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A One-Step Mechanochemical Synthesis and Characterization of SnSe and $SnSe_2$

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Tin selenides belong to the $A^{IV}B^{VI}$ group of semiconductors and have brilliant application prospects due to their excellent optical and electrical properties, which can be applied in film electrodes, infrared optoelectronic devices, thermoelectric refrigerators and solar cells [1]. Various methods have been developed to prepare metal selenides such as solid-state reactions [2], solvothermal method [3], self-propagating high-temperature synthesis [4] and mechanical alloying of metal and elemental selenium at room temperature [5].

In the present work, a simple mechanochemical synthesis of binary tin selenides was performed by high-energy milling in a planetary ball mill Pulverisette 6 (Fritsch, Germany). SnSe and $SnSe_2$ were prepared from powdered elements (Sn 99.85 %, Se 99.5 %) at ambient temperature and in a relatively short reaction time. The products were characterized by XRD, transmission electron microscopy and ^{119}Sn Mössbauer spectroscopy. The XRD pattern (Fig. 1A) confirmed that the mechanochemical synthesis of orthorhombic SnSe (JCPDS 32-1382) takes place, and the degree of conversion of the reaction reaches 83% after 10 min of milling. Similarly, the degree of conversion of the mechanochemical synthesis of $SnSe_2$ (JCPDS 23-0602) reaches 72 % after 20 min of milling (Fig. 1B). It was revealed that in addition to the hexagonal $SnSe_2$, the milled Sn/2Se mixture contains also the orthorhombic SnSe phase. TEM analysis of the mechanochemically synthesized SnSe demonstrated the formation of crystals with the orthorhombic shape and the size between 2 and 8 nm. Note that several hexagonal crystallites were also found in the mechanosynthesized selenides. The room-temperature ^{119}Sn Mössbauer spectra of the mechanosynthesized selenides are shown in Fig. 2. A striking feature observed is the broad shape of the spectral lines of the mechanosynthesized products, implying the presence of a broad distribution of local environments around the Sn nuclei due to the mechanically induced deformation of Sn-Se polyhedra. The detailed analysis of Mössbauer spectra of the mechanosynthesized SnSe and SnSe$_2$ nanomaterials is in progress.

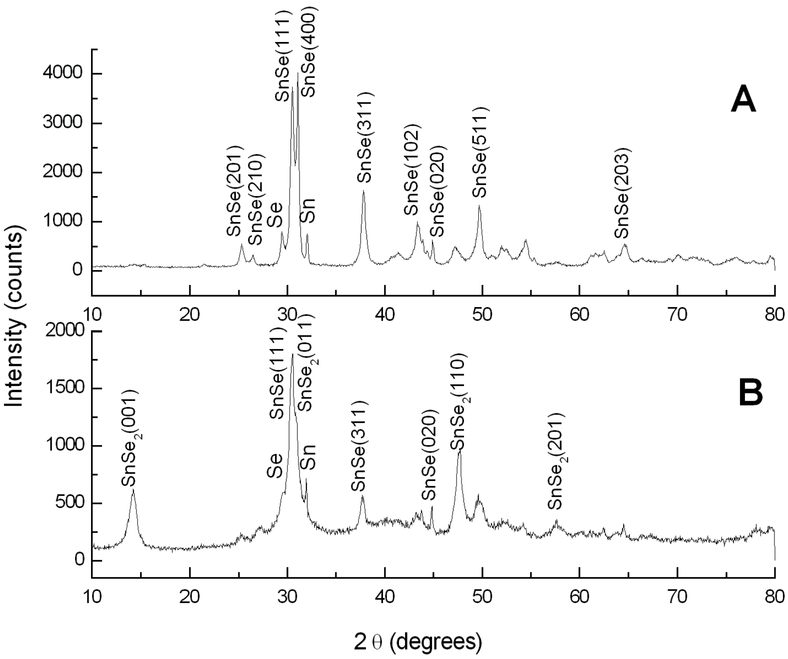

Fig. 1 XRD patterns of mechanochemically synthesized SnSe (A) and SnSe$_2$ (B).

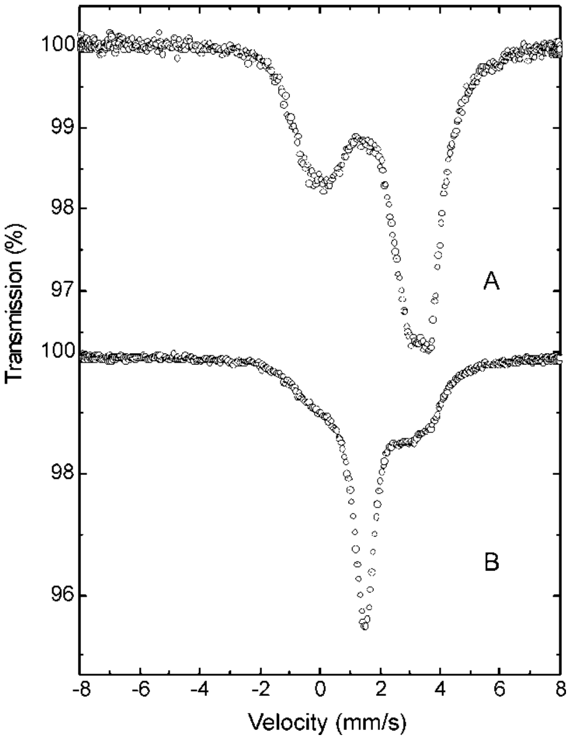

Fig. 2 ^{119}Sn Mössbauer spectra of mechanochemically synthesized SnSe (A) and SnSe$_2$ (B).

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