Ionic thermoelectric phenomena in copper(I) selenide during the α→β phase transition and beyond

Thermoelectricity is a phenomenon based on a conjunction of transport of charge carriers (typically electrons) with the transport of heat. In some materials, the thermoelectric effect is strong enough to make the material applicable in thermoelectric devices, in which electric current is used to transport heat. They are used *e.g.* in portable refrigerators or radioisotope thermoelectric generator, often used in spaceships. One of these materials is copper selenide (Cu_2Se).

Another interesting property of the copper selenide is a change of material's structure about 130°C. In this transition, copper ions are released from their positions in the crystal structure. In higher temperatures behave like a liquid. In this form, the ions have relatively high mobility. Consequently, the Cu^+ ions can conduct electric current and have their thermoelectric effect, distinct from the thermoelectric effect of electrons. The transport effects of electrons and ions are conjugated by one thermal gradient and one electric field in the material. The transition hasn't been accurately investigated and explained yet. *E.g.*, in preliminary research we have observed, that electrical conductivity and Seebeck coefficient (a measure of the thermoelectric effect) changes differ between measurements during heating and cooling.

Ions-related thermoelectric effect is still a gap in the knowledge of ion-conducting thermoelectric materials. There is only one scientific report regarding ionic thermoelectric phenomena in copper selenide, and that measurements were performed only above 300°C. Considering, that during the transition, ordering of Cu^+ ions changes, investigation of the ionic thermoelectric effects is important for a good understanding of the transformation.

Typically, in the equipment for electrical measurements, metallic parts, which conduct electrons, are used. This makes the apparatus sensible for electrons-related properties. For measurements of ionic electrical properties, we need to build a measurement setup with electrodes conducting only copper ions.

Having this apparatus, we will perform measurements of the thermoelectric effects, both related to electrons and ions, in different thermal cycles. This will allow to find out, how the thermoelectric properties change with time and temperature and look for stability of the properties. Additionally, the reproducibility of the results will be evaluated. In parallel, the structure and thermal characteristics of the material will be investigated. We will look for relationships between structure and thermoelectric properties to explain changes in these properties occurring during the transition as well as in other temperatures.

The ionic measurements will be performed not only in a temperature region of the transition but also in higher temperatures, in which copper selenide will operate if used in thermoelectric devices. Properties of Cu_2Se are dependent on a deficiency of copper (less than 2 in the stoichiometric formula). Moreover, additives can be used to modify the material. For example, copper selenide with indium addition was found to be more stable. Structures with different copper deficiency and those, in which some Cu atoms are replaced by silver or indium and some Se atoms by tellurium, will be investigated. We will check, how these modifications influence the ionic transport properties and stability of the material.