

Acoustical Analysis of Alkaline Earth Oxides

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An attempt has been made for obtaining higher order elastic constants of BaO, SrO, MnO, CaO and MgO having NaCl-structure starting from basic parameters viz. nearest neighbor distance and hardness parameter using Coulomb and Börn-Mayer potentials. These values are utilized to obtain Grüneisen parameters and non-linearity constants. Ultrasonic velocity, non-linearity constants ratio, ultrasonic attenuation due to phonon-phonon interaction $(\alpha/f^2)_{p-p}$ and thermo elastic loss $(\alpha/f^2)_{th}$ are then calculated at room temperature along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ crystallographic directions of propagation for longitudinal and shear waves.

1. Introduction

The oxides of alkaline earth metals are a group of chemical elements in the periodic table with very similar properties. The fellows of this family show patterns in their electronic configuration. These oxides are basic (alkaline) when combined with water. The magnesium, calcium, strontium and barium are the alkaline earth metals. This group lies in the s-block of the periodic table as all these materials have their outermost electron in an s-orbital. The alkaline earth metals are named after their oxides, the alkaline earths, whose old-fashioned names were magnesia, lime, strontia, and baryta. Earth is an old term used for nonmetallic substances that are insoluble in water and resistant to heating—properties shared by these oxides. Barium oxide (BaO) is a white hygroscopic non-flammable cubical compound and used in cathode ray tubes, crown glass and hot cathodes coating. Calcium oxide (CaO) generally known as quicklime or burnt lime, is a widely used compound. It is used in cement, biodiesel, kraft pulp and petroleum industry. There is archeological evidence that pre-pottery Neolithic humans used limestone-based plaster for flooring. Magnesium oxide (MgO), or magnesia, is a white hygroscopic solid mineral that occurs naturally as periclase. It is used as an insulator in industrial cables, as a raw materials for making Portland cement, as a basic material for crucibles, as a protective coating in plasma displays, as an optical material, and as a principal fireproofing ingredient in construction materials. It is physically and chemically stable at high temperatures and have several attractive

characteristics like fire resistance, moisture resistance, mold, and mildew resistance and strength. About 8% by weight of television picture tube glass is strontium oxide (SrO). Color TVs and other devices containing color cathode ray tubes use strontium in the faceplate. Manganese oxide (MnO) is the simplest ionic oxide, which is a component of fertilizer and food additives. Other uses include: a catalyst in the manufacture of allyl alcohol, ceramics, paints, colored glass, bleaching tallow and textile printing.

Currently alkaline earth oxides (MgO, CaO, SrO, BaO etc.) have been a subject of intense experimental and theoretical study [1-5] and determination of anharmonic properties at high temperatures is of common attention [1-4]; therefore we have evaluated the ultrasonic attenuation in oxides. Ultrasonic velocity and attenuation studies are widely used as a versatile tool in studying the inherent properties and internal structure of different material. In various types of solids, the attenuation of acoustic waves are attributed due to different causes, which are lattice imperfection, electron-phonon interaction, ferromagnetic and ferroelectric properties, phonon-viscosity, thermo elastic losses, and thermal relaxation. The phonon viscosity and non-elastic phenomena are the principal causes [6] of ultrasonic attenuation in all types of substances at higher temperature. The prominent mechanism for the absorption of sound wave in solids is the Akhiezer [7] mechanism in which the attenuation results because, in the presence of ultrasound, the thermal phonons are not in equilibrium. In the process of coming to equilibrium, entropy is produced and energy of the sound wave is lost. In

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the present work, Börn-Mayer [8] and electrostatic potentials have been used to obtain second and third order elastic constants taking nearest neighbor distance and hardness parameter of alkaline earth oxides. These values have been used to obtain Grüneisen numbers hence non-linearity constants along different directions for longitudinal and shear waves. Thermal relaxation time, non-linearity constants ratio, thermo elastic losses, and ultrasonic attenuation due to p-p interaction are then calculated for these compounds. $(\alpha/f^2)_{p-p}$ and $(\alpha/f^2)_{th}$ has been evaluated at room temperature for longitudinal waves along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions and for shear waves, along $\langle 100 \rangle$, $\langle 110 \rangle$ (polarized along $\langle 001 \rangle$ and $\langle \bar{1}10 \rangle$ direction) and $\langle 111 \rangle$ (polarized along $\langle \bar{1}10 \rangle$ and $\langle 11\bar{2} \rangle$ directions) crystallographic directions of propagation. The results are compared with available theoretical and experimental values. From microstructure characterization point of view, it is well identified that acoustic properties of materials are very essential. Since our interest is in acoustical studies at high temperatures, we have concentrated on this aspect of alkaline oxide systems. We have calculated the acoustical attenuation due to different foundations and the nature of the acoustic behavior in these compounds has analyzed.

2. Theory

The second and third order elastic constants play a crucial role in the investigation of ultrasonic attenuation. These constants may be used [3] for the purpose of investigating anharmonic properties. Assuming electrostatic potential $\{\pm (e^2/r)\}$ and Börn-Mayer type potential $Q_{uv}(r_0) = A \exp(-r_0/q)$; e , r_0 and q being electronic charge, nearest-neighbour distance and hardness parameter, and following Brügger's [9] definition of elastic constants at absolute zero, second and third order elastic constants are obtained. Leibfried et al. [10,11] have developed the theory of anharmonic properties of crystals, which has been used to obtain higher order elastic constants at different temperatures. As elastic constants evaluation is done, Grüneisen numbers (γ_i^j) are calculated using Grüneisen number tables [12]. These parameters directly give Mason's [13,14] non-linearity coupling constant (D) presented below as

$$D = 9 \langle \gamma_i^{j2} \rangle - (3C_v T / E_0) \langle \gamma_i^j \rangle^2 \quad (1)$$

Where, $\langle \gamma_i^j \rangle^2$ and $\langle \gamma_i^{j2} \rangle$ are average Grüneisen and square average Grüneisen numbers, C_v is

specific heat per unit volume, T is temperature and E_0 is the thermal energy density.

The thermo elastic losses $(\alpha/f^2)_{th}$ and attenuation [15] due to phonon-phonon interaction $(\alpha/f^2)_{p-p}$ are given by

$$(\alpha/f^2)_{th} = (2\pi)^2 \langle \gamma_i^j \rangle^2 KT / 2d v^5 \quad (2)$$

$$(\alpha/f^2)_{p-p} = (2\pi)^2 E_0 (D/3) \tau_{th} / d v^3 (1 + \omega^2 \tau_{th}^2) \quad (3)$$

In our case, $\omega \tau_{th} \ll 1$, therefore the relation reduces to

$$(\alpha/f^2)_{p-p} = (2\pi)^2 E_0 D \tau_{th} / 3dv^3 \quad (4)$$

The attenuation coefficients for longitudinal (l) and shear (s) waves are given by

$$(\alpha/f^2)_l = (2\pi)^2 E_0 D_l \tau_l / 6dv_l^3 \quad (5)$$

$$(\alpha/f^2)_s = (2\pi)^2 E_0 D_s \tau_s / 3dv_s^3 \quad (6)$$

Where, α is the ultrasonic attenuation coefficient, γ is the Grüneisen parameter, ω is the natural angular frequency ($= 2\pi f$) of lattice vibration, f is frequency of ultrasonic waves, d is crystal mass density, K is thermal conductivity, τ_{th} is thermal relaxation time, D_l and D_s are non-linearity coupling constants, τ_l and τ_s are relaxation times, v is sound wave velocity, and v_l and v_s are sound wave velocities for longitudinal (l) and shear (s) waves, respectively.

3. Evaluation

This paper contains the details of temperature dependent non-linear acoustical properties in oxides by means of force constant model investigation. Firstly, the second and third order elastic constants are considered. Then, we deal with temperature dependence on ultrasonic attenuation defining which we use the data on elastic constants. Second and third order elastic constants for oxides are calculated at elevated temperature using the theory described. Grüneisen parameters have been evaluated using Mason's Grüneisen tables [12]. With the help of Eqn. (1), non-linearity constants have been obtained. On taking specific heat and crystal energy density at different temperatures [16-20] as a function of θ_D/T , where θ_D is Debye temperature, thermo elastic losses and ultrasonic attenuation at different temperatures obtained and shown in Tables 1-4. The applicability of present model has been tested by several workers [1,3,4,6,21,22] and it looks to be reasonably

effective in clarifying the basic features of materials. In spite of its wide-ranging applicability it may be proven that mechanism used in present

model delivers much better analysis of the crystal properties.

Table 1: Nearest neighbor distance (r_0), hardness parameter (q), second and third order elastic constants (in 10^{11} dyne/cm²), thermal relaxation time (in 10^{-12} sec.), and ultrasonic velocities (in 10^5 m/s) for oxides

	Melting point (K)	r_0	q	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}	τ_{th}	v_{long}	v_{shear}	v_{ave}
BaO	2196	2.8764	0.345	15.00	5.54	5.74	-229.57	-22.84	8.22	9.20	-23.53	9.14	0.96	5.64	3.49	3.85
SrO	2804	2.5143	0.345	17.85	10.14	10.37	-254.52	-41.66	14.83	15.75	-42.35	15.66	1.11	6.16	4.69	5.03
MnO	2218	2.105	0.345	18.26	22.19	22.48	-238.42	-88.94	31.20	32.01	-89.61	31.88	4.18	5.82	6.46	6.22
CaO	2886	2.390	0.345	18.56	12.71	12.95	-257.90	-51.93	18.39	19.28	-52.62	19.18	0.21	7.45	6.22	6.54
MgO	3125	2.014	0.345	17.86	27.00	27.29	-217.41	-106.7	37.45	38.23	-107.4	38.08	2.00	6.89	8.71	7.90

Table 2: Ratio of non-linearity constants (D_l/D_s) for oxides at room temperature

Prop. Direction	D_l/D_s					
	[BaO]	[SrO]	[MnO]	[CaO]	[MgO]	(18)
<100>	9.81	6.42	1.68	4.76	1.13	(1.10)
<110>Pola. along<001>	1.99	2.92	5.43	4.02	1.47	(1.42)
<1 $\bar{1}0$ >	0.41	1.05	3.95	1.97	1.47	(1.37)
<111>Pola. along< $\bar{1}10$ >	3.49	2.60	2.54	2.56	1.46	(1.42)
<11 $\bar{2}$ >	3.57	3.36	2.35	3.32	0.64	(0.77)

Table 3: Grüneisen numbers at 300K (experimental values are given in bold)

Prop. Direction	$\langle \gamma_i^2 \rangle$					
	[BaO]	[SrO]	[MnO]	[CaO]	[MgO]	(18) (19)
<100>long.	3.99	4.54	9.38	6.05	3.94	(3.71) 3.27
shear	0.29	0.57	5.57	0.94	3.12	(0.52) 0.15
<110>long.	4.53	7.17	3.11	12.23	7.89	(1.88) 1.28
shear(pol.<001>)	1.43	1.96	5.64	2.34	5.32	(0.41) 0.23
(pol.<1 $\bar{1}0$ >)	6.95	5.46	7.75	4.78	5.32	(1.87) 1.58
<111>long.	2.37	2.13	0.11	2.21	0.78	(1.59) 0.90
shear(pol.< $\bar{1}10$ >)	3.55	2.84	5.15	2.57	3.33	(3.29) --
(pol.<11 $\bar{2}$ >)	3.46	2.17	5.56	1.98	7.53	(6.01) --

Table 4: Ultrasonic attenuation (in 10^{-18} dBSec²cm⁻¹) due to p-p interaction & due to thermo-elastic losses at room temperature

Prop. Direction	$(\alpha/F^2)_p$						$(\alpha/F^2)_{th}$				
	[BaO]	[SrO]	[MnO]	[CaO]	[MgO]	(18)	[BaO]	[SrO]	[MnO]	[CaO]	MgO]
<100>long.	0.36	0.99	0.14	0.15	1.27	(1.23)	0.012	0.027	0.002	0.006	0.03
shear	0.16	0.35	5.90	0.05	0.55	(0.26)					
<110>long.	0.37	1.56	0.44	0.32	2.81	(0.25)	0.016	0.043	0.11	0.011	0.04
shear(pol.<001>)	0.78	1.21	5.97	0.14	0.94	(0.05)					
(pol.<1 $\bar{1}0$ >)	3.79	3.36	8.20	0.27	0.94	(0.07)					
<111>long.	1.60	2.01	0.19	0.22	1.74	(1.60)	0.043	0.064	0.002	0.013	0.05
shear(pol.< $\bar{1}10$ >)	1.93	1.74	5.45	0.15	0.59	(0.25)					
(pol.<11 $\bar{2}$ >)	1.89	1.34	5.89	0.12	1.33	(0.50)					

4. Results and Discussions

We have efficaciously assessed [1,3,4,21-24] temperature dependency of the higher order elastic constants and allied parameters of face centered cubic compounds. Such types of studies are essential for considering the suitability of materials for several practical problems. An investigation of the acoustical properties provides useful information on the inter-atomic forces, inter-ionic potentials, equation of state, phonon spectra, and on anharmonic properties of crystalline solids. Today ultrasound is one of the several effective methods used in the field of Non Destructive Testing (NDT) and inspection. Non-destructive ultrasonic techniques are used to study physical properties of the materials through the process of evaluating and measuring the ultrasonic velocities and attenuation. These physical parameters are very important to characterize the material and well related to several physical quantities like thermal conductivity, specific heat, thermal energy density, elastic constants, etc. The elastic constants play primary role for understanding the anharmonic and non-linear properties of solids [1]. The knowledge of elastic constants is essential for many practical applications related to mechanical properties of solids such as load diffraction, thermo-elastic stress, internal strain (residual stress) and sound velocity, and fracture toughness. Elastic properties are also linked thermodynamically to thermal expansion, Debye temperature and Grunesien parameter.

It is clear that the value of $(\alpha/f^2)_{th}$ is negligible in comparison to $(\alpha/f^2)_{p-p}$ (Tables 1-4) in all substances, which divulges the fact that a major part of ultrasonic energy loss is used in achieving the equilibrium along different phonon branches and directions at various temperatures. The variation of attenuation at different temperatures is the same for both cases: phonon-phonon interaction and thermo-elastic phenomena. From these results, one may say that attenuation is very low for shear wave than longitudinal wave for $\langle 100 \rangle$ direction. It increases as molecular weight increases from MgO to BaO. It is seen that attenuation for longitudinal wave is more than shear wave. From the attenuation values along different directions, it is evident that the ultrasonic attenuation is different along different directions of propagation and varies with the orientation of the crystal. One can say that the attenuation is direction and polarization of propagation dependent property. Similar behavior has been observed by other investigators in solids [18-20]. Some additional properties observed in

these substances using the only method can be applied to all type of substances [3,4,18]. Due to some extensive physical significance, it will be advantageous to study these substances for various devices as it is used in industries, oil exploration and electronic equipments. It can be used in medical equipments to collect the knowledge for various deceases and is thus an important application of ultrasonics.

The study of ultrasonic attenuation in the materials has gained new dimensions with the progress in material science. Investigators have aimed their study for explaining the temperature-dependent part of the attenuation in terms of model where ultrasonic phonon interacts with thermal phonon in the lattice. All these studies indicate that a major portion of attenuation is caused by direct conversion of acoustic energy into heat via phonon-phonon interaction. The ultrasonic wave propagation is influenced by the microstructure of the material through which it propagates. Ultrasonic attenuation, which is the sum of absorption and scattering, is mainly depending upon the damping capacity and scattering from the grain boundary in the material. Loss due to scattering is dominant in polycrystalline solids. However, for complete characterization of the material, the attenuation requires the knowledge of a large number of thermo physical parameters.

We have stated the ultrasonic attenuation for alkaline earth oxides calculated at the higher temperatures and using Mason's approach. The attenuation is found to be very advantageous in material characterization; therefore it is anticipated that this study may be significant for various industrial purposes. We have displayed that by obtaining the ultrasonic absorption, a deep insight into the micro structural properties can be attained. More importantly, because of its relatively few assumptions, the present theory yields a trustworthy output. As a consequence, it represents an excellent starting point for a systematic many-body description of the process. These results, together with other well-known physical properties of these materials, may be expanded to further prospects for the application of these oxides. This treatment gave the chance to understand the temperature dependences of anharmonic properties, as well as to secure more exact values of parameters for characterizing the material. The results obtained in this research can be used for further study of these materials. Our entire theoretical approach can be applied for the evaluation of ultrasonic attenuation and related

parameters to study the micro-structural properties of face centered cubic structured materials.

The general interpretations made above in the case of oxides are true in the other crystals of the similar nature [23-25]. It can be concluded that the present approach is correct and we can claim that our results are satisfactory for further studies. This model has already been used successfully for the study of acoustical properties of different types of materials [3,4,18,23-25]. Due to the easiness of this method, it can be applied to more complicated solids, like minerals of geophysical importance and applications. The results on different types of solids at different temperatures and composition are in progress.

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