

Structural complexity of intermetallic compounds by TEM

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Atomic-resolution TEM and STEM allow to shed light on the structural features of complex intermetallic compounds, which cannot be resolved by conventional X-ray diffraction analysis. Orthorhombic o -Al₁₃Co₄ contains about 102 atoms in the unit cell. Most positions are described by split technique. Atomic-resolution microscopy reveals the local atomic arrangements. In lead telluride, TEM study revealed temperature-dependent appearance of extended dislocations caused by a shift of atomic slabs along [100] which influence the electronic transport properties. Furthermore, the TEM is used for the preparation of nanocrystals of PbTe.

Orthorhombic o -Al₁₃Co₄ is a low-scale prototype from the family of complex intermetallic compounds (CMA) considered to be promising catalysts. In order to reveal the real local structure of o -Al₁₃Co₄ (Fig. 1), crucial for understanding potential catalytic behavior, combined TEM and X-ray investigations were performed on the single crystal [1]. By applying atomic-resolution spherical aberration corrected TEM and annual dark field (ADF) STEM of the [100] zone, strong disorder in the aluminum substructure indicated by XRD study was visualized. Regardless of this positional disorder within the aluminum substructure, the cobalt positions defining the corners of the large pentagonal units remain stable (Fig. 1a-d). The local arrangement of the Al atoms in every unit cell is different (Fig. 1e,f). The disorder (Fig. 1h) is caused by covalent bonds formed in the Al-Co-Al group (Fig. 1g) located within the large cages in the structure. Even though the whole single crystal shows long-range order, due to disorder in the aluminum substructure every unit cell becomes unique.

Lead telluride is a prominent thermoelectric material already in use since the sixties for power supply, *e.g.* in space missions. Despite its long-standing technical application, certain basic physical features are still not completely understood, such as the reversible change in transport behavior from metallic to semiconducting around 270 °C (Fig. 2, right). A single crystal of PbTe was investigated by *in-situ* and *ex-situ* temperature-dependent high-resolution electron microscopy [2]. At room-temperature, the whole sample is interstratified by shifted atomic layers normal to [100] (Fig. 2, middle) forming a dense dislocation network (Fig. 2, left).

In-situ experiments show that upon heating the dislocation, the strips undergo a qualitative transformation over 300 °C (Fig. 3). The strips broaden up and become diffuse. At 400 °C, the strips start to vanish. At the atomic level, the strips may be understood by means of the stereo-chemically active

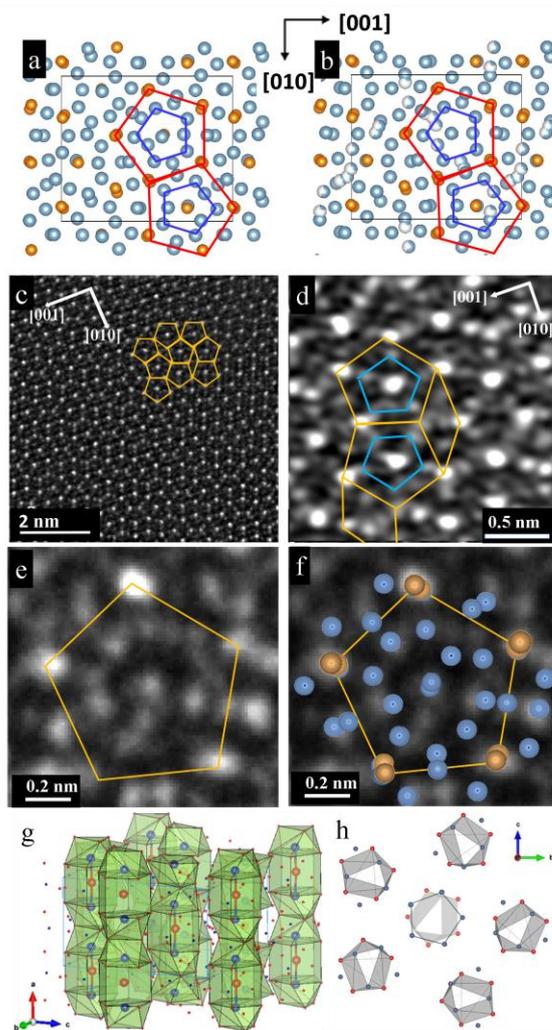


Fig. 1: Crystal structure of o -Al₁₃Co₄ in projection along [100]: (a) ordered and (b) disordered models (Al - blue, Co - orange); (c) HR-STEM overview with overlaid pentagonal Co arrangement; (d) magnified area around one of the pentagonal arrangements of Co (orange) and Al atoms (blue); (e) atomic-resolution TEM of pentagonal arrangement (orange) with local atomic disorder; (f) HR-TEM image overlapped with possible positions of Al tailored for this pentagon; (g) 3D framework composed of cages bearing three-atomic Al-Co-Al groups; (h) pentagonal caps of the cages with trigonal distortion.

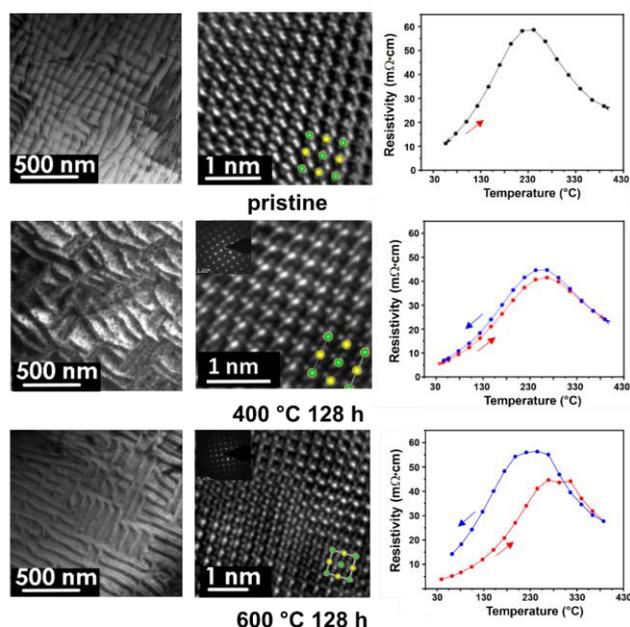


Fig. 2: Local atomic arrangements and electrical conductivity of PbTe: (left) Overview of dislocation pattern; (middle) HR-TEM of dislocation region; (right) electric resistivity vs. temperature.

lone pairs between shifted atomic slabs along the dislocation. The order of the lone pairs causes the slab shift and results in gap closure in the band structure leading to metallic transport behavior. Over 270 °C, the lone-pair disorder reappears, the crystal slabs move in a row and regain the regular rock-salt lattice, and the material becomes semiconducting. The process is reversible.

Focused studies showed that pulverized PbTe single crystal is unstable in the TEM beam and starts to evaporate. In this way, perfect nanocrystals of PbTe are obtained by *in-situ* recrystallization *via* the gas phase (Fig. 4) [3].

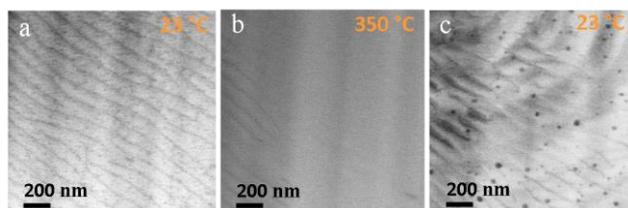


Fig. 3: Reversible dislocation dynamics in PbTe recorded by STEM at different temperatures. (a) strips at starting room temperature (metallic material); (b) strips start to vanish at 350 °C (semiconductor); (c) strips reappear after sample cooled down to room temperature (metallic).

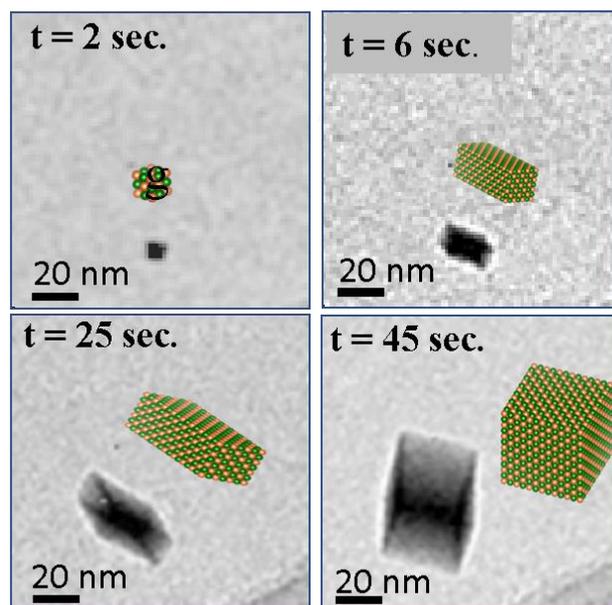


Fig. 4: Time-dependent growth of PbTe nanobar (*in-situ* sequence). During growth, the nanoparticle changes its aspect ratio.

External Cooperation Partners

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