MERIT self-directed research

Ultra-fast lattice dynamics of polar one-dimensional ion conductor candidate Ln_3AgGeX_7

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Summary

We made single crystals of the one-dimensional chiral polar magnetic ion conduction semiconductor candidate material $Nd_3AgGeSe_7$, and an attempt was made to capture the dynamics of Ag ions through electron beam diffraction experiments.

Authors

Yusuke Chiashi : Real-space observation of lattice dynamics based on electron beam diffraction

Aki Kitaori : Material search / selection, single crystal sample growth

Back ground

Ion conductors, which are solid but whose ionic positions in crystals change, are substances that have been studied for a long time due to their characteristics. In addition, the behavior in which the position of ions in a solid, which can be said to be its precursor phenomenon, is unstable is also expected to enhance the thermoelectric effect through inhibition of heat conduction. [1]. The mechanism of microscopic ion diffusion that explains such physical properties has been the subject of discussion, and it is important to experimentally obtain information on the dynamics of microscopic ions and their interaction with the surrounding environment. Especially LISICON The dynamics of ionic conductors with one-dimensional conduction paths, including Li ion solid-state battery materials such as [2], should be elucidated from an applied point of view.

$Ln_3M^1M^2X_7$ (Ln: lanthanoid, M^1 : Ag, Cu , etc. , M^2 : Si, Ge, Sn, X: S, Se) that we focused on this time is belonging to $CuLa_3SiS_7$ type structure of $P6_3$. From the viewpoint of symmetry, it has both polarity and chirality, and it is possible to introduce magnetic

ions such as Ce, Pr, Nd, Sm, Gd, Tb, and Er into the Ln^{3+} site. In addition, although it depends on the composition, it is often a semiconductor with a bandgap of 1-2 eV, and some studies have focused on the opto-electrical characteristics. Among them, this time, the target system was a composition in which the M^1 site is Ag.

This substance has a crystal structure in which Ag atoms are arranged one-dimensionally (Fig. 1), and a large atomic displacement of the ion position has been reported in the related substance $La_3AgSnSe_7$ [3]. If ion dynamics are observed in this material as well, it will be an example of a system for evaluating the effect of one-dimensional Ag ion arrangement on the dynamics of ions.

$Nd_3AgGeSe_7$ has the same crystal structure in the system, and we attempted to observe the dynamics of Ag ions by electron diffraction of this material.

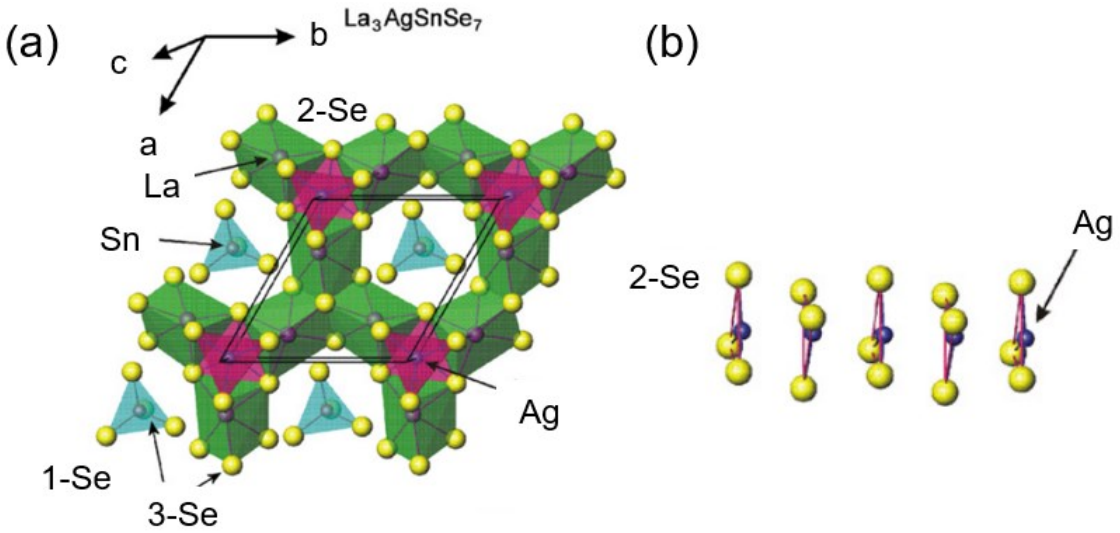

Figure 1 ：Crystal structure of $Ln_3M^1M^2X_7$

(a) Crystal structure of $La_3AgSnSe_7$. (b)Ag and Se around Ag. We can see 1-dimensional Ag chain.

Experimental method

Sample preparation

The sample was prepared by the flux method. 10 times the amount of KI was mixed with the elemental powder mixed in the stoichiometric ratio of the target product, and sealed in a vacuumed quartz tube. The KI used was one that had been repeatedly heated, dried and crushed several times in advance. The quartz tube was kept at 1000 ° C at 100 ° C / h and then held for 20 hours, then slowly cooled at 20 ° C / h , cooled to room temperature, and then the flux was dissolved in water to obtain the desired crystals. This recipe was newly designed for this study. The obtained crystal was confirmed to be a single crystal by a Laue camera and its orientation, and it was confirmed by powder X-ray diffraction that it was a target product.

The obtained single crystal is a hexagonal columnar crystal with a total length of about 4 mm, and has a volume more than 10000 times that of the similar single crystal reported in the previous research. (Figure. 2)

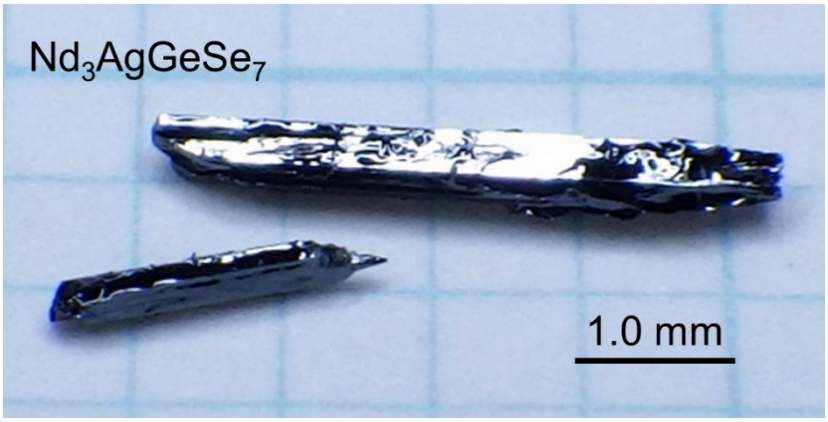

Figure 1: Obtained single crystal

Electron diffraction experiment with an electron microscope

An electron diffraction experiment was performed using a FEI transmission electron microscope Technai Femto. This device can perform pump-probe spectroscopy in combination with the femtosecond laser PHAROS as shown in Figure 3.

The sample was processed into flakes using a Hitachi FIB device to allow electron beams to pass through (Fig. 4 (a)). The sample surface was processed so as to include the a * axis of the crystal, and an electron beam was incident horizontally to the b-axis direction of the crystal.

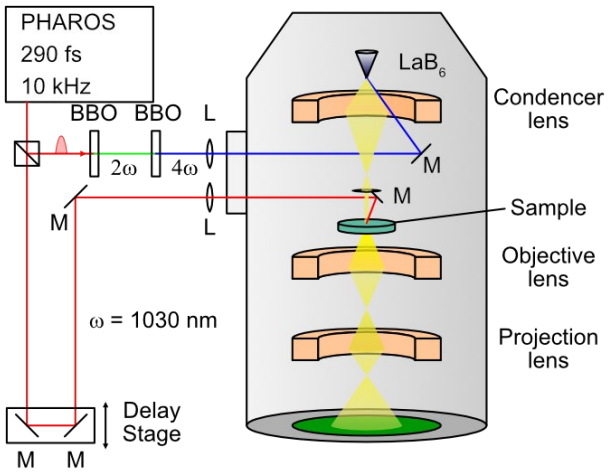

Figure 3: Measurement setup

Results and discussion

An electron diffraction experiment was performed and its temperature dependence was measured. First, an electron diffraction experiment was performed at 300 K (Fig. 4 (b)) . The electron diffraction pattern shows Bragg diffraction points in the a * and c *

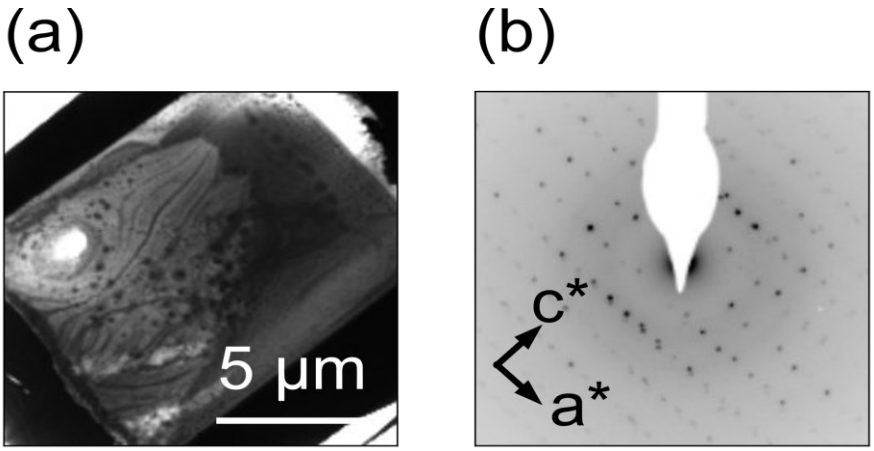

Figure 4：Fragment sample and corresponding diffraction pattern

(a) Bright field image of the sample. (b) Electronic diffraction pattern.

directions. When the lattice constant is calculated from the obtained Bragg diffraction point, it becomes a = b = 9.80 Å, c = 5.56 Å, which is compared with the value a = b = 10.58 Å, c = 5.99 Å of the related substance $La_3AgSnSe_7$. It's one size smaller. It is considered that the difference in the ionic radii of the constituent elements S n and Ge has an effect.

Next, the temperature change of the electron diffraction pattern was observed. At 300 K an electron diffraction pattern in Fig. 5 (a) was shown, but when the temperature rose to 400 K, it became as shown in Fig. 5 (b). It can be seen that the intensity of the Bragg reflection that satisfies the condition $h \neq 3n$ is strongly attenuated. The Debye-Waller effect and the crystal structure factor are considered as components that attenuate the intensity of Bragg reflection. However, the Debye-Waller effect cannot attenuate the intensity of a particular Bragg reflection, resulting in a contribution from crystal structure factors.

When considered as a crystal structure factor, it suggests that the atomic displacement inside the unit cell has brought the crystal period in the $\frac{1}{3}$a * direction closer to. This phenomenon cannot be explained because the period itself does not change when the Ag ion position is disordered, and it is necessary to change the position of other atoms. Also, the halo diffraction that occurs when the Ag position is disordered. [4] could not be observed through temperature experiments. It can be seen that the A g position is not disordered due to this temperature change. From this, it is considered that while the atomic positions other than the Ag ion change at 400 K in this material, they do not show the disorder of the Ag position unlike $La_3AgSnSe_7$. It is considered that the cause of this is that the path through which Ag ions can move is narrowed due to the small unit cell.

The temperature was further raised to 550 K, an irreversible change occurred in which Bragg reflection points appeared in a polycrystalline form (Fig. 5 (c)). Since the bulk sample did not break due to heating, it is considered that the thinning of the sample had an effect. Specifically, when the surface of the ionic conductor Ag_2S is irradiated with electrons, Ag precipitates at a certain temperature. It is probable that changes such as [5] have occurred.

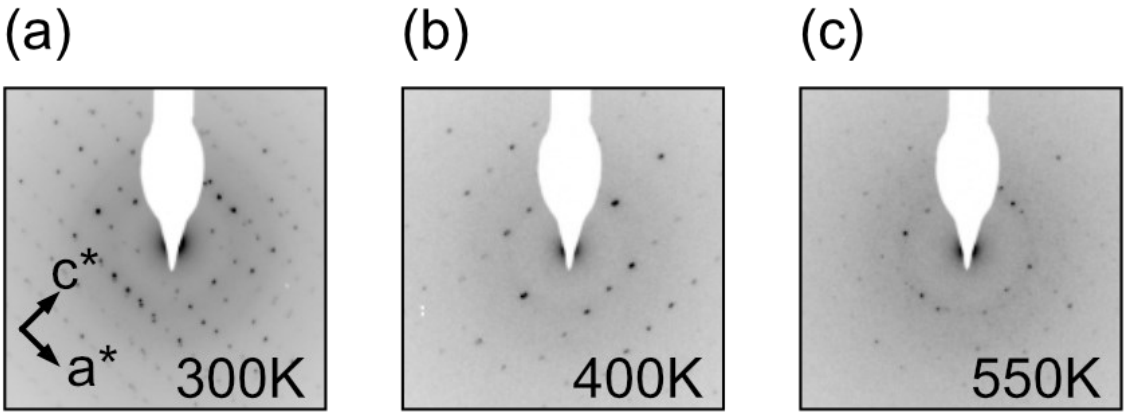

Figure 5：Temperature dependence of electronic diffraction pattern

(a) Electronic diffraction pattern at 300 K. (b) Electronic diffraction pattern at 400 K. The exponent in the a* direction is significantly reduced. (c) Electronic diffraction pattern at 550 K. Some of the diffraction points become circular and the crystals collapse to become polycrystals.

Conclusion

In this study, we achieved single crystal synthesis with a novel composition for the one-dimensional ion conductor candidate substance $Ln_3M^1M^2X_7$, and attempted to observe the dynamics of Ag ions in an electron diffraction experiment using a transmission electron microscope. This substance with a new composition has a crystal structure in which Ag atoms are arranged one-dimensionally, and one-dimensional ion conduction is expected. In the electron diffraction experiment, a large atomic displacement of the ion position was confirmed due to the temperature rise. On the other hand, the disorder of Ag ion position due to the temperature rise was not observed in this material. It is considered that this is because the conduction path around the Ag ion is narrowed and the activation energy of ion conduction is increased. It is expected that one-dimensional ion conduction can be observed by creating $Ln_3M^1M^2X_7$ whose constituent elements include those with a large ionic radius.

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