

Room and High-Temperature Study of Rare Earth Chalcogenides

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Phase transformation analysis of ScS and ScSe, including temperature effects, is reported in this investigation. The theoretical exploration by means of the Realistic Interaction Potential Approach (RIPA) model is carried out. A volume collapse occurs in the transition phenomena. This transformation is described in a high-temperature range of 0-900 K. The consequences of this investigation demonstrate generally very good agreement with the available reports. In addition, the elastic behavior and pressure derivatives are premeditated. The performance of bulk modulus for the present compounds as a function of temperature and pressure is accounted for. Innovation estimates are made for the elastic assets of the current compounds. Various moduli of elasticity of these compounds are reported with temperature as well as pressure variations. The temperature and pressure behavior of the present compounds is in good agreement with the previously published results. This study confirms the phase transformation from NaCl to the CsCl structure of these compounds.

Keywords: Scandium, Phase transformation, Crystal structure, Temperature, Pressure.

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1. INTRODUCTION

Monochalcogenides of rare earth (RE) metals have been deliberated lengthily to make use of high-temperature thermoelectric relevance. In solid-state physics, the study of their peculiar electronic, optical, phonon, and magnetic properties are significant. The occurrence of 4*f*-electron in these compounds is essentially accountable for these inquisitive physical possessions. Among these compounds, some chalcogenides show non-integral valence. This is due to *f*-electron hybridization at ambient temperature and pressure. They demonstrate metallic temperament when the rare earth ion is in a trivalent state and semi-conducting in the case of a divalent state [1-4].

Amongst scandium is a grave raw substance that is vital for its potential application in enabling technologies such as fuel cells and lightweight resources. The scandium monochalcogenides belong to the wide class of binary rare-earth compounds with the NaCl-type structure, which has been the least, studied material. The pressure applying deeds of these have been scrutinized up to 300 kbar experimentally using high-pressure X-ray-diffraction techniques [5]. The experimental high-pressure X-ray diffraction examination demonstrates an inconsistent decrease in volume with pressure in present chalcogenides [6]. This is predictable to the 4*f*-5*d* electronic transition. Maachou et al. [7] stated the high-pressure structural (*B*₁ – *B*₂) phase transition (PT) and the elastic properties of ScSe using the FP-APW + LO computation method.

ScS and ScSe fall into place in six-fold synchronized

NaCl-type composition with space group symmetry *Fm*3*m* (225) and distorted into CsCl-type (*B*₂) composition with space group symmetry *Pm*3*m* (221). To the best of our comprehension, not a bit of the study we found about these chalcogenides deals with the development of their properties at high temperatures by means of model calculations. We have deliberated structural high pressure and temperature exploration of these compounds hypothetically through the Realistic Interaction Potential Approach (RIPA) together with temperature effect. To acquire enhanced comparability of theoretical outcomes, we have taken into account room temperature in pressure to stimulate approximation in view of the fact that the majority of the calculations are accomplished at zero temperature. In the subsequent section 2, we symbolize the technique of computation. Section 3 presents the fallouts attain for present chalcogenides. As a final point, section 4 finishes the paper with a summing-up of present outcomes.

2. TECHNIQUE OF COMPUTATION

2.1 Computations of Structural Assets

The function of pressure implies an amendment in the volume of the crystal, and accordingly, it modifies the charge allocation of the electron shells. Accordingly, a bend of the overlapping electron shells of the adjacent ions takes place which leads to an augmented charge transfer (or three-body interaction (TBI)) [8]:

$$f(r) = f_0 \exp(-r / \rho). \quad (1)$$

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Here, f_0 is a constant.

This commenced in the terminology of Gibbs free energy to attain the immovability stipulation. These Gibbs free energies planned for rock-salt (NaCl, B_1) and cesium-chloride (CsCl, B_2) configuration at $T = 300$ K are given by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1}(r) - TS_1, \quad (2)$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2}(r') - TS_2 \quad (3)$$

with $V_{B_1} = 2.00r^3$ and $V_{B_2} = 1.54r'^3$ as unit cell volumes,

$$\Delta G = \Delta H - T\Delta S. \quad (4)$$

The first terms in (2) and (3) are lattice energies for B_1 and B_2 configurations and are articulated as:

$$U_{B_1}(r) = \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f(r))}{r} - \left[\frac{C}{r^6} + \frac{D}{r^8} \right] + 6b\beta_{ij} \exp[(r_i + r_j - r) / \rho] + 6b\beta_{ii} \exp[(2r_i - 1.414r) / \rho] + 6b\beta_{jj} \exp[(2r_j - 1.414r) / \rho] \quad (5)$$

$$U_{B_2}(r') = \frac{-\alpha'_m z'^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f(r'))}{r'} - \left[\frac{C'}{r'^6} + \frac{D'}{r'^8} \right] + 8b\beta_{ij} \exp[(r_i + r_j - r') / \rho] + 3b\beta_{ii} \exp[(2r_i - 1.154r') / \rho] + 3b\beta_{jj} \exp[(2r_j - 1.154r') / \rho] \quad (6)$$

where the symbols have their usual meanings [9, 10].

At present, the differences in entropy in the last terms of equations (2) and (3) can be predicted in the formulation of our earlier work [9]:

$$S_1 - S_2 = \int_1^2 \left[\frac{C_1 - C_2}{T} \right], \quad (7)$$

$$C_i = \frac{\{\beta V_i B\}_i}{\gamma_i}. \quad (8)$$

Here, the Gruneisen parameter (γ) can be calculated by the well-known formula as follows [9]:

$$\gamma = -r_0 / 6 \left[U'''(r_0) / U''(r_0) \right]. \quad (9)$$

The current prospective model has three model parameters [b , ρ , $f(r)$]. They are computed by means of the subsequent conditions [10]:

$$\left[\frac{dU}{dr} \right]_{r=r_0} = 0, \quad (10)$$

$$B_1 + B_2 = -1.165 Z_m^2. \quad (11)$$

Here, $Z_m^2 = Z(Z + 12f(r))$.

By means of these model parameters and the minimization technique, PT pressures of the current compounds have been computed.

2.2 Calculations of Elastic Assets

Elasticity is an essential asset of a material. Elastic properties of a material are significant as they transmit to an assortment of elementary solid-state properties, such as interatomic potentials, equation of state, and phonon spectra. Accordingly, it is imperative to establish the elastic constants of the material. The terminology for the second-order elastic constants (SOECs) was approved in our earlier work [9].

3. RESULTS AND DISCUSSION

3.1 Structural Assets

In the beginning, we assess the key factors and after that estimate the model parameters of current compounds. These inputs [7, 11] and output parameters are prearranged in Table 1. These parameters are used in underhanded the structural and elastic possessions are illustrated by means of calculating the lattice energies of the B_1 and B_2 configurations. The PT is deliberated via minimizing the Gibbs free energies for the equilibrium lattice parameters r_0 and r_0' corresponding to the B_1 - and B_2 -structures. The lattice energies U_{B_1} and U_{B_2} are obtained to calculate the Gibbs free energy difference $\Delta G = (G_{B_1} - G_{B_2})$ at different pressures.

Table 1 – Input parameters and computed model parameters for ScS and ScSe

Solid	Input parameters		Model parameters		
	r_0 (Å)	B (GPa)	B (10^{-12} ergs)	ρ (Å)	$f(r)$
ScS	2.599 ^a	115.33 ^b	14.3106	0.275	0.0020
ScSe	2.699 ^a	95.92 ^b	12.0584	0.252	0.0021

a – ref [11], b – ref [7]

We designed this energy change ΔG as a role of pressure in Fig. 1 and Fig. 2 for ScS and ScSe, respectively. From the figures, it is noticeable that at $P = 0$ all the compounds lie in the B_1 configuration, demonstrating the fact that the B_1 configuration is the ground state structure for these compounds. Gibbs free energy differences ΔG are plotted at different temperatures (0-900 K). The structural PT is associated with an abrupt change in the arrangement of atoms at high pressure. An abrupt volume collapse with a change in pressure is acquired as in the phase diagram. The relative volume changes V/V_0 are also observed at different pressures and planned alongside the pressure in Fig. 3 for both ScS and ScSe.

The deliberated consequences of PT and volume collapse are abridged in Table 2 all along with the hypothetical outcomes. The outcomes of PT are 86.8 GPa and 52.5 GPa, and volume collapses are 5.78 % and 5.63 %, respectively, for ScS and ScSe, which is in good agreement with other theoretical results [7]. For studying the temperature behavior of PT pressure, we have computed the values of PT pressure at temperatures. This variation is plotted in Fig. 4 for the temperature range 0-900 K. It is perceptible from this stature to facilitate the PT pressures decrease with increasing the temperature for together the compounds.

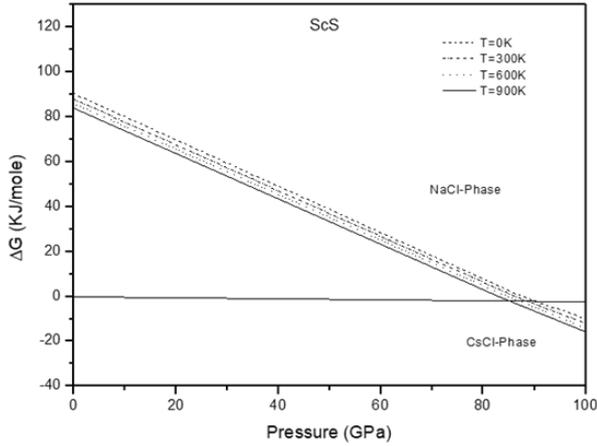


Fig. 1 – Variation of ΔG (KJ/mole) with pressure for ScS at different temperatures

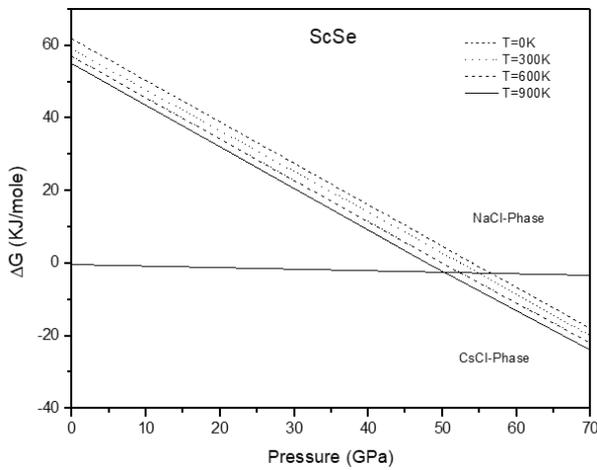


Fig. 2 – Variation of ΔG (KJ/mole) with pressure for ScSe at different temperatures

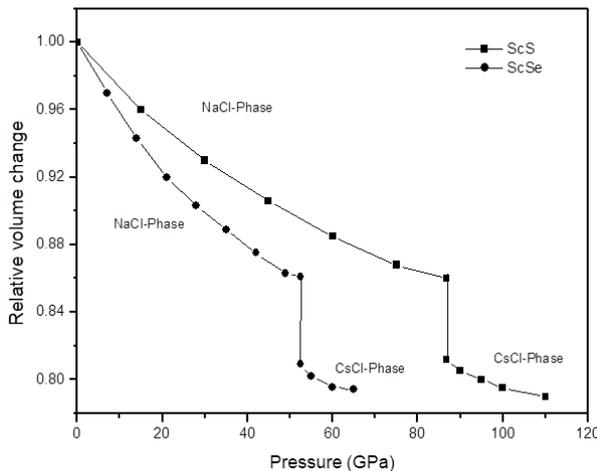


Fig. 3 – Variation of volume change V_P/V_0 with pressure for ScS and ScSe

3.2 Elastic Assets

The comprehension of second-order elastic constants (SOECs) and their pressure derivatives is imperative for the indulgence of the interatomic forces in solids. The values of these SOECs are given in Table 3.

Our results are similar to those values with other obtainable experimental [12] and theoretical [7] data for ScS and ScSe. These constants are computed at high pressures. The pressure variation of SOECs at $T = 0$ K is presented in Fig. 5 for ScS and ScSe, respectively. In both cases, the SOECs of ScS and ScSe increase with increasing pressure. The pressure variation in C_{11} is large, because C_{11} corresponds to elasticity in length. While in the case of C_{12} and C_{44} this variation is small, because they are related to the elasticity in shape, which is a shear constant. These results have been compared with the FP-APW + LO [7].

Table 2 – Phase transition and volume change of ScS and ScSe

Solid	PT pressure (GPa)		Volume collapse, %	
	Present	Others	Present	Others
ScS	86.8	87.25 ^a	5.78	5.29 ^a
ScSe	52.5	53.65 ^a	5.63	5.24 ^a

a – ref [7]

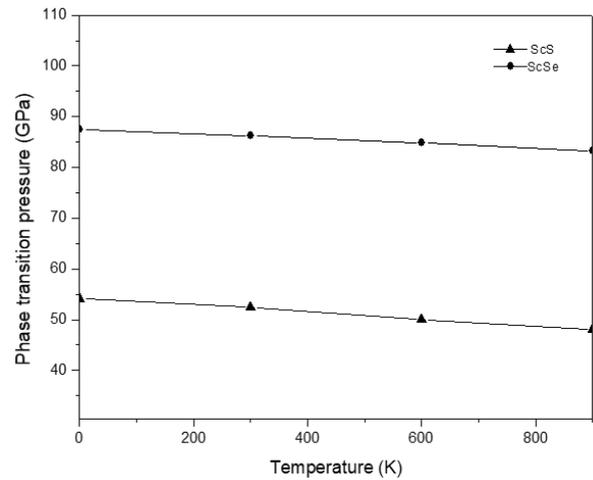


Fig. 4 – Variation of PT pressure with temperature (in K) for ScS and ScSe

Table 3 – Calculated values of SOECs (C_{11} , C_{12} , C_{44} in GPa), bulk modulus (B in GPa) and its pressure derivative (B') for ScS and ScSe

Solid	C_{11}	C_{12}	C_{44}	B	B'	
ScS	Present	272.50	26.89	114.35	108.59	3.24
	Others	287.07 ^a	29.46 ^a	126.83 ^a	115.33 ^a	3.51 ^a
	Expt.	–	–	–	103±11 ^b	–
ScSe	Present	238.00	21.55	98.85	93.70	3.56
	Others	239.76 ^a	23.99 ^a	104.50 ^a	95.92 ^a	3.64 ^a

a – ref [7], b – ref [12]

Bulk modulus is a combination of elastic constants that describe the elastic properties of a solid when it is under pressure on all surfaces. The formula for calculating the bulk modulus and its pressure derivative is given in Eq. (12). The calculated values of bulk modulus and its pressure derivative of the present compounds are summarized in Table 3. It is apparent from these results that ScSe is more compressible than ScS. Furthermore, to study the high-temperature behavior of bulk modulus (B) we have plotted its variations with different temperatures up to 900 K for ScS and ScSe, which are represented in Fig. 6. At the same time, as

temperature increases, the bulk modulus of both compounds decreases monotonically. Our results have been equated with the first-principles calculations in different temperature range [7].

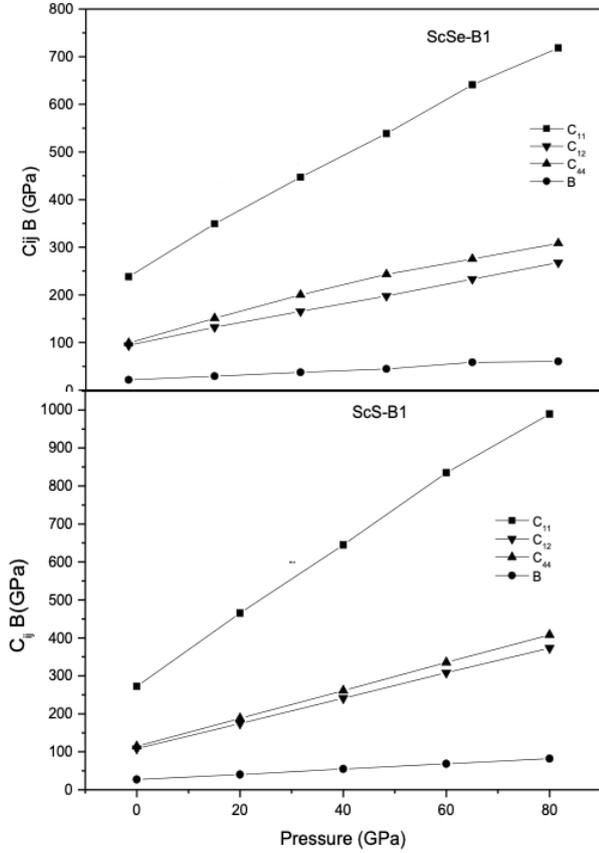


Fig. 5 – Variation of elastic constant and bulk modulus with pressure for ScS and ScSe

The shear modulus G can be defined by the subsequent equation:

$$G = (G_V + G_R) / 2, \quad (12)$$

where $G_V = (2C + 3C_{44}) / 5$ and $G_R = 15(6/C + 9/C_{44})^{-1}$ with $C = (C_{11} - C_{12}) / 2$, G_V is the Voigt shear modulus and G_R is the Reuses shear modulus.

We have also calculated the Young modulus Y , which is related to the bulk modulus B and the shear modulus G by the following equation [13]:

$$Y = 9BG(3B + G). \quad (13)$$

The cubic crystal has elastic anisotropy as a result of a fourth rank tensor property of elasticity. We have calculated the elastic anisotropic parameter of scandium compounds, using the following relation:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}. \quad (14)$$

As the Poisson ratio is an important property to know the properties of compounds, it influences the speed of propagation and reflection of stress waves. We

have calculated the Poisson ratio (σ) of the present chalcogenides, the expression of σ can be given in the following form:

$$\sigma = \frac{3B - 2G}{6B + 2G}. \quad (15)$$

The calculated values of shear modulus G , Young modulus Y , anisotropic parameter A and Poisson ratio σ of ScS and ScSe are illustrated in Table 4. It is clear from the table that our values of G , A , Y , and σ for the present compounds agree well with other results [13].

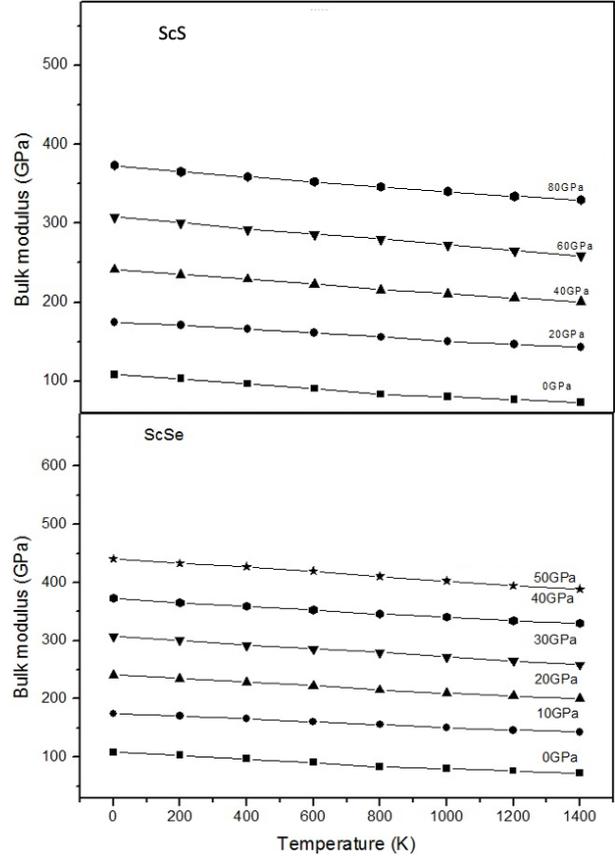


Fig. 6 – Variation of bulk modulus with temperature for ScS and ScSe

Table 4 – Calculated values of Young modulus (Y in GPa), shear modulus (G in GPa), Poisson ratio (σ) and anisotropy factor (A)

Solid	G	Y	A	σ
ScS Present	117.66	259.32	0.931	0.105
Others	127.62 ^a	279.69 ^a	0.98 ^a	0.095 ^a
ScSe Present	102.49	225.33	0.913	0.099
Others	116.65 ^a	149.00 ^a	0.77 ^a	0.07 ^a

a – ref [7]

4. CONCLUSIONS

We have pertained the Temperature Interaction Potential Realistic Approach (TIPRA) model to explore the structural, mechanical, and thermophysical assets at elevated temperature of the scandium compounds. The outcomes are abridged as go after:

- Existing rare earth compounds reline in the NaCl-type configuration (B_1) under ambient conditions, they transform to the CsCl-type configuration (B_2).
- At the phase transition pressure from the NaCl to CsCl configuration, the occurrence of an abrupt volume collapse identifies the occurrence of the first-order phase transition.
- The temperature and pressure performance of bulk modulus demonstrates similar deeds as testified beforehand.
- It is apparent from current efforts that ScSe is more compressible than ScS. The current outcomes are better identified with other hypothetical consequences.

REFERENCES

1. Franziska Klimpel, Michael Bau, Torsten Graupner, *Sci. Rep.* **11**, 5306 (2021).
2. A.A. Ahmad, S. Mahmoud, Burhan Alshafaay, F. El Haj Hassan, *Indian J. Phys.* **93** No 9, 1129 (2019).
3. Chun-Gang Duan, R.F. Sabirianov, W.N. Mei, P.A. Dowben, S.S. Jaswal, E.Y. Tsymbal, *J. Phys. Condens. Matter.* **19**, 315220 (2007).
4. C.G. Duan, R.F. Sabirianov, J. Liu, W.N. Mei, P.A. Dowben, J.R. Hardy, *Phys. Rev. Lett.* **94**, 237201 (2005).
5. A. Chatterjee, A.K. Singh, A. Jayaraman, *Phys. Rev. B* **6**, 2285 (1972).
6. A.K. Singh, A. Jayaraman, A. Chatterjee, *Solid State Commun.* **9**, 1459 (1971).
7. A. Maachou, H. Aboura, B. Amrani, R. Khenata, S. Bin Omran, D. Varshney, *Comput. Mater. Sci.* **50**, 3123 (2011).
8. Purvee Bhardwaj, Sadhna Singh, *Curr. Appl. Phys.* **14**, 496 (2014).
9. P. Bhardwaj, S. Singh, *J. Mater. Sci. Semicond. Proc.* **31**, 44 (2015).
10. Sadhna Singh, Purvee Bhardwaj, *J. Alloy. Compd.* **509**, 7047 (2011).
11. A. Svane, P. Strange, W.M. Temmerman, Z. Szotek, H. Winter, L. Petit, *phys. status solidi b* **229**, 1459 (2002).
12. Suhithi M. Peiris, Michael T. Green, Dion L. Heinz, Jeremy K. Burdett, *Inorg. Chem.* **35**, 6933 (1996).
13. P. Bhardwaj, S. Singh, *Mater. Chem. Phys.* **125** No 3, 440 (2011).

Кімнатне та високотемпературне дослідження рідкісноземельних халькогенідів

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У дослідженні представлено аналіз фазової трансформації ScS і ScSe, включаючи температурні ефекти. Проведено теоретичне дослідження за допомогою моделі Realistic Interaction Potential Approach (RIPA). У перехідних явищах відбувається колапс об'єму. Це перетворення описано для високотемпературного діапазону 0-900 К. Результати дослідження загалом демонструють дуже гарне узгодження з наявними повідомленнями. Крім того, пружна поведінка та похідні тиску є заздалегідь обдуманими. Враховано характеристики модуля об'ємної пружності для сполук, що розглядаються, як функції температури та тиску. Інноваційні оцінки зроблені для еластичних активів сполук. Повідомляються різні модулі пружності сполук із зміною температури та тиску. Поведінка температури та тиску сполук добре узгоджується з раніше опублікованими даними. Представлене дослідження підтверджує фазове перетворення від NaCl до структури CsCl цих сполук.

Ключові слова: Скандій, Фазове перетворення, Кристалічна структура, Температура, Тиск.