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High-pressure phase transformation and the equation of state of SrSe

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The crystalline structure of the heavy alkaline earth chalcogenide SrSe was studied at high pressure by x-ray diffraction using a synchrotron source. The NaCl-type ($B1$) structure of SrSe was found to be stable on loading to 14.2 GPa where the CsCl-type ($B2$) structure was evidenced with a 10.7% decrease in relative atomic volume. The $B2$ phase of SrSe persists to 40 GPa, the highest pressure attempted in the experiments. The $B1$-$B2$ phase transition was found to be reversible with small hysteresis. The bulk modulus and its pressure derivative were determined for both phases. Systematic behavior among the strontium chalcogenides is discussed.

Three of the four strontium chalcogenides SrX (X=O, S, Se, Te) have been found to undergo a pressure-induced first-order phase transformation from the sixfold-coordinated NaCl-type ($B1$) structure to the eightfold-coordinated CsCl-type ($B2$) structure at 36 GPa in SrO,[1] 18 GPa in SrS,[2] and 12 GPa in SrTe.[3] The still nonmetallic SrX after $B1$-$B2$ phase transition were predicted to become metallic at higher pressures through a band-gap overlap mechanism.[4,5] Also, among these compounds, a systematic trend between the ionic radius and transition pressure to eightfold coordination has been examined.[4,5] However, in comparison to the neighboring chalcogenides, BaX, in which both structural transition and insulator-metal transition have been extensively studied,[6–9] less experimental results have been obtained on SrX, especially on the structural transition in SrSe and insulator-metal transitions of all SrX.

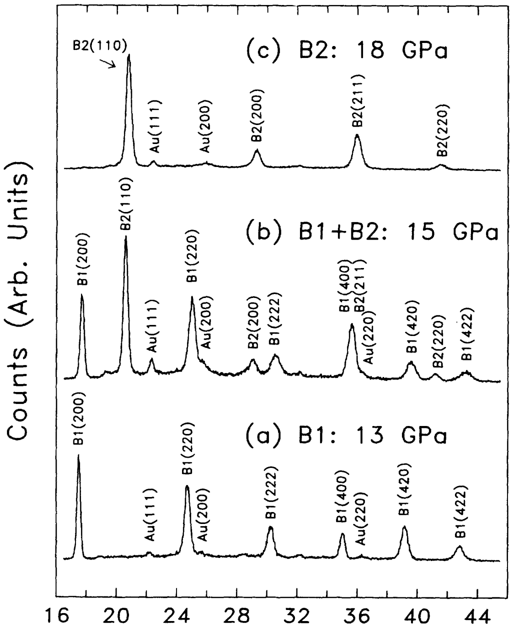

FIG. 1. EDXD spectra of SrSe around the B1-B2 transition. Those labeled by Au are diffraction peaks from the gold marker. The diffraction angle 2θ was 13.89°.

In this paper we present the results of an x-ray-diffraction study on SrSe to 40 GPa at room temperature. This work, whose aim was to determine the high-pressure

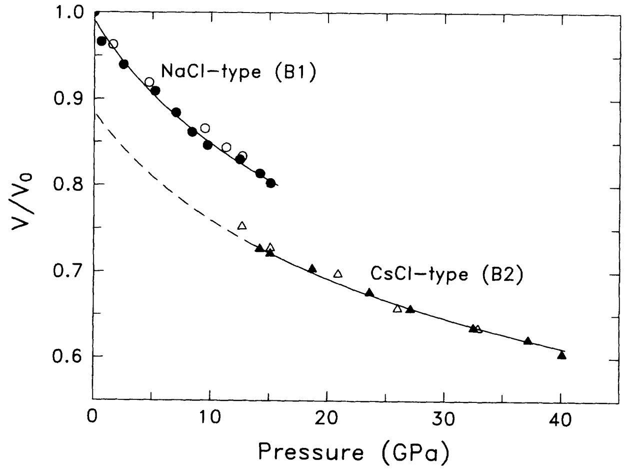

FIG. 2. Plot of the relative atomic volume V/V_0 of SrSe vs pressure. Different symbols correspond to different phases and the decreasing pressure data are shown by open symbols. The solid curves show the first-order Birch fits to the increasing pressure data points only.

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TABLE I. Bulk modulus B_0 and its pressure derivative B_0' of SrSe obtained by fits of the first-order Birch equation of state to the relative volume vs pressure data. $(V/V_0)_{P=0}$ is the extrapolated zero-pressure atomic volume divided by the atomic volume of the NaCl-type ($B1$) phase.

Phase	Pressure range (GPa)	B_0 (GPa)	B_0'	$(V/V_0)_{P=O}$
$B1$	0–14	45.2	4.5	1
$B2$	14–40	46.5	4.5	0.884

TABLE II. Summary of experimental results for SrX (X =O, S, Se, and Te). P_t is the $B1$-$B2$ transition pressure. V_t/V_0 ($B1$) and $-\Delta V/V_0$ ($B1$) are relative volume and relative volume change at the transition to the $B2$ phase. B_0 is the bulk modulus of the $B1$ phase.

Compound	P_t (GPa)		$-\Delta V/V_0$ ($B1$) (%)	B_0 (GPa)	Ref.
SrO	36	0.80	13.0	91	1
SrS	18	0.815	11.4	58	2
SrSe	14	0.813	10.7	45	This work
SrTe	12	0.828	11.1	40	3

structural behavior of SrSe, was initiated to complete the study of the structural behavior of strontium chalcogenides under high pressure.

Energy-dispersive x-ray-diffraction (EDXD) experiments on SrSe were performed at the Cornell High-Energy Synchrotron Source (CHESS). Details of the experimental techniques are given in Refs. 10 and 11. SrSe powder with a purity of 99.99% was pressurized in a diamond-anvil cell along with gold powder which served as an internal pressure marker.[12] A rhenium gasket was used to form a sample chamber between the diamond anvils because rhenium has a very high strength. To avoid decomposition of this hygroscopic sample, no pressure medium was used.

The ambient pressure x-ray-diffraction spectrum confirms the crystal structure of SrSe to the NaCl-type ($B1$) with $a_0=6.234$ Å. The $B1$ structure is stable with increasing pressure until 14 GPa, at which the relative volume V/V_0 is 0.813. Starting at 14.2 GPa new diffraction peaks emerge which can be fitted fully to the CsCl-type ($B2$) structure. The $B2$ phase of SrSe coexists with the $B1$ phase for about 3 GPa before completing its formation at about 17 GPa. The diffraction spectra around $B1$-$B2$ transition are shown in Fig. 1. The atomic volume (the unit-cell volume divided by the number of atoms per unit cell) at the starting pressure of the $B1$-$B2$ transition, namely 14.2 GPa, is 24.64 Å^3 for the $B1$ phase and 22.00 Å^3 for the $B2$ phase. Therefore, the decrease in relative atomic volume on transformation is $-\Delta V/V(B1)=10.7\%$. The $B2$ phase is stable with further increasing pressure to at least 40 GPa, the highest pressure attempted in this experiment.

Upon decreasing pressure from 40 GPa, a completely reverse process was observed with the $B2$-$B1$ transition first observed at 12.7 GPa. The hysteresis in phase transition is small in SrSe. The equilibrium transformation pressure is determined to be at 13.5±0.7 GPa.

The P-V relation of SrSe is plotted in Fig. 2 and the data points are fitted to the first-order Birch equation.[13] The resulting values of fitting parameters for both $B1$ and $B2$ phases are tabulated in Table I. The Birch parameters, i.e., B_0 and B_0' are approximately the same for both phases in our fitting. Similar results have been seen in other strontium chalcogenides. The physical reason that makes the B_0 of the high-pressure phase of SrX not significantly larger than the low-pressure phase is that the nearest-neighbor distance increases at the $B1$-$B2$ transition. For SrSe, this distance increases from 2.91 to 3.06 Å.

In the following, we briefly discuss some systematic behaviors among the strontium chalcogenides under compression. First, all the SrX (X=O, S, Se, Te) have now been found to transform from the NaCl-type (B1) to the CsCl-type ($B2$) structure under high pressure with a volume decrease of 11–13 %. The transition pressures P_t, the relative volumes and the volume changes at the $B1$-$B2$ transition are summarized in Table II. As shown in Table II, the $B1$-$B2$ transition pressure is sensitively dependent on the anion component. A fit of data points between P_t and the zero-pressure cation-anion ratio r_c/r_a (after Ref. 14) yields

$$\ln P_t\ (\mathrm{GPa})=0.532+3.781(r_c/r_a)_{P=0}\ . \qquad (1)$$

Second, the volume decreases of SrX at the B1-B2 transition range from 11–13 %. If experimental uncertainties are considered, the relative volume change at transition is about constant, barely dependent on the anion species. A volume change of about 17% has been found in the III-V compounds as they transform from the fourfold to the sixfold coordination.[15,16]

In conclusion, SrSe transforms from the sixfold-coordinated NaCl-type B1 phase to the eightfold-coordinated CsCl-type B2 phase at 14.2 GPa with a volume decrease of 10.7%. The transition pressure, the bulk modulus and the volume change obtained in SrSe are in good agreement with trends observed in other strontium chalcogenides under high pressure.

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