

Crystal Structure Analysis of $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ Oxynitride Photocatalyst

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Abstract

Gallium zinc oxynitride $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ is a new type of photocatalyst that is capable of overall water splitting under visible light. The crystal structure of the $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ was refined by Rietveld analyses of neutron powder diffraction data. The $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ was confirmed to have a Wurtzite-type structure (space group: P63mc). The present work demonstrates that oxygen substitutes for nitrogen in the crystal structure, and may be responsible for the desirable optical properties of $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ as a photocatalyst for visible light-driven overall water splitting. The neutron scattering amplitude distribution through the maximum-entropy method (MEM) and MEM-based pattern fitting revealed that the crystal structure of the $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ is free of interstitial sites and large disorder.

(1) Introduction

Overall water splitting using a photocatalyst can supply the clean and recyclable hydrogen energy. Maeda et al. reported the gallium zinc oxynitride $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ as a new type of photocatalyst. This is the first example of photocatalyst that is capable of overall water splitting under visible light. The $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ photocatalyst was identified by x-ray powder diffraction to be a single phase with a wurtzite-type structure. The x-ray diffraction peak positions changed with composition x in the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$,

suggesting the formation of solid solution $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$. However, the position and occupancy of nitrogen and oxygen atoms have not yet been known yet, probably due to the difficulty in distinguishing the nitrogen atoms from oxygen atoms through X-ray diffraction method. On the contrary, neutron diffraction can distinguish them from each other, because the neutron scattering length of nitrogen atom (9.36 fm) is different from that of oxygen atom (5.803 fm).

The present work [1] reports a neutron powder diffraction study of the $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$, which was determined in the previous study¹⁾ to be an active composition for overall water splitting.

(2) Experiments and Data Processing

Powders of $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ were prepared by solid-state reaction under NH_3 gas flow. A mixture of Ga_2O_3 (High Purity Chemicals, 99.9%) and ZnO (Kanto Chemicals, 99%) powders was heated under NH_3 flow (250 mL/min) at 1123 K for 5.4×10^4 s to afford the $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ photocatalyst as a yellow powder.

For neutron diffraction measurement, the $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ powder was placed in a $\varnothing 10$ mm \times 50 mm vanadium cylinder. Neutron diffraction data were collected at 299 K using a multi-detector fixed-wavelength powder diffractometer (HERMES) of the Institute of Materials Research, Tohoku University, which is installed at the JRR-3M research reactor of the Tokai Research Laboratories, Japan Atomic Energy

Agency. A neutron beam with wavelength of 0.18207 nm was obtained using the (331) plane of a germanium monochromator.

The crystal structure of the $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ powder was refined by Rietveld analysis of the neutron diffraction data using the computer program RIETAN-2000 with neutron scattering lengths of Ga, 7.288; Zn, 5.60; N, 9.36; and O, 5.803 fm. Scattering amplitude distributions were obtained by a maximum-entropy method (MEM) for the structure factors obtained in the Rietveld analysis.

(3) Results and Discussion

The $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ photocatalyst was confirmed to achieve overall water splitting to H_2 and O_2 under irradiation with visible light. Chemical analysis indicated the average composition of the powder to be $\text{Ga}_{0.933(1)}\text{Zn}_{0.067(3)}\text{N}_{0.896(1)}\text{O}_{0.104(0)}$ where the values in parenthesis are standard errors. Neutron diffraction data for the $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ were successfully analyzed assuming a single hexagonal wurtzite-type phase with space group $P6_3mc$. In a preliminary analysis, we refined the occupancy factors of Ga atom $g(\text{Ga})$ and Zn atom $g(\text{Zn})$ with a constraint $g(\text{Ga})+g(\text{Zn})=1$. The refined $g(\text{Ga})$ and $g(\text{Zn})$ agreed with those obtained in the chemical analysis. In another analysis, we refined the z coordinate of Ga atom $z(\text{Ga})$ and $z(\text{Zn})$ independently. The refined $z(\text{Ga})$ agreed with the refined $z(\text{Zn})$. Therefore, we fixed the occupancy factors: $g(\text{Ga})=0.933$ and $g(\text{Zn})=0.067$, and used a constraint: $z(\text{Ga})=z(\text{Zn})$ in the final analysis. The refined unit cell parameters were $a = 0.31900(2)$ and $c = 0.51835(2)$ nm, and the refined fractional coordinate z for the (Ga,Zn) cation in $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ (0.3782(2)) is in good agreement with that in GaN (0.377(1)). The (Ga,Zn) cation is coordinated with four anions (N,O) to form a $(\text{Ga,Zn})(\text{N,O})_4$ tetrahedron. The interatomic distance between the cation and

anions is in the range of 0.19473–0.1960 nm. The estimated quadratic elongation and angle variance⁶⁾ are 1.000 and 0.35 (deg²), respectively, indicating that the $(\text{Ga,Zn})(\text{N,O})_4$ tetrahedron is regular.

The refined occupancies of N and O atoms determined by Rietveld analysis are $g(\text{N}) = 0.89(2)$ and $g(\text{O}) = 0.11(2)$, where the constraint $g(\text{N}) + g(\text{O}) = 1.000$ was assumed. The corresponding chemical formula $\text{Ga}_{0.93}\text{Zn}_{0.07}\text{N}_{0.89(2)}\text{O}_{0.11(2)}$ agrees well with that determined by chemical analysis $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$, indicating that oxygen substitutes for nitrogen in this material. In the previous study, the variation of the x-ray powder diffraction profile and diffuse reflectance spectra with x in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ suggested this substitution. The present results thus provide direct evidence of the substitution of oxygen for nitrogen in this structure.

The validity of the refined crystal structure and the possible disorder in $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ were investigated by calculating the scattering amplitude distribution using a maximum-entropy method (MEM) and MEM-based pattern fitting (MPF). The MEM equicontour map reproduces the atomic positions determined by the Rietveld analysis, but does not indicate any interstitial sites. This result confirms the validity of the refined crystal structure. The MEM density map also indicates that the structure is free of large positional disorder. Since all the atoms are localized near the stable position and do not exhibit large positional disorder, the reliability factors in the MPF analysis are nearly equaled to those in the Rietveld analysis.

Reference

- [1] M. Yashima, K. Maeda, K. Teramura, T. Takata and K. Domen, "Crystal Structure Analysis of $(\text{Ga}_{0.93}\text{Zn}_{0.07})(\text{N}_{0.90}\text{O}_{0.10})$ Oxynitride Photocatalyst", *Mater Trans.*, 47 [2] 295-297 (2006).