

# Ultrasonic attenuation in divalent fcc crystal CaO due to phonon-phonon interaction in temperature range 100-1500K

Kailash<sup>1</sup> and Jitendra Kumar<sup>2</sup>

1. Department of Physics, BN PG College, Rath, Hamirpur, U.P., 210 431, Bharat  
2. Department of Physics, Govt. Girls P. G. College, Banda, U.P., 210 001, Bharat  
Email: [kailash.rath@yahoo.co.in](mailto:kailash.rath@yahoo.co.in), [jitendra\\_sharma50@yahoo.com](mailto:jitendra_sharma50@yahoo.com)

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## ABSTRACT

*Ultrasonic velocity and attenuation parameters are well connected to the micro- structural and mechanical properties of the materials. Ultrasonic absorption coefficients can be used for non-destructive techniques to characterize the materials. The most important causes of ultrasonic attenuation in solids are electron-phonon, phonon-phonon interaction and that due to thermo elastic relaxation. At room temperature, electron mean free path is not comparable to phonon mean free path and no coupling will take place. Thus the attenuation due to electron-phonon interaction will be absent. The two dominant processes that will give rise to appreciable ultrasonic attenuation at higher temperature are the phonon-phonon interaction and that due to thermo elastic relaxation. Both type of attenuation are observed in calcium oxide crystal. It has been established that at frequencies of ultrasonic range and at higher temperatures in solids, phonon-phonon interaction mechanism is dominating cause for attenuation. The temperature dependent part of ultrasonic attenuation has been explained in terms of model where the acoustic phonon interacts with a number of thermal phonons in the lattice. CaO is a key ingredient in the nixtamalization process used to create corn hominy and tortilla dough. Calcium oxide is used for many construction purposes, as in the manufacture of bricks, mortar, plaster, and stucco. Its high melting point makes it attractive as a refractory material, as in the lining of furnaces. The compound is also used in the manufacture of various types of glass. Common soda-lime glass, for example, contains about 12% calcium oxide, while high-melting alumino- silicate glass contains about 20% calcium oxide. One of the new forms of glass used to coat surgical implants contains an even higher ratio of calcium oxide about 24%. The CaO crystal possesses well developed structure of the NaCl-type and is divalent in nature. Oxides and silicates make up the bulk of the Earth's mantle and crust, and thus it is important to predict their behaviour. In this work ultrasonic attenuation due to phonon-phonon interaction  $(\alpha f^2)_{p-p}$  and thermo elastic relaxation  $(\alpha f^2)_{th}$  are studied in CaO crystal from 100K-1500K along different crystallographic directions. For the evaluation of the ultrasonic coefficients the second and third order coefficients are also calculated using Coulomb and Born Mayer potentials utilizing nearest neighbour distance and hardness parameter data. Several investigators have given different theories; here the one given by Mason has been used. Mason's theory relates the Gruneisen constants with SOECs and TOECs. Temperature dependence of ultrasonic absorption in CaO crystal along different crystallographic direction reveals some typical characteristic features.*

## INTRODUCTION

Ultrasonic velocity and attenuation parameters are well connected to the micro structural and mechanical properties of the materials. The ultrasonic attenuation study of the materials has gained new dimensions with the progress in the material science [1-8]. Ultrasonic absorption coefficients can be used for non-destructive techniques to characterize the materials. The most important causes of ultrasonic attenuation in solids are electron-phonon, phonon-phonon interaction and that due to thermo elastic relaxation. At room temperature, electron mean free path is not comparable to phonon mean free path and no coupling will take place. Thus the attenuation due to electron-phonon interaction will be absent. The two dominant processes that will give rise to appreciable ultrasonic attenuation at higher temperature are the phonon-phonon interaction also known as Alkeiser loss and that due to thermo elastic relaxation. Both these type of attenuation are observed in calcium oxide crystal. It has been established that at frequencies of ultrasonic range and at higher temperatures in solids, phonon-phonon interaction mechanism is dominating cause for attenuation. The temperature dependent part of ultrasonic attenuation has been explained in terms of model where the acoustic phonon interacts with a number of thermal phonons in the lattice.

In recent years, the ultrasonic attenuation techniques [9-12] are widely used as versatile tool in studying the inherent properties and internal structure of solids. In several types of solids, viz. metallic dielectric and semiconducting crystals, the attenuation occurs due to various causes e.g. lattice imperfection, ferromagnetic and ferroelectric, NMR and thermal relaxation and thermoelastic loss at different temperature regions. The temperature dependent part of ultrasonic attenuation has been explained in terms of model where the acoustic phonon interacts with a number of thermal phonons in the lattice. Accurately determining the attenuation along the propagation path leading to a region of interest could significantly improve diagnostic ultrasound tissue characterization [13] in medical science since tissue characterization requires exact compensation for the frequency-dependent attenuation along the propagation path.

The most important causes of ultrasonic attenuation in solids are electron-phonon, phonon-phonon interaction and that due to thermo elastic relaxation. At low temperature region, the interaction of acoustical phonons and conducting electrons is more dominating in metals [14, 15]. At room temperature, electron mean free path is not comparable to phonon mean path and no coupling will take place. Thus the attenuation due to electron-phonon interaction will be absent. The two dominant processes that will give rise to appreciable ultrasonic attenuation at higher temperature are the phonon-phonon interaction [16] also known as Alkeiser loss [17] and that due to thermo elastic relaxation. Both these type of attenuation are observed in calcium oxide crystal. It has been established that at frequencies of ultrasonic range and at higher temperatures in solids, phonon-phonon interaction mechanism is dominating cause for attenuation.

CaO is a key ingredient in the nixtamalization process used to create corn hominy and tortilla dough. Calcium oxide is used for many construction purposes, as in the manufacture of bricks, mortar, plaster, and stucco. Its high melting point makes it attractive as a refractory material, as in the lining of furnaces. The compound is also used in the manufacture of various types of glass. Common

soda-lime glass, for example, contains about 12% calcium oxide, while high-melting aluminosilicate glass contains about 20% calcium oxide. One of the new forms of glass used to coat surgical implants contains an even higher ratio of calcium oxide about 24%. Among the many other applications of calcium oxide are its uses in the production of pulp and paper, in the removal of hair from animal hides, in clarifying cane and beet sugar, in poultry feeds, and as a drilling fluid.

W. P. Mason theory which was initially proposed by Alkeiser has been established for the temperature dependence of ultrasonic attenuation and other related parameter for dielectrics, metals along some propagation directions of the wave. This theory is still to be established for the variety of semiconductors, intermetallics and mixed crystal systems for different crystallographic direction and at different temperatures. In the present work, the efforts have been made to establish this theory to evaluate ultrasonic absorption coefficients and other parameters at an elevated temperature along <100>, <110> and <111> directions. The behaviour of ultrasonic absorption and other parameters as a function of higher temperature have been discussed as the characteristic features of calcium oxide.

The calcium oxide crystal possesses well developed structure of the NaCl-type. Oxides and silicates make up the bulk of the Earth's mantle and crust, and thus it is important to predict their behaviour. In this work ultrasonic attenuation due to phonon-phonon interaction  $(\alpha/f^2)_{p-p}$  and thermo elastic relaxation  $(\alpha/f^2)_{th}$  are studied in calcium oxide at an elevated temperatures along <100>, <110> and <111> crystallographic directions. For the evaluation of the ultrasonic coefficients the second and third order coefficients (SOECs and TOECs) are also calculated using Coulomb and Born Mayer [18] potentials utilizing nearest neighbour distance and hardness parameter data. Several investigators have given different theories; here the one given by Mason has been used. Mason's theory relates the Gruneisen constants with SOECs and TOECs. A successful attempt is made to conclude that attenuation is one of the basic properties of substance.

## FORMULATION

The expressions for ultrasonic attenuation coefficient due to phonon-phonon interaction [19] over frequency square  $(\alpha/f^2)_{p-p}$  are as

$$(\alpha/f^2)_{Akh.long} = \frac{4\pi^2 E_0 \left(\frac{D_l}{3}\right) \tau_l}{2\rho V_l^3} \quad (1)$$

$$(\alpha/f^2)_{Akh.shear} = \frac{4\pi^2 E_0 \left(\frac{D_s}{3}\right) \tau_s}{2\rho V_s^3} \quad (2)$$

where the condition  $\omega \tau_{th} \ll 1$  has already been assumed. Here  $E_0$  is thermal energy density,  $\omega$  is the angular frequency ( $=2\pi f$ ),  $f$  is frequency of ultrasonic waves,  $\rho$  is the density and  $V_l$ ,  $V_s$  are the ultrasonic velocities for longitudinal and shear waves respectively.

The  $V_l$ ,  $V_s$  and  $V_D$  are given as

Along the <100> crystallographic direction

$$V_l = \sqrt{\frac{C_{11}}{\rho}} \quad (3)$$

$$V_{s1} = V_{s2} = \sqrt{\frac{C_{44}}{\rho}} \quad (4)$$

Along the <110> crystallographic direction

$$V_l = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}} \quad (5)$$

$$V_{s1} = \sqrt{\frac{C_{44}}{\rho}} \quad (6)$$

$$V_{s2} = \sqrt{\frac{C_{11} - C_{12}}{\rho}} \quad (7)$$

Along the <111> crystallographic direction

$$V_l = \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho}} \quad (8)$$

$$V_{s1} = V_{s2} = \sqrt{\frac{C_{11} - C_{12} + C_{44}}{3\rho}} \quad (9)$$

$$\bar{V}_D = \left[ \frac{1}{3} \left( \frac{1}{V_l^3} + \frac{2}{V_s^3} \right) \right]^{-\frac{1}{3}} \quad (10)$$

Two relaxation times are related as

$$\frac{1}{2} \tau_l = \tau_s = \tau_{th} = \frac{3K}{C_V \bar{V}_D^2} \quad (11)$$

Where  $\tau_{th}$  is the thermal relaxation time for the exchange of acoustic and thermal energy, K is the thermal conductivity,  $C_V$  is specific heat and  $\bar{V}_D$  is the Debye average velocity. The acoustic coupling constant D in eqns. (1) and (2) is obtained from the values of the SOEC and TOEC data using theoretical formulae for  $\langle \gamma_i^j \rangle$  and  $\langle \gamma_i^j \rangle^2$  and given as

$$D = 9 \langle \gamma_i^j \rangle^2 > - \left( \frac{3C_V T}{E_0} \right) \langle \gamma_i^j \rangle >^2 \quad (12)$$

Where  $\gamma_i^j$  are the Grüneisen parameters corresponding to particular direction of propagation and polarization. The thermoelastic attenuation is obtained as

$$(\alpha / f^2)_{th} = \frac{4\pi^2 \langle \gamma_i^j \rangle^2 >^2 KT}{2\rho V^5} \quad (13)$$

We have calculated the SOEC and TOEC for the evaluations of acoustic coupling constants D, thermal relaxation time  $\tau_{th}$  and ultrasonic absorption coefficients over frequency square of the ultrasonic wave with the method described by Mori and Hiki [20] using Born-Mayer [18] potential.

## EVALUATION

The temperature dependence of second and third order elastic constants for CaO has been evaluated at different temperatures (100 to 1500 K) following Brugger's approach [21] and the method given by Mori and are presented in Tables 1, 2 at room temperature along with melting point, nearest neighbour distance and hardness parameter. Using equations (3-12)  $V_l$ ,  $V_s$ ,  $\bar{V}_D$ ,  $\tau_{th}$  and non linearity constants (D) have been obtained and presented in Table 3 at room temperature. Grüneisen parameters have been evaluated using Mason's Grüneisen parameters tables [22] at different temperatures along different crystallographic directions with the help of SOECs and TOECs. The non-linearity constants are evaluated using the average square Grüneisen parameters  $\langle \gamma_i^j \rangle^2$  and square average Grüneisen parameters  $\langle \gamma_i^j \rangle$ . The values of  $\langle \gamma_i^j \rangle$  and ultrasonic attenuation  $(\alpha / f^2)_{p-p}$  and  $(\alpha / f^2)_{th}$  are presented in Table 4 at room temperature along different crystallographic directions. The temperature variations of all these properties are presented graphically given in Figures. 1 – 10.

## RESULTS AND DISCUSSIONS

In the present study all the SOECs are positive, while among TOECs three are positive and three are negative in nature. The magnitude of SOECs and TOECs and their temperature variation plays a crucial role in the investigation of ultrasonic attenuation in crystals. The temperature variation of thermal relaxation time is presented in Figure.1. It is clear from the figure that the value of thermal relaxation time  $\tau_{th}$  is very high at low temperature and decreases as temperature is increased along all crystallographic directions under consideration and of the order of  $10^{-12}$  sec, which is also expected but at any particular temperature its value is more along  $\langle 111 \rangle$  direction. The temperature variation of ultrasonic velocities is presented in Figures.2 - 4 for  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  crystallographic directions. It is clear from the figures that the ultrasonic velocity for longitudinal wave increases as temperature increases, while for shear wave it decreases also the Debye average velocity decreases with temperature along  $\langle 100 \rangle$  direction. Along  $\langle 110 \rangle$  direction the situation is different where longitudinal wave velocity and shear wave velocities decreases with temperature. While looking on  $\langle 111 \rangle$  direction one can conclude that longitudinal wave velocity decreases and shear wave velocity increases with temperature.

From Figure5. one can see that ratio of non-linearity constants  $D_l/D_s$  increases with temperature. The D is a measure of acoustic energy converted to thermal energy under the relaxation process, thus the increase in  $D_l/D_s$  with temperature shows that longitudinal loss increases with temperature and vice versa along  $\langle 100 \rangle$  direction. Figure.6 represents the variation of average Square and square average Gruneisen Numbers with temperature. It is clear from the figure that both of these decrease with temperature.

The thermal ultrasonic attenuation along different directions is presented in Figure7. It is clear from the figure that thermal attenuation increases with temperature along all these directions and of the order of  $10^{-18}$  Nps<sup>2</sup>/m which is expected for the type of crystal under inspection. Figures. 8 - 10 represents the ultrasonic attenuation due to phonon-phonon interaction along  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  crystallographic directions respectively. Along all these directions the ultrasonic attenuation increases with increase in

temperature, the situation is little different for shear wave along  $\langle 110 \rangle$  direction (pol.  $\langle 1 \bar{1} 0 \rangle$ ) for which the ultrasonic attenuation decreases with temperature. It is also observed that along  $\langle 100 \rangle$  direction the attenuation for longitudinal wave is more in comparison to that for shear wave and along rest of the two directions it is more for shear waves. From the above results one can reach to the conclusion that the thermal relaxation time, ultrasonic wave velocities and attenuation are the properties which depends on the crystallographic directions or one can say that these properties are orientation dependent which strongly supports the results given by other investigators [23] for the same type of crystals that all these properties are strongly dependent on direction of polarization. The results obtained in this study can be used for further investigations [24, 25] and industrial purposes.

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**Table 1.** The nearest neighbour distance ( $r_0$ ) and hardness parameter ( $q$ ) in  $10^{-10}$  m and SOECs in  $10^{10}$  N/m<sup>2</sup> for CaO crystal at roomtemperature.

Melting Point (K)	$r_0$	$q$	$C_{11}$	$C_{12}$	$C_{44}$
2843K	2.3925	0.345	20.6744	12.527	12.718

**Table 2.** The TOECs in  $10^{10}$  N/m<sup>2</sup> for CaO crystal at room temperature

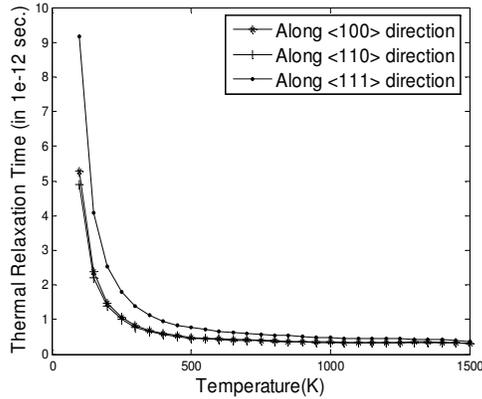
$C_{111}$	$C_{112}$	$C_{123}$	$C_{144}$	$C_{166}$	$C_{456}$
-252.887	-65.105	20.349	19.439	-51.266	4.713

**Table 3.** Longitudinal and shear wave velocities, Debye average velocity in  $10^3$  m/sec, thermal relaxation time in  $10^{-12}$  sec and non linearity constants for CaO crystal along different crystallographic directions at room temperature.

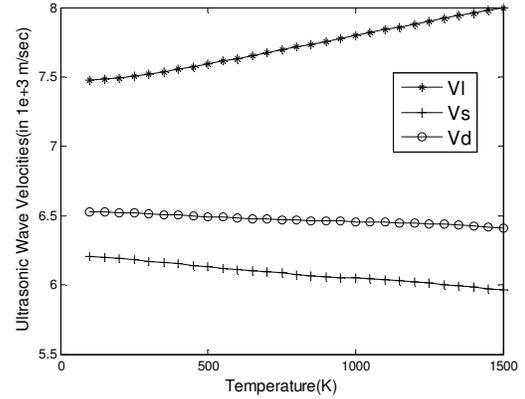
Direction of propagation	V	$\overline{V_D}$	$\tau_{th}$	D
<100>longitudinal	7.520	6.512	0.836	15.414
shear	6.171	-	-	2.886
<110>longitudinal	9.124	6.733	0.782	12.248
shear(pol.<001>)	6.171	-	-	5.777
(pol.<1 $\bar{1}$ 0>)	3.375	-	-	13.838
<111>longitudinal	9.599	5.070	1.379	14.115
shear(pol.< $\bar{1}$ 10>)	4.504	-	-	8.786
(pol.<11 $\bar{2}$ >)	4.504	-	-	13.529

**Table 4.** Grüneisen parameter, p-p attenuation for long. and shear waves in  $10^{-16}$  Nps<sup>2</sup>/m and thermal attenuation in  $10^{-18}$  Nps<sup>2</sup>/m for CaO crystal along different crystallographic directions at room temperature

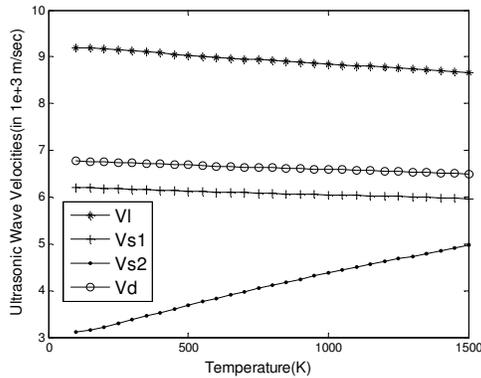
Direction of propagation	$\langle \gamma \rangle$	$(\alpha/f^2)_{p-p}$	$(\alpha/f^2)_{th}$
<100>longitudinal	-0.601	0.218	0.373
shear	-0.015	0.037	-
<110>longitudinal	-0.673	0.091	0.178
shear(pol.<001>)	-0.039	0.069	-
shear(pol.<1 $\bar{1}$ 0>)	-0.512	6.253	-
<111>longitudinal	-0.665	0.158	0.135
shear(pol.< $\bar{1}$ 10>)	-0.203	0.954	-
shear(pol.<11 $\bar{2}$ >)	-0.082	1.469	-



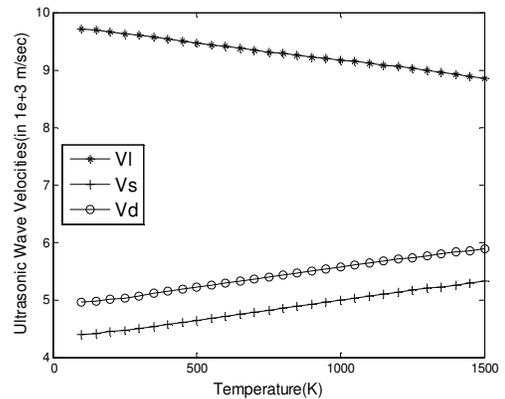
**Figure 1.** Thermal relaxation time Vs Temp



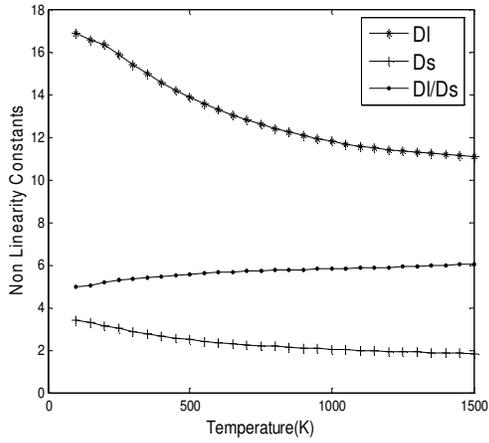
**Figure 2.** Ultrasonic velocities Vs Temp. along <100> direction



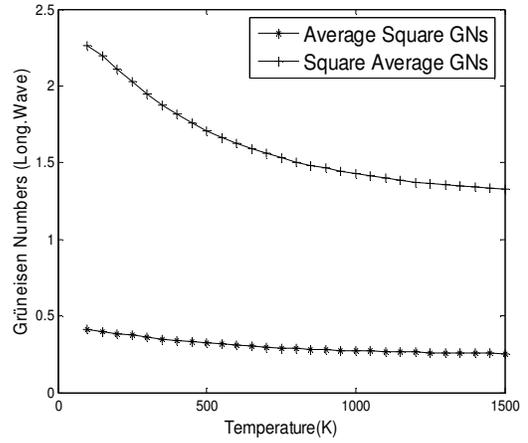
**Figure 3.** Ultrasonic velocities Vs Temp. along <110> direction



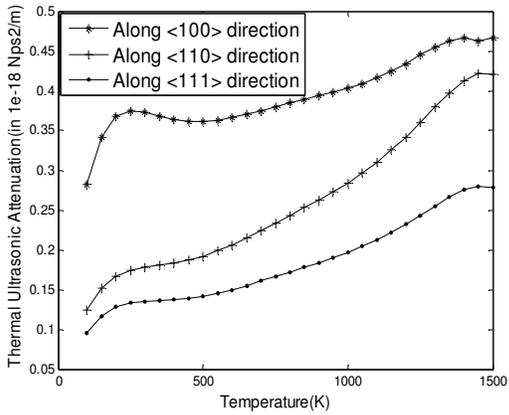
**Figure 4.** Ultrasonic velocities Vs Temp. along <111> direction



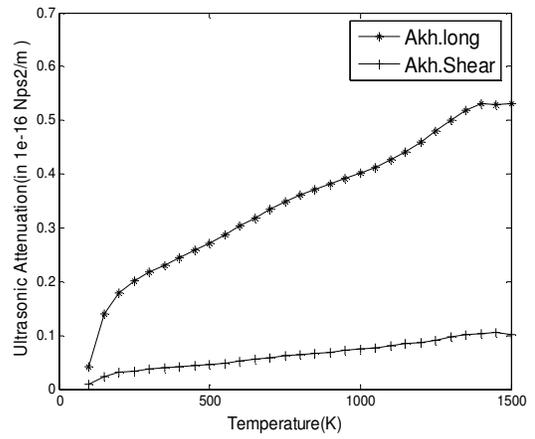
**Figure 5.** Nonlinearity constants Vs Temp.



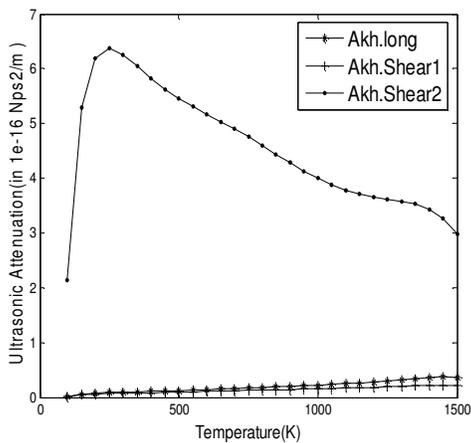
**Figure 6.** Gruneisen Numbers Vs Temp.



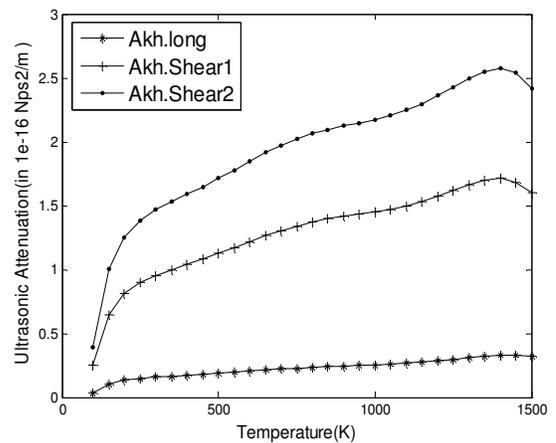
**Figure 7.** Thermal ultrasonic attenuation Vs Temp.



**Figure 8.** Ultrasonic attenuation Vs Temp. along <100> direction



**Figure 9.** Ultrasonic attenuation Vs Temp. Along <110> direction



**Figure 10.** Ultrasonic attenuation Vs Temp. along <111> direction