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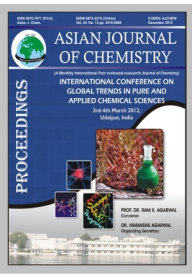

Crystal Anharmonicity in Strontium Monochalcogenides†

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This paper describes the temperature dependence of the ultrasonic velocities of Strontium chalcogenides SrX (X: S, Se and Te) for longitudinal and shear waves along <100>, <110> and <111> crystallographic directions in the temperature range 100-500 K. The second- and third- order elastic constants have also been evaluated for these chalcogenides using Coulomb and Born-Mayer potential. The second and third order elastic constants are used to find out ultrasonic velocities. The values of elastic constants and ultrasonic velocities are highest for SrS. Hence the mechanical properties and crystallography of SrS are better than SrSe and SrTe. Obtained results are discussed and compared with available results of same type of materials.

Key Words: Strontium monochalcogenides, Elastic constants, Ultrasonic velocity.

INTRODUCTION

Nowadays, the strontium monochalcogenides have much attention because of their scientific and technological importance with many applications ranging from catalysis and microelectronics. These materials are useful in the area of radiation dosimetry, luminescent devices and infrared sensitive devices[1-4]. The electron band structure, optical properties, volume dependence of energy gap; structural phase stability, elastic properties and metallization process of strontium monochalcogenides are studied by various investigators[5-10]. Marinelli and Lichanot investigated elastic constants and electronic properties of SrS and SrSe at quantum mechanical level with periodic CRYSTAL 98 program[11]. The full potential linearized augmented plane wave method (FP-LAPW) within the generalized gradient approximation (GGA) was applied to calculate the electronic band structure, bulk modulus and second order elastic constants of SrS, SrSe and SrTe in NaCl structure[12]. The discussion on systematic trends in structural transitions and changes in optical properties of SrS, SrSe and SrTe have been made by Syassen[13]. The study of temperature dependence of ultrasonic velocity in perfect crystal is a powerful tool for understanding microscopic properties with crystallographic texture[14]. The theory enumerated by Mason[15] in terms of second and third order elastic constants has been widely used to account for the temperature dependence of ultrasonic velocity in a variety of crystals[16-21]. So for to our knowledge, the crystal anharmonicity of strontium monochalcogenides have not been studied systematically. Therefore, we computed and presented a set of physical parameters of these compounds in B_1 structured phase along <100>, <110> and <111> crystallographic directions in the temperature range 100-500 K, such as second and third order elastic constants, bulk modulus, shear modulus, tetragonal modulus, ultrasonic velocities for longitudinal waves as well as shear waves.

THEORETICAL APPROACH

The strontium monochalcogenides possess face centered cubic crystal structure. The potential used for evaluation of second and third order elastic constants (SOECs and TOECs) is taken as the sum of Coulomb and Born-Mayer potentials.

$$\phi(R) = \phi(C) + \phi(B) \quad (1)$$

where, $\phi(C)$ is the Coulomb potential and $\phi(B)$ is the Born-Mayer potential, given as:

$$\phi(C) = \pm\frac{e^2}{r} \text{ and } \phi(B) = A\exp\left(\frac{-r}{b}\right) \quad (2)$$

where, e is the electronic charge, r is the nearest-neighbor distance, b is the hardness parameter and A is the strength

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TABLE-1
TEMPERATURE DEPENDENT SOEC AND TOEC OF STRONTIUM MONOCHALCOGENIDES (10^{10} N/m^2) OF SrX

Materials	Temp. (K)	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
SrS	100	4.956	1.013	1.101	-84.606	-4.05	1.353	1.915	-4.428	1.901
	200	5.117	0.931	1.105	-85.322	-3.706	0.805	1.929	-4.444	1.901
	300	5.297	0.848	1.109	-86.262	-3.358	0.257	1.943	-4.463	1.901
	400	5.483	0.765	1.113	-87.267	-3.009	-0.291	1.956	-4.482	1.901
	500	5.671	0.682	1.117	-88.298	-2.661	-0.839	1.972	-4.501	1.901
SrSe	100	4.579	0.863	0.947	-79.885	-3.413	1.101	1.667	-3.783	1.655
	200	4.748	0.782	0.95	-80.747	-3.064	0.547	1.679	-3.798	1.655
	300	4.927	0.701	0.954	-81.74	-2.714	-0.006	1.691	-3.815	1.655
	400	5.109	0.621	0.957	-82.769	-2.364	-0.559	1.703	-3.831	1.655
	500	5.293	0.54	0.96	-83.813	-2.014	-1.113	1.715	-3.848	1.655
SrTe	100	3.957	0.634	0.713	-71.738	-2.442	0.709	1.281	-2.808	1.272
	200	4.119	0.557	0.715	-72.64	-2.09	0.145	1.29	-2.819	1.272
	300	4.05	0.66	0.713	-73.249	-2.467	0.989	1.278	-2.816	1.272
	400	4.461	0.405	0.72	-74.663	-1.385	-0.981	1.308	-2.844	1.272
	500	4.633	0.328	0.722	-75.698	-1.033	-1.544	1.317	-2.856	1.272
NpS[19]	300	5.794	1.332	1.598	-88.7	-5.51	1.196	2.679	-6.52	2.620
NpSe[19]	300	4.935	1.068	1.304	-76.1	-4.40	0.852	2.203	-5.31	2.153
NpTe[19]	300	4.389	0.743	0.966	-70.3	-2.98	0.276	1.679	-3.90	1.641

parameter. Following Brugger's[22] definition of elastic constants at absolute zero, the second and third order elastic constants are obtained. According to lattice dynamics developed by Leibfried and Ludwig[23] and Mori and Hiki[24] lattice energy changes with temperatures. Hence adding vibrational energy contribution to the static elastic constants, one gets second and third order elastic constants (C_{ij} and C_{ijk}) at the required temperature.

$$C_{ij} = C_{ij}^{0} + C_{ij}^{Vib} \text{ and } C_{ijK} = C_{ijK}^{0} + C_{ijK}^{Vib} \quad (3)$$

C_{ij}^{0} and C_{ijK}^{0} are second order elastic constants and third order elastic constant at absolute zero temperature and C_{ij}^{Vib} and C_{ijK}^{Vib} are second order elastic constants and third order elastic constant at particular temperature like 100, 200 and 300 K.

The expressions for direction dependent ultrasonic velocities in cubic crystals are as follows: Along <100> crystallographic direction;

$$V_L = \sqrt{\frac{C_{11}}{d}} \;\; ; \;\; V_{S1} = V_{S2} = \sqrt{\frac{C_{44}}{d}} \Bigg\} \quad (4)$$

Along <111> crystallographic direction;

$$V_L = \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3d}}; V_{S1} = V_{S2} = \sqrt{\frac{C_{11} - C_{12} + C_{44}}{3d}} \Bigg\} (5)$$

Along <110> crystallographic direction;

$$V_L = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2d}}; V_{S1} = \sqrt{\frac{C_{44}}{d}}; V_{S2} = \sqrt{\frac{C_{11} - C_{12}}{d}} \Bigg\} \quad (6)$$

The ultrasonic velocities are worked out using calculated values of second order elastic constants.

RESULTS AND DISCUSSION

The elastic constants are important characteristic parameters of solids. The investigation of them is essential to understand many of their physical properties such as elasticity, mechanical stability, stiffness of materials and concerning the nature of forces operating in solids. The elastic constants of materials are directly related to their microstructure and are used to obtain the ultrasonic velocities. These are of great interest in applications where the mechanical strength and durability are important. The second- and third- order elastic constants have been evaluated using two basic parameters *i.e.*, lattice parameter and hardness parameter. The lattice parameters[4] for SrS, SrSe and SrTe are 6.024 Å, 6.236 Å and 6.660 Å and the value of hardness parameter for each material is 0.293 Å. The computed results of temperature dependent second order elastic constants and third order elastic constant are listed in Tables-1. We found no experimental/theoretical result of second order elastic constants and third order elastic constant of the strontium monochalcogenides directly in existing literature. So we compare our achieved results with other monochalcogenides of neptunium[19]. These compared results are available with obtained results.

It is clear from the Table-1 that, out of nine elastic constants, four (*i.e.*, C_{11}, C_{44}, C_{112} and C_{144}) are increasing and four (*i.e.*, C_{12}, C_{111}, C_{166} and C_{123}) are decreasing with the temperature while C_{456} is found to be unaffected. The increase or decrease in stiffness constants is due increase or decrease in atomic interaction with temperature. If inter-atomic distance increases or decreases with temperature then interaction potential decreases/increases, which causes due to decrease or increase in stiffness constants. Our calculations of second order elastic constants and third order elastic constant are reasonable since we have made calculations for the temperature variation of elastic constants of these alkaline earth monochalcogenides. Most simple theories are able to get a reasonable estimate of elastic constants at room temperature only by using two basic parameters *i.e.* nearest neighbour distance and hardness parameter. Table-1 depicts that SrS has highest valued second order elastic constants and third order elastic constant in contrast to SrSe, SrTe. Hence mechanical influence of SrS is better than SrSe and SrTe.

The known mechanical stability condition for cubic materials led to the restriction on the elastic constants known

as $B_T = (C_{11}+2C_{12})/3 > 0$, $C_{44} > 0$, $C_{11} > 0$ and $C_S = (C_{11}-C_{12})/2 > 0$, where C_{ij} are the conventional elastic constants and B_T bulk modulus and C_S the tetragonal moduli. The temperature dependent C_{11}, C_{12} and C_{44} are presented in Table-1, while the values B_T and C_S are tabulated in Table-2 at room temperature. The other cubic stability condition, $C_{12} < B < C_{11}$ for strontium monochalcogenides is also satisfied.

TABLE-2
BULK MODULI AND TETERGONAL MODULI OF SrX (10^{10} N/m^2) AT ROOM TEMPERATURE

Material	B_T	C_S
SrS	2.331	2.22
SrSe	2.110	2.11
SrTe	1.750	1.737

The ultrasonic velocity is a key factor to characterize the material's properties. It is directly related to second order elastic constants and density of that particular material as shown in eqns. (4-6) and presented in Table-3.

TABLE-3
TEMPERATURE DEPENDENT ULTRASONIC VELOCITIES (10^3m/s) OF SrX

Materials		Temp. (K)	100	200	300	400	500
SrS	<100>	V_L	3.687	3.746	3.811	3.878	3.944
		$V_{S_1}=V_{S_2}$	1.738	1.741	1.744	1.747	1.750
	<111>	V_L	3.227	3.228	3.233	3.238	3.243
		$V_{S_1}=V_{S_2}$	2.147	2.199	2.254	2.309	2.362
	<110>	V_L	3.348	3.365	3.387	3.409	3.432
		V_{S1}	1.738	1.741	1.744	1.747	1.750
		V_{S2}	3.288	3.388	3.493	3.597	3.699
SrSe	<100>	V_L	3.164	3.222	3.282	3.342	3.402
		$V_{S_1}=V_{S_2}$	1.439	1.441	1.444	1.446	1.449
	<111>	V_L	2.712	2.715	2.719	2.724	2.729
		$V_{S_1}=V_{S_2}$	1.843	1.892	1.943	1.992	2.040
	<110>	V_L	2.832	2.850	2.870	2.891	2.911
		V_{S1}	1.439	1.441	1.444	1.446	1.449
		V_{S2}	2.850	2.944	3.039	3.132	3.223
SrTe	<100>	V_L	2.816	2.873	2.932	2.990	3.047
		$V_{S_1}=V_{S_2}$	1.195	1.197	1.199	1.201	1.203
	<111>	V_L	2.323	2.325	2.329	2.333	2.337
		$V_{S_1}=V_{S_2}$	1.642	1.690	1.738	1.786	1.832
	<110>	V_L	2.455	2.474	2.493	2.513	2.533
		V_{S1}	1.195	1.197	1.199	1.201	1.203
		V_{S2}	2.580	2.671	2.762	2.851	2.937

The ultrasonic velocity is directly related to C_{ij} and density of that particular material. It can be seen that the velocities of the chosen materials along longitudinal and shear waves increase with increase in temperature. Due to unavailability of experimental results of these materials for ultrasonic velocities of SrX, we compare our results with other B_1 structured materials like semiconductor[25], rare-earth monochalcogenides[26] and metallic alloys[20] and is found that the order and nature of ultrasonic velocities. It is clear from Table-3 that the computed values of ultrasonic velocities are highest in case of SrS. So we can say that the propagation of sound waves through SrS will be better than that of other chosen materials.

Conclusion

On the basis of obtained results of present investigation, we say that:

ˆ We have used the Coulomb and Born-Mayer potential having two basic parameters *i.e.*, lattice parameter and hardness parameter to compute second- and third order elastic constant. Evaluated values of second- and third order elastic constant have been compared with available B_1 structured materials, which are near to agreement, hence our approach to calculate second- and third order elastic constant appears to justify.

ˆ All the chosen materials satisfied the Born critera of mechanical stability.

ˆ Second- and third order elastic constant have been used to find out the ultrasonic velocities for longitudinal and shear waves in SrX.

ˆ Ultrasonic velocity is found to be highest for SrS along all chosen direction, so SrS will be most suitable compound for wave propagation.

Thus our theoretical approach to calculate the second- and third-order elastic constants, ultrasonic velocity for longitudinal and shear waves is justified and obtained results will be interesting to explore any further possible physical information of the chosen materials.

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