Crystal structure refinement of a high-performance thermoelectric material Mg_3Sb_2

R. Sakagami, K. Ono, C. H. Lee

AIST, Japan

Thermoelectric materials have been intensively studied because they can generate electric power from waste heat contributing to energy conservation. A high performance can be attained by low thermal but high electronic conductivity. Mg_3Sb_2 belongs to a family of 122-Zintl phase compounds and is one of well-known n-type high thermoelectric material showing the value of dimensionless figure of merit (ZT) to be 1.65 at T = 725 K [1,2]. Recently, we developed Te-free Mg_3Sb_2 that is an environmental-harmony compound [3]. Remarkably, it exhibits extremely low lattice thermal conductivity (κ_L) with high electronic power factor (S^2/ρ), where S is Seebeck coefficient and ρ is resistivity. The high-power factor can be attributed to the multi-valley structure of electronic bands. In contrast, the origin of κ_L is still controversial. Thus, crystal refinement is important for further understanding.

In this experiment, we conducted powder diffraction measurements of Mg_3Sb_2 at temperatures from 100K to 700K using HERMES diffractometer. The wavelength of incident neutron was 2.2 A. Powder samples were installed in a vanadium cell with size of 6 mm in diameter.

Figure 1 shows a typical neutron diffraction pattern of Mg_3Sb_2 at a room temperature. A green line depicts calculated values of the Rietveld method using RIETAN-FP. The solid line at the bottom indicates the difference between observations and calculations. Table 1 shows the obtained atomic parameters for Mg_3Sb_2. Mg atoms located at two different sites forming ionic [Mg(1)] and covalent [Mg(2)] bonding. The atomic displacement parameters demonstrate that Mg with ionic bonding vibrate quite largely resulted from a large free space. This can contribute to suppress the lattice thermal conductivity. The Mg(2) atoms form two kinds of bonding with Sb atoms. The bond-length of in-plane Mg(2)-Sb is 2.82 Å, which is consistent with a typical covalent bonding. On the other hand, the bond-length of out-of-plane Mg(2)-Sb is longer with the value of 2.95 Å. This indicates the formation of polar bonding. The Mg(2)-Sb layers can, thus, be interpreted as forming a biplanar structure in terms of electronic states where electronic conduction layers split along the c-axis.

In conclusion, we determined atomic parameters of Mg_3Sb_2 by neutron powder diffraction measurements. The obtained results provide required parameters for the first principle calculation of electronic and phonon bands that are essential for understanding its thermoelectric properties.

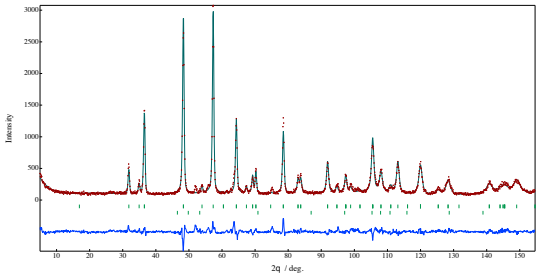

Fig. 1. Neutron diffraction patterns of Mg_3Sb_2. at a room temperature. Vertical bars show the calculated positions of the diffraction peaks.

Atom	Site	*g*	*x*	*y*	*z*	*B* (Å^2)
Mg_3Sb_2						
a = 4.568(7) Å, *c* = 7.240(8) Å, R_{wp} = 10.98 %						
Mg(1)	1a	1	0	0	0	3.1(3)
Mg(2)	2d	1	1/3	2/3	0.6348(5)	2.1(2)
Sb	2d	1	1/3	2/3	0.2269(5)	1.4(2)

Table 1. Atomic parameters for Mg_3Sb_2.

[1] H. Tamaki et al., Adv. Mater. 28, 10182 (2016).

[2] J. Zhang et al., Nat. Commun. 8, 13901 (2017).

[3] K. Kihou *et al.*, J. Mater. Res. Technol. 10, 438 (2021).