_4\text{O}_9$), and 10 ($\text{LiNaGe}_4\text{O}_9$) obtained by crystallization of the corresponding precursor glasses; (b) internal QY of the red emission as a function of x .

Fig. 3. (a) Mn⁴⁺-doped tetragermanate phases under UV-irradiation at room temperature (RT; above) and on a stage heated to ~180°C (below). (b) Integrated red-emission peak intensity as a function of temperature for the samples with $x = 0, 2$, and 10 . The data for $x = 0$ are cited from Ref. 11. The inset is a picture of the emission observed upon excitation by blue-laser irradiation at RT.

good red-emission performance among the tetragermanate samples examined in this study. Thus we decided to assess the LiNaGe₄O₉ phase in more detail.

3.3 Assessment of Mn-doped LiNaGe₄O₉ obtained by solid-state reaction

To study the effect of Na substitution, the respective samples were obtained by a glass-ceramic route because the base tetragermanate phase of Li₂Ge₄O₉ can only be obtained by crystallization of the stoichiometric glass. Since the synthesis of the non-doped LiNaGe₄O₉ phase by solid-state reaction has been reported,¹⁹⁾ we attempted to synthesize the Mn⁴⁺-doped LiNaGe₄O₉ phase in a similar manner. The nominal composition was 10Li₂O–10Na₂O–80GeO₂–0.1MnO₂ (the same as that of the glass-ceramic sample with $x = 10$), and the chemical reagents were mixed and sintered at 730°C for 6 h in air. The product appeared as a white polycrystalline body, and was finally identified as the LiNaGe₄O₉ phase by means of powder XRD analysis [Fig. 4(a)].

PL and PLE measurements of the sintered phase revealed similar spectral features to those of the crystallized LiNaGe₄O₉ sample, i.e., broad PLE peaks around the near-UV and blue regions and a sharp red emission, and in particular the PL spectrum was completely superimposed on that of the crystallized sample [Fig. 4(b)]. In addition, the chromaticity coordinates of the sintered sample were located in the red region with high color purity, i.e., (0.698, 0.272). Interestingly, the internal QY of the sintered sample was considerably improved to 61% as compared to that of the crystallized sample (43%).

A glassy (disordered) state transforms into an ordered structure, which is reflected in the medium-order structure, i.e., crystallization. Imperfection of the atomic arrangement in the resulting crystallized phase (or crystal defect) is attributed to the presence of nanometric inhomogeneity in the glass.^{20,21)} This leads us to consider that the tetragermanate phase obtained by the glass-ceramic technique contains many more defects than the phase obtained by solid-state reaction. Therefore, it is supposed

Fig. 4. (a) Powder XRD pattern of product of 10Li₂O–10Na₂O–80GeO₂–0.1MnO₂ subjected to solid-state reaction (SSR), together with the ICDD data of LiNaGe₄O₉; (b) PL and PLE spectra of the Mn⁴⁺-doped phases obtained by SSR (red point) and the glass-ceramic (GC) route (gray curves), and the chromaticity coordinates of the doped phase obtained by SSR in a CIE diagram.

that the improvement in the QY of the sample obtained by the solid-state route is due to the suppression of defects, which act as non-radiative centers. However, we would like to emphasize that we do not deny the effectiveness of the glass-ceramic technique for material processing because defect-activation enables oxide crystals to appear as a new functionality and can improve the performance.^{22)–24)}

4. Summary and concluding remarks

The red-emission properties of Mn⁴⁺-doped mixed tetragermanate phases synthesized by crystallization in the stoichiometric precursor glasses in the Li₂Ge₄O₉–LiNaGe₄O₉ system have been investigated. The tetragermanate phases displayed clear PL with peaks at ~660–670 nm in the red region. Substitution of Na at Li sites led to an improvement in T_q , and in particular the doped LiNaGe₄O₉ phase showed an increase in T_q of ~40 K. Moreover, we found the LiNaGe₄O₉ phase synthesized by solid-state reaction to be better suited for use as a red-emitting phosphor than the metastable Li₂Ge₄O₉ phase because its QY value and red color purity are considerably superior, demonstrating its potential as an RE-free red phosphor.

Na-substitution caused not only an increase in T_q , but also in the lattice constant. However, according to Paulusz, in Mn⁴⁺-doped emissive crystals, e.g., CsXF₆ (X : Si, Ge, Ti, Sn, etc.), an increase in the lattice constant due to substitution by a larger ion causes a decrease in T_q , and this can be reasonably explained on the basis of the behavior of the Franck–Condon off-set, Δr , in configurational coordinate models.²⁵⁾ Our result in this study apparently contradicts this (Fig. 3), and as yet the reason is still

unresolved. Since Δr is related to the site size of Mn^{4+} in the host crystal, in order to elucidate the reason, it is necessary to know the environment of Mn^{4+} in the tetragermanate phase and its crystallographic structure in more detail.

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