

Studies on crystal structures and
anharmonic thermal vibration of
thermoelectric materials Cu_{2-x}S

< Abridged version of Doctoral Thesis >

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1. Introduction

Thermoelectric technology

Currently, eco-friendly energy and energy efficiency enhancement are emerging as important issues. Thermoelectric (TE) technology is a strong candidate for such needs.

The TE technology can convert heat to electricity and vice versa directly without the conventional thermodynamic engine. Therefore, it can be applied to increase energy efficiency by using wasted heat, making a generator using body heat, or developing a small-size refrigerator. There is a dimensionless figure of merit of TE materials called ZT ($ZT = S^2 \sigma T / \kappa$, S , σ , T , and κ indicate Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively). The physical parameters consisting of ZT have strong carrier concentration dependence and trade-off relations. Therefore, it is necessary to find an optimized carrier concentration. However, the lattice thermal conductivity is independent of the carrier conductivity, so lowering lattice thermal conductivity is an essential strategy for enhancing TE materials.

Promising thermoelectric materials $\text{Cu}_{2-x}(\text{S}, \text{Se})$

Among many TE materials, $\text{Cu}_{2-x}(\text{S}, \text{Se})$ have been reported to have a high ZT of about 2. Their high ZT is due to their very low thermal conductivity.

In common, the $\text{Cu}_{2-x}(\text{S}, \text{Se})$ (near $x = 0$) have an Fm-3m space group, anions form the fcc framework, and cations exist in 8c and 32f sites making tetrahedron distribution. Moreover, $\text{Cu}_{2-x}(\text{S}, \text{Se})$ are classified as non-stoichiometric compounds that allow a wide Cu defect range. Furthermore, $\text{Cu}_{2-x}(\text{S}, \text{Se})$ shows very high ionic conductivities in the high-temperature region.

Controversy of origin of low thermal conductivity on $\text{Cu}_{2-x}(\text{S}, \text{Se})$

The physical origin of low thermal conductivities of $\text{Cu}_{2-x}(\text{S}, \text{Se})$ is somewhat controversial. In 2012, H. Liu et al. firstly insisted that the low thermal conductivity of Cu_2Se is maybe its high ionic mobility of the Cu atom, and proposed a terminology PLEC (Phonon-Liquid Electron-Crystal). However, in 2017, Voneshen et al showed, using neutron spectroscopy, that the energy

suppressed by ion hopping is too low to explain the low thermal conductivity. In addition, Voneshen speculated that the origin of low thermal conductivity might be due to its large anharmonicity. In 2020, W. Zhang et al. reproduced the low thermal conductivity of Cu_2Se by theoretical calculation introducing up to 4th order anharmonic potential.

Cu defect dependent lattice thermal conductivity

Meanwhile, several researchers have reported the lattice thermal conductivity of $\text{Cu}_{2-x}(\text{S}, \text{Se})$ according to the temperature variation and amount of Cu defects. The lattice thermal conductivity showed an increasing trend when the Cu defects increased.

However, this increasing trend is somewhat unconventional when considering the heat capacity and the point defects. We speculated that anharmonicity is a possible reason for increasing lattice thermal conductivity.

2. Experiment

Sample synthesis

In this study, we synthesized Cu_{2-x}S ($x= 0, 0.08, 0.12, 0.16, 0.2$) through the liquid-solid reaction method.

After the synthesis process, the room temperature phases of the samples were checked by X-ray diffraction (XRD) measurements.

Each compositional sample is expected to have different phases and the obtained XRD patterns are all explained as the peak positions of expected phases.

X-ray absorption spectroscopy at Cu K-edge

Cu K-edge X-ray absorption spectroscopy (XAS) of the Cu_{2-x}S powder samples was conducted at 8C beamline in Pohang Light Source, Korea, using transmission yield mode.

We performed XAS at room temperature to estimate the Cu-valences in Cu_{2-x}S .

The absorption coefficient, which represents the probability of electron excitation from the core level to the unoccupied electronic states (conduction band), is collected as a function of the incident X-ray's energy. The energy at the steepest slope in the XAS spectra or at the maximum in the derivative spectra can be utilized to roughly estimate the valence of the Cu ions. The peak position of derivative spectra were estimated by a Gaussian fitting.

If the Cu-S bonding in Cu_{2-x}S were purely ionic (without covalent nature), Cu valences in Cu_2S and $\text{Cu}_{1.8}\text{S}$ should have been +1 and +1.11, respectively, because the S anions would possess a fixed valence of -2. Meanwhile, S has a lower electronegativity than O so that the bonding character of the Cu-S bonds tends to be more covalent compared to Cu-O bonds. Thus, the overall small oxidation numbers in Cu_{2-x}S is reasonable. Although the XAS analysis was done at room temperature, the information on the Cu valences would be valid even for high-temperature phases, namely in the cubic structure as well.

Sulfur evaporation and quartz capillary sealing

At high temperatures, sulfur evaporations on the Cu_{2-x}S sample were observed.

We conducted a thermogravimetric (TG) measurement and high temperature X-ray diffraction (HT XRD) on $\text{Cu}_{1.8}\text{S}$ to confirm thermal stability. However, $\text{Cu}_{1.8}\text{S}$ sample emitted sulfur gas at 700°C inducing the compositional changes.

Since compositional change during high temperature measurement is fatal, so we tried to seal the bulk form of samples to quartz capillary.

High temperature powder diffraction

We conducted high-temperature neutron powder diffraction experiments at high-resolution diffractometer BL08 SuperHRPD and BL09 SPICA, MLF, J-PARC in Japan.

3. Crystal structure analysis

Rietveld analysis

The crystal structure of Cu_{2-x}S were refined by the Rietveld method.

In the unit cell of Cu_{2-x}S , the S atom has one site (4a). However, for the Cu atom, the split atom model was used by introducing the Cu2 site; that is, one (or less) Cu atom is split into 5 sites, 1-Cu1 site (8c) and 4-Cu2 site(32f). Split Cu atom expresses anisotropic thermal vibration. The anisotropic vibration implies the existence of the deformed anharmonic potential of the Cu atom.

At all compositions, as temperature increases, the lattice constant shows a linearly increasing trend; moreover, as Cu defects increase, the lattice constant a show linearly decreasing trend. For the temperature factor of the Cu and S atoms, at all the temperature ranges, $B(\text{Cu})$ is larger than $B(\text{S})$. It is consistent with the reported ionic conduction property in which the S atom forms a rigid framework, and the Cu atom is loosely bound. However, there is no clear Cu defect dependence.

As temperature increases, the atomic coordinate of Cu_2 $x(\text{Cu}_2)$ shows clear increasing trends in all compositions. However, $x(\text{Cu}_2)$ does not show clear compositional trends on Cu defects.

As the temperature increased, the occupancy of the Cu2 site, $g(\text{Cu}_2)$, increased. But as Cu defects increased, $g(\text{Cu}_2)$ decreased.

4. Nuclear density distribution analysis

The Nuclear density distributions of Cu_{2-x}S were analyzed by the Maximum entropy method (MEM). The Cu atom showed an anharmonic feature compared to the S atom.

The temperature and compositional MEM density of the Cu and S atoms are compared.

For the Cu atom, as temperature increases, densities are spread to outward from the Cu1 site. Moreover, as Cu defects increased, density distribution showed concentrating trend on the Cu1 site.

For the S atom, there is no clear dependence on temperature and Cu defect.

The Rietveld analysis and MEM analysis results show similar results. Since the split Cu₂ site expresses the anharmonic thermal vibration of the Cu atom. These results indicate that the anharmonicity reduces when the Cu defect decreases and when the temperature increases.

5. One-particle potential analysis

We introduced One-particle potential using Boltzmann distribution on MEM nuclear density for a more direct discussion on anharmonicity.

The feature of the One-particle potential of the Cu atom is obviously deformed compared to the S atom. The temperature and compositional One-particle potential of the Cu and S atoms are compared.

For the one particle potential of the Cu atom, as temperature increased, potential became sharper, and as Cu defect increased, potential became sharper.

For one particle potential of the S atom, there are no clear temperature and compositional trends.

Furthermore, the obtained One-particle potential was fitted by a three-dimensional potential function considering the cubic symmetry, and the physical meaning was examined from each coefficient obtained as a result of the fitting.

The coefficient (corresponding to the spring constant) α of the harmonic term of the three-dimensional potential function was smaller in Cu than in S. This reflects that the system is a Cu ionic conductor, with the S atoms forming the cage and copper atoms loosely bound within the cage. In addition, the larger Cu defect x showed the larger α , indicating that the harmonicity increases with the increase of defects.

Furthermore, the ratio β / α , where β is the anharmonicity term, indicates that the anharmonicity decreases with the increase of x . In addition, β / α is smaller as the temperature increases, indicating that the anharmonicity is reduced.

6. Summary

The anharmonicity ratio is the largest in Cu_2S .

The anharmonicity ratio decreases as Cu-vacancy defects increase in Cu_{2-x}S .

The increase of lattice thermal conductivities on Cu-defects is ascribable to the decrease of the anharmonicity ratio.