

Structural Study on a New Mineral, Hitachiite, $Pb_5Bi_2Te_2S_6$

A new mineral, hitachiite (2018-027), ideal chemical formula $Pb_5Bi_2Te_2S_6$, discovered from the Hitachi Mine, Ibaraki Prefecture, Japan, has been approved. Its crystal structure was determined by the SC-XRD method with synchrotron radiation. Hitachiite has a layer-type structure, and the galena-like structural units are sandwiched by the tetradymite-like structural unit in its structure. Obtained structural features indicate that hitachiite can be regarded as a member of the homologous series on the join of Bi_2Te_2S (tetradymite)-PbS (galena).

Hitachiite, ideal chemical formula $Pb_5Bi_2Te_2S_6$, is a new mineral discovered from the Hitachi Mine, Ibaraki Prefecture, Japan [1]. The primary formation age of the ore deposit including hitachiite in the mine is estimated to be at least 5.3 Ga [2-3], and the ore deposit is the oldest in Japan.

The chemical formula of hitachiite lies on the join of Bi_2Te_2S -PbS in the system Pb-Bi-(Te, S) (Fig. 1). Some of the minerals on this join such as tetradymite, aleksite, and saddlebackite are classified into the tetradymite group defined by Strunz and Nickel (2001) [4], and can be regarded as homologous series minerals based on the chemical formula of $Pb_nBi_4Te_4S_{n+2}$ [5]. Many of this group of minerals such as Bi_2Te_3 and Bi_2Se_3 are of interest as materials for topological insulators and superconductors. However, at present, many of the crystal structures of the tetradymite group minerals with Pb have not been determined or refined. Therefore, it is necessary to obtain structural information on these minerals to understand their structural classification.

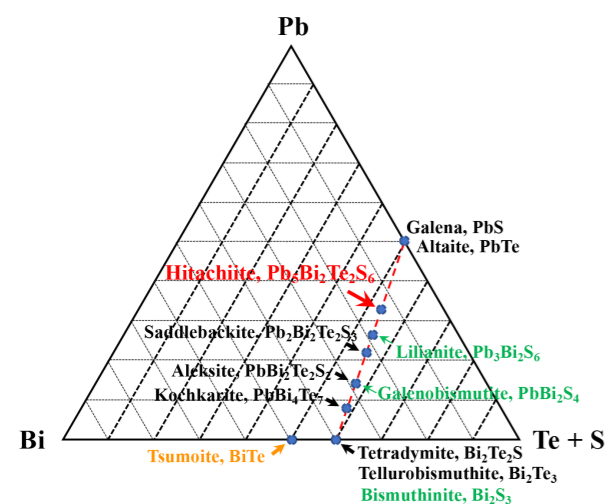


Figure 1: Minerals on the join of PbS - Bi_2Te_2S in the system Pb-Bi-(Te, S).

Single-crystal X-ray diffraction (SC-XRD) experiments were conducted at the beamline BL-10A. In the preliminary check by X-ray oscillation photographs, most of the hitachiite samples showed a streak pattern along the c^* direction due to stacking faults. The sample (0.05 mm x 0.02 mm x 0.02 mm in size) used for SC-XRD was picked up by hand from the polished section after chemical analysis (Fig. 2). The chemical formula of the examined sample was $(Pb_{4.60}Fe_{0.25})_{\Sigma 4.85}(Bi_{2.24}Sb_{0.02})_{\Sigma 2.26}Te_{2.15}(S_{5.62}Se_{0.13})_{\Sigma 5.75}$, which is slightly Bi and Te rich, and Pb and S poor.

The lattice parameters showed trigonal symmetry: $a = 4.2200(13) \text{ \AA}$, $c = 27.02(4) \text{ \AA}$ and $V = 416.7(7) \text{ \AA}^3$. The space group was determined as $P\bar{3}m1$ from the systematic absence in the measured intensities. The crystal structure of hitachiite is based on an ABC-type close-packing of each single element atomic sheet stacking along the c -axis with a periodicity of $\sim 27 \text{ \AA}$ and can be regarded as a layer-type structure (tetradymite archetype) (Fig. 3). The stacking sequence in the unit cell of hitachiite is -Te-Bi-S-Pb-S-Pb-S-Pb-S-Pb-S-Bi-Te- (15 layers). Hitachiite has two types of structural basic units in its structure: galena and tetradymite units.

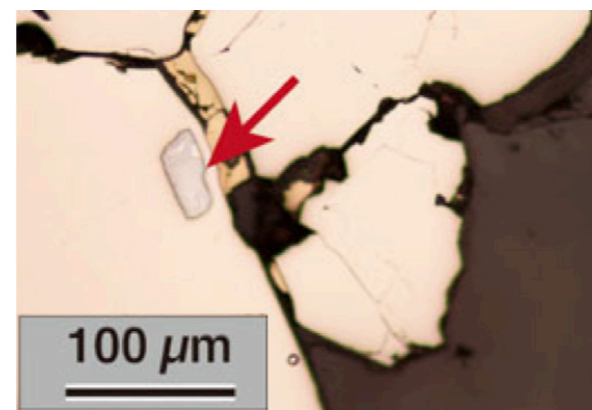


Figure 2: Hitachiite within pyrite under reflection microscope.

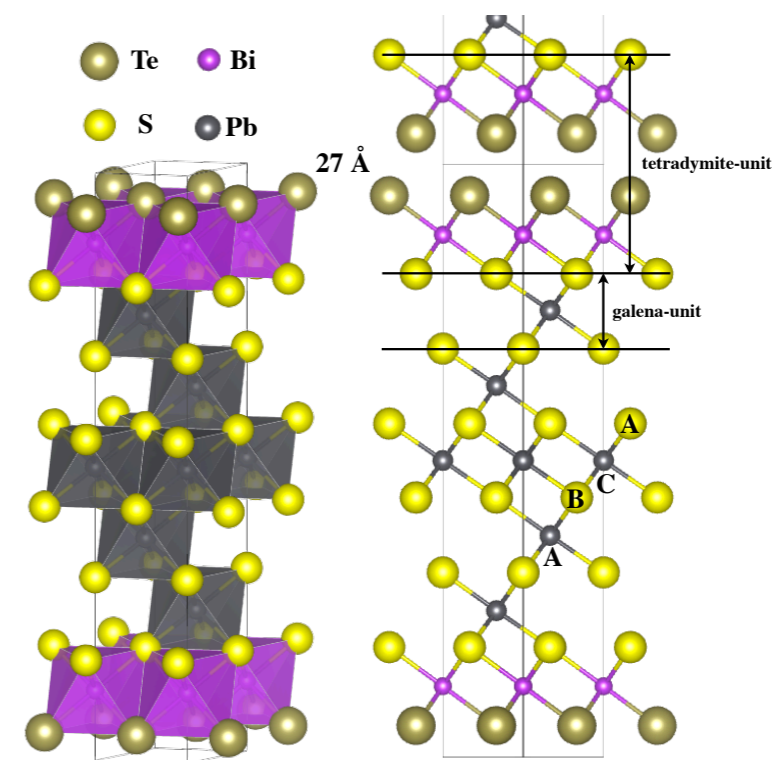


Figure 3: Crystal structure of hitachiite.

The compositional limit for forming the tetradymite archetype structure in the Bi_2Te_3 - Bi_2S_3 system was reported to be $Bi_2S_2Te_2$ - $Bi_2S_{1.3}Te_{1.7}$ [6]. These structural differences due to composition imply that the role of Te in the tetradymite structures due to the differences of chemical properties from S need to be considered. In order to form the tetradymite archetype structure, the key is to have a tetradymite unit (-S-Bi-Te-Te-Bi-S-), which has an anion-anion interlayer except for S-S. In actuality, although rucklidgeite ($PbBi_2Te_4$) and kochkarite ($PbBi_4Te_7$) have tetradymite archetype structures, galenobismutite ($PbBi_2S_4$) and mozgovaite ($PbBi_4S_7$) have different ones. Our findings imply that hitachiite can be regarded as a member of the homologous series of $Pb_nBi_2Te_2S_{n+1}$. In addition, natural hitachiite includes some impurities such as Fe and Sb. Further study is needed, especially to obtain the positional information on Fe in its structure because the Fe-Te layer in the tetradymite archetype structure plays an important role in controlling electric properties [7].

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