Pressure induced Structural Phase Transition in SrS

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Abstract. Pressure induced structural phase transition in SrS from NaCl (B1) structure to CsCl (B2) structure has been studied using plane wave pseudopotential density functional theory as implemented in Quantum Espresso code. Ultrasoft pseudopotential along with generalised gradient approximation (GGA) has been used for total energy calculation. The electronic band structure has been calculated for B1 phase of SrS. We also report the vibrational properties such as phonon frequencies along major symmetry directions using density functional perturbation theory. The phase transition pressure is calculated by comparing enthalpies of both phases and its presently calculated value is 17.95 GPa, in very good agreement with the experimental results.

1. Introduction

The alkaline earth chalcogenides are technologically important material as they have found application ranging from catalysis to microelectronics [1-3]. They are important closed-shell ionic system crystallizing in the NaCl-type (B1) structure at ambient condition except for the MgTe and the beryllium chalcogenides. Among the alkaline earth chalcogenides, very little information is available for SrS. By X-ray diffraction experiment [4], SrS was found to undergo the structural phase transition from B1 to B2 at 18 GPa pressure. Kenata et al. [5] found the structural phase transformation occurring at 18 GPa, and reported the elastic constants in B1 phase at ambient condition. The non-metallic SrS after B1 to B2 phase transition was predicted to become metallic through band gap overlap mechanism [6-7]. Üğur et al. [8] have studied phonon properties of SrS under high pressure. Yan et al. [9] studied the elastic properties of SrS. The electronic band structure and optical properties of SrS are mainly discussed in other literature [10-12]. In present paper, we report the results of our theoretical study of structural and vibrational properties of SrS using plane wave pseudopotential density functional theory as implemented in Quantum Espresso code [13]. We have also calculated the phase transition pressure of SrS from B1 to B2 phase. In this section, we give the basic introduction. In the second section we give the information about methodology of the calculation and third section us discussed results and finally we conclude in the fourth section.

2. Calculation

The calculation of total energy of B1 and B2 phases of SrS has been carried out using ultrasoft pseudopotential within the generalised gradient approximation (GGA) using the scheme of Perdew et al. [14]. Convergence test gave a K.E. cut off of 55 Ry and 8x8x8 Monkhorst-Pack special k-point grid for Brillouin zone sampling. The calculated total energies were fitted to Murnaghan equation of state [15] in order to estimate structural parameters.
We have calculated the phonon dispersion curve and elastic constants of SrS. In phonon calculation, Brillouin zone sampling was performed with a line width of $10^{-3}$ Ry. To obtain the full phonon spectrum, dynamical matrices were evaluated on a 4x4x4 grid in q space for the B1 structure. These matrices were then Fourier-interpolated to obtain the phonon dispersion curve. From the phonon frequencies, we have calculated the phonon density of state (p-dos). Further, electronic band structure is also calculated.

The phase transition pressure from B1 to B2 phase is calculated by calculating enthalpies of both the phases. At T=0 K, enthalpy is given by,

$$H(P) = E_{\text{tot}}(V) + V P(V).$$

At a given pressure, the stable structure is the one whose enthalpy has the lowest value. The phase transition pressure is the pressure at which, the enthalpies of the two phases are equal.

### 3. Results and Discussions

In order to calculate the ground state properties of SrS, the total energies are calculated in both phases for different volume around the equilibrium cell volume $V_0$. The plot of total energy versus volume for SrS in both the phases are shown in Figure 1. It can be seen from E-V curves that the NaCl-type structure is the most stable at ambient conditions. The calculated total energies are fitted to Murnaghan equation of state [15] to determine the ground state properties namely lattice parameter ($a_0$), bulk modulus ($B_0$), first order pressure derivative of bulk modulus ($B'_0$). The calculated equilibrium parameters in both structures are given in Table 1, which also contains the results of previous first principal calculation and experimental data. Our present lattice constant is slightly larger than experimental work. This is essentially due to the GGA.

#### Table 1. The calculated ground state properties of B1 and B2 phases of SrS along with experimental and theoretical data.

| Properties      | B1 phase | B2 phase |
|-----------------|----------|----------|
|                 | Present  | Exp.     | Others  | Present | Exp.     | Others  |
| $a_0$ (Å)       | 6.040    | 6.024$^a$| 6.035$^b$, 6.076$^c$ | 3.655   | 3.61$^a$ | 3.655$^b$, 3.680$^c$ |
| $B_0$ (GPa)     | 53.6     | 58.0$^a$ | 48.0$^b$, 53.9$^c$ | 49.1    | ...      | 51.0$^b$, 50.6$^c$ |
| $B'_0$          | 3.55     | ...      | 3.96$^b$, 4.66$^c$ | 4.35    | ...      | 4.38$^b$, 4.50$^c$ |

$^a$ Ref.[5], $^b$ Ref.[8], $^c$ Ref.[16].

#### Table 2. Elastic constant (in GPa) of SrS in B1 phase.

| Present       | Others          |
|---------------|-----------------|
| $C_{11}$      | 129.1           |
|               | 141.0 [4], 113.9 [22] |
| $C_{12}$      | 15.85           |
|               | 17.2 [4], 19.4 [22] |
| $C_{44}$      | 74.53           |
|               | 62.5 [4], 30.3 [22] |

#### Table 3. Transition pressures and Volume collapse for the B1→B2 transition in SrS

| Present       | Exp.     | Others           |
|---------------|----------|------------------|
| Phase transition pressure | 17.95    | 18$^a$           |
| Volume collapse ($\Delta V/V (%)$) | 11.34    | 11.4$^c$        |

$^a$ Ref.[5], $^b$ Ref.[17], $^c$ Ref.[18], $^d$ Ref.[19], $^e$ Ref.[20], $^f$ Ref.[4], $^g$ Ref.[21].
The calculated electronic-band structure for the B1 phase along the various symmetry directions is shown in Figure 2. From the plot of band structure, we predict that SrS in B1 phase is insulator, which is in agreement with the experimental data.

Figure 3 shows the phonon dispersion curve along the high-symmetry direction for SrS in B1 phases at various pressures. We see that all the phonon frequencies have positive value at ambient condition; no modes appear to be soft, indicating that this structure is mechanically stable. The experimental results of phonon dispersion curve for SrS is not available yet. Phonon dispersion relation is also calculated at 10 GPa and 18 GPa pressure. The longitudinal phonon frequencies along [100] plane become hard with pressure. On the other hand, transverse phonon frequencies become soft. Thus, we believe that softness of phonon frequencies along [100] and [110] plane might be one of the reasons behind phase transition under pressure. From the phonon frequencies, we have also calculated the pressure dependent phonon density of state (p-dos), which is having the sharp peak is at 250 cm\(^{-1}\) at ambient condition, as shown in Figure 4. The computed p-dos at high pressure show that peak shifts towards heavy frequency side. We have also calculated the elastic constants (\(C_{11}\), \(C_{12}\) and \(C_{44}\)) in B1 phase of SrS using long wavelength limit of phonon frequencies. The experimental values of elastic constants are not available yet. On the other hand, clear difference is observed in the previously reported
theoretical elastic constants in Ref. [4] and Ref. [22]. Thus, in the absence of any experimental results, presently computed values form a new set of reliable data of elastic constants of B1-SrS at ambient condition. Figure 5 shows the pressure-volume relation for SrS along with the experimental results. It is evident from the figure that presently calculated results agree well with available experimental values. Figure 6 represents the pressure variation of enthalpy for both phases. It is evident from the graph that upon compression SrS undergoes a first order structural phase transition at about 17.95 GPa pressure, which is in excellent agreement with the experimental results of 18 GPa. The volume collapse due to phase transition is calculated. Table 2 summarized the transition pressures \( p_t \) and the volume collapse of SrS, along with the other theoretical and experimental data. The presently calculated value of volume collapse is 11.34 \%, which is in very good agreement with the experimental value of 11.4 \%.

4. Conclusion

The structural stabilities under pressure, elastic and vibrational properties of SrS are investigated using first principles calculations based on density functional theory. The presently calculated cohesive properties of B1 and B2 phase of SrS namely lattice constant, bulk modulus, first order pressure derivative of bulk modulus are found to be in good agreement with experimental and other theoretical results. The electronic band structure of B1-SrS shows the insulating nature, in agreement with the experimental and other theoretical findings. The calculated values of phonon frequencies along major symmetry directions and elastic constants confirm that SrS is mechanically stable in B1 structure. Further, it is observed that softening of phonon frequencies with pressure may be one of the reasons behind the structural phase transition from B1 to B2 phase. The phase transition pressure and volume collapse from B1 to B2 phase is also in excellent agreement with experimental results.

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6. References

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