

Super-Broadband Near-Infrared Phosphors via Multiple-Cation Control of $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$ for Application in Light-Emitting Diodes

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Abstract

Near-infrared (NIR) phosphors are fascinating materials that have numerous applications in different fields. In this study, a series of $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$ phosphors, incorporated with Sn^{4+} , Ba^{2+} , and Sc^{3+} , were successfully synthesized using the solid-state reaction method to explore every cationic site in-depth. All the structures are well-resolved by synchrotron X-ray diffraction and neutron powder diffraction following with joint refinement. Trapping of free electrons induced by charge unbalances and lattice vacancies leads to the change of magnetic properties, which is well explained by a Dyson curve in electron paramagnetic resonance. Temperature and pressure-dependent photoluminescence reveal a variety of luminescent properties between strong and weak field in different dopant centers. Light-emitting diode (LED) package demonstrates a superior broadband emission covering the near-infrared region of 650 - 1050 nm. This study can provide the researchers with new insight into the control mechanism of multiple-cation-site phosphors and reveal a potential phosphor candidate for practical LED NIR application.

Key Words: Near-infrared phosphor, $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$, Light-emitting diode

Introduction

Through the rapid advancement of modern technology, the lighting industry has played a significant role in the development of cutting-edge devices. The use of light emitting diodes (LEDs) has been the key into some of these devices, particularly with near-infrared (NIR) phosphors as the main component. Ever since its discovery, NIR phosphors have been studied all over the world due to its numerous applications in different fields such as characterizations practiced in chemistry, medicine, food sciences, agriculture, and many more.^[1] The common ground between these applications is that they all rely on the characteristic absorptions of chemical components in the NIR region of the electromagnetic spectrum. Therefore, it requires a broad emitting NIR phosphor in order to maximize these applications. One particular phosphor that fits this category is the $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$ (LGGO) with a superior broadband NIR emission which has already been reported for applications such as ultraviolet (UV) and NIR excitable persistent phosphorescence,^[2] upconversion luminescence,^[3] and UV excitable photoluminescence.^[4] Rajendran et al.^[5] first studied this phosphor for blue-excited photoluminescence applications. Nevertheless, there are still some questions to be addressed regarding the maximum potential that the LGGO phosphor can give such as the crystallographic sites of this compound, factors affecting the photoluminescence, and the effects of multiple site substitutions.

Therefore, in this study, a series of $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$ phosphors, incorporated with Sn^{4+} , Ba^{2+} , and Sc^{3+} were

synthesized using the solid-state reaction method to explore every cationic site in-depth (Figure 1).

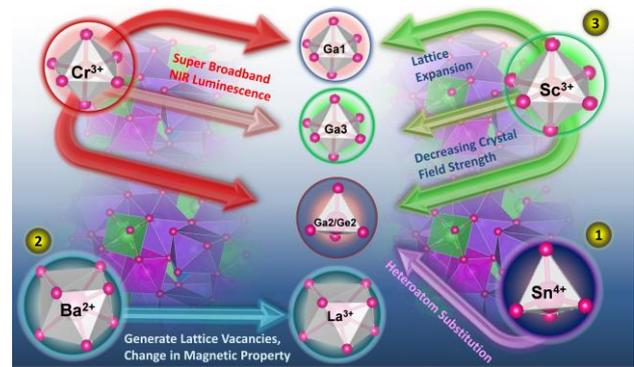


Fig. 1. Schematic representation of the multiple site substitutions in the LGGO compound.

Experiments

The $\text{La}_{3(1-z)}\text{Ga}_{5(1-w-y)}\text{Ge}_{1-x}\text{O}_{14}:5w\text{Cr}^{3+}$, $x\text{Sn}^{4+}$, $3z\text{Ba}^{2+}$, $5y\text{Sc}^{3+}$ phosphors were synthesized using the conventional solid-state reaction method. The phase and purity of the samples were characterized by X-ray diffraction (XRD) using a D2 PHASER diffractometer (Bruker) with $\text{CuK}\alpha$ radiation source ($\lambda = 1.5418 \text{ \AA}$). The fine structure data, lattice parameters, and atom positions, and bond lengths were obtained by synchrotron XRD analysis ($\lambda = 0.77491 \text{ \AA}$) of BL01C2 beamline with a Debye-Scherrer camera at the National Synchrotron Radiation Research Center, Taiwan.

Results

The Joint Rietveld refinements were performed by the neutron powder diffraction (NPD) and synchrotron X-ray

diffraction (XRD) data simultaneously. As shown in Fig. 2a and 2b, almost all peaks aside from the impurity (Ga_2O_3) were indexed by a trigonal cell (P-321). The occupancies of Cr ions were well refined with low R-factors in all Ga sites assuming that the total occupancy is equal to 1. The refinements also reveal that all Ga sites (Ga1; Ga2/Ge; Ga3) were occupied by Cr^{3+} ions indicating the successful incorporation of Cr^{3+} into the host. Furthermore, the coordinates of atoms and the main bond lengths show with the Ga3 site showing two additional contacts with O confirming that the Ga3 site forms a distorted octahedron (CN = 6) instead of a tetrahedron (CN = 4). Therefore, the Cr^{3+} ions have three types of local environments in the LGGO compound with two octahedral sites and one tetrahedral site.

Each site was partially replaced with an element that has a greater ionic radius in order to investigate its effects. The cationic substitutions were systematic starting off with Sn^{4+} replacing Ge^{4+} , Ba^{2+} in place of La^{3+} , and Sc^{3+} substituting for Ga^{3+} . Fig. 2c shows the XRD characterizations of all LGGO samples with additional dopants. The diffraction peaks of all samples show good accordance with the ICSD – 20783 standard. In addition, the lattice parameters (Fig. 2d) show an increasing trend with each additional dopant which gives further proof to the successful incorporation of the dopants into the host lattice.

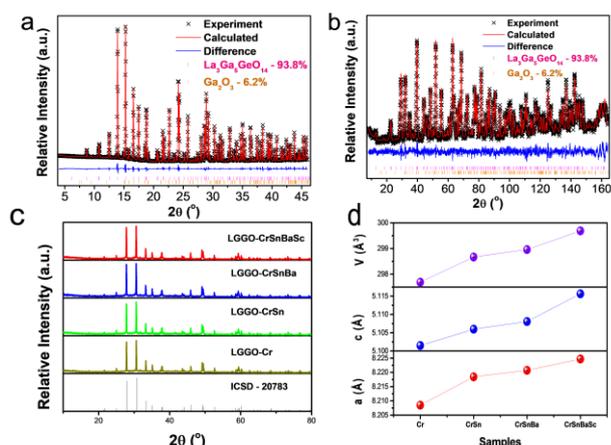


Fig. 2. (a) XRD refinements of $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$. (b) NPD refinements of $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$. (c) XRD of $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$ samples with additional dopants (Sn^{4+} , Ba^{2+} , Sc^{3+}). (d) Lattice parameters of $\text{La}_3\text{Ga}_5\text{GeO}_{14}:\text{Cr}^{3+}$ samples with additional dopants (Sn^{4+} , Ba^{2+} , Sc^{3+}).

The EPR signal at middle magnetic induction confirms that chromium ions occupy the tetrahedral site with a weak crystal field. Conversely, in the EPR signals at low magnetic inductions, chromium ions occupy two octahedral sites with intermediate crystal fields. The shape of the EPR signal consists also the Dyson line assigned to conductive electrons, which have a significant influence on the transport of interactions between chromium ions in octahedral sites. The occurrence of defects due to Ba^{2+} -doping affects the trapping of conductive electrons and their localization in vacancies of the crystal lattice with a considerable change of magnetic

property from ferromagnetic to antiferromagnetic behavior.

The PL measurements exhibited a superior broadband emission covering 650 nm – 1050 nm range for all samples. The temperature dependent and pressure dependent studies demonstrated the variation of crystal field strength as an effect of the cationic substitution. The incorporation of Sc^{3+} caused a significant decrease of the crystal field strength which leads to a red shift in the emission and an enhancement of quantum efficiency. The LED packaging results demonstrated similar results with the PL with an electroluminescent emission covering 650 nm – 1050 nm exhibiting a maximum radiant flux of 23.8mW making the LGGO phosphor a promising candidate for NIR-LED applications.

Discussion

To summarize, a series of LGGO phosphors were synthesized via solid-state reaction. All structures are well-resolved by X-ray diffraction and neutron powder diffraction following with joint refinements. The effects of multiple site substitutions were resolved using EPR, temperature and pressure dependent PL. The heteroatom substitution with Sn^{4+} exhibited no significant effect. The Ba^{2+} substitution generated lattice vacancies via a charge-unbalance mechanism, leading to a change in the magnetic property. The Sc^{3+} substitution exhibited the greatest effects with a significant reduction of crystal field strength, causing a red shift in the emission of the LGGO phosphor with a notable enhancement in the quantum efficiency. Finally, the LED packaging demonstrated that the LGGO phosphor co-doped with Sn^{3+} , Ba^{2+} , and Sc^{3+} is a promising candidate for NIR-LED applications.

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