Identification of New Nano-Scale Phases in $AgPb_{18}SbSe_{20}$ Crystals by Electron Crystallography Methods

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Lead telluride (PbTe) and lead selenide (PbSe) are well-known thermoelectric material used for power generation [1]. Doping of PbTe with Ag and Sb is expected to improve the thermoelectric properties. Interesting members of this family are $AgPb_{18}SbTe_{20}$ and $AgPb_{10}SbTe_{12}$, which show promising figures of merit and have an interesting nanostructure [2,3]. In the present work the selenium analog $AgPb_{18}SbSe_{20}$ is studied by electron microscopy and the new phases found in the nanocrystals are identified.

The electron microscopy study reveals the existence of a very large number of nanocrystals within the matrix material (PbSe). Their size ranges from a few nm up to about 50 nm. The distribution of these nanocrystals in the matrix appears rather homogeneous.

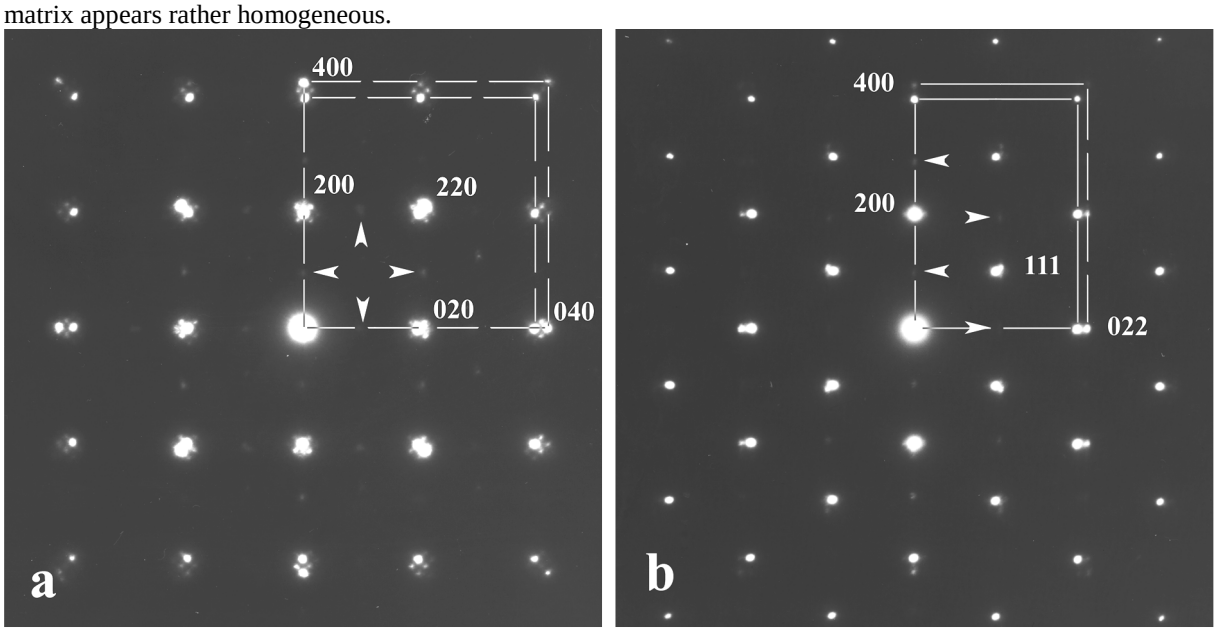

Figure 1: Electron diffraction patterns taken along: a) [001] and b) $[01\bar{1}]$ cubic axes.

Electron diffraction patterns (Fig. 1) contain spots which can be distinguished as coming from three different structures. The strongest ones, corresponding to the smaller frame in Fig.1, are absolutely consistent to a face centered cubic (fcc) NaCl-type of structure. They belong to the matrix PbSe (phase A), which it is known to have a NaCl-type of structure with a_0= 0.6134 nm.

The second group of reflections, corresponding to the larger frame, can also be interpreted as coming from a cubic (phase B). The two lattices are almost perfect parallel one to the other, denoting that the new phase was grown "endotaxially" in the matrix cubic phase. Taking as an internal standard the PbSe matrix reflections the lattice parameter of this cubic phase is deduced as: $a_1=0.579 \pm 0.01$ nm. Such a constant is identical with that of the compound $AgSbTe_2$, which is known to posess the NaCl structure. However the very weak intensity of the 200 reflections of phase B, in both patterns, is not consistent with a NaCl-type of structure, which is characterized by strong 200 reflections. Calculation of intensities for a a zinc-blende type of structure and for $AgSbTe_2$ yields to very weak 200 reflections and denotes that this is the type of structure for phase B.

In most of the cases of the diffraction patterns, weak spots, indicated by arrows in Fig. 1, appear close to the positions 100 and 011, which are forbidden reflections for the NaCl structure. This indicates the presence of a superstructure (phase C) at least in some of the nanocrystals, with approximately the same lattice parameters as the basic one, but with tetragonal (or even lower, i.e. orthorhombic) symmetry.

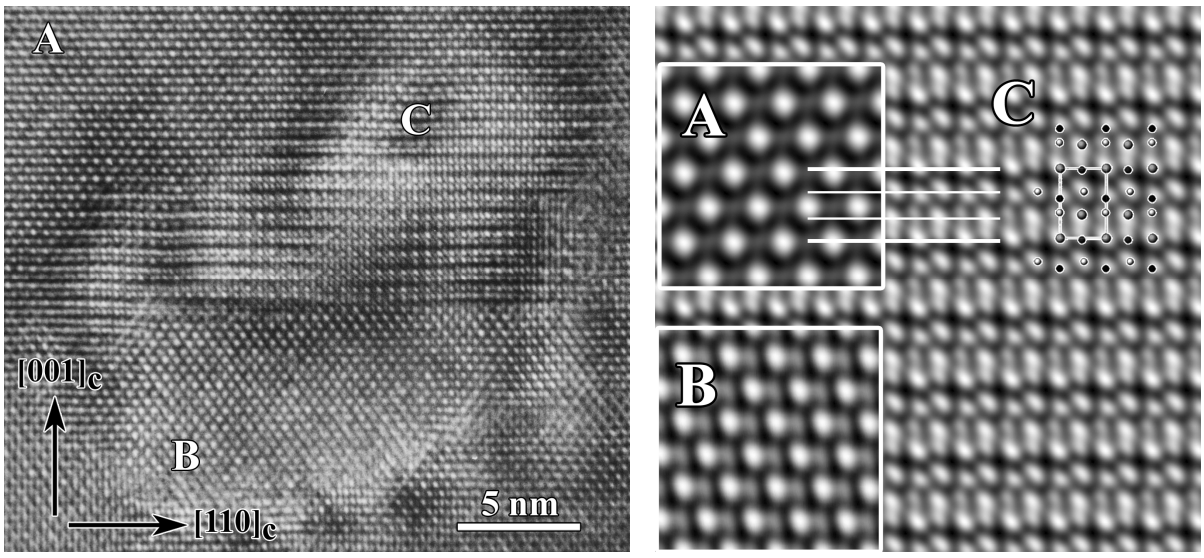

Figure 1: A HREM image from a nanocrystal taken along the $[01\bar{1}]$ cubic axis. In the right panel the averaged images, taking with the use of the appropriate software, for the three phases are shown.

High-resolution electron microscopy (HRTEM) images, as the one in Fig. 2, confirm the above ideas. Usually, both the phases B and C exist in the same nanocrystal, surrounded by the PbSe matrix. Careful measurements from the diffraction patterns and HRTEM images lead to values $c=0.625 \pm 0.01$ nm and $a= 0.588 \pm 0.01$ nm, for the tetragonal superstructure, i.e. to a ratio $c/a=1.07 \pm 0.01$. The **c** tetragonal axis is found to be parallel to one of the <100> cubic axes and the **a**, **b** axes parallel to the other two <100> cubic axes, i.e. this phase is also grown "endotaxially" in the matrix cubic phase. It can exist in three variants in relation with the cubic basic structure. In each of the variant the tetragonal axis is parallel to one of the three cubic basic axes. So, the presence of the superstructure spots at both the 010 and 001 positions in the diffraction pattern of Fig. 1a is attributed to the presence of two of these variants. The third type of variant has its tetragonal axis parallel to the electron beam and hence does not give any extra spot in the diffraction pattern.

Analysis of the morphological features of HRTEM images from phase C allows concluding that this structure is a deformed cubic structure, with coordination polyhedra similar to those observed in the compounds Ag_2Se and $AgSbS_2$. Computer image simulations were performed, involving ordering of Pb, Ag and Sb in the cationic sublattice. The most successfull model assumes the distribution of Pb atoms in deformed octahedral sites and those of Ag and Sb in the tetrahedral ones.

In conclusion two new phases were found in $AgPb_{18}SbSe_{20}$ nanocrystals, embedded in the PbSe matrix (phase A). A cubic one (phase B), with a zinc-blende structure and a tetragonal superstructure (phase C) which is the result of ordering of Pb, Ag and Sb in the cationic sublattice.

[1] D. M. Rowe ed., CRC Handbook of Thermoelectrics, (CRC Press, Boca Raton, FL, 1995).
[2] Hsu K.F., Loo S., Guo F., Chen W., Dyck J.S,. Uher C., Hogan T., Polychroniadis E. K., Kanatzidis M. G., Science, 303, 818 (2004).
[3] Quarez E, Hsu K.F., Pcionek R., Frangis N., Polychroniadis E. K. and Kanatzidis M., J. Amer. Chem. Soc., 127, 9177 (2005).