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Incommensurate structure analyses of Bi-Te and Sb-Te binary system

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Sb-Te binary compounds are well known as base materials for optical data storage media. They have long-period cubic close-packed ABC stacking structures [1]. Two kinds of fundamental structural units form an intergroth along the stacking direction at the atomic level. Chemical formulae of Sb-Te binary compounds are expressed as $(\text{Sb}_2)_n(\text{Sb}_2\text{Te}_3)_m$, where n and m are integers. The period of stacking structure is considered to be determined by the ratio of the two atomic species. However, our recent study revealed that stacking period of this system changes with temperature [2]. Bi-Te binary compounds which have similar crystal structures also show this tendency. We then performed synchrotron powder diffraction experiments and crystal structure analyses in order to clarify the temperature dependence of these stacking period in Sb-Te and Bi-Te binary systems.

$\text{Bi}_{14}\text{Te}_{15}$, $\text{Bi}_{10}\text{Te}_{11}$, Bi_8Te_9 and Bi_3Te_4 compounds were synthesized by melting method and $\text{Sb}_{67}\text{Te}_{33}$ and $\text{Sb}_{60}\text{Te}_{40}$ compounds were synthesized by sputtering method, as specimens. Powder X-ray diffraction experiments were carried out using a large diameter Debye-Scherrer camera with an imaging plate at the SPring-8 BL02B2 beamline. Temperature of powdered specimens were controlled by blowing high-temperature N_2 gas. Measurements were carried out every 50 K from room temperature to 773 K.

The specimens synthesized by sputtering method were amorphous and they crystallized with increasing temperature. It was found from the peak positions of diffraction pattern that the specimens have incommensurate structure at early stage of crystallization. Crystal structure analyses were performed under the superspace group approach, using JANA2006[3]. The basic unit cell consists of cubic close-packed three layers, and modulation of the atomic displacement is characterized by a single modulation vector $q = \gamma c^*$, where γ is a modulation period.

In the case of $\text{Sb}_{67}\text{Te}_{33}$ compound, as-deposited specimen was amorphous up to 388 K. It crystallized into an incommensurate

structure with $\gamma = 1.633$ at 423 K. The γ value then continuously changed with increasing temperature and drastically rised from 1.633 to 1.656 at around 700 K. However, it did not change in the following cooling down measurement. Final γ value 1.656 showed very good accordance with that expected from its composition. Similarly, as for all other specimens, changes of γ values and stacking structures were demonstrated.

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Structural conditionality of proton conductivity in $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2}$ crystals

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Compounds $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2}$ ($M = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$; $X = \text{S}, \text{Se}, \text{P}, \text{As}$) are of considerable interest for extending current knowledge about the nature of hydrogen bonds and their influence on the properties of crystalline compounds. At the same time, these compounds are of importance for applied research due to the formation of phases with conductivity of the 10–2 Ω/cm order of magnitude at relatively low temperatures. The characteristic features of this crystal family are low-temperature ferroelectric or antiferroelectric phase transitions, which result in the ordering of protons in the two-minimum hydrogen-bond potential, and high-temperature superionic phase transitions associated with the disordering of the positions of hydrogen atoms. “Superprotonic” crystals form a specific class of compounds, in which changes in hydrogen bonds in the course of phase transitions result in radical changes in the physical and physico-chemical properties. This crystal family is unique in a class of proton conductors since proton conductivity is property of their structure, instead of consequence of impurity doping process.

X-ray structural data allow to draw a conclusion on the distinction of structural mechanisms of conductivity in $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2} \cdot \text{H}_2\text{O}$ compounds. In $\text{K}_3\text{H}(\text{SO}_4)_2$ crystals high proton conductivity is caused by the formation of dynamically disordered hydrogen-bond network similarly to $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ [1], [2], which enables protons to move over vacant crystallographically equivalent positions, and also by the formation of a multiphase state at further heating (with the retention of the crystal state). In $\text{K}_9\text{H}_7(\text{SO}_4)_8 \cdot \text{H}_2\text{O}$ crystals an essential contribution to conductivity is brought also by crystalline water and K atoms.

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