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Phase transformation and conductivity in nanocrystal PbS under pressure

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The grain-size effect on the phase transition induced by pressure in PbS was studied by *in situ* high-pressure electrical resistance and synchrotron radiation x-ray powder diffraction measurements. The mean transition pressure of the B1-to-B16 phase transformation was found to be 6.3 ± 1.3 GPa in 8 ± 1 nm PbS while it is 3.1 ± 0.7 GPa for 10 μm PbS. The resistivity of the B16 PbS phase decreases exponentially with pressure in both samples at ambient temperature. They follow $R \propto \exp(-CP)$, where $C = -0.64$ GPa^{-1} for 10 μm PbS and $C = -0.34$ GPa^{-1} for 8 ± 1 nm PbS. These results are discussed in terms of a decrease of energy band gap with increasing pressure. © *2000 American Institute of Physics.* [S0021-8979(00)02102-2]

Nanocrystals, consisting of small crystallites with diameters 1–100 nm, often have novel physical and chemical properties, differing from those of the corresponding bulk materials.[1] For example, nanometer-sized semiconductors exhibit particle size dependence of electronic and optical properties, making them potential candidates for applications involving tunability of these properties.[2,3] Recently, Tolbert *et al.*[4–6] studied structural phase transformations in Si, CdSe, and CdS nanocrystals, and found that the smaller the crystallite, the higher the transformation pressure. They explained the increase in transition pressure for the nanocrystals in terms of surface-energy differences between the phases involved. A similar explanation to the enhancement of transition pressure was also reported in nanocrystals of ZnS in Ref. 7 and of ZnO in Ref. 8 compared with corresponding bulk materials. However, Jiang *et al.*[9] reported that for nanometer-sized γ-Fe$_2$O$_3$ particles the phase transition pressure (from γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$) is lower than that for bulk material. They suggested that the larger volume change upon transition in the nanocrystals is the main factor in this case. A reduction of the transition pressure was also found in nanocrystals of TiO$_2$ for the rutile-to-α-PbO$_2$ transition.[10] It seems that the grain-size effect on the transition pressure can be of either sign, depending on the system under investigation. However, the mechanisms governing the structural stability of nanocrystals are not well understood. More data for the grain-size effect on structural stability in various systems are desirable.

At ambient temperature, bulk PbS has a phase transformation at 2.2 GPa from a NaCl-type structure (B1) to a black phosphorus-type orthorhombic structure (B16).[11] Qadri

et al.[12] have reported synchrotron radiation energy-dispersive high-pressure x-ray powder diffraction measurements of PbS with three different grain sizes. They found that onset and completion pressures of the B1-to-B16 transition increase with decreasing grain size. However, due to small grain sizes and the fact that B16 is a distorted cubic B1 phase, the broad diffraction lines of B1 and B16 phases strongly overlap. Consequently, the determination of the transition pressure for the B1-to-B16 transformation in PbS using the x-ray powder diffraction technique becomes questionable. In addition, the behavior of the mean transition pressure versus grain size in PbS is still unclear. Therefore, a reexamination of grain-size effect on the phase transition using different techniques in PbS is warranted. In this communication, we present *in situ* high-pressure conductivity and x-ray powder diffraction investigations on the phase transition in bulk and nanostructured PbS.

Two PbS samples with average grain sizes of approximately 10 μm (hereafter called bulk) and 8 ± 1 nm (hereafter called nanocrystals) were investigated. PbS powder (10 μm) with a 99.9% purity was used as a starting material for the synthesis of nanometer-sized PbS samples using a Planetary ball mill (Fritsch Pulverisette 5), with tungsten carbide vials and balls. A single phase with a NaCl-type structure (B1) in the samples studied was confirmed by x-ray powder diffraction. The average grain sizes of milled samples and the starting material were estimated by x-ray powder diffraction and by scanning electron microscopy, respectively. High resolution transmission electron microscopy measurements revealed the presence of lattice fringes and confirmed the B1 structure in the samples. Tungsten contamination in the milled samples, originating from abrasion of the vial and balls, was found to be less than 0.5 at. % from energy-dispersive x-ray analysis. High-pressure *in situ* electrical re-

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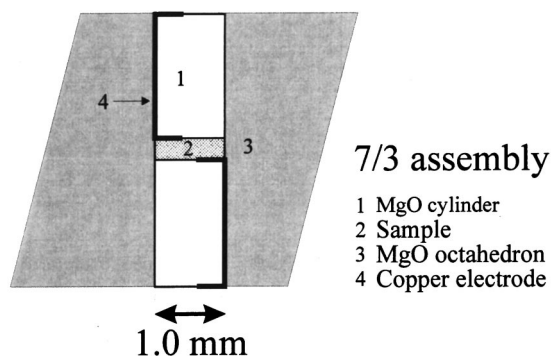
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FIG. 1. Sample assembly for high-pressure *in situ* electrical resistance measurements at ambient temperature.

sistance measurements at ambient temperature were carried out at Bayerisches Geoinstitut in Bayreuth, Germany, in a 1200 ton multianvil apparatus using 7 mm edge length octahedral pressure cells (Fig. 1). Copper foils were used as electrodes to measure the dc resistance across a sample disk approximately 1 mm in diameter and 0.2 mm thick. Resistance measurements were made on increasing pressure using a previous determined pressure calibration that is based on several pressure standards. High-pressure x-ray powder diffraction measurements (<6 GPa) were performed by the white-beam energy-dispersive method using synchrotron radiation and a multianvil press, MAX80, at HASYLAB in Hamburg, Germany. The sample was mixed with a fine NaCl powder which was used both as a pressure calibrator and a pressure medium. The pressure was estimated from the lattice constant of NaCl using the Decker equation of state at room temperature.[13]

Figure 2 shows high-pressure *in situ* electrical resistivity for bulk and nanocrystal PbS. For bulk PbS, the resistivity at low pressures is found to be a few $k\Omega$ cm and remains almost unchanged by 2.3 GPa. At 2.4–3.8 GPa there is a sharp rise in resistivity by three orders of magnitude. The mean transition pressure is about 3.1 ± 0.7 GPa. The transition is essentially complete by 4 GPa, at which point the resistivity starts to decrease again, which will be discussed later. For nanocrystal PbS, the resistivity at low pressures is slight higher than that for bulk PbS, which could be explained by
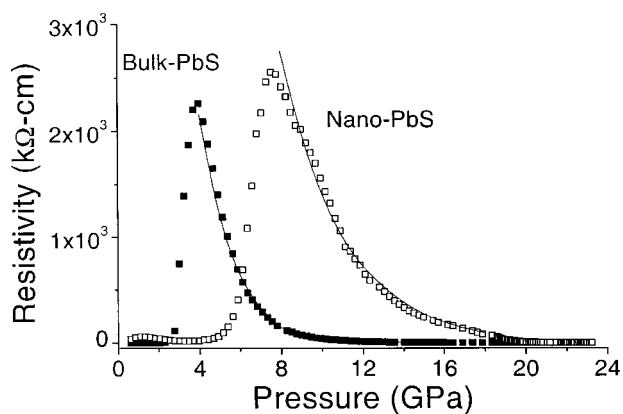

FIG. 2. High-pressure *in situ* electrical resistance for PbS materials with average grain sizes of 10 μm and 8 ± 1 nm at ambient temperature.
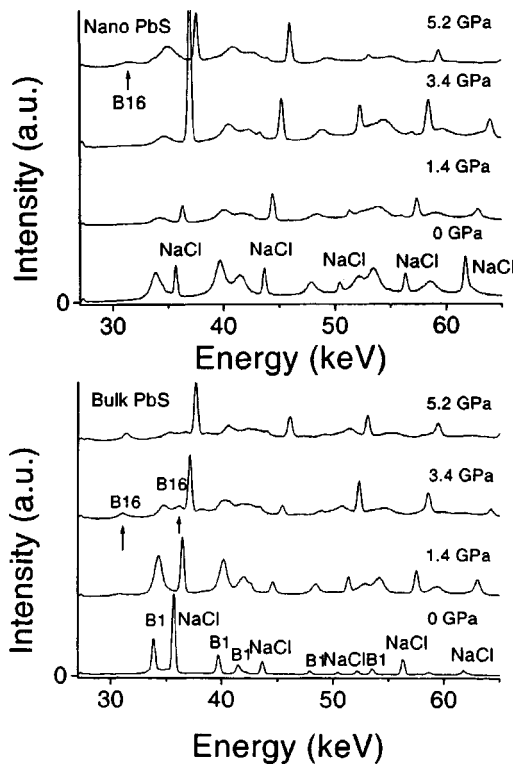

FIG. 3. Examples of *in situ* high-pressure synchrotron radiation x-ray powder diffraction patterns at room temperature with increasing pressures for 10 μm and 8 ± 1 nm PbS B1 and B16 are the low- and high-pressure phases, respectively.

an enhancement of the energy band gap of the B1 phase with decreasing grain size.[14] No appreciable change of the resistivity was detected up to 5 GPa and a sharp rise in resistivity was observed from 5 to 7.6 GPa. The mean transition pressure is about 6.3 ± 1.3 GPa. Figure 3 shows high-pressure x-ray powder diffraction patterns for both bulk and nanocrystal PbS. The quality of data recorded here is similar to that reported by Qadri *et al.*[12] Although the patterns of NaCl and PbS are superimposed, it is clear that in bulk PbS, the high-pressure B16 phase can be detected at 3.4 GPa while it is not observable at this pressure within experimental uncertainty for nanocrystal PbS. At 5.2 GPa, one peak of the B16 phase is visible also for nanocrystal PbS. These results are consistent with the resistivity data above and confirm the sharp rise in resistivity originating from the B1-to-B16 phase transformation. Table I lists the onset, completion, and mean transition pressures of the B1-to-B16 phase transformation in PbS. It can be seen that the onset pressure reported by Qadri *et al.*[12] for 8.8 nm PbS crystals is lower than that obtained in

TABLE I. Transition pressures of the B1-to-B16 phase transformation in PbS.

Grain size (nm)	Onset (GPa)	Completion (GPa)	Mean (GPa)	Reference
10^4	2.4 ± 0.2	3.8 ± 0.2	3.1 ± 0.7	Present work
8.8	2.4	5.8		Qadri *et al.* (Ref. 12)
8 ± 1	5.0 ± 0.2	7.6 ± 0.2	6.3 ± 1.3	Present work
5.4	3.0	8.0		Qadri *et al.* (Ref. 12)
2.6	3.3	9.0		Qadri *et al.* (Ref. 12)

this work for 8 ± 1 nm Pbs nanocrystals. This discrepancy could be due to (1) different sample preparation methods used and (2) different techniques used to estimate transition pressures. On the basis of the combined *in situ* high-pressure conductivity and x-ray powder diffraction measurements, it can be concluded that the mean transition pressure of the B1-to-B16 phase transformation in nanocrystal PbS is higher than that in bulk PbS.

As seen in Fig. 2, the resistivity of the high-pressure phase (B16) in both bulk and nanocrystal PbS drops rapidly with increasing pressure. For bulk PbS, it decreases by about three orders of magnitude between 4 and 10 GPa, and above 10 GPa, the resistivity levels off rapidly, decreasing only by about a factor of 10 over the range of 10–23 GPa. Similar behavior of the resistivity of the B16 phase versus pressure was also detected in nanocrystal PbS. The data obtained from a pressure range of 4–14 GPa for bulk PbS and of 8–18 GPa for nanocrystal PbS were fitted by $d(\ln R)/dP=C$, where C is constant. It found $C=-0.64\,\text{GPa}^{-1}$ for bulk PbS and $C=-0.34\,\text{GPa}^{-1}$ for nanocrystal PbS, as is shown by the solid lines in Fig. 2. In general, resistivity of a semiconductor and a semimetal is determined by the energy band gap at a given temperature, as $R\propto\exp(-\Delta E_g)$.[15] These results indicate a negative pressure coefficient for the energy gap of the B16 phase of PbS. The magnitude of the slope, $d(\Delta E_g)/dP$, in nanocrystal PbS is found to be smaller than that in bulk PbS. In fact, the high-pressure B16 PbS phase is isostructural with the black phosphorus B16 phase, in which both experimental and theoretical data[16] did show $d(\Delta E_g)/dP<0$.

In summary, phase transition (B1-to-B16) in PbS with average grain sizes of 10 μm and 8 ± 1 nm has been investigated by *in situ* high-pressure electrical resistance and synchrotron radiation x-ray powder diffraction measurements. The mean transition pressure of the B1-to-B16 phase transformation was found to be 6.3 ± 1.3 GPa for 8 ± 1 nm PbS while it is 3.1 ± 0.7 GPa for 10 μm PbS. Thus, the smaller the crystallite, the higher the transition pressure. A similar grain-size effect on transition pressure has also been found in CdSe, ZnO, and ZnS. The resistivity of the B16 PbS phase

decreases exponentially with pressure in both samples. They follow the empirical law $R\propto\exp(-CP)$, where $C=-0.64\,\text{GPa}^{-1}$ for 10 μm PbS and $C=-0.34\,\text{GPa}^{-1}$ for 8 ± 1 nm PbS. This behavior can be explained by the decrease of the energy band gap of the B16 PbS phase with increasing pressure.

[1] See, for example, *Nanophase Materials: Synthesis–Properties–Applications*, edited by G. C. Hadjipanayis and R. W. Siegel (Kluwer Academic, Dordrecht, 1994); *Fundamental Properties of Nanostructured Materials*, edited by D. Fiorani and G. Sberveglieri (World Scientific, Singapore, 1994).

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