

Article

Pressure-Induced YbFe₂O₄-Type to Spinel Structural Change of InGaMgO₄

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Abstract: Spinel-type InGaMgO₄ with $a = 8.56615(3)$ Å was prepared by treating layered YbFe₂O₄-type InGaMgO₄ at 6 GPa and 1473 K. DFT calculation and Rietveld analysis of synchrotron X-ray powder diffraction data revealed the inverse spinel structure with $\text{In}^{3+}:\text{Ga}^{3+}/\text{Mg}^{2+} = 0.726:0.274$ in the tetrahedral site and 0.137:0.863 in the octahedral site. InGaMgO₄ spinel is an insulator with an experimental band gap of 2.80 eV, and the attempt at hole doping by post-annealing in a reducing atmosphere to introduce an oxygen defect was unsuccessful. This is the first report of the bulk synthesis of AB₂O₄ compounds with both YbFe₂O₄ and spinel polymorphs.

Keywords: high-pressure synthesis; phase transition; YbFe₂O₄-type structure; spinel structure



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1. Introduction

Transparent conductive oxides (TCOs) find applications in various fields, including flat-panel displays and solar cells. Among them, amorphous indium gallium zinc oxide (a-IGZO) is widely used in smartphones and displays in thin films [1–7]. a-IGZO allows for low-temperature deposition, enabling the fabrication of complex devices on plastic substrates. However, due to its random structural nature, variations in oxygen binding strength occur, leading to the easy removal of some oxygen. As the free electron density is related to oxygen defects, a-IGZO is electrically unstable. Crystalline IGZO is known to have a layered YbFe₂O₄-type structure with space group $R\bar{3}m$ (166). MgIn₂O_{4-x} with the other AB₂O₄ structure, spinel, is also known as a TCO [8,9]. Spinel has a closed packing oxygen sublattice with the ABCABCA sequence of a triangular lattice, while the sequence of oxygen layers in the YbFe₂O₄ structure is ABABCACABCBCA, as shown in Figure 1 [10]. Divalent A-cation in the normal spinel structure has an oxygen tetrahedral coordination (T_d), while trivalent B-cation has an octahedral coordination (O_h). Recently, the synthesis of the polycrystalline spinel phase of IGZO by physical vapor deposition (PVD) on a Ga₂ZnO₄ (GZO) template layer has been reported [11]. However, no AB₂O₄ composition having both YbFe₂O₄ and spinel polymorphs is known in bulk form. Since the spinel phase generally has a higher density, the transformation of YbFe₂O₄ into spinel structures is expected to

occur under high pressure. In this work, we focus on MgInGaO_4 . Inverse spinel structures of MgIn_2O_4 ($\text{In}^{3+}[\text{Mg}^{2+}\text{In}^{3+}]\text{O}_4$) and MgGa_2O_4 ($\text{Ga}^{3+}[\text{Mg}^{2+}\text{Ga}^{3+}]\text{O}_4$) were reported, while $\text{MgIn}_{2-x}\text{Ga}_x\text{O}_4$ ($0.8 \leq x \leq 1.0$) has a YbFe_2O_4 -type structure when prepared at ambient pressure [9,12,13]. We first investigated the stable cation distribution of spinel MgInGaO_4 by density functional theory (DFT) calculations and Monte Carlo simulation, which indicated that the tetrahedral site was mainly occupied by In^{3+} . Treatment of the YbFe_2O_4 -type phase at 6 GPa and 1473 K resulted in the formation of a spinel phase. Our structural analysis using synchrotron X-ray diffraction (SXRD) data revealed that the resultant spinel phase adopts an inverse-type structure with a cation distribution of $\text{In}^{3+}:\text{Ga}^{3+}/\text{Mg}^{2+} = 0.726:0.274$ in the tetrahedral site, whereas the distribution in the octahedral sites was $\text{In}^{3+}:\text{Ga}^{3+}/\text{Mg}^{2+} = 0.137:0.863$, consistent with our theoretical investigation. This is the first report of the bulk synthesis of AB_2O_4 compounds with both YbFe_2O_4 and spinel polymorphs.

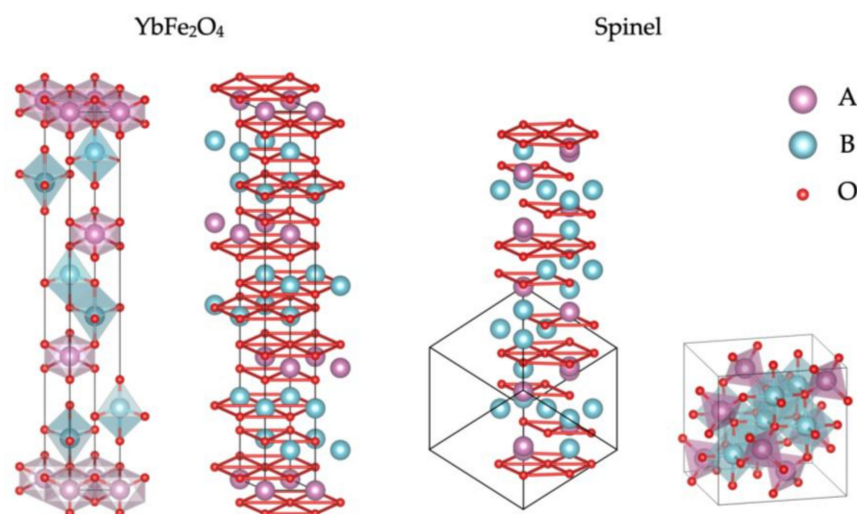


Figure 1. Crystal structures of YbFe_2O_4 and spinel types AB_2O_4 drawn using VESTA 3 software [14].

2. Materials and Methods

2.1. Computational Details

To determine the lowest-energy cation arrangements in the InGaMgO_4 system, we developed In-Ga-Mg ternary models using the cluster expansion (CE) method [15–17] as implemented in the Cluster Approach to Statistical Mechanics (CASM) software [18]. The ternary model Hamiltonian was expanded as a functional of occupation variable σ as, $E(\sigma) = E_0 + \sum_{\gamma} m_{\gamma} J_{\gamma} \Phi_{\gamma}$, where m_{γ} , J_{γ} and Φ_{γ} represent the multiplicity of inequivalent cluster, effective cluster interactions (ECI) and cluster function, respectively. E_0 denotes the point energy and γ represents a cluster lattice size. The basis is defined as $\{1, \sigma, \sigma^2\}$ to construct the cluster function [19]. The lattice Hamiltonian was expanded up to four-site clusters. We employed the linear regression method with the genetic algorithm to fit the ternary Hamiltonian with the first principles of density functional theory (DFT) calculated energies. The final Hamiltonian was optimized to a ~ 8 meV/f.u cross-validation (CV) score. Canonical Monte Carlo simulations based on the DFT-constructed In-Ga-Mg ternary model considering up to $9 \times 9 \times 9$ supercell size were performed. We considered an energy convergence criteria of 10^{-4} eV to detect phase transitions.

In addition, to model the effect of cation disorder within DFT tractable cell size, we generated special quasi-random structures (SQS) [20], considering a supercell consisting of a maximum of 112 atoms and various cation configurations. Within a supercell, a perfectly random network for the selected shells around a given site was closely generated to create an SQS structure by using the Alloy Theoretic Automated Toolkit (ATAT) [21].

First-principles calculations were performed using DFT [22,23] by employing the projector augmented-wave (PAW) method [24,25] as implemented in the Vienna ab initio

simulation package (VASP) [26,27]. We used an energy cutoff of 600 eV and sampled the k-points according to crystal symmetry. The lowest-energy cation-ordered structures were determined by considering the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) approximation for the exchange-correlation functionals developed for solids (PBEsol) [28,29]. The Hellmann-Feynman forces were converged to 0.001 eV/Å. We cross-checked our electronic energy bands and optical properties by using the meta-GGA functional r²SCAN [30] as well as the hybrid functional HSE06 [31]. We selected PAW potentials for Mg, In, Ga and O with the electronic configurations 2s²2p⁶3s², 5s²4d¹⁰5p¹, 5s²4d¹⁰5p¹, 2s²2p⁴, respectively. Additionally, we cross-checked our results, considering other electronic configurations.

To estimate the value of electron effective mass for each structure, we performed a calculation of the band structure considering the multiple symmetry lines and computed the effective masses along the band-structure symmetry lines using the AMSET package [32], which employs the Fourier interpolation of the band structure using BoltzTraP2 [33]. The average effective electron masses are listed in Table 1.

Table 1. Estimated values of electronic band gap (E_g) and mean effective electron mass (m_e^*) for $\text{MgIn}_x\text{Ga}_{2-x}\text{O}_4$ compositions at levels of GGA PBEsol, Meta-GGA r²SCAN and hybrid functional HSE06. The values of the direct band gap are given within parenthesis.

Exchange-Correlation Functional	MgIn ₂ O ₄	MgGa ₂ O ₄	InGaMgO ₄ (IS)	InGaMgO ₄ (L)
	E_g (eV)	E_g (eV)	E_g (eV)	E_g (eV)
PBEsol	1.45 (1.48)	2.88 (3.01)	1.90 (2.05)	2.10 (2.14)
r ² SCAN	2.09 (2.11)	3.62 (3.75)	2.57 (2.72)	2.77 (2.80)
HSE06	3.04 (3.07)	4.71 (4.85)	3.58 (3.72)	3.77 (3.83)
Exchange-Correlation Functional	MgIn ₂ O ₄	MgGa ₂ O ₄	InGaMgO ₄ (IS)	InGaMgO ₄ (L)
	m_e^*	m_e^*	m_e^*	m_e^*
PBEsol	0.324	0.407	0.346	0.285
r ² SCAN	0.391	0.465	0.423	0.305
HSE06	0.160	0.180	0.170	0.206

2.2. Experimental

YbFe₂O₄-type InGaMgO₄ was prepared by calcining a stoichiometric mixture of In₂O₃, Ga₂O₃ and MgO at atmospheric pressure and 1573 K for 6 days [12]. The obtained powder was packed in Pt capsules, loaded into pyrophyllite cells and then treated at 6 GPa and 1473 K for 30 min using a cubic anvil-type high-pressure apparatus. The powder X-ray diffraction patterns were obtained with a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source. SXRD data for structural refinements were collected at the BL02B2 beamline of SPring-8 with a wavelength of $\lambda = 0.50061$ Å. The Rietveld analysis of SXRD data was conducted using the RIETAN-FP program [34]. Transmission electron microscope (TEM) and electron diffraction (ED) images were obtained with a scanning transmission electron microscope (STEM, JEOL JEM-2800). Optical reflectance measurements were carried out using a U-4100 Hitachi High-Tech Co. ultraviolet–visible (UV–vis) spectrophotometer.

3. Results and Discussion

3.1. Theoretical Comparative Analysis between the Layered and the Inverse Spinel Phase

The $Fd\bar{3}m$ cubic phase of spinel MgAl_2O_4 -type structure has two types of cation sites: tetrahedral (T_d) and octahedral (O_h). In agreement with experimental observations [35], both MgIn_2O_4 and MgGa_2O_4 were found to be crystallized in the inverse spinel $P4_122$

structure (see Figure 2a) with $[\text{In}_{1.0}]_{\text{T}_d} [\text{Mg}_{1.0}\text{In}_{1.0}]_{\text{O}_h} \text{O}_4$ and $[\text{Ga}_{1.0}]_{\text{T}_d} [\text{Mg}_{1.0}\text{Ga}_{1.0}]_{\text{O}_h} \text{O}_4$ configurations, respectively. As Mg^{2+} ions exhibit a strong tendency to occupy the octahedral site, we generated MgInGaO_4 configurations by distributing the cations in both the T_d and O_h sub-lattices. The ground state structure predicted by DFT + CE within eight formula units of cell size has inverse spinel $P4_322$ symmetry with $[\text{In}_{1.0}]_{\text{T}_d} [\text{Mg}_{1.0}\text{Ga}_{1.0}]_{\text{O}_h} \text{O}_4$ configuration, with In^{3+} ions showing a higher tendency to occupy the four-fold oxygen-coordinated T_d sites compared to the six-fold oxygen coordination (O_h) sites. The CE model was constructed by fitting the In-Ga-Mg ternary Hamiltonian with DFT calculated energies of 370 configurations, resulting in a CV score of ~ 8 meV/f.u. The calculated formation energies and estimated ECI values are shown in Figure 2. The formation energy of the InGaMgO_4 composition was calculated with respect to the end members, MgIn_2O_4 and MgGa_2O_4 stable compositions, as

$$\Delta_f E = E[\text{InGaMgO}_4] - \frac{1}{2}E[\text{MgIn}_2\text{O}_4] - \frac{1}{2}E[\text{MgGa}_2\text{O}_4] \quad (1)$$

where $E[\text{InGaMgO}_4]$, $E[\text{MgIn}_2\text{O}_4]$ and $E[\text{MgGa}_2\text{O}_4]$ denote the corresponding DFT calculated internal energies. The formation energy of the lowest-energy cation-ordered inverse spinel structure is ~ 0.018 eV/oxygen, which agrees with experimental observations [9] that the inverse spinel phase is less likely to crystallize under ambient conditions. Canonical MC simulations do not clearly indicate any temperature-induced cation order-disorder transition; rather, at 305 K, stabilize structures having $[\text{In}_{0.74}\text{Ga}_{0.17}\text{Mg}_{0.09}]_{\text{T}_d} [\text{In}_{0.26}\text{Ga}_{0.82}\text{Mg}_{0.92}]_{\text{O}_h} \text{O}_4$ cation configurations. Interestingly, the lowest-energy SQS model has a $[\text{In}_{1.0}]_{\text{T}_d} [\text{Mg}_{1.0}\text{Ga}_{1.0}]_{\text{O}_h} \text{O}_4$ configuration. Therefore, the key observations are the following: (1) while In^{3+} ions tend to form at the T_d sites, the Mg^{2+} and Ga^{3+} ions occupy the O_h sites with anti-site disorder, which is in line with the estimated ECI values of binary and ternary clusters; (2) the inverse spinel phase is less likely to form at ambient conditions in contrast to the parent systems; and (3) at finite temperatures, the cations are less likely to form a long-range order. These predictions were experimentally confirmed, as discussed later. In fact, T. Moriga et al. [9] synthesized the YbFe_2O_4 -type layered phase of InGaMgO_4 at ambient conditions. By studying the energies of 200 ordered cation structures, where cations are distributed within the trigonal bipyramidal and octahedral sites of the layered phase, the lowest-energy cation-ordered structure was found to have $P2m$ symmetry and was 0.030 eV/oxygen lower in energy compared to the inverse spinel phase. The calculated formation energy is ~ -0.012 eV/oxygen. In the layered phase, while the In^{3+} ions sit within an oxygen octahedral environment, the Mg^{2+} and Ga^{3+} occupy the five-fold coordinated trigonal bipyramid sites. A phase transition from the layered to inverse spinel structure is expected to take place at around ~ 9.5 GPa of applied pressure, accompanied by a 2% volume reduction.

The band structures of the layered and inverse spinel phases of InGaMgO_4 calculated using HSE functionals, as shown in Figure 3, show an indirect nature of the band gap with values of 3.77 eV ($E \rightarrow \Gamma$) and 3.58 eV ($X \rightarrow \Gamma$), respectively, like the parent compounds MgIn_2O_4 and MgGa_2O_4 . The various band structures corresponding to the inverse spinel phase of $\text{MgIn}_x\text{Ga}_{2-x}\text{O}_4$ compositions display striking similarities across a range of functionalities. These sets of common behavioral patterns are as follows: (1) the valence bands are dominated by O 2p states forming valence band maxima (VBM) at the X $(0, \frac{1}{2}, 0)$ point; (2) valence bands near Fermi energy are flat with localized oxygen 2p bonding character and large hole effective mass; (3) the conduction bands, on the other hand, are primarily composed of post-transition metal 5s states having a strong dispersion and low electron effective mass, originating from the strong antibonding interaction between the cation 5s and oxygen 2p states, a common feature in the post-transition metal-based TCOs such as In_2O_3 , SnO_2 and Ga_2O_3 ; and (4) a direct band gap at the Γ point lies close to an indirect band gap between the X and Γ points. The calculated band gaps (E_g) and mean effective electron masses (m_e^*) for $\text{MgIn}_x\text{Ga}_{2-x}\text{O}_4$ compositions using various exchange-correlation functionals are listed in Table 1. The calculated band gaps at the HSE level for MgIn_2O_4

and MgGa_2O_4 compositions, 3.04 eV and 4.71 eV, respectively, are in close agreement with previous reports [8,9]. The estimated values of electron mean effective masses and reduced effective masses indicate high electron mobility and are comparable to those of known post-transition metal-based TCOs [35,36]. The direct band-to-band absorption spectrum calculated by employing the hybrid HSE06 functional is shown in Figure 3 for both the layered and inverse spinel phases of InGaMgO_4 . In the case of the MgIn_2O_4 parent system, the absorption coefficient reaches a value of 10^4 cm^{-1} at an energy of 3.43 eV, which is close to the optical band gap of 3.4 eV reported for $\text{MgIn}_2\text{O}_{4-x}$ [8,9]. The theoretically estimated optical band gap of MgGa_2O_4 at the level of HSE06, ~ 4.9 eV, is also in good agreement with the experiment. Therefore, according to the HSE06 results, an optical band gap of ~ 3.8 eV is predicted to be observed for InGaMgO_4 . The optical band gap of the layered phase is expected to be slightly higher than that of the inverse spinel phase. We calculated the electronic structures for multiple cation configurations with and without anti-site disorder energetically lying within 50 meV above the energy hull and observed that the value of the indirect band gap varies within 0.1 eV energy around that of the lowest-energy cation-ordered phase (see Table 1) and hence does not significantly depend on the cation ordering or anti-site disorder. Therefore, even if a situation of the formation of cation-disordered states arises at a finite temperature, as observed in the MC simulations, the electronic structure and optical properties of the system are least likely to register any significant alteration.

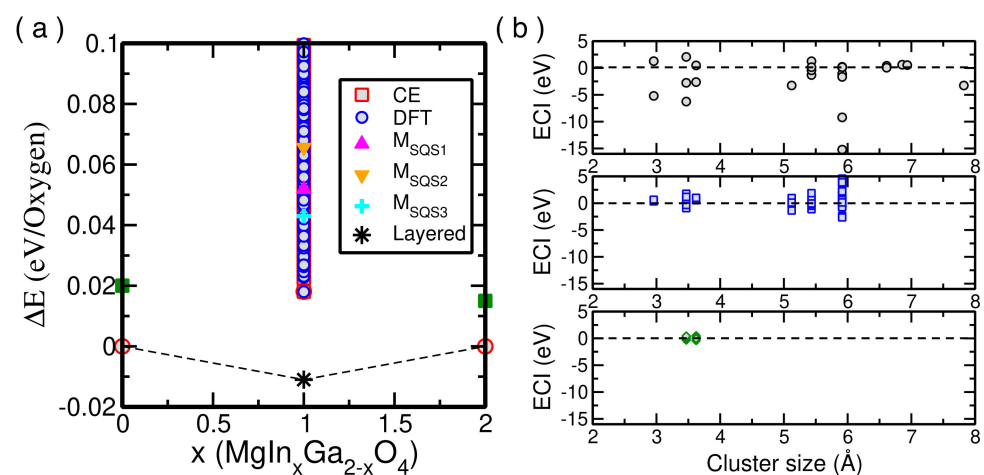


Figure 2. DFT-calculated and cluster-expanded formation energies of the inverse spinel phase of MgInGaO_4 composition as a function of In^{3+} concentration (x). (a) The calculated energies of the spinel and inverse spinel phases of the end members MgGa_2O_4 and MgIn_2O_4 are denoted as green solid squares and red circles, respectively. The special quasi-random structures (SQS) models M_{SQS1} , M_{SQS2} and M_{SQS3} correspond to $[\text{In}_{0.5}\text{Ga}_{0.5}]_{\text{Td}}[\text{Mg}_{1.0}\text{In}_{0.5}\text{Ga}_{0.5}]_{\text{Oh}}\text{O}_4$, $[\text{In}_{0.5}\text{Ga}_{0.25}\text{Mg}_{0.25}]_{\text{Td}}[\text{Mg}_{0.75}\text{In}_{0.5}\text{Ga}_{0.75}]_{\text{Oh}}\text{O}_4$ and $[\text{In}_{1.0}]_{\text{Td}}[\text{Mg}_{1.0}\text{Ga}_{1.0}]_{\text{Oh}}\text{O}_4$ configurations, where Td and Oh denote tetrahedral (multiplicity = 8) and octahedra (multiplicity = 16) sites, respectively. (b) Estimated values of effective cluster interactions (ECI) for two sites (top panel), three sites (middle panel) and four sites (bottom panel) clusters.

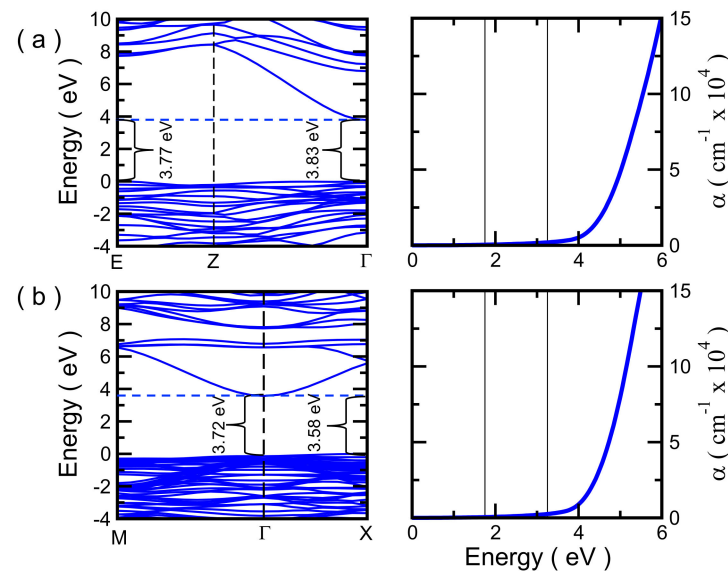


Figure 3. (a) Calculated band structure (left panel) and optical absorption (right panel) for the layered phase of InGaMnO_4 , corresponding to the lowest-energy cation-ordered structure using hybrid potential. (b) Calculated band structure (left panel) and optical absorption (right panel) for the inverse spinel phase of InGaMnO_4 , corresponding to the lowest-energy cation-ordered structure using hybrid potential. The gray band in (b) represents the visible spectrum of light.

Next, to develop insights into the probability of oxygen formation and hence its impact on the electronic and optical properties of InGaMnO_{4-x} compositions, we calculated oxygen vacancy formation energy as a function of oxygen pressure and temperature by using the following equation:

$$\Delta E^f = E_{V_0} - E_0 + \mu_0 + qE_f \quad (2)$$

Here, E_{V_0} and E_0 denote the total energies with and without an oxygen vacancy in a charge state of q , respectively. The oxygen chemical potential and the electronic chemical potential are denoted as μ_0 and E_f , respectively. The chemical potential of oxygen as a function of oxygen pressure (p) and temperature (T) was estimated from the following equation:

$$\mu_0(p, T) = \mu_0(p_0, T_0) + \mu_0(p_1, T) + \frac{1}{2}k_B T \ln\left(\frac{p}{p_1}\right) \quad (3)$$

Here, $\mu_0(p_0, T_0)$ and $\mu_0(p_1, T)$ represent oxygen chemical potential at zero pressure ($p_0 = 0$), zero temperature ($T_0 = 0$ K) and at $p_1 = 1$ atm pressure and finite temperature (T), respectively. The value of the former parameter was estimated from the DFT calculations, $\mu_0(p_0, T_0) = \frac{1}{2}E(\text{O}_2)$, where $E(\text{O}_2)$ denotes the total energy of an oxygen molecule. The second term, $\mu_0(p_1, T)$, was obtained from the experimental data [37]. We estimated the formation energy of a charged (2+) vacancy by performing a total energy calculation in a charge-neutralized cell using a jellium background. The energy shift associated with the jellium neutralization was adjusted by using the total energy of a positively charged perfect crystal. In the inverse spinel structure, each oxygen is connected to one T_d and three O_h sites. Therefore, a 3D distribution of oxygen vacancies is expected. The formation of charged vacancies is ($V_O^\bullet$) ~3.7 eV lower in energy compared to that of neutral vacancies ($V_O^\times$). At the oxidation limit and 0 K, the formation energy of $V_O^\bullet$ is ~0.23 eV, indicating a high probability of oxygen vacancy formation similar to the parent system MgIn_2O_4 [8,9]. The calculated formation energies at a finite temperature and oxygen pressure are given in Figure 4a. In the layered structure, oxygen vacancies can form at the octahedral and trigonal bipyramid layers. Our results show that the charged $V_O^\bullet$ vacancies exhibit a high tendency of becoming accumulated in the 2D $\text{In}_{1-\delta_1-\delta_2}\text{Ga}_{\delta_1}\text{Mg}_{\delta_2}\text{O}$ layer (values of δ_1 and δ_2 are negligibly small), as the formation energy of $V_O^\bullet$ in the trigonal bipyramid layer is

~ 1.2 eV higher in energy compared to that in the octahedral layer. At the oxidation limit and 0 K, the formation of $V_{\text{O}}^{\bullet\bullet}$ in the layered phase is ~ 0.37 eV lower in energy compared to that in the inverse spinel phase. The calculated formation energies at a finite temperature and oxygen pressure are given in Figure 4b. The pressure-induced phase transition can be accompanied by a change in the spatial distribution of oxygen vacancies from 2D $\rightarrow$ 3D. Interestingly, the charged $V_{\text{O}}^{\bullet\bullet}$ vacancy formation was found to have a considerable impact on the electronic structure of InGaMgO_4 , as depicted in Figure 4c. An almost linear decrease in the indirect and direct band gap with the increase in oxygen defects has been observed for the inverse spinel phase. Moreover, a similar trend has also been observed in the case of charged cation defects (see Figure 4d), indicating that the optical properties are expected to be influenced by the cation or oxygen deficiencies.

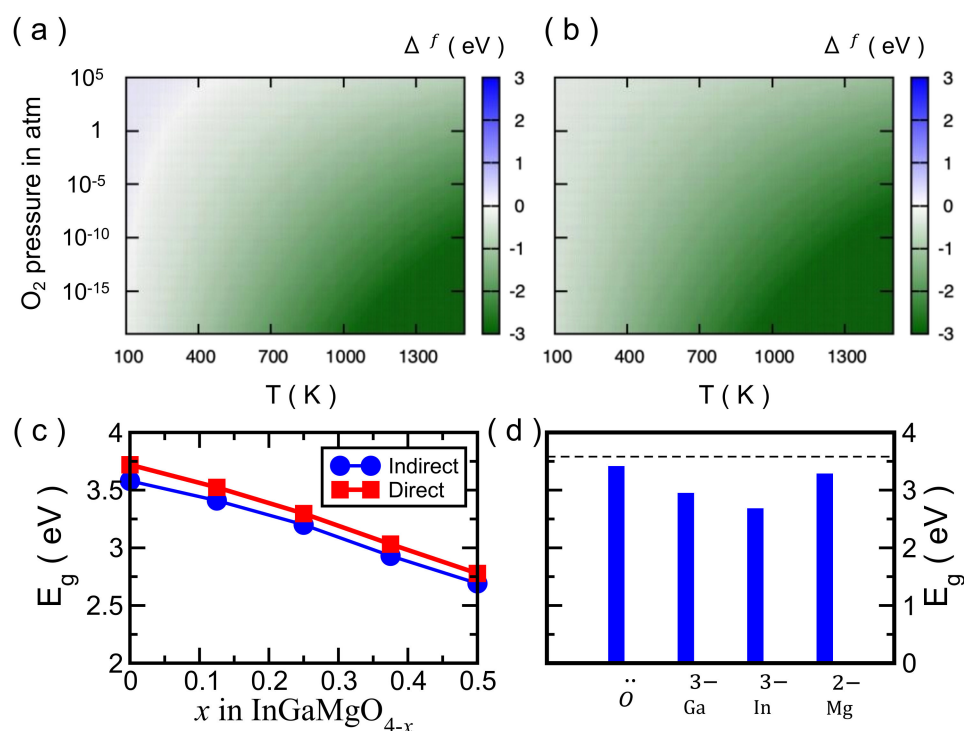


Figure 4. Calculated formation energies (ΔE_f) of charged oxygen vacancy $V_{\text{O}}^{\bullet\bullet}$ as a function of oxygen partial pressure and temperature for the inverse spinel (a) and layered (b) phases of InGaMgO_4 . The E_f was set at the valence band maximum. (c) Calculated energy band gap (E_g) of the inverse spinel phase of InGaMgO_{4-x} as a function of oxygen defect concentration x at the level of HSE06. (d) Estimated band gap values corresponding to the crystals with charged cation and oxygen defects with 0.125 concentration at the level of HSE06. The dashed line denotes the band gap value for the perfect crystal.

3.2. Experimental Investigations of the Structural Transition

Figure 5 shows the result of the Rietveld analysis of the SXRD data of YbFe_2O_4 -type InGaMgO_4 . The refined crystallographic parameters are summarized in Table 2. The refinement indicates the occupations of In in the octahedral sites and Ga/Mg in the trigonal pyramid sites, consistent with the previous report [10]. The site preference is governed by the ionic size rather than the valence of the cations. This phase was further investigated by TEM. Figure 6 shows the TEM image, ED and nano-beam diffraction (NBD) patterns. Twin boundaries, denoted as TB, are observed. NBD reveals that the c -axis is coherent, while the a - and b - axes are inverted at TB.

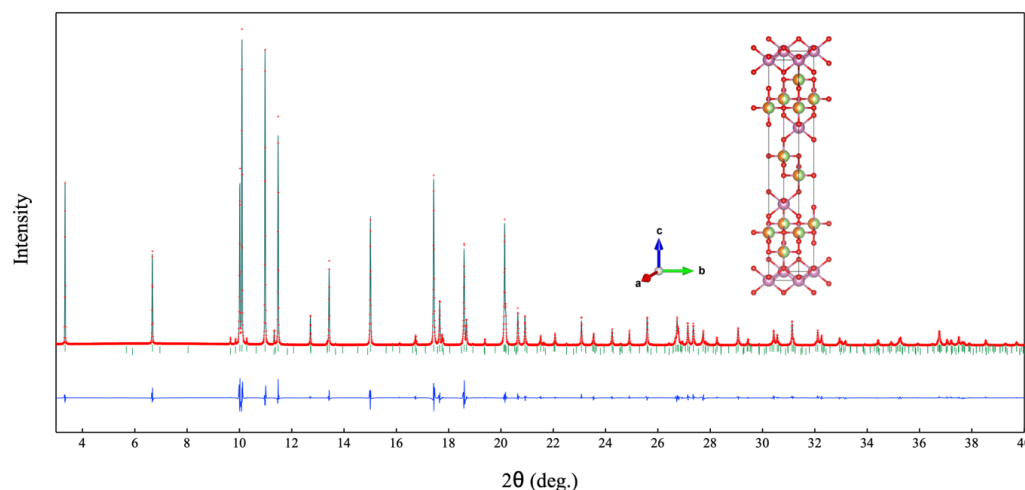


Figure 5. Observed (red points), calculated (green line) and difference (blue line) patterns of YbFe₂O₄-type InGaMgO₄ from the result of the Rietveld analysis of the SXRD data at room temperature ($\lambda = 0.500606$ Å). The green tick marks indicate the positions of Bragg reflections of YbFe₂O₄-type InGaMgO₄, In₂O₃ and MgGa₂O₄ phases from top to bottom. The reliability factors of the refinement were $R_{WP} = 9.62\%$ and $R_I = 1.67\%$. The weight fractions of the impurity of In₂O₃ and MgGa₂O₄ phases were estimated to be 0.3 and 1.7 wt%, respectively. The crystal structure of YbFe₂O₄-type InGaMgO₄ was visualized using VESTA 3 software [14].

Table 2. Refined structural parameters for YbFe₂O₄-type InGaMgO₄ from SXRD data at room temperature.

Atoms	Site	g	x	y	z	$U_{iso}/\text{\AA}^2$
In	3a	0.964 (2)	0	0	0	0.0046 (2)
Ga		0.018				
Mg		0.018				
In	6c	0.034 (3)	0	0	0.21671 (3)	0.0047 (3)
Ga		0.483				
Mg		0.483				
O	6c	1	0	0	0.1289 (1)	0.011 (1)
O	6c	1	0	0	0.2915 (1)	0.005 (1)

Space group $R\bar{3}m$ (No.166), $a = 3.30397(2)$ Å, $c = 25.8047(2)$ Å. The occupation factors g of Mg and Ga are constrained to have identical values for the refinement. The sum of occupation factors for each distinct site is constrained to be unity.

The SXRD patterns of high-pressure processed InGaMgO₄ shown in Figure 7 were indexed, assuming a cubic unit cell with a ~ 8.56 Å indicating the formation of the spinel phase. The calculated density of 5.77 g/cm³ is higher than that of the YbFe₂O₄-type phase, 5.61 g/cm³, in accordance with the pressure-induced phase transition. Since the DFT calculation indicated the structure with In in the T_d site and Mg/Ga in the O_h site was energetically stable and Monte Carlo simulation also showed the tendency of In in the T_d site and 1:1 mixing of Mg and Ga, the Rietveld analysis was performed assuming the presence of Mg/Ga in the 1:1 ratio both in the T_d and O_h sites. It should be noted that the cation occupancies cannot be freely refined in this case, and such a constraint must be applied. The refinement gave reasonable reliability factors of $R_{WP} = 7.960\%$ and $R_I = 2.648\%$. The refined crystal structure is shown as the inset of Figure 7, with the crystallographic parameters summarized in Table 3. The T_d site is predominantly occupied by In³⁺, with a compositional ratio of $\text{In}^{3+}:\text{Ga}^{3+}/\text{Mg}^{2+} = 0.726:0.274$, indicative of the inverse spinel structure as anticipated by DFT calculations and Monte Carlo simulations, while the occupancy factors of the O_h site are $\text{In}^{3+}:\text{Ga}^{3+}/\text{Mg}^{2+} = 0.137:0.863$. The refined u parameter for the oxygen position (u, u, u), 0.3828 , is close to the ideal value $u = 0.375$.

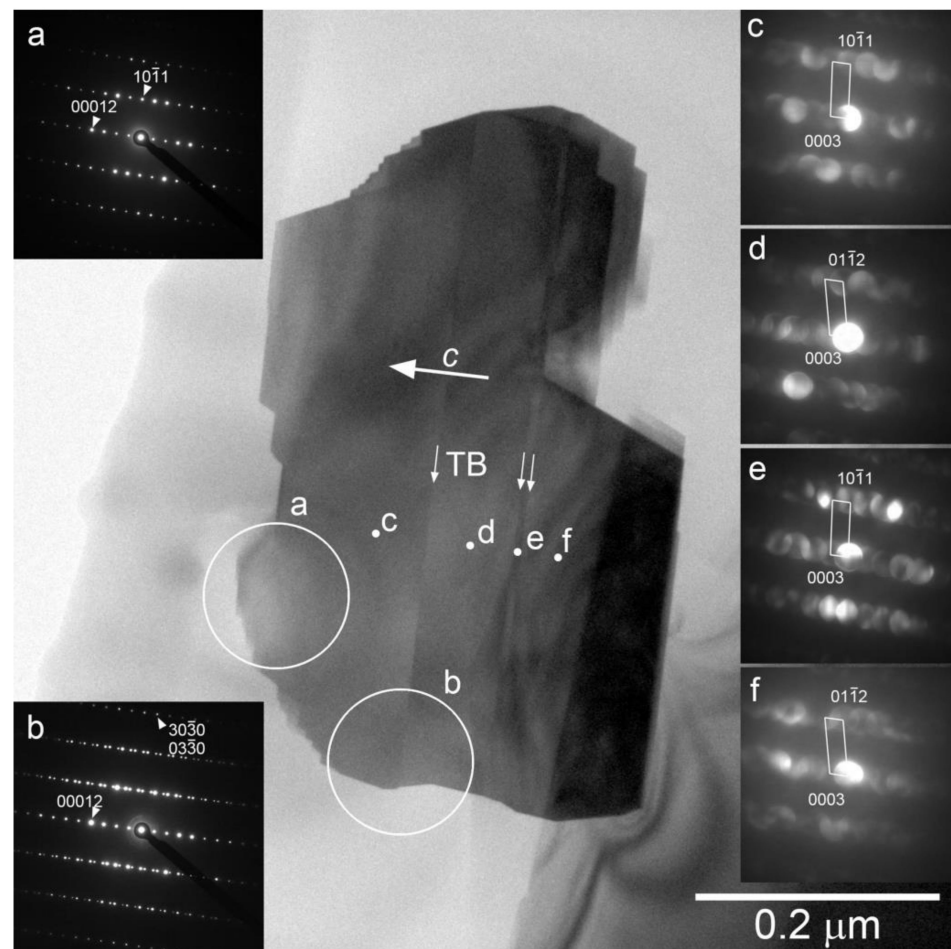


Figure 6. TEM image, ED and NBD patterns of YbFe_2O_4 -type InGaMgO_4 . a and b are the ED images of the corresponding area in the main panel. c–f are the NBD patterns of the corresponding area in the main panel.

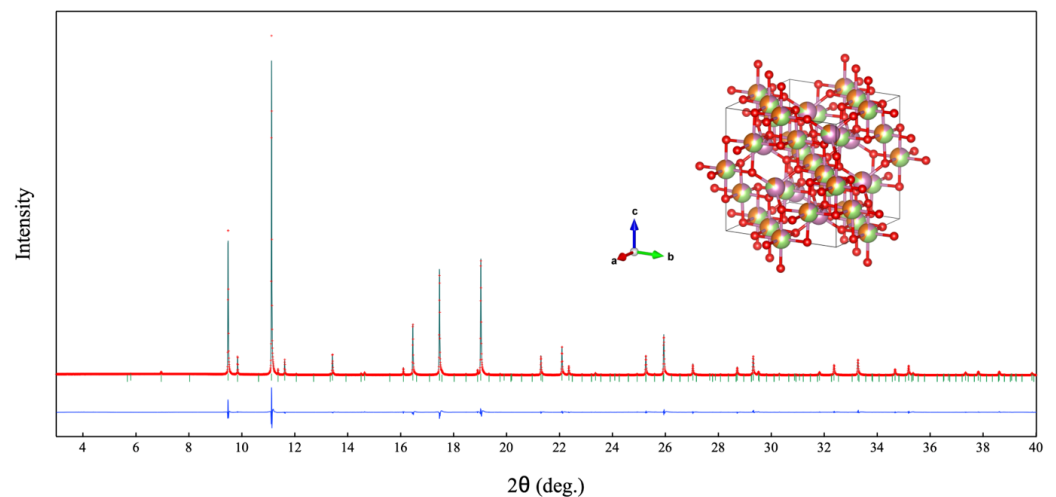


Figure 7. Observed (red points), calculated (green line) and difference (blue line) patterns of spinel InGaMgO_4 from the result of the Rietveld analysis of the SXR D data at room temperature ($\lambda = 0.500606 \text{ \AA}$). The tick marks correspond to the positions of Bragg reflections of the InGaMgO_4 spinel and In_2O_3 phases from top to bottom. The reliability factors of the refinement were $R_{\text{WP}} = 7.960\%$ and $R_1 = 2.648\%$. The weight fraction of the impurity of In_2O_3 was estimated to be 3.3 wt%. The crystal structure of the InGaMgO_4 spinel phase was visualized using VESTA 3 software [14].

Table 3. Refined structural parameters for high-pressure processed InGaMgO₄ spinel from SXRD data at room temperature.

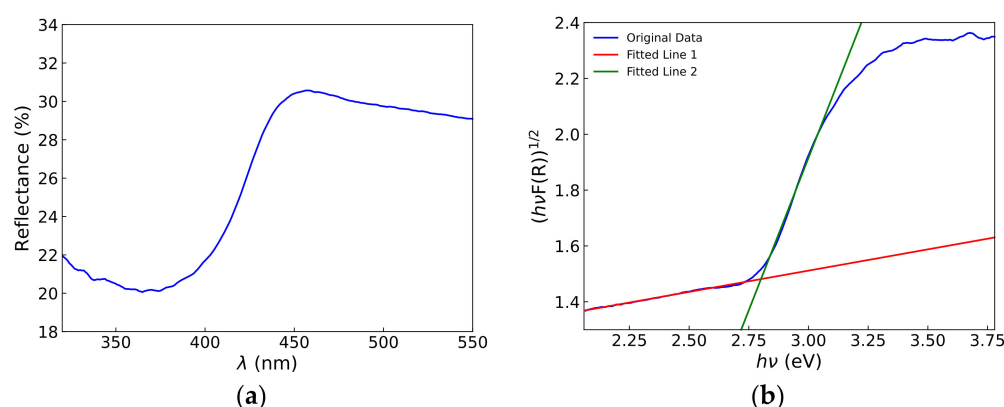
Atoms	Site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> /Å ²
In	8a	0.726 (3)	0	0	0	0.0058 (2)
Ga		0.137				
Mg		0.137				
In	16d	0.432	0.625	0.625	0.625	0.0071 (2)
Ga		0.432				
Mg	32e	1	0.3828 (2)	0.3828	0.3828	0.0118 (6)
O		1				

Space group *Fd-3m* (No. 227), *a* = 8.56615(3) Å. The occupation factors *g* of Mg and Ga are constrained to have identical values for the refinement. The sum of occupation factors is constrained to be unity for each distinct site and maintain the chemical composition of InGaMgO₄.

Figure 8a shows the diffuse reflectance spectrum of the spinel phase. The absorption edge is around 410 nm, corresponding to the band gap of 3.0 eV. To further accurately determine the band gap, the diffuse reflectance data were converted using the Kubelka–Munk function and the Tauc plot was made in Figure 8b using the following Tauc equation:

$$(h\nu F(R))^{1/n} = A(h\nu - E_g), \quad (4)$$

where *F(R)* is the Kubelka–Munk function, *h* is Planck's constant, *A* is a proportionality constant, *ν* is the frequency of light and *E_g* is the band gap energy. Based on the results of the band structure from DFT calculations, direct transitions (indirect transitions) were assumed, with *n* = 2. The band gap was determined by locating the intersection of the linear region and the baseline. The estimated band gap for the spinel InGaMgO₄ is 2.80 eV, close to the calculated value employing *r*²SCAN, but is considerably smaller than the HSE06 value (3.58 eV) and the experimental values reported for MgIn₂O₄ (3.45 eV) and MgGa₂O₄ (4.95 eV) [8,9]. The origin of the smaller band gap is not clear at this stage, but a small amount of cation deficiency under the detection limit of the Rietveld analysis might affect the band gap.

**Figure 8.** (a) The diffuse reflectance spectrum and (b) Tauc plots of spinel phase.

The electrical resistance of spinel InGaMgO₄ was above the range of our measurement system, indicating the sample is highly insulating. The attempt at hole doping by inducing oxygen vacancy by post-annealing in 5% H₂ gas at 723 K as performed for MgIn₂O₄ and MgGa₂O₄ was unsuccessful. No change in the lattice constant or the electrical resistivity was observed.

4. Conclusions

In conclusion, we have successfully obtained the spinel-type InGaMgO₄ phase by treating the layered YbFe₂O₄-type phase at 6 GPa and 1473 K. The formation of an in-

verse spinel structure with $\text{In}^{3+}:\text{Ga}^{3+}/\text{Mg}^{2+} = 0.726:0.274$ in the T_d and $\text{In}^{3+}:\text{Ga}^{3+}/\text{Mg}^{2+} = 0.137:0.863$ in the O_h sites was confirmed by a comprehensive DFT calculation, Monte Carlo simulation and the Rietveld analysis of SXRD patterns. The spinel phase is an insulator with an experimental band gap of 2.80 eV. The attempt at hole-doping by introducing oxygen deficiency was not successful. This is the first report of the bulk synthesis of AB_2O_4 compounds with both YbFe_2O_4 and spinel polymorphs.

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