Systematic Tuning of the Luminescent Properties of Self-Activated ZnGa$_2$O$_4$ Phosphors by Cd Ion Substitution

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The effect of host compositions on the luminescent properties of spinel-type ZnGa$_2$O$_4$ phosphors was investigated by systematic substitution of Cd^{2+} for Zn^{2+} in the host lattice. A continuous solid solution with the composition (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ ($0 \leq x \leq 1.0$) was synthesized at 950°C as self-activated phosphors, as indicated by X-ray diffraction (XRD) analysis. With increasing substitution of Cd^{2+} the emission and excitation wavelengths (λ_{em} and λ_{exc}) of self-activated (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ were observed to exhibit a red shift, as indicated by photoluminescence spectral analysis. Similar results were also confirmed by cathodoluminescence data. Our observations are attributed to the systematic narrowing of the energy gap of the host attributed to expanding lattice dimensions induced by Cd^{2+} substitution. A CIE chromaticity diagram manifests the effect of Cd^{2+} doping on variation of hue for the (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ gallate phosphors. © 2000 Academic Press

Key Words: (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ phosphor; Cd^{2+} substitution; self-activation; photoluminescence; chromaticity diagram.

INTRODUCTION

Identification of suitable phosphors for applications in electroluminescent displays (ELDs), plasma display panels (PDPs), and field emission displays (FEDs) has been a great challenge to materials chemists in the area of flat panel display technology. The luminescent properties of ZnGa$_2$O$_4$ phosphor have been actively investigated recently for use in thin-film ELDs (1, 2) and low-voltage FEDs (3), owing to its excellent chemical and thermal stability (4) as compared with sulfide phosphors. It has been suggested that low electrical resistance, low threshold voltage, and excellent crystallinity are highly desirable for applications in low-voltage cathodoluminescence FEDs (5). Furthermore, undoped ZnGa$_2$O$_4$ host lattice (with bandgap ca. 4.4 eV) itself emits strong blue light which was attributed to a transition via a self-activation center under ultraviolet or

low-voltage electron (e.g., 30 V dc) excitation (4, 6, 7). Most importantly, high luminance multicolor emissions have been realized in thin-film ELDs with a Mn^{2+}-, Cr^{3+}-, or rare earth-activated ZnGa$_2$O$_4$ thin-film emitting layer (1). One of the effective alternatives to identify the possible applications of ZnGa$_2$O$_4$ and related phosphors for FED or thin-film ELD uses is to tune the luminescent properties of ZnGa$_2$O$_4$ by modifying the host constituents or compositions (i.e., substitution of Zn^{2+} with Cd^{2+} or Ga^{3+} with Al^{3+}). However, only a limited number of investigations on the host compositional dependence of photoluminescence (PL) or cathodoluminescence (CL) of ZnGa$_2$O$_4$ have appeared in the literature (8, 9). This work is essentially motivated by the quest to acquire a deeper insight into the materials nature of ZnGa$_2$O$_4$, by the possibility of identifying more promising gallate phosphors, and by the ability to tune their luminescent properties. We report the composition and constituent effects (i.e., substitution of Zn^{2+} with different amounts of Cd^{2+}) on PL and CL spectra and hue variations of self-activated ZnGa$_2$O$_4$ phosphors.

EXPERIMENTAL

Samples of (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ (ZCGO) phases with $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0 were synthesized by grinding a mixture of stoichiometric amounts of ZnO (99.9%), CdO (99.5%), and Ga$_2$O$_3$ (99.99%). The mixture was placed in the furnace and heated in air at several trial temperatures of 950, 1000, and 1300°C for 12 h, respectively, and then slowly cooled to ambient temperature. Sample purity was first checked and structure analysis was then carried out by X-ray diffraction (XRD) by using a Mac Science MXP-3 automatic diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). The excitation and fluorescence emission spectra of ZCGO phases were measured at ambient temperature with a Shimadzu RF5301 PC spectrofluorophotometer equipped with a 150-W Xe lamp. The excitation spectra could be obtained by scanning the wavelength from 220 to 700 nm monitored at optimal emission wavelength (λ_{em}) of 438 to 540 nm. λ_{em} was scanned and recorded from 400 to

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700 nm excited at 254 nm. CL spectra of ZCGO phases were measured with a Topcon DS-CL-B CL spectrometer using an electron beam with excitation voltage of 10 kV and current density of 10 mA/cm^2.

RESULTS AND DISCUSSION

Synthesis of (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ Phases

The conditions for synthesis of (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ phases are uncertain and, hence, attempts to obtain pure samples with different Cd^{2+} contents have been made by investigating several trial synthesis conditions and characterizing their purity by XRD profile analysis. The results are summarized in Figs. 1a to 1e and the XRD profile of CdGa$_2$O$_4$ shown in Fig. 1e was found to be essentially X-ray pure. Synthesis temperatures higher than 950°C were discovered to drastically promote the volatility of CdO, and cause loss of CdO and the profiles for samples in Figs. 1a through 1d indicate the presence of Ga$_2$O$_3$ (labeled with asterisks) as an impurity phase. We found that the key to success in synthesizing ZCGO is to adopt a temperature of 950°C or lower so that the volatility of CdO can be effectively minimized. However, our results are apparently inconsistent with those reported by Choi et al. (9) who claimed that a solid solution of (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ could only be synthesized at 1200°C for 4 h in the composition range $0 \le x \le 0.6$. At the temperature adopted by Choi et al. we found that CdO is extremely volatile and stoichiometry is not conserved, as indicated by the XRD profiles shown in Figs. 1a to 1d.

XRD Profiles and Structure Analysis

The indexed XRD profiles of (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ phases with $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0 are represented in Figs. 2a to 2f, respectively. All of the diffraction peaks of ZCGO phases with different x values have been indexed with a cubic spinel structure. Furthermore, the lattice constants (a_0) as a function of x for cubic (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ phases shown in Fig. 3 were calculated by using a least-squares refinement program based on the indexed XRD profiles shown in Fig. 2. The magnitude of a_0 was found to increase steadily with increasing x. Furthermore, the possibility of Ga^{3+} substitution by Cd^{2+} ions has been ruled out due to the large difference in ionic radii between six-coordinated Cd^{2+} (0.95 Å) and Ga^{3+} (0.62 Å) ions (10). Hence, a complete solid solution of (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ is expected to form, as revealed by the excellent linear relationship between a_0 and x shown in Fig. 3.
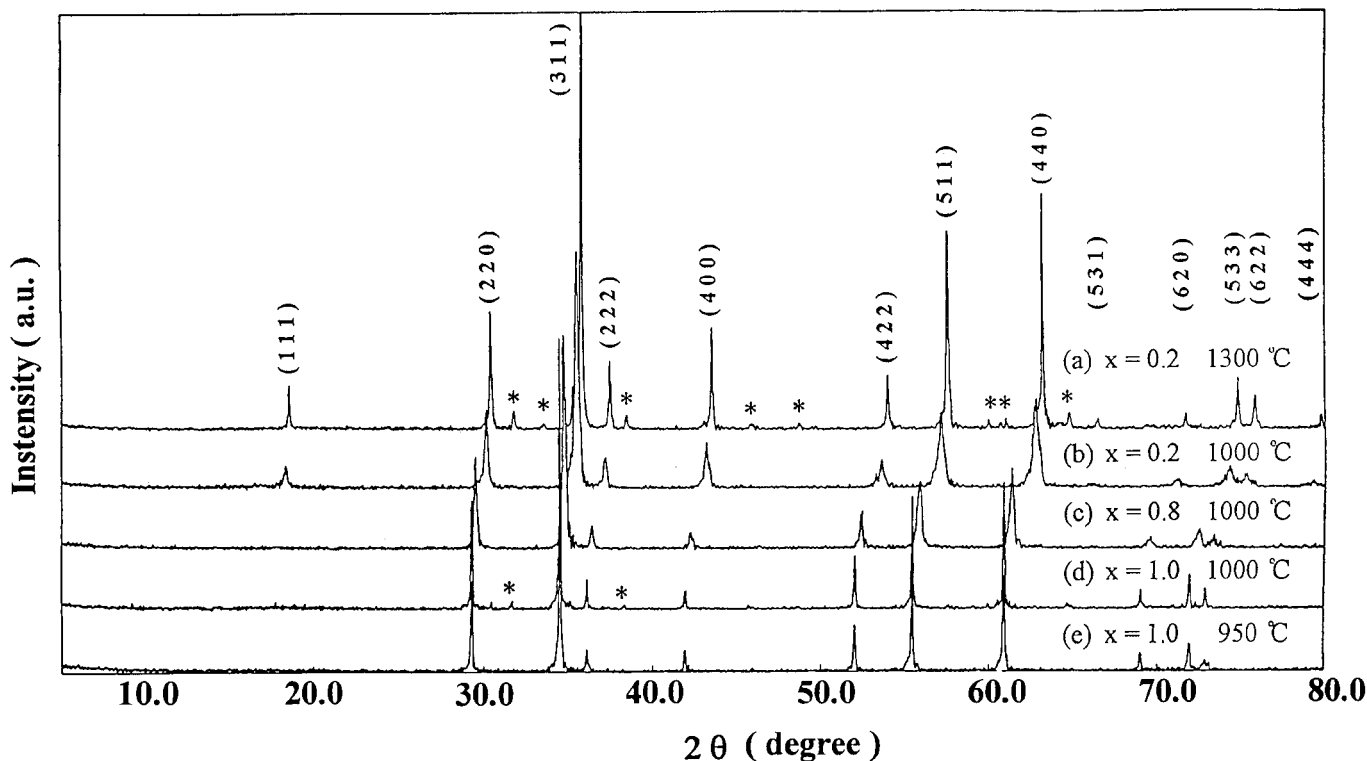

FIG. 1. XRD profiles of samples with nominal (Zn$_{1-x}$Cd$_x$)Ga$_2$O$_4$ composition prepared under different synthetic conditions (asterisks indicate Ga$_2$O$_3$ as an impurity).
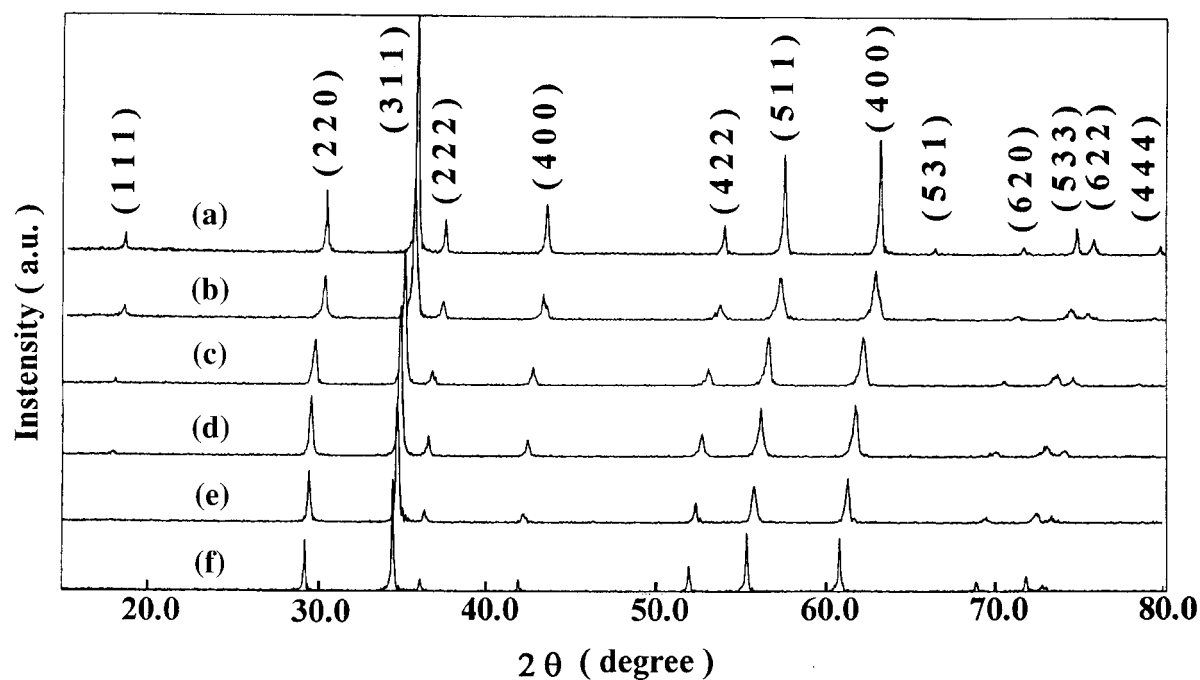
FIG. 2. Indexed XRD profiles for ZCGO phases synthesized at the optimal temperature of 950°C for 12 h: $x =$ (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0.

Photoluminescence and Cathodoluminescence Spectra

In an attempt to understand how host compositions or structural changes affect the excitation and fluorescence emission spectra of $(Zn_{1-x}Cd_x)Ga_2O_4$ phases, we have measured the PL excitation and emission spectra of $(Zn_{1-x}Cd_x)Ga_2O_4$ phases with a Shimadzu RF5301 PC spectrofluorophotometer and the data are summarized in

Figs. 4A and 4B, respectively. As expected, with increasing substitutional level of Cd^{2+} from 0 to 1.0 the emission and excitation wavelengths (λ_{em} and λ_{exc}) of self-activated $(Zn_{1-x}Cd_x)Ga_2O_4$ were observed to exhibit a continuous red shift from 438 nm ($x = 0$) to 538.4 nm ($x = 1.0$) and from 255 nm ($x = 0$) to 326 nm ($x = 1.0$), respectively, as indicated by PL spectral analysis. These observed red shifts of λ_{em} and λ_{exc} can be rationalized by the fact that the relative
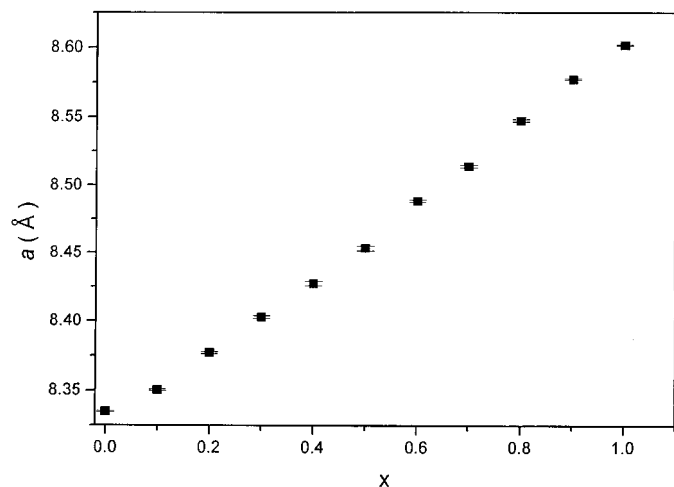

FIG. 3. Lattice constants as a function of x for cubic $(Zn_{1-x}Cd_x)Ga_2O_4$ solid solution.

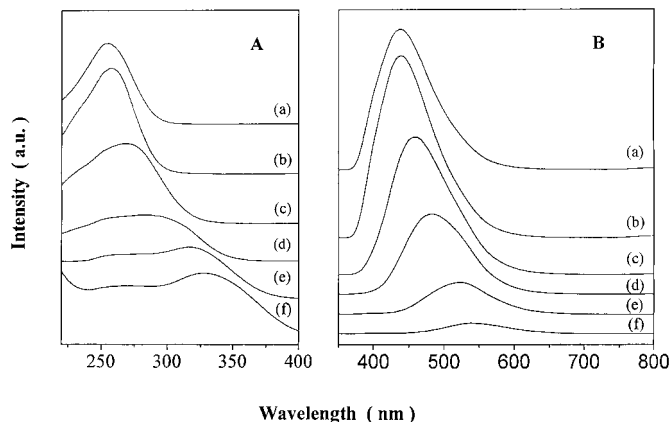**FIG. 4.** PL spectra for self-activated $(Zn_{1-x}Cd_x)Ga_2O_4$ phases as a function of x: (A) excitation, (B) emission.

four-coordinated (spinel A site) ionic radius of Cd^{2+} (0.84 Å) is 28% larger than that of Zn^{2+} (0.60 Å) (10) and the optical bandgap of $(Zn_{1-x}Cd_x)Ga_2O_4$ phases tends to become narrower on increasing the substitution level of Cd^{2+}. The latter observation can be attributed to the expansion of host lattice dimensions. Furthermore, the intensity of both excitation and emission peaks was found to decrease with increasing Cd^{2+} content and eventually flatten out as the Cd^{2+} content increases up to 1.0. A similar trend in the deterioration of luminescence intensity of ZnGa$_2$O$_4$ on cation doping has also been observed and reported by Jeong *et al.* in the investigation of self-activated Zn(Ga$_{1-x}$Al$_x$)$_2$O$_4$ phases (8). In principle, this problem can be foreseen in doped phosphors and may be solved by improving the transition probability or energy efficiency involved in the emission process, which is beyond the scope of this work. Or otherwise, in practical applications appropriate pigments are generally coated on the particle surfaces to compensate for the deterioration in luminescence intensity of phosphor materials on cation doping.

The comparison of Stokes shifts for $(Zn_{1-x}Cd_x)Ga_2O_4$ phases with $0 \leq x \leq 1.0$ is also summarized in Table 1 to illustrate the effect of Cd^{2+} substitution on energy efficiency. Similar Stokes shifts ranging from 17,000 to 20,500 cm^{-1} have also been observed in oxo compounds with d^{10} or d^0 configuration such as LiGaO$_2$ (18,000 cm^{-1}), Zn$_4$B$_6$O$_{13}$ (18,000 cm^{-1}), and KSbSiO$_5$ (20,500 cm^{-1}) (11). The observed intrinsic broad optical emission of gallate host lattice present in $(Zn_{1-x}Cd_x)Ga_2O_4$ phases has been attributed to a self-trapped exciton (12) or a charge transfer (13)-type mechanism and is expected to shift to lower energies if the formal charge of the central cation increases (11). On the other hand, a large Stokes shift of the emission peaks is also expected in view of the considerable relaxation or mobility of the excited state after optical absorption.

In addition, the composition-dependent CL spectra of ZCGO phases were measured with a Topcon DS-CL-B CL spectrometer using an electron beam with excitation voltage of 10 kV and current density of 10 mA/cm^2 and the spectra are shown in Fig. 5. Our data are again inconsistent with those reported by Choi *et al.* (9) in both the full width at half-maximum (FWHM) and λ_{em} in the CL spectra which
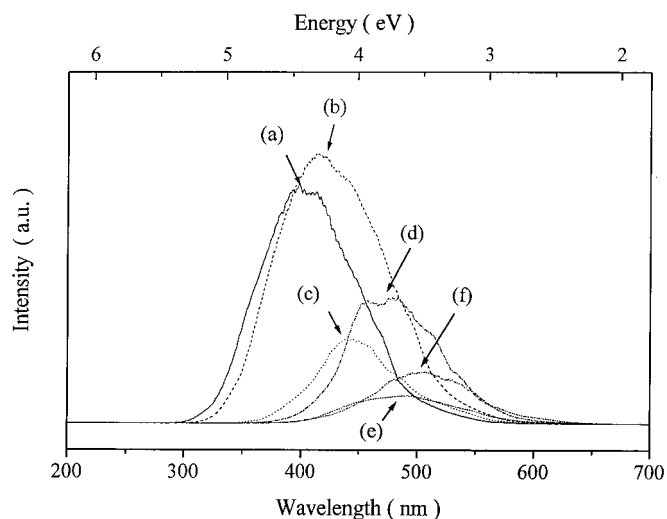

FIG. 5. CL spectra for self-activated $(Zn_{1-x}Cd_x)Ga_2O_4$ phases with $x =$ (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0.

requires further investigations. The emission peaks of ZCGO phases were also found to shift toward longer wavelength and this trend is in good agreement with that observed in the corresponding PL spectra for the ZCGO phases described previously. The electron beam heats up the $(Zn_{1-x}Cd_x)Ga_2O_4$ lattice when the samples are excited. Due to the thermal effect, the FWHM of the CL spectrum was observed to become much wider than those observed in the corresponding PL spectra as shown in Fig. 5.

Chromaticity Diagram

To determine the variation of hue attributed to the composition changes in ZCGO phases, we calculated the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates for ZCGO phases with different Cd^{2+} dopant contents from the corresponding PL spectra; a chromaticity diagram is presented in Fig. 6. We have found that the hue of $(Zn_{1-x}Cd_x)Ga_2O_4$ phases under ultraviolet excitation varied from blue ($x = 0$) with chromaticity coordinates 0.156, 0.124 to greenish blue, aqua, green, and eventually yellowish green ($x = 1.0$) with coordinates 0.347, 0.527. These observations are consistent with the observed shifting of λ_{em} from 438 nm ($x = 0$) to 538 nm ($x = 1.0$) observed in the PL spectra shown in Fig. 4B.

CONCLUSION

We have investigated the synthesis of a series of self-activated Cd^{2+}-doped ZnGa$_2$O$_4$ phosphors and studied the effect of host compositions and constituents on their luminescence properties. Both λ_{exc} and λ_{em} measured from the PL and CL spectra of $(Zn_{1-x}Cd_x)Ga_2O_4$ phases exhibited significant red shifts when Cd^{2+} was doped into the

TABLE 1
Comparison of Stokes Shifts for $(Zn_{1-x}Cd_x)Ga_2O_4$ Phases with $0 \leq x \leq 1.0$

λ (cm^{-1})	x					
	0	0.2	0.4	0.6	0.8	1.0
Excitation maximum	39,277	39,032	37,258	35,286	31,646	30,581
Emission maximum	22,831	22,769	21,786	20,747	19,135	18,574
Stokes shift	16,446	16,263	15,471	14,539	12,510	12,007

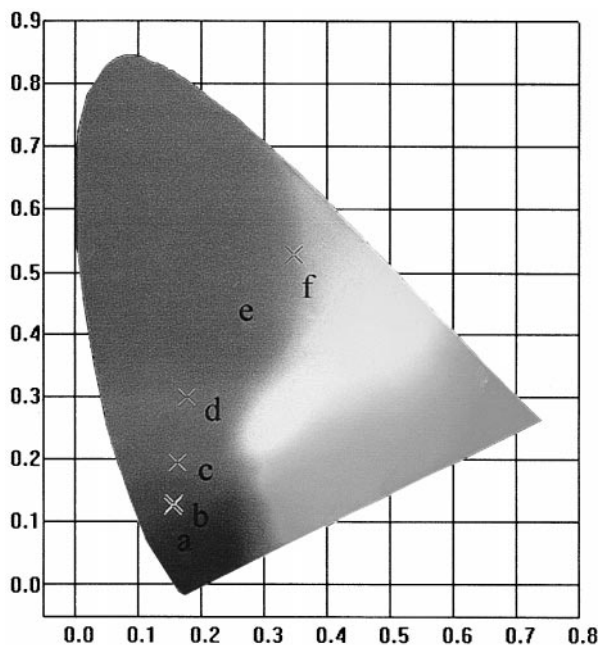**FIG. 6.** CIE chromaticity diagram for $(Zn_{1-x}Cd_x)Ga_2O_4$ phases with $x =$ (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1.0.

host lattice and replaced tetrahedrally coordinated Zn^{2+} cations. This work has demonstrated an innovative method of systematically tuning emissive hues through the formation of a series of $(Zn_{1-x}Cd_x)Ga_2O_4$ solid solutions.

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