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Structural properties of PbTe quantum dots revealed by high-energy X-ray diffraction

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Abstract. High-energy X-ray diffraction (HE-XRD) experiments combined with an analysis based on atomic-pair-distribution functions can be an effective tool for probing low-dimensional materials. Here, we show how such an analysis can be used to gain insight into structural properties of PbTe nanoparticles. We interpret our HE-XRD data using an orthorhombic Pnma phase of PbTe, which is an orthorhombic distortion of the rocksalt phase. Although local crystal geometry can vary substantially with particle size at scales below 10 nm, and for very small nanoparticles the particle size itself influences X-ray diffraction patterns, our study shows that HE-XRD can provide a unique nano-characterization tool for unraveling structural properties of nanoscale systems.

1. introduction

With the advent of high-energy synchrotron X-ray beamlines, high-energy X-ray diffraction (HE-XRD) has emerged as a viable tool for characterizing the structure of nanoparticles [1, 2]. HE-XRD probes the scattering cross-section for high momentum-transfers, Q , and thus allows the recovery of accurate pair distribution functions (PDFs) with higher spatial resolution. In contrast with the conventional (lower energy) X-ray diffraction techniques, HE-XRD takes advantage of both the Bragg peaks and the diffuse scattering components of the spectra, where the latter component originates from the perturbation of the crystalline order.

Third generation synchrotron sources with advanced insertion devices enable diffraction with very hard (energies greater than 50 keV) X-rays for quantitative studies of structures of disordered materials [3]. Following the study of Poulsen *et al.* [4, 5] on amorphous silica, many similar experiments followed on the HE-XRD beamline BL04B2 at SPring-8 [3, 6, 7]. Nanostructured materials are of great current interest because their properties can be tailored by varying the size and geometry of their constituents. In particular, amorphous nanomaterials have demonstrated desirable characteristics in mechanical, catalytic, and magnetic performance [8]. Nanoparticles (NPs) can support high surface-to-volume ratios and display features driven by disorder to host properties distinct from their bulk parents [9], and as a result NPs offer rich possibilities for applications [10].

Lead chalcogenides with chemical formula PbX ($X = \text{S, Se, Te}$) belong to the IV-VI group semiconductors. In comparison to the III-V compounds, these lead salts exhibit different properties. For example, their lattices are relatively stable over a significant range of non-stoichiometric compositions and their energy gaps increase with increasing temperature, which is opposite to the behavior of other semiconductors. Lead chalcogenides also host narrow band-gaps, high mobilities for electrons and holes and large dielectric constants. The band gaps decrease with hydrostatic pressure and increase with temperature, and external pressure can induce topological phase transitions [11]. This rich phenomenology makes lead chalcogenides interesting compounds for applications ranging from photocatalysis [12] to optoelectronics and photovoltaics [13].

In this paper, we discuss structural aspects of lead telluride (PbTe) NPs deposited onto a Si substrate [14]. A comprehensive account of PbTe is given by Lalonde *et al.* [15]. An in-depth high-resolution transmission electron microscopy (HR-TEM) investigation of PbTe has been reported by Lambert *et al.* [16]. PbTe hosts a large exciton, good carrier-mobility, multi-exciton generation, interesting dielectric properties and a high melting temperature [17]. An unusual property of PbTe is that it displays the appearance of a new phonon mode with increasing temperature, an effect that has not been reported in any other pure material [18, 19]. This new phonon mode may partly explain the longstanding puzzle of anomalous temperature dependence of the above-mentioned semiconducting energy gap in PbTe . PbTe also exhibits a relatively high thermoelectric figure of merit, which makes it an excellent solid-state thermoelectric material [20, 21, 22, 23], which can be deployed over 323 – 900 K range in photodetectors and energy generators. PbTe hosts interesting

Figure 1. Crystal structures of PbTe: (a) rocksalt, (b) orthorhombic Pnma, and (c) CsCl type. Yellow balls denote Te atoms and the gray balls refer to the Pb atoms lying within the polyhedra outlined by Te-Te bonds. The number of Pb-Te bonds forming the polyhedra increases from six in the rocksalt structure to seven in Pnma and finally to eight in the CsCl structure. Figure created by VESTA [33].

topological properties [24, 25, 26, 27, 28]. Thermoelectric properties of PbTe are reviewed by Yana *et al.* [29], and the material has been used for a variety of device applications since the 1960s [30]. PbTe quantum dots have a small carrier-cooling rate, which makes them an interesting material for solar cells [31, 32].

PbTe crystallizes in the rocksalt structure (Fm-3m group) under normal temperature and pressure with a lattice parameter of 6.462(1) Å [34]. The structure consists of two interpenetrating fcc lattices (Pb at [0.5 0.5 0.5] and Te at [0 0 0]) connected by mixed ionic and covalent bonds. Each atom is coordinated with six nearest-neighbors of the other type of atom at a distance of 3.23 Å. n- and p-type semiconductors can be realized via appropriate doping. PbTe assumes other crystal structures under high pressure conditions. Ab initio electronic structure calculations [35] and X-ray diffraction studies [36, 37] show structural phase transitions induced by pressure. These include the orthorhombic Pnma phase, which is an orthorhombic distortion of the rocksalt phase [37]. The CsCl phase (Pm-3m group) has also been predicted [35]. Various crystal structures for PbTe are shown in Figure 1.

X-rays [38] can be used for characterizing the geometry of NPs and for qualitatively accessing morphological features, both of which are involved in determining properties of the NPs. Photons, which are generally non-destructive, probe an ensemble average of many

Figure 2. An HR-TEM image of our PbTe nanocrystalline sample. The inset is an FFT image from the marked NP showing good crystallinity. (200)-plane spacing (red circles) is 0.32 nm, while the (220)-plane spacing (green circles) is 0.22 nm.

NPs. In this sense, X-ray techniques are complementary to direct-imaging techniques such as electron microscopy. For ordered crystals, the X-ray scattering pattern consists of Bragg reflections corresponding to various atomic planes in the lattice. Crystal structures can be characterized in terms of point-group symmetry, lattice constants, and atomic-basis positions, and thus involve relatively few parameters.

X-ray scattering signal from nanostructures is significantly less intense than that from bulk materials, so that measurements must be performed over long periods of time and/or with intense beams. Standard crystallography in nanomaterials is difficult because diffraction results only in a few Bragg reflections. Also, symmetry arguments used in the analysis of crystals can miss important details related to the presence of disorder in nanostructures, where much information is contained in the diffuse scattering, which is often not included in the conventional X-ray analysis.

In this connection, HE-XRD measurements combined with a PDF analysis can provide valuable information concerning atomic orderings in nanocrystalline materials displaying some degree of geometrical coherence and periodicity [39, 40, 41, 42, 43, 2, 18, 19, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54]. Here, all the scattered intensity is used, and effects of deviations from perfect crystallinity are included in the analysis. This is relevant, because even though nanocrystalline materials can be similar to bulk crystals, they can also contain disordered glass-like structural features.

Notably, the diffuse scattering amplitude is typically orders of magnitude weaker than the Bragg signal. By Fourier transforming the total scattering data, one can obtain the PDF from which the real-space features of the nanostructure can be inferred. The size of the Q -space probed, which determines the accuracy of the real-space data, depends on the energy of the radiation source used. Q_{max} of more than $20 \text{ \AA}^{-1}$ is needed for extracting atomic-scale information via the PDF such as the distribution of atom-atom distances in nanostructures. Peak positions in the PDF yield atomic-pair distances. Coordination numbers can be obtained from the integral of the intensity under the spectral peaks in the PDF, while the peak shapes

provide information concerning the static and dynamic disorder in the system. Finally, the attenuation of the PDF peaks reveals the coherence range of the scattering process.

2. Experimental

PbTe nanoparticles were produced using hot-injection colloidal synthesis [55]. We started by preparing a tellurium solution of 1 M by dissolving 12.76 g of Te shots (100 mmol) in 100 ml of trioctylphosphine overnight at 100 °C. Next, 2.25 g of lead (II) oxide (10.08 mmol), 12.54 ml of oleic acid, and 65 ml of 1-octadecene solvent were mixed in a round-bottom flask (250 ml) linked to a Schlenk line. This combination was degassed while stirring for half-hour at a temperature of 25 °C, followed by stirring at a temperature of 90 °C for another half-hour. After changing vacuum to Ar atmosphere, the flask temperature was raised to 165 °C. Then 10 ml of 1 M solution of tellurium in trioctylphosphine at 60 °C was inserted into the combination. The reaction was quenched by rapidly cooling the flask with a bath of ice after the mixture had been left for one minute to stir. The NPs were extracted by adding ethanol and centrifuge (9000 rpm) for ten minutes. The NPs were dispersed again in hexane, cleaned with ethanol, and separated in the centrifuge tube. After drying in vacuo, the NPs were put in toluene and a solution of colloidal PbTe NPs with a concentration of $10 \text{ mg}(\text{ml})^{-1}$ was finally obtained.

Si substrates of $1\text{cm} \times 1\text{cm}$ size were cleaned with ultrasonication in three different liquids (acetone, ethanol, and isopropanol) and dried with compressed air. NPs dissolved in toluene were deposited onto the Si substrate, and then, toluene was evaporated. HR-TEM was used to characterize the NPs. The average NP diameter was extracted from a Gaussian fit to the measured diameters of 200 NPs. A representative visualization of the PbTe sample is shown in Figure 2. The image of the fast Fourier transform in the inset of Figure 2 shows the crystallinity of the NPs. The HR-TEM picture of the NPs was taken before deposition onto the substrate. This deposition of NPs, in fact, alters the crystallinity of nanoparticles as discussed by Pussi *et al.* [54]. In particular, atomic structures of the NPs can relax in the presence of surfactant ligands, and result in significant geometrical rearrangements of the NPs surface as suggested by simulations [56, 57] as well as experiments [45, 58].

Measurements with X-rays of $0.21 \text{ \AA}$ wavelength were carried out at the SPring-8 synchrotron facility in Japan at beamline BL04B2. The incident intensity was monitored with an ionization chamber, while the scattered intensity was measured with three CdTe detectors. Notably, the two-axis diffractometer installed at the BL04B2 beamline can also cover the low- Q region ($\sim 0.1 \text{ \AA}^{-1}$), see Ref. [6] for details.

Experimental $I(Q)$ data were measured for amorphous PbTe NPs of about 10 nm size. The range for Q was $0.16 - 25.75 \text{ \AA}^{-1}$. The background intensity, which is subtracted from the data, was measured by carrying out a scattering experiment without the sample. Proper handling of the background signal is especially important in the case of amorphous samples, where significant information is contained in the diffuse scattering contribution. Figure 3(a) shows the lower- Q region of the experimental data as a function of 2Θ . Positions of the most intense Bragg reflections from powder diffraction are also shown for the rocksalt (PbTe) and

Figure 3. (a) Intensity vs. 2θ for the PbTe nanoparticles. Positions of most intense Bragg reflections, calculated using VESTA [33], are marked for the rocksalt and Pnma phases. The corresponding Q -values in $\text{\AA}^{-1}$ are marked on the top x-axis. (b) PDF, $G(r)$, calculated from the experimental $I(Q)$ data in (a) for amorphous PbTe nanoparticles.

Pnma phases. The orthorhombic Pnma phase shows a dense set of Bragg peaks in the same range of 2θ values where the NPs yield the most intense peaks.

3. Results and discussion

Experimental HE-XRD data were converted into PDF with the PDFgetX3 software [59]. The Fourier transform was performed using data up to $Q = 25.75 \text{ \AA}^{-1}$. This Q_{max} corresponds to a resolution of $\Delta r \sim 0.25 \text{ \AA}$. The PDF obtained from the experimental data is shown in Fig. 3(b). As expected for amorphous samples, the data show no long-range order. The size of the coherent scattering domain is estimated to be about $10 \text{ \AA}$, which indicates that the analysis

is only sensitive to intra-particle spacings. We checked the robustness of our results using the DiffPy-CMI software [60], which is a Python library for modelling crystalline nanostructures and amorphous nanomaterials.

For the analysis of the experimental data, three different structural phases known for PbTe were considered: rocksalt, orthorhombic Pnma, and CsCl. Since the experimental PDF for PbTe nanoparticles shows no long-range order (see Fig. 3(b)), we concentrated on the first few nearest-neighbor distances [45]. Figure 4 shows the partial PDFs for bulk PbTe in rocksalt, orthorhombic (Pmna), and CsCl phases. Visual inspection reveals that the experimentally measured data fit best to the orthorhombic structure, which supports a more versatile setting of bond lengths compared to other bulk PbTe structures. The Pnma structure is an orthorhombic distortion of the rocksalt phase, and thus it is a reasonable starting point for analyzing the structure of PbTe NPs.

Figure 1(b) shows the unit cell for the orthorhombic Pnma phase. The structure of the orthorhombic phase of PbTe can be derived from the rocksalt phase using the following equations [37]:

$$a_O = a_C - b_C \quad (1)$$

$$b_O = (a_C + b_C)/2 \quad (2)$$

$$c_O = c_C. \quad (3)$$

Here the subscript O refers to the Pnma orthorhombic cell, and subscript C to the rocksalt cell with cubic symmetry. [One needs to take into account an adjustment of the origin by $(1/4, 1/2, 3/4)$ in the rocksalt case]. In the orthorhombic structure, atoms are slightly shifted in the $(a - c)$ plane and they occupy $4c$ sites. In the rocksalt phase the atoms have a simpler arrangement, while in the Pnma phase the atomic ordering becomes modulated as shown in Fig. 5(b). Pb and Te atomic positions are still placed consecutively, but a modulation is created by their small movements away the $(a - c)$ plane. [The atoms are displaced from their cubic positions by $0.4 - 0.5$ Å in the a and c directions]. The rocksalt to Pnma transition is a first order displacive transition. Atomic displacements during the transition process are large enough to change the atomic coordination numbers of the original rocksalt structure. Pb(Te) atoms have seven neighboring Te(Pb) atoms and two extra neighbors at slightly larger distances. The seven unlike neighbors lie at distances ranging from 2.93 to 3.81 Å [37]. The Pnma structure has twelve Te-Te and Pb-Pb distances ranging from 3.97 to 5.80 Å for tellurium sites and from 3.46 to 4.89 Å for lead sites [37]. Figure 5(a) shows the link between the unit cells of the rocksalt and orthorhombic phases.

We have performed a relatively simple PDF fit starting from the orthorhombic cell. Details of the starting [37] and optimized structures are shown in Table 1. Optimized unit cell is non-uniformly contracted with respect to the starting structure. Figure 7 shows the results, where we have focused on the $2.5 - 6$ Å range, which includes the first two Pb-Te distances and the first Pb-Pb and Te-Te distances.

The hard sphere radius for Pb is 1.75 Å and for Te it is 1.37 Å. These values give an estimate of the bonding distances expected in PbTe NPs. The first three peaks in Figure 7

Figure 4. Partial PDFs for bulk PbTe in: (a) rocksalt phase, (b) orthorhombic Pnma phase, and (c) CsCl phase.

Figure 5. (a) A schematic illustration of the relationship between the rocksalt (solid line) and orthorhombic (dotted line) unit cells. (b) Modulated ordering of lead and tellurium sites in the Pnma structure. View is along the a-c plane. Yellow balls denote Te atoms and the gray balls represent Pb atoms. Figure created using VESTA [33].

<i>Starting structure</i>	<i>Optimized structure</i>
$a = 8.177 \text{ \AA}, b = 4.495 \text{ \AA}, c = 6.23 \text{ \AA}$	$a = 8.149 \text{ \AA}, b = 4.375 \text{ \AA}, c = 6.188 \text{ \AA}$
Pb (0.56, 0.25, -0.19)	Pb (0.56, 0.25, -0.19)
Te (0.82, 0.75, 0.87)	Te (0.82, 0.75, 0.84)

Table 1. Geometrical parameters for the starting [37] and optimized structures. Pb and Te atoms are on the 4c sites.

lying between $2.5 \text{ \AA}$ and $3.5 \text{ \AA}$ are all contributed by Pb-Te distances. The Pb atoms are enclosed inside the polyhedron formed by Te atoms. In the rocksalt phase the polyhedra are all regular octahedra with Pb atom at the center and six Te atoms at the corners. All Pb-Te bonds have equal length of $3.23 \text{ \AA}$. In the orthorhombic Pnma phase Pb-Te bonds (seven nearest-neighbors) range over $2.93 - 3.81 \text{ \AA}$, so that the polyhedra enclosing Pb atoms are distorted. In the CsCl phase Pb atoms have eight neighboring Te atoms at an equal distance of $3.46 \text{ \AA}$. In our fitting we could match three different Pb-Te lengths: $2.7 \text{ \AA}$, $3.1 \text{ \AA}$, and $3.4 \text{ \AA}$. Keeping the real-space accuracy of our data of $0.25 \text{ \AA}$ in mind, all these values are realistic for the Pb-Te bonds. The next set of peaks in Fig. 7 lying between $3.5 \text{ \AA}$ and $6.0 \text{ \AA}$ are contributed by the Pb-Pb and Te-Te distances. In the rocksalt structure, the shortest Pb-Pb (Te-Te) distance is $4.57 \text{ \AA}$, but in the Pnma phase there is greater variation with Pb-Pb and Te-Te bond lengths ranging from $3.5 \text{ \AA}$ to $6 \text{ \AA}$. In our analysis of the experimental data, five distinct distances could be fitted: $3.9 \text{ \AA}$, $4.2 \text{ \AA}$, $4.5 \text{ \AA}$, $4.7 \text{ \AA}$, and $5 \text{ \AA}$, all of which fall within the range of distances observed in the orthorhombic PbTe phase. Figure 6(a) shows that the three shortest of these five distances can be assigned to Te-Te bonds.

Figure 6. Distorted polyhedral building block for a PbTe nanoparticle. Yellow balls denote Te atoms while the gray balls refer to Pb atoms in the middle of the polyhedra outlined by Te-Te bonds. Various (a) Te-Te and (b) Pb-Te bond lengths are shown. Figure created by VESTA [33].

Figure 7. A simple PDF fit to the orthorhombic unit cell discussed in the text.

4. Conclusion

We have investigated the structure of PbTe nanoparticles by combining our HE-XRD measurements with an analysis based on atomic pair distribution functions. Although local geometry can vary substantially with particle size, and for very small nanoparticles the size itself influences the XRD patterns [61], we show how we can still identify structural features of nanoparticles with sizes of about 10 nm. Our experimental HE-XRD data can be interpreted using an orthorhombic $Pnma$ phase of PbTe, which is an orthorhombic distortion of the rocksalt phase. The nanoparticle structure can be described in terms of the distorted polyhedron shown in Fig. 6. This three-dimensional arrangement of atoms in PbTe NPs revealed by HE-XRD will be difficult to access via other probes [42, 62]. Notably, positron-annihilation spectroscopy (PAS) [13] has recently provided information

concerning the surface of semiconductor quantum dots [63]. The complementary combination of HE-XRD and PAS techniques can thus provide a more complete characterization of the microstructure of PbTe NPs [64], which show much promise for optoelectronics applications.

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