REACTIVITY OF SOLIDS

Melt synthesis of oxide phosphors with K_2NiF_4 structures: $CaLa_{1−x}Eu_xGaO_4$

**Tadashi Ishigaki · Kenji Toda · Tomoaki Watanabe ·
Naonori Sakamoto · Nobuhiro Matsushita ·
Masahiro Yoshimura**

Abstract In order to synthesize compounds of various Perovskite-related structures, we have utilized a novel "melt synthesis technique" for phosphors rather than the conventional solid state reaction techniques. The solid state reactions require multi-step processes of heating/cooling with intermediate grindings to make homogeneous samples. However, for the melt synthesis, it is possible to make a homogeneous sample in a single step within a short period of time (1–60 s) due to the liquid phase reaction in the molten samples, which were melted by strong light radiation in an imaging furnace. In this study, we have prepared a red-phosphor $CaLaGaO_4:Eu^{3+}$ which has a perovskite—related layered K_2NiF_4 structure. Well-crystallized $CaLa_{1−x}Eu_xGaO_4$ samples with the K_2NiF_4 structure have been obtained up to $x = 0.25$, but there was the formation of an olivine phase when $x = 0.5–1.0$. The red emission at 618 nm increased with the increasing value of x up to $x = 0.25$.
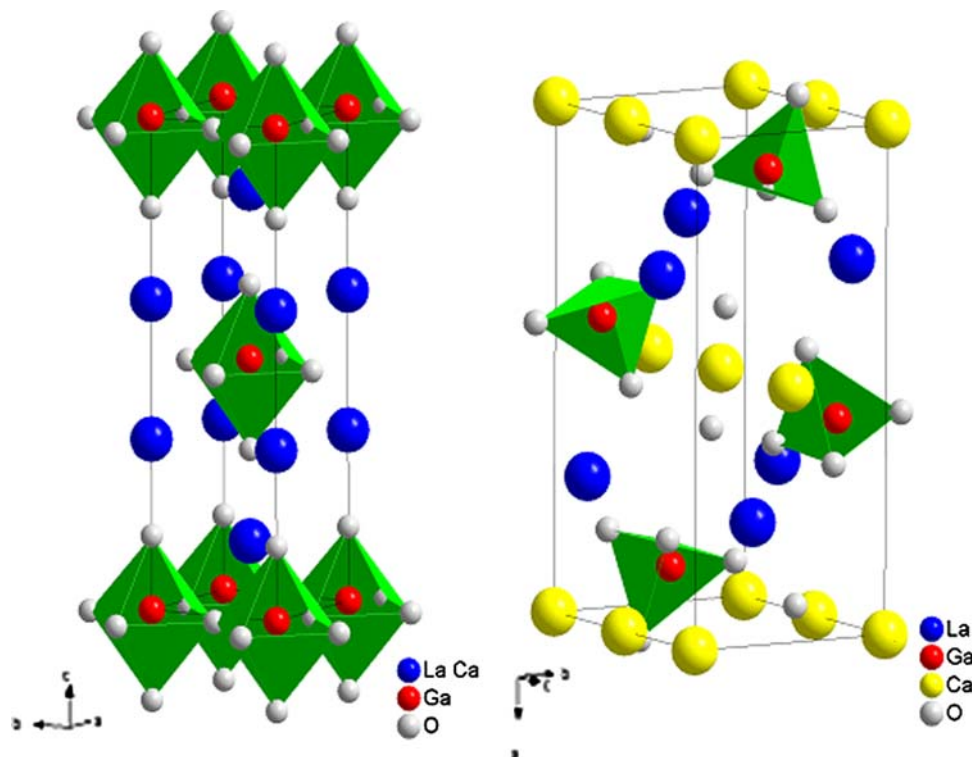
T. Ishigaki · T. Watanabe · N. Sakamoto · N. Matsushita ·
M. Yoshimura (✉)
Materials and Structures Laboratory, Tokyo Institute
of Technology, R3-20 4259, Nagatsuta Midori,
Yokohama, Kanagawa, Japan
e-mail: yoshimura@msl.titech.ac.jp

Present Address:
T. Ishigaki
Center for Transdisciplinary Research, Niigata University,
8050 Ikarashi Ninocho, Niigata 950-2181, Japan
e-mail: tishigaki@eng.niigata-u.ac.jp

K. Toda
Center for Transdisciplinary Research, Niigata University,
8050 Ikarashi Ninocho, Niigata 950-2181, Japan

Introduction

Complex oxide compounds like the perovskite-type ABO_3, spinel-type AB_2O_4, and scheelite-type ABO_4 have been investigated in many fields like ferroelectrics, magnetics, optics, phosphors, electronics, ionics, superconductors, sensors, catalysts, and because they have various but unique properties due to their compositions and structures which are characterized by the various combinations of the constituent A and B ions.

Recently, we reported a series of complex perovskites made by the melt synthesis technique that demonstrated a single-step easy route to make such complex perovskites [1]. We have now extended these studies to a series of ternary mixed oxides with the composition of $AA'BO_4$, structurally related to K_2NiF_4. Such complex oxides are not easy to synthesize by conventional solid state reaction techniques because the reaction rates among oxides are so slow by solid state diffusions that they form homogeneous compounds or solid solutions. On the other hand, melt reactions are very fast and homogeneous due to liquid mixing and fast diffusion in the liquid phase. Therefore, these melt synthesis techniques are suitable for synthesizing multi-component compounds and solid solutions in which homogeneous cation mixing is essentially required.

Moreover, the melt synthesis has another interesting feature, i.e., the synthetic temperature. It is a high-temperature approach for the synthesis whereas the solid state synthesis is a low-temperature approach. That is, the melt-synthesis may produce metastable phases at higher temperatures, which may not be formed by the solid state reactions even after a prolonged heating [2]. However, the melt synthesis process has not yet been studied in detail, probably because it is not easy to attain such a high temperature and to obtain a non-reactive container

Fig. 1 The structure of
$CaLaGaO_4$. (**a**) tetragonal (t-)
phase (K_2NiF_4-type) and (**b**)
olivine (o-) phase according to
Ref. 11

for the molten oxides at such high temperatures of
1,500–2,000 °C. By using an arc-imaging furnace, how-
ever, we have succeeded in synthesizing a series of
perovskite-type solid solutions in the systems of
$A^{2+}B^{4+}O_3 - A^{3+}B^{3+}O_3$, etc. [3]. Melting by using the arc-
imaging furnace does not require any container in various
atmospheres even at high temperatures, i.e., above
2,000 °C [4, 5]. While only a small amount of sample
can be prepared in the arc-imaging furnace, it can be
useful when investigating new materials.

$CaLnGaO_4$ (Ln = Y, lanthanide) under normal tem-
perature and pressure modification of these compound has
an olivine-type (o-phase) crystal structure. At high tem-
peratures (Ln = La, Pr, Nd, Sm) or under high pressures
(Ln = Eu, Gd, Tb, Dy), the tetragonal (t-phase) K_2NiF_4 or
a distorted tetragonal K_2NiF_4 was synthesized (Fig. 1)
[6–8]. The compound K_2NiF_4 doped with luminescent
activators (e.g., Eu^{3+} or Bi^{3+}) has been studied for the
phosphors [9–11]. Thus it seems interesting to investigate
the influence of the crystal structure due to the modification
of both temperature and pressure on the luminescence
properties of the activated compounds.

Combining these advantages of the melt synthesis and
the arc-imaging furnace, we prepared K_2NiF_4-type solid
solutions for forming phosphors at a rapid rate, in which
homogeneous Eu^{3+} doping is highly required [6, 7].

Experimental

The starting materials were high-purity carbonate and
oxide ($CaCO_3$ (99.5%, Kanto Kagaku Co., Ltd.), Eu_2O_3
(99.99%, Shin-Etsu Chemical Co., Ltd.), Ga_2O_3 (99.99%,
Kojundo Chemical Lab. Co., Ltd.), and La_2O_3 (99.99%,
Shin-Etsu Chemical Co., Ltd.)) powders. They were mixed
by dry and wet mixing in a high-purity alumina mortar.
The mixed powder or their molded samples were placed on
a copper hearth and melted in air under normal pressure
using the arc-imaging furnace as described elsewhere
[1, 3]. By the focused radiation of a 10 kW-Xe lamp, the
sample was melted into a 3–5 mm spherical globule on the
copper hearth, then rapidly cooled by dosing a shutter to
cut-off the radiation. It took generally 5–15 s from the
molten state at around 2,000 °C to reach the solid state
with a dark color at around 600 °C after closing the shutter.
Therefore, the cooling rate was estimated to be more than
100 °C/s.

Powder X-ray diffraction patterns were obtained for the
arc-melted samples after their grinding using an alumina
mortar. $CuK\alpha$ radiation in a curved graphite-beam mon-
ochrometer (MXP3VA, MAC Science, Tokyo, Japan) was
the X-ray source.

A spectrofluorometer (Perkin-Elmer, LS-55) equipped
with a Xe-arc lamp was used for the photoluminescence

(PL) measurement at room temperature for the powder sample.

Results and discussion

The CaLaGaO$_4$:Eu^{3+} solid solution with $0 < x < 0.25$ in Ca(La$_{1-x}$Eu$_x$)GaO$_4$ could be synthesized by the melt technique within a short period of time, i.e., 5–60 s, in a single step from the mixed powders. The sample was of globular shape with about 5 mm diameter.

Figure 2 shows the powder X-ray diffraction patterns of the CaLaGaO$_4$:Eu^{3+} samples that had the K$_2$NiF$_4$-type tetragonal single phase. Doped activator Eu^{3+} is replaced by the La site which is a member of the rare earth elements. With the increasing Eu^{3+} content, the peaks were shifted to higher angles due to the smaller ionic radius of Eu^{3+} in comparison with La^{3+}. Ronde et al. [8] reported that they failed to prepare a completely olivine phase (o-phase) or free tetragonal phase (t-phase) by their solid state synthesis. However, we succeeded in preparing the single t-phase sample by the melt synthesis. With reference to the lattice parameters $a = 3.8187$, $c = 12.3477$ for the t-phase cell and $a = 11.8083$, $b = 5.3529$, $c = 6.8603$ for the o-phase[1,2], we calculated the lattice energies for the t-phase and o-phase to be 4,841 and 4,776 kcal/mol, respectively. This indicates that the t-phase is more stable than the o-phase in the site of the lattice energies. The stability of phases can be determined by their Gibbs energies (ΔG). The enthalpy difference (ΔH) seems to be dominant more than the stability of t-phase because the energy difference due to the entropy difference (ΔS) would be much smaller than the enthalpy difference (ΔH) even at high temperatures like 2,000 K, $\Delta G = \Delta H - T\Delta S$. Therefore we can estimate the t-phase stability according to the lattice energy difference, $4{,}841 - 4{,}776 = 65$ kcal/mol, because the lattice energy is the enthalpy of formation at 0 K.

According to Li et al. [12], the t-phase is also the high temperature phase. Hence, the melt synthesis, which is a very high temperature process, can easily synthesize the pure t-phase. On the other hand, when $x > 0.5$, the samples are composed of the o-phase and unknown mixed phase (Fig. 3). Comparing the ionic radius, Eu^{3+} is smaller than La^{3+}. This is the reason why no single o-phase was obtained for the CaEuGaO$_4$ compound which has not been reported elsewhere until now. In fact, the lattice energy of the o-phase indicates that it is not stable at low temperatures.

Figure 4 shows the emission spectra of the CaLaGaO$_4$:Eu^{3+} phosphor samples. The spectral intensity

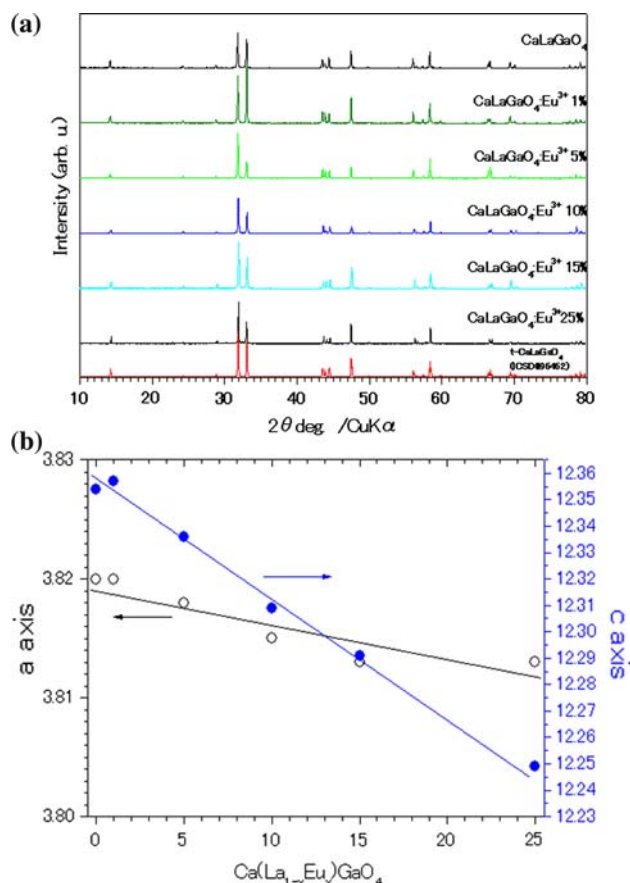¹ ICSD # 96462.

² ICSD # 96463.

Fig. 2 (a) XRD patterns of CaLaGaO$_4$:Eu^{3+} samples (Ca(La$_{1-x}$Eu$_x$)GaO$_4$: $0 < x < 0.25$) indicating t-phase and (b) calculated lattice parameters
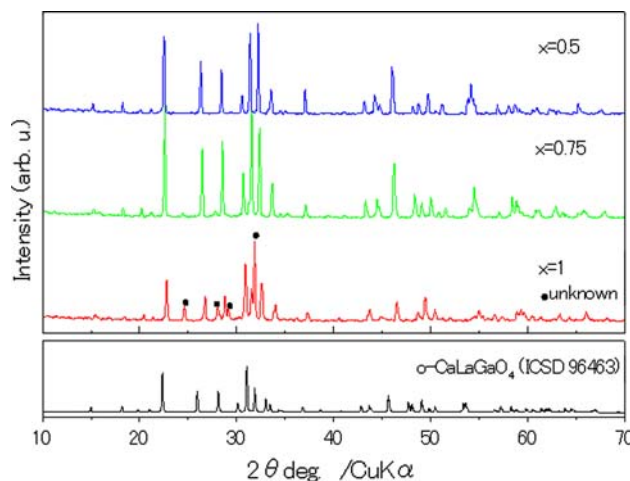
Fig. 3 XRD patterns of CaLaGaO$_4$:Eu^{3+} samples (Ca(La$_{1-x}$Eu$_x$)GaO$_4$: $0.5 < x < 1$), which belong to o-phase

of ^{5}D$_0 \rightarrow {}^7$F$_1$ and ^{5}D$_0 \rightarrow {}^7$F$_2$ increased with the Eu^{3+} contents. The spectral intensities measured by Ronde et al. were almost the same for ^{5}D$_0 \rightarrow {}^7$F$_1$ and ^{5}D$_0 \rightarrow {}^7$F$_2$. However, in this case, the relative intensity difference
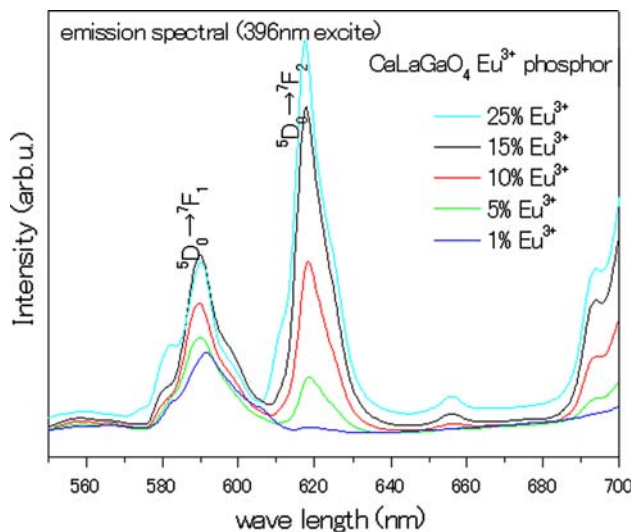
Fig. 4 Emission spectra of CaLaGaO$_4$:Eu^{3+} phosphor samples showing Ca(La$_{1-x}$Eu$_x$)GaO$_4$: $0 < x < 0.25$

between $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ was greater than Ronde et al.'s report and it was almost twice that of 15% Eu^{3+}. The rare earth ions, such as Eu^{3+} and Nd^{3+}, show a fine emission based on electron transitions among the 4f orbitals. The rare earth doped compounds have been paid much attention due to their high luminescence efficiencies. However, an excessive doping of emission ions would generally significantly decrease the emission intensity. This phenomenon is called "concentration quenching," which is caused by the migration of the excitation energy between the emission ions; thus it is closely related to the crystal structure [13]. These results suggest that we can prevent concentration quenching by preparing K$_2$NiF$_4$ structural samples.

The K$_2$NiF$_4$-type layered perovskite structure is composed of the two-dimensional arrangement of the rare earth ions. These low-dimensional arrangements of the rare earth ions would allow for their long separations; thus these compounds show a high critical concentration up to 25% Eu^{3+}. On the other hand, the long separation results in a decreased emission center concentration in unit volume.

According to Honma et al. [14], the low-dimensional arrangement of the emission ions may avoid contact with killers, such as impurities or vacancies, and a heavier framework will reduce the non-radiative relaxation of the excitation energy through phonons.

For the compounds with short separations and low-dimensional arrangements of the rare earth ions, these phenomena could overcome the concentration quenching

in the melt-synthesized CaLaGaO$_4$:Eu^{3+}. The relationship between the critical concentration of luminescence and the structural arrangement of the rare earth ions in the Eu^{3+}-activated samples will be investigated.

Conclusions

- Oxide phosphors were synthesized by a rapid reaction via a melt-solidification technique using an arc-imaging furnace.
- It was possible to synthesize the single t-phases of the phosphor CaLa$_{1-x}$Eu$_x$GaO$_4$ which is a stable lattice.
- The PL-measurement results revealed that the intensity ratio of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ were changed by the Eu^{3+} concentration.
- Because of the low-dimensional ordering of Eu^{3+}, the concentration quenching slightly decreased in this compound.

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