

Ultrasonic Wave Propagation in Hexagonal SrMnO₃ Compound

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ABSTRACT

In the present study, the ultrasonic attenuation due to phonon-phonon interaction has been investigated in hexagonal SrMnO₃ compound. Higher order elastic constants have been computed at temperature dependent following the Lenard-Jones Potentials. Second order elastic constants are used for the determination of other ultrasonic parameters. The temperature variation of the ultrasonic velocities is evaluated along different angles with unique axis of the crystal using the second order elastic constants. Temperature variation of the thermal relaxation time and Debye average velocities is also calculated along the same orientation. The temperature dependency of the ultrasonic properties is discussed in correlation with elastic, thermal and electrical properties. It has been found that the thermal conductivity and thermal relaxation times is the main contributor to the behaviour of ultrasonic attenuation as a function of temperature and the responsible cause of attenuation is phonon-phonon interaction. The mechanical properties of SrMnO₃ material at low temperature (50K) are better than room temperatures because at this temperature it has low ultrasonic attenuation

Keywords: Elastic constants, Ultrasonic velocity, Ultrasonic attenuation, Thermal properties

I. INTRODUCTION

Perovskite manganese oxides, commonly represented as AMnO₃ (A: rare-earth alkaline earth metals), have been instrumental in condensed matter physics as well as in technical applications. Perovskite SrMnO₃ (SMO) is a polymorphism that has complex magnetic ordering and dielectric polarization and thus attracted a lot of attention as a multiferroic material [1, 2]. An inorganic chameleon has been inorganic chameleon because of the great flexibility of the hexagonal perovskite structure. Many different compounds take it or the corresponding structure, as the mother structure is easily deformed or diffused to the relative sizes of the ions of the compounds [3]. The hexagonal

SrMnO₃ is antiferromagnetic below at Néel temperature. Néel temperatures is reported to be 260 K by Takeda and Ohara [4]. Hexagonal polymorphisms are semiconductors. The hexagonal SrMnO₃ when heated in air is stoichiometric at room temperature but loses oxygen at high temperature [5].

In the present work, we have worked diligently to make the relationship between thermo physical and microstructural properties for hexagonal SrMnO₃ compound. SrMnO₃ compound will help in understanding the mechanical behaviour of this compound and it will play an important role in the illustration of industrial applications with useful physical properties under moderate operating

conditions. For that, we have considered ultrasonic attenuation, thermal relaxation time and ultrasonic velocity for SrMnO₃ compound have also been evaluated and discussed for this perovskite manganese oxides.

II. METHODS AND MATERIAL

In the present consideration, the theory is divided into two parts:

2.1 Second-and third order Elastic constants

The second (C_{ij}) and third (C_{ijk}) order elastic constants of material are specified by following expressions.

$$C_{ij} = \frac{\partial^2 U}{\partial e_i \partial e_j}; \quad I \text{ or } J = 1, \dots, 6 \quad (1)$$

$$C_{ijk} = \frac{\partial^3 U}{\partial e_i \partial e_j \partial e_k}; \quad I \text{ or } J \text{ or } K = 1, \dots, 6 \quad (2)$$

where, U is elastic energy density, e_i=e_{ij} (i or j = x, y, z, I=1, ...6) is component of strain tensor. Eqs. (1) and (2) leads six second and ten third order elastic constants (SOEC and TOEC) for the hexagonal structure materials [6, 7].

$$\left. \begin{aligned} C_{11} &= 24.1 p^4 C' & C_{12} &= 5.918 p^4 C' \\ C_{13} &= 1.925 p^6 C' & C_{33} &= 3.464 p^8 C' \\ C_{44} &= 2.309 p^4 C' & C_{66} &= 9.851 p^4 C' \end{aligned} \right\} \quad (3a)$$

$$\left. \begin{aligned} C_{111} &= 126.9 p^2 B + 8.853 p^4 C' & C_{112} &= 19.168 p^2 B - 1.61 p^4 C' \\ C_{113} &= 1.924 p^4 B + 1.155 p^6 C' & C_{123} &= 1.617 p^4 B - 1.155 p^6 C' \\ C_{133} &= 3.695 p^6 B & C_{155} &= 1.539 p^4 B \\ C_{144} &= 2.309 p^4 B & C_{344} &= 3.464 p^6 B \\ C_{222} &= 101.039 p^2 B + 9.007 p^4 C' & C_{333} &= 5.196 p^8 B \end{aligned} \right\} \quad (3b)$$

where p = c/a: axial ratio; C' = χ a / p⁵; B = ψ a³ / p³; χ = (1/8)[{nb₀(n-m)}/{aⁿ⁺⁴}] ψ = -χ / {6a²(m+n+6)}; m, n=integer quantity; b₀=Lennard- Jones parameter

2.2 Ultrasonic attenuation and allied Parameters

Phonon-phonon (Akhieser loss) interaction and thermo elastic relaxation mechanism are basic reasons for the ultrasonic attenuation in solid at room temperature. The following equation expressed attenuation coefficient's (A)_{Akh} due to phonon -

phonon interaction mechanism and thermo elastic relaxation mechanism respectively [8, 9].

$$(A/f^2)_{Akh} = 4\pi^2 (3E_0 \langle \gamma_i^j \rangle^2 - \langle \gamma_i^j \rangle^2 C_V T) \tau / 2\rho V^3 \quad (4)$$

$$(A/f^2)_{Th} = 4\pi^2 \langle \gamma_i^j \rangle^2 kT / 2\rho V_L^5 \quad (5)$$

where, f: frequency of the ultrasonic wave; V: ultrasonic velocity for longitudinal and shear wave; V_L: longitudinal ultrasonic velocity; E₀: thermal energy density; γ_i^j: Grüneisen number (i, j are the mode and direction of propagation).

The Grüneisen number for hexagonal structured crystal along <001> orientation or θ=0° is direct significance of second and third order elastic constants. D = 3(3E₀ <γ_i^j>² - <γ_i^j>² C_VT) / E₀ is identified as acoustic coupling constant, which is the measure of acoustic energy improved to thermal energy. When the ultrasonic wave propagates through crystalline material, the equilibrium of phonon distribution is concerned. The time for renew of equilibrium of the thermal phonon distribution is called thermal relaxation time (τ) and is given by following expression:

$$\tau = \tau_s = \tau_L / 2 = 3k / C_V V_D^2 \quad (6)$$

Here 'τ_L' and 'τ_s' are the thermal relaxation time for longitudinal and shear wave. 'k' and 'C_V' are the thermal conductivity and specific heat per unit volume of the compound respectively. The Debye average velocity (V_D) is well connected to longitudinal (V_L) and shear wave (V_{S1}, V_{S2}) velocities. The expressions for ultrasonic velocities are known in our prior papers [8, 9].

III. RESULTS AND DISCUSSION

3.1 Higher order elastic constants

In the current analysis we have calculate the elastic constants (six second order elastic constants and ten third order elastic constants) using the theory given by Eqn. (3) and Eqn. (4). The unit cell parameters 'a' (basal plane parameter) and 'p' (axial ratio) for

SrMnO₃ compound is 5.489Å, and 1.66 respectively [10]. The value of m and n for chosen materials are 6 and 7. The value of b₀ is 5.5x10⁻⁶² erg cm⁷ for SrMnO₃ compound. The calculated values of SOEC and TOEC have been calculated for this compound at room temperature are offered in Table 1.

Table1. Second and third order elastic constants (SOEC and TOEC) in the unit of 10¹⁰Nm⁻² of SrMnO₃ compound at room temperature.

	C ₁₁	C ₁	C ₁₃	C ₃₃	C ₄	C ₆₆				
	2				4					
Th	28.1	6.	6.194	30.71	7.	11.				
is	4	91			43	03				
wo										
rk										
[10	28.	9.	9.36	30.5		9.6				
]]	52	25				4				
	C ₁₁	C ₁	C ₁₁	C ₁₂	C ₁₃	C ₃	C ₁₄	C ₁	C ₂	C ₃
	1	12	3	3	3	44	4	55	22	33
	-	-	-16	-20	-	-	-24	-	-	-
	459	73			10	97		15	36	40
					3			7	3	2

SrMnO₃ compound had the highest elastic constant values, which are important for the material, as these are associated with the stiffness parameter. Second-order elastic constants are used to determine the ultrasonic attenuation and associated parameters. The highest elastic constant values found for superhard materials are indicative of their better mechanical properties over other hexagonal materials. Clearly, for a steady hexagonal structure the five independent second order elastic constants (C_{ij}, namely C₁₁, C₁₂, C₁₃, C₃₃, C₄₄) should satisfy the well-known Born-Huang's stability norms [11, 12] i.e. C₁₁ - |C₁₂| > 0, (C₁₁+C₁₂) C₃₃ - 2C₁₃² > 0, C₁₁ > 0 and C₄₄ > 0. It is understandable from Table-1. It is evident that the values of elastic constant are positive and satisfies the Born-Huang's mechanical stability constraints and therefore all these compounds are mechanically stable. The calculated values of C₁₂ and C₆₆ are few different than some other theoretical [10] results for SrMnO₃ compound. Actually R. Sondena et al. [10] were theoretically evaluated using DFT investigations, which is quite different from present approach. Although obtained

order of SOEC are of the same as given in Table. 1 [10]. Relative magnitude of C₁₁ and C₃₃ are well presented by our theoretical approach. Thus, there is good agreement between the presented and the reported values which is correlated with elastic constants. Thus, our theoretical approach is well justified for the calculation of second order elastic constants. We present the calculated values of TOECs in table 1. The negative values of TOECs indicate a negative strain in the solid. The negative TOECs appear in the previous paper on hexagonal structure material. Hence the theory applied for evaluation of higher order elastic constants is justified [13, 14]. Hence the applied theory for the valuation of higher order elastic constants, at room temperature, is acceptable.

3.2 Ultrasonic Velocity and allied parameters

In the present investigation, we have correlated the mechanical and isotropic behavior of the material with the ultrasonic velocity. We have calculated the longitudinal ultrasonic velocity (V_L), shear ultrasonic velocity (V_s), the Debye average velocity (V_D) and the thermal relaxation time (τ) for SrMnO₃ compound. The data for the temperature dependent density (ρ) SrMnO₃ compound presented in Table 3 and have been taken from literature [15]. Thermal conductivity (k) of SrMnO₃ compound presented in Table 3 has been taken form the literature [15]. The values of temperature dependent specific heat per unit volume (C_v) and the thermal energy density (E₀) have been calculated using the tables of physical constant and Debye temperatures and calculated values of temperature dependent acoustic coupling constant D_L and D_s are presented in Table.3.

Table 3. Density (ρ: in 10³ kg m⁻³), specific heat per unit volume (C_v: in 10⁵Jm⁻³K⁻¹), thermal energy density (E₀: in 10⁷Jm⁻³), thermal conductivity (k: in Wm⁻¹K⁻¹) and acoustic coupling constant (D_L, D_s) of SrMnO₃ compound.

Temp	ρ	E_0	C_V	k	D_L	D_s
50	5.345	1.27	0.96	4.367	48.32	1.758
100	5.340	1.25	3.52	5.633	49.66	1.758
150	5.3335	3.35	4.99	5.483	50.49	1.758
200	5.330	6.16	5.77	4.950	51.01	1.758
250	5.325	9.16	6.17	4.517	51.28	1.758
300	5.320	12.31	6.39	4.467	51.46	1.758

It is clear from Table 3 that for all temperature, the values of D_L are larger than those of D_s for all temperatures. It indicates that for the shear ultrasonic wave the conversion of ultrasonic energy into thermal energy is less than that for the longitudinal ultrasonic wave.

The orientation dependences of ultrasonic wave velocity (V_L , V_{S1} , V_{S2} and V_D) at different temperature are shown in Figs 1-4. The angles are measured from the unique axis of the crystal. From Fig. 1-2 the velocity V_L and V_{S1} of SrMnO₃ compound have minima and maxima at 45° with the unique axis of the crystal and Fig. 3, we find that V_{S2} increases with angle from the unique axis. The abnormal behavior of angle dependent velocity is due to the combined effect of second order elastic constants and density. The nature of the angle dependent velocity curves in the present work is similar to the nature of angle dependent velocity curve found for other hexagonal structured material [16, 17]. Thus the angle dependence of the velocities in SrMnO₃ compound is justified.

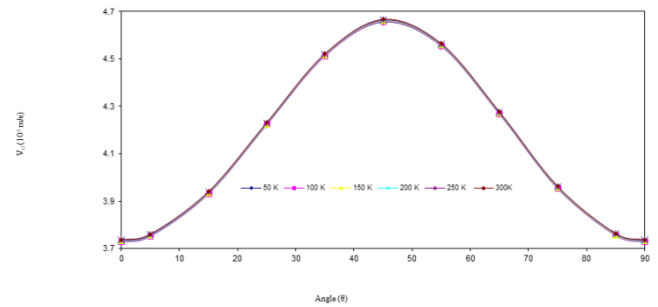


Figure 2. VS1 vs angle with unique axis of crystal

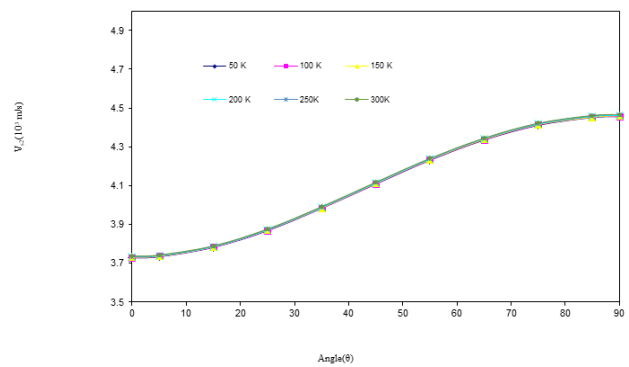


Figure 3. VS2 vs angle with unique axis of crystal

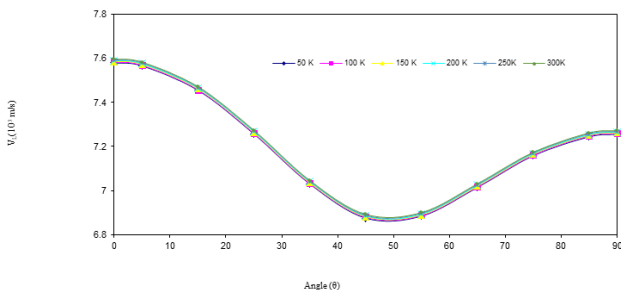


Figure 1. VL vs angle with unique axis of crystal

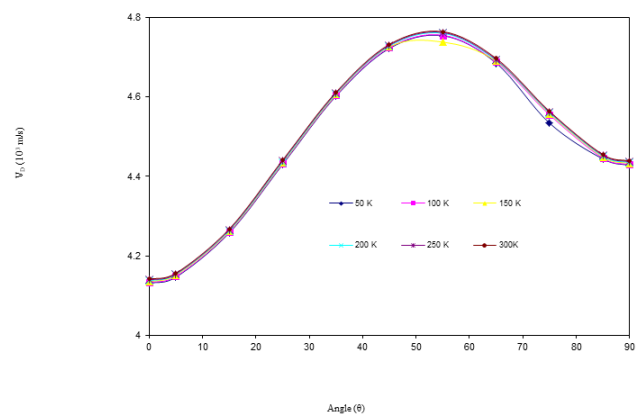


Figure 4. VD vs angle with unique axis of crystal

Fig. 4 shows the variation of the Debye average velocity (V_D) with the angle made with the unique

axis of the crystal. It is clear that V_D increases with the angle and reaches maximum at 55° for SrMnO_3 compound. As the calculation of V_D involves the velocities V_L , V_{S1} and V_{S2} [18,19], It is understandable that the variation of V_D is affected by the constituent ultrasonic velocities. The maximum V_D at 55° is due to a significant increase in longitudinal and pure shear (V_{S2}) wave velocities and a decrease in quasi-shear (V_{S1}) wave velocity. It may be concluded that the average sound wave velocity is maximum when a sound wave travels at 55° angles with the unique axis of these crystal.

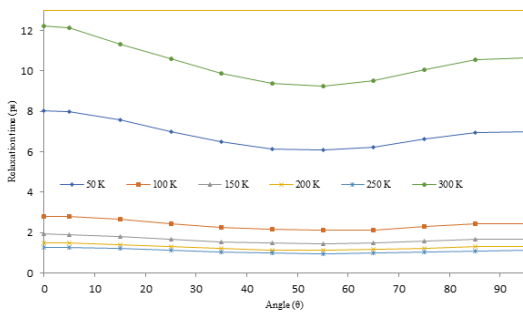


Figure 5. Relaxation time vs angle with unique axis of crystal

Fig. 5 shows a plot of the calculated thermal relaxation time ' τ ' with the angle. The angle dependent thermal relaxation time curves follow the reciprocal nature of V_D as $\tau \propto 3K/C_V V_D^2$. It is clear that thermal relaxation time for SrMnO_3 compound is mainly affected by the thermal conductivity. For hexagonal structured material ' τ ' is of the order at picoseconds [16, 20]. Hence the calculated ' τ ' justifies the hexagonal structure of SrMnO_3 compound. The minimum ' τ ' for wave propagation along $\theta = 55^\circ$ implies that the re-establishment time for the equilibrium distribution of thermal phonons will be minimum for propagation of wave along this direction.

3.3 Ultrasonic attenuation due to phonon-phonon interaction and thermal relaxation phenomena

While evaluating the ultrasonic attenuation, it is assumed that the wave is propagating along the

unique axis [$\langle 001 \rangle$ direction] of SrMnO_3 compound. The attenuation coefficient divided by frequency squared $(A/f^2)_{\text{Akh}}$ is calculated for longitudinal wave $(A/f^2)_L$ and for shear wave $(A/f^2)_S$ using Eqn. 4 under the condition $\omega\tau \ll 1$ at different temperature. Eqn. 5 has been used to calculate the thermo-elastic loss divided by frequency squared $(A/f^2)_{\text{Th}}$. Figs. 6-7 present the values of the temperature dependent $(A/f^2)_L$, $(A/f^2)_S$, $(A/f^2)_{\text{Th}}$ and total attenuation $(A/f^2)_{\text{total}}$ of SrMnO_3 compound.

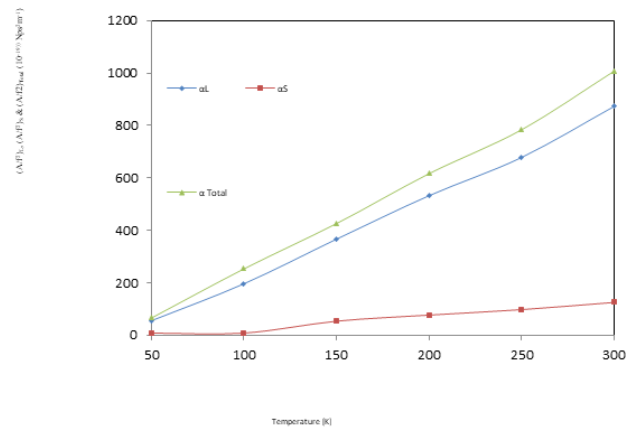


Fig. 6. Long. & Shear attenuation vs temp. of SrMnO_3

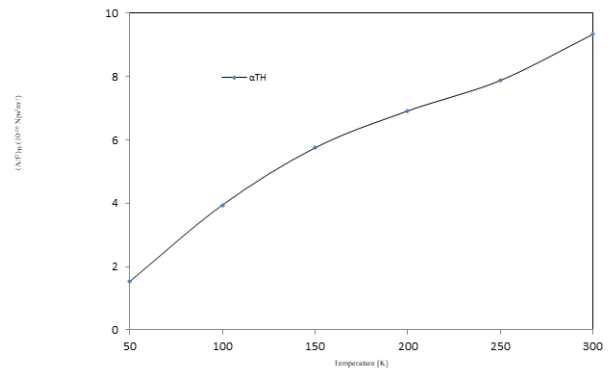


Fig. 7 Th. attenuation vs temp of SrMnO_3

In the present work, the ultrasonic wave is propagating along the unique axis of the crystal from figs. 6-7. It is evident that the Akhieser type of energy losses for longitudinal and shear waves have minimum at temperature at 50K and the thermo-electric loss increase with the temperature of material. $(A/f^2)_{\text{Akh}}$ is proportional to D , E_0 , τ and V^{-3} (Eqns. 4 and 6). Table 3 shows that ' E_0 ' and ' V ' are increasing with

temperature, while thermal relaxation time is decreasing with temperatures. Hence Akhieser losses in SrMnO₃ compound is overwhelmingly affected by thermal energy density E_0 and the thermal conductivity 'k' and relaxation time. Therefore, the ultrasonic attenuation is combined effect of thermal conductivity and relaxation time. Thus, ultrasonic attenuation is mainly governed by the phonon-phonon interaction mechanism. A comparison of the ultrasonic attenuation could not be made due to lack of experimental data in the literature.

From figs. 6-7, it is clear that the thermo-elastic loss is very small in comparison to Akhieser loss for SrMnO₃ compound, and also the ultrasonic attenuation for the longitudinal wave $(A/f^2)_L$ is greater than that for the shear wave $(A/f^2)_S$ of the total attenuation $(A/f^2)_{Total} = (A/f^2)_{Th} + (A/f^2)_L + (A/f^2)_S$. The ultrasonic attenuation due to phonon-phonon interaction for longitudinal wave is governing factor. The thermal relaxation time, thermal energy density and the thermal conductivity are the main factor that affects the total attenuation. Thus, it may be predicted that SrMnO₃ compound behave as its purest form at 50K and are more ductile demonstrated by the minimum attenuation while at other temperatures of SrMnO₃ compound are least ductile. Therefore, at low temperature (50K) there will be least impurity in SrMnO₃ compound.

IV. CONCLUSION

Based on the above discussion is worthwhile to state that:

- The theory formed on a simple interaction potential model for the calculation of higher-order elastic constants is supported for the hexagonal SrMnO₃ compound.
- For SrMnO₃ compound, the thermal relaxation time is found to be of the order of pico seconds, which defends their hexagonal structure. As ' τ ' has smallest value along $\theta = 55^\circ$ at all temperatures, the time for re-establishment of

equilibrium distribution of phonons, will be minimum, for the wave propagation in this direction.

- The acoustic coupling constant of SrMnO₃ compound for the longitudinal waves is found larger than other hexagonal materials. Hence the change of acoustic energy into thermal energy will be large for SrMnO₃ compound.
- The ultrasonic attenuation due to phonon-phonon interaction mechanism is intense over total attenuation as a governing factor thermal conductivity and thermal relaxation time.
- The mechanical properties of SrMnO₃ compound at low temperature 50K are better than at room temperature because at this temperature it has low ultrasonic attenuation.

The study may be fruitful for the processing and non-destructing characterization of SrMnO₃ compound. These findings will provide a base for further investigation of crucial thermophysical properties in the field of other perovskite polymorph compounds.

V. REFERENCES

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