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Microstructure of Thermoelectric Material - $Pb_{1-x}Sn_xSe$ and PbSe

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Lead Selenide (PbSe) has been used for thermoelectric materials since 1950's due to its high thermoelectric figure of merit zT (~0.8 at ~700K where $zT = S^2\sigma T/\kappa$, which depends on the Seebaeck coefficient [the thermopower] S, absolute temperature T, electrical conductivity σ, and thermal conductivity κ) [1]. To extend the temperature range for thermoelectric materials, i.e., to increase the zT, defect engineering by reducing the thermal conductivity has been the most popular approach. The defect engineering used in PbTe(Se) polycrystallites such as the large area grain boundaries, non-stoichiometric of Pb or Te(Se) depletion region and dopant precipitates has been widely studied [2]. However, literature for PbSe and Pb1-xSnxSe have primary focused on special physical properties of topological crystalline insulator [3], and the study of formation of defects in PbSe and $Pb_{1-x}Sn_xSe$ single crystals has been scarce. A microstructure study of the intrinsic defects in PbSe and $Pb_{1-x}Sn_xSe$ single crystals was thus undertaken using conventional and aberration corrected TEM/STEMs.

PbSe and $Pb_{1-x}Sn_xSe$ single crystals were grown by the vertical Bridgman method [3]. The sealed Pb/Se/Sn ingot was first heated to 1223 K in a vacuum quartz tube (~10^{-4} torr) to melt the ingot. It was then pulled out from the hot zone area at the rate of 1 mm/hr. to cool down to room temperature. Thin TEM specimens were prepared by tripod polishing technique, and followed by Ar^+ ion milling. Microstructure and elemental composition were examined using JEOL 2100F TEM/STEM equipped with Gatan Tridiem 863 EELS/GIF and Oxford EDS systems. Atomic resolution STEM high-angle annular dark field (HAADF) imaging was carried out by a probe Cs corrected (CEOS GmbH) JEOL-2100F TEM/STEM. The defect density was measured by the number of defects in HRTEM/HAADF images (more than 50 images), and divided by the total observation area.

EDS spectra of PbSe and $Pb_{1-x}Sn_xSe$ single crystals (inset) reveal the lack of Sn peak at ~3.5 keV in PbSe sample (Fig. 1). TEM images of both PbSe and $Pb_{1-x}Sn_xSe$ single crystals clearly show the high density of strain contrast with ellipsoidal shape morphology (10~20 nm in length and 3~6 nm in width) along <100> direction (Figs. 2a and c) while the electron diffraction (ED) patterns (Figs. 2b and d) also reveal streaks running parallel to <100>, forming the interlink intensity network, and the appearance of supplementary weak {110} forbidden spots (arrows) due to electron scattering by π electrons at $\bar{M}$ [3]. It was also found that the density of strain contrast increases from ~$4x10^{11}/cm^2$ to $8x10^{11}/cm^2$ with the increases in Sn concentration. HRTEM and atomic resolution HAADF images of pure PbSe single crystal reveal typical dislocation defects (Fig. 3a). The weak intensity of Se atoms in HAADF images and slightly distorted lattice arrangement (Figs. 3b and c) are believed to be interstitial due to the accommodation of highly diffused Se in the ordered crystal at high temperature (1223 K) and high vapor pressure. The EELS line-scan result also confirmed the loss of Se (reduced EELS spectral intensity) but non-stoichiometric surrounding defect regions. Accompanying ellipsoidal shape defects with significant lattice distortion were clearly seen in $Pb_{1-x}Sn_xSe$ (Figs. 3d and e), and increases its density with the increase of Sn concentration. Results of EELS line-scan analysis (Fig. 3e) indicate that the defect in $Pb_{1-x}Sn_xSe$ single crystal was dominantly attributed to the loss of Sn/Se at local region, which in turn induced the lattice distortion and formed strain contrast in HRTEM images. Non-stoichiometric of Se atoms played an important role in the formation of defects in the single crystals.

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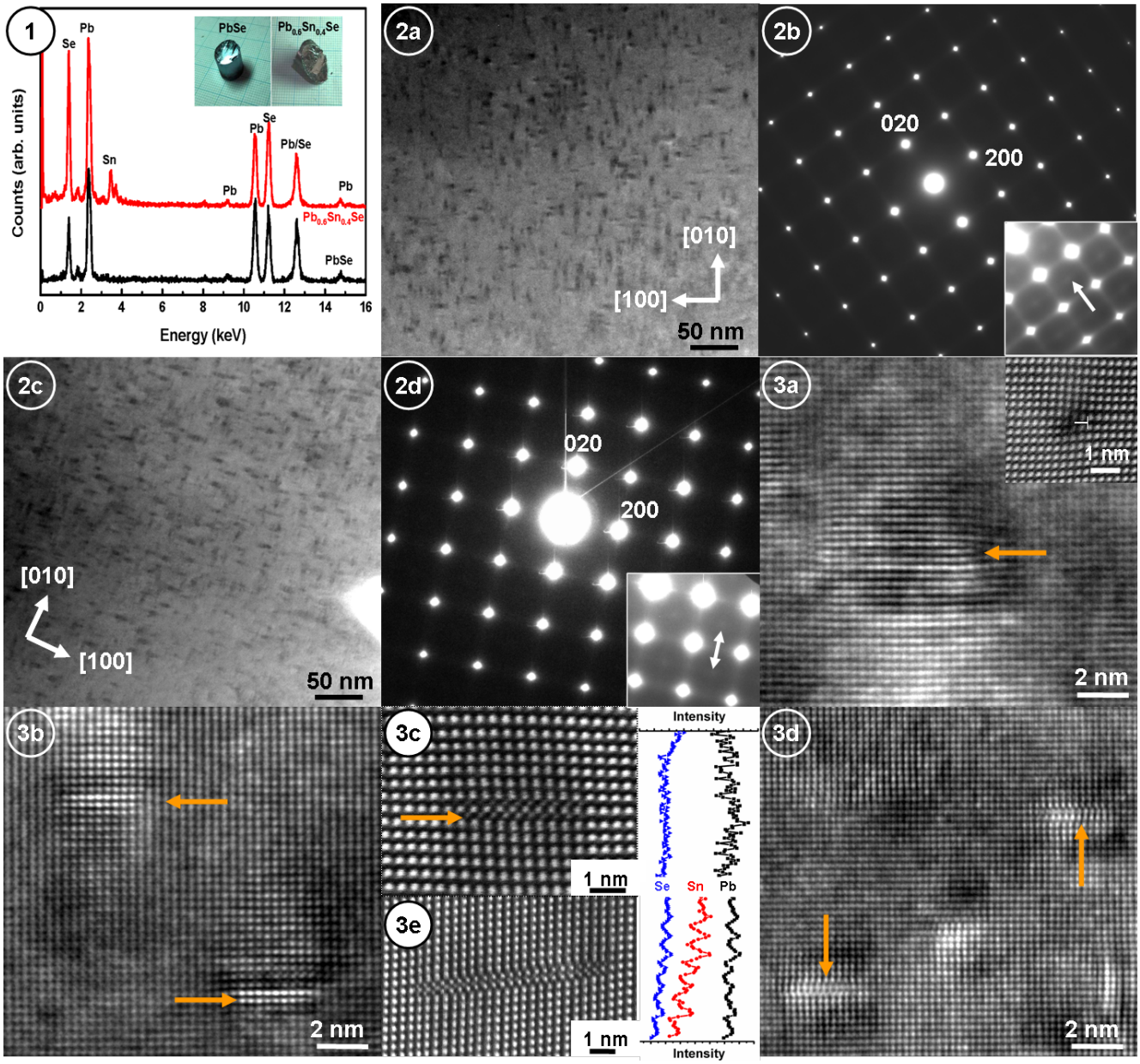

Fig. 1. EDS spectra of single crystal PbSe and $Pb_{1-x}Sn_xSe$. Inset shows ingots of these single crystals.

Fig. 2. TEM images and corresponding ED patterns of PbSe (a and b) and $Pb_{1-x}Sn_xSe$ (c and d) along [001] direction reveals high density of strain contrast with ellipsoidal shaped morphology. With longer exposure time ED patterns clearly depict the streaks and forbidden {110} spots (arrows in inset).

Fig. 3. HRTEM images and atomic resolution HAADF images of defects in PbSe single crystal (a-c) and in $Pb_{1-x}Sn_xSe$ single crystal (d and e). The typical dislocation (a) and the Se interstitial defects (b and c), with decreasing the EELS spectral intensity of Se in regular column position, are major defects in PbSe. In contrast, the defect induced by the additional lattice rearrangement is observed in the $Pb_{1-x}Sn_xSe$ sample. Results of EELS analysis reveal that the lattice distortion was due mainly to non-stoichiometric loss of Sn/Se.

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