



Structural Study on a Layered Thermoelectric Material: InGaZnO₄

Thermoelectric energy conversion is attracting much interest as a possible application for “environmentally friendly” electric-power generators and highly reliable, accurate temperature-controllable refrigerators used as electronic devices. The performance of a thermoelectric device is defined by its material properties through the figure of merit, $ZT = S^2T / \rho(\kappa_e + \kappa_l)$, where S is Seebeck coefficient, T is operating temperature, ρ is resistivity, and κ_e and κ_l are carrier and lattice thermal conductivities, respectively. Although a thermoelectric material, such as Bi₂Te₃, which has a ZT of about 1, is used in particular fields, its performance is still insufficient for wider commercial use. Thus, the development of new materials with large ZT is the one of the main issues in thermoelectric research.

Electronically and structurally two-dimensional (2-D) materials can be good thermoelectrics, because S increases in a 2-D electronic state [1] and κ_l is reduced in the 2-D crystal structure. A

YFe₂O₄-type layered compound, InGaZnO₄, is a candidate for 2-D material. It has a 2-D crystal structure, as shown in Fig. 1, with InO₂ layers and double GaZnO₂ layers. Moreover, calculation of the electronic structure by means of a cluster model predicted that only the InO₂ layers provide 2-D electrical conduction, if the z coordinates of Ga and Zn sites are significantly different [2]. However, no experimental results on the local structure around Ga and Zn sites have been reported, though such a structural feature plays a key role in understanding the electrical structure of InGaZnO₄. We have, thus, studied the crystal structure of InGaZnO₄ to discuss the 2-D electronic and structural properties by using synchrotron radiation X-rays.

A powder sample of InGaZnO₄ was prepared by solid-state reaction. X-ray powder diffraction data were collected with a Debye-Scherrer-type diffractometer at beamline **BL02B2**. The crystal structure was refined by the Rietveld method using the program RIETAN.

Figure 2 shows the X-ray diffraction pattern and its Rietveld refinement profile. The crystal structure of InGaZnO₄ is rhombohedral space group $R\bar{3}m$, and Ga and Zn atoms are distributed randomly at 6c crystallographic positions between InO₂ layers.

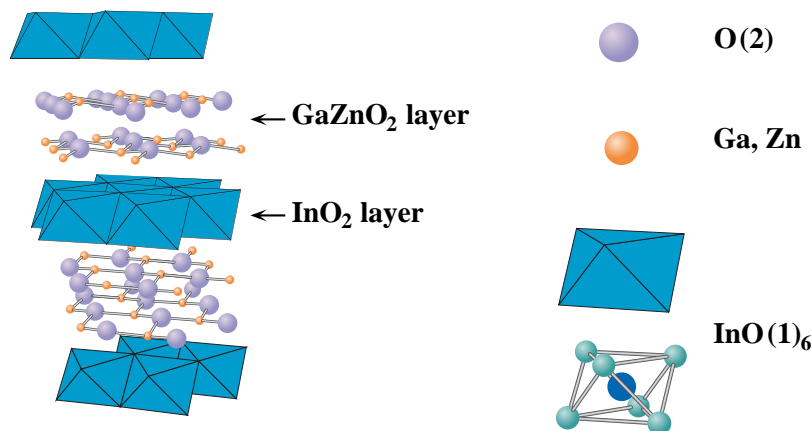


Fig. 1. Crystal structure of InGaZnO₄.

However, since the valence state and ionic radii of Ga and Zn are different, the positions of these atoms are also different. The structure refinement based on a model with different z coordinates for Ga and Zn gives a fairly good fit to the observed diffraction pattern.

The results of Rietveld refinement show that the z coordinates of the Ga and Zn sites differ by 3 to 4%. The difference in local structures around the Ga and Zn atoms is shown in Fig. 3. The random displacement of Ga and Zn atoms causes small overlapping of the 4s orbital of Ga and/or Zn as predicted by the cluster-model calculation, leading to the insulating nature of the GaZnO₂ layer. The In-In atomic distance in the InO₂ layer, on the other hand, is smaller than that in the Sn-doped In₂O₃ (ITO: a transparent conducting oxide with high carrier mobility). This suggests that the direct overlapping of In 5s orbitals causes the high electrical conductivity in the layer. These structural features revealed by our analysis are consistent with the 2-D model in the cluster calculation. However, a preliminary result of the band-structure calculation indicates nearly 3-D electrical conduction due to the orbital overlap between In 5s and Ga 4s, in spite of the difference in the z coordinates of Ga and Zn [3]. A precise electronic-band-structure calculation using the refined structural parameters is now in progress.

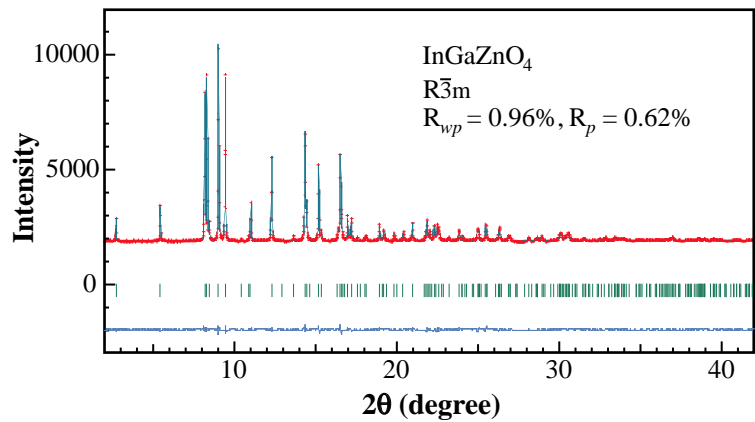


Fig. 2. High-resolution X-ray diffraction pattern of InGaZnO₄ and its Rietveld profile.

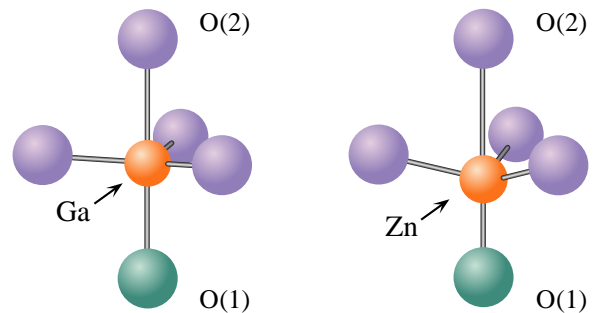


Fig. 3. Schematic of refined local structures around Ga and Zn atoms.

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References

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