Study of elastic, mechanical, thermophysical and ultrasonic properties of divalent metal fluorides $XF_2$ ($X = \text{Ca, Sr, Cd and Ba}$)

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MS received 20 February 2021; revised 26 October 2021; accepted 30 November 2021

Abstract. This paper described the behaviours of four divalent metal fluorides ($\text{CaF}_2, \text{SrF}_2, \text{CdF}_2$ and $\text{BaF}_2$) in terms of their superior elastic, mechanical and thermophysical properties. Initially, higher-order elastic constants of the chosen divalent metal fluorides have been calculated using the Coulomb and Born–Mayer interaction potential in the temperature regime $100–300$ K. With the help of these constants, other elastic moduli, such as Young’s modulus ($Y$), bulk modulus ($B$), shear modulus ($G$), Poisson’s ratio ($\sigma$) and Pugh’s ratio ($B/G$) have been computed using Voigt–Reuss–Hill approximation. The Born stability criteria and Vicker’s hardness parameter ($H_v$) have been used for analysing the nature and strength of the materials. Later on, ultrasonic velocities including Debye average velocities were evaluated using calculated values of second-order elastic constants and density in the same physical conditions. Thermal properties such as the lattice thermal conductivity, thermal relaxation time, thermal energy density and acoustic coupling constant have also been computed at the same physical conditions and along $\langle 100 \rangle$. The temperature-dependent ultrasonic properties have been correlated with other thermophysical properties to extract important information about the microstructural quality and the nature of the materials. The obtained results have been analysed to explore the inherent properties of the chosen divalent metal fluorides, which are useful for numerous industrial applications.

Keywords. Divalent metal fluorides; elastic constants; mechanical property; thermophysical property; ultrasonic attenuation.

PACS Nos 43.35.Cg; 62.20.dc; 63.20.kr

1. Introduction

Divalent metal fluorides $XF_2$ ($X = \text{Ca, Sr, Cd and Ba}$) fascinate material scientists and researchers due to their intrinsic low phonon energies and high physical and chemical stability [1–4]. The divalent metal fluorides exhibit extensive optical, electrical, thermal, superconducting, semiconducting, thermo-optical and wide transmission band properties [3–6]. The potential applications of the divalent metal fluorides are raw materials for manufacturing optical elements for average and high power lasers, elementary particle and $\gamma$ -ray detectors, sensors, high-temperature batteries, chemical filters, etc. [7–10]. In recent years, several studies have been conducted on the optical, thermal and electronic properties of divalent metal fluorides. In particular, optical anisotropy parameters and Euler angles of crystallographic axis orientation of $\text{CaF}_2$, $\text{SrF}_2$ and $\text{BaF}_2$ cubic crystals were measured by Snetkov et al [3]. The structural phase stability of the alkaline-earth divalent metal fluorides had been studied by Kanchana et al [4]. Band structures of divalent metal fluorides were reported by Ching et al [5]. A detailed study considering the effect of pressure in the electronic and optical properties of $\text{BaF}_2$, by applying the equation of state has been done by Jiang et al [6]. Heise et al [7] investigated pressure dependency of the elastic constants of $\text{CaF}_2$ using phase comparison and Cook’s method. The thermodynamic and phonon transport properties of FCC structured divalent metal fluorides at high temperature
and pressure were investigated by Yan et al [8]. Aleksandrov et al [9] developed an elastic model of the layered structure and investigated the Brillouin scattering of surface acoustical wave in divalent metal fluorides.

Ultrasonic offers the possibility to characterise solid-state characteristics such as thermal relaxation time, thermal conductivity, specific heat and thermal energy density of the crystals [11–13]. These thermophysical properties are well related to ultrasonic absorption and velocity. The study of the interaction of sound waves with materials is a versatile tool for the determination of the elastic properties of the materials. The elastic constants of materials are associated with the thermophysical properties of the materials, such as specific heat, Debye temperature and Gr"uneisen parameters, which provide a better understanding of the solid-state behaviour of the materials [14–16]. The behaviour of crystal in external stress can also be understood by knowing elastic constants. The second and third-order elastic constants (SOECs and TOECs) of the materials can provide valuable information about the nature of atomic bonding, mechanical strength, nonlinearity and anharmonicity of the materials [16,17].

Given the above investigations, to the best of the authors’ knowledge, elastic, mechanical, thermophysical properties of divalent metal fluorides have not been reported comprehensively. This lack of information regarding these properties of divalent metal fluorides motivated us to conduct the present study. Here, we have accomplished theoretical analysis of temperature-dependent linear/nonlinear elastic constants and the concerned mechanical and thermoelastic properties by using a simple interaction potential model.

2. Theoretical approach

The whole theory has been divided into three phases. In the primary phase, the formulation used for calculating SOECs and TOECs has been discussed. In the second phase, the approach towards the evaluation of stability, mechanical parameters and nature of the materials has been discussed. The thermophysical properties and their correlation with ultrasonic attenuation have been elucidated in the third phase.

2.1 SOECs and TOECs

The SOECs and TOECs for NaCl-type crystals type X\[F\] (X = Ca, Sr, Cd and Ba) have been calculated using the models established by Brugger’s definition (at absolute zero) [18,19] and Mori and Hiki approach (at preferred temperature) [20]. The interaction potential $\phi_{\mu\nu}(r)$, which is the sum of the attractive Coulomb potential $\phi_{\mu\nu}^C(r)$ and the short-range repulsive Born–Mayer potential, have been used for calculating SOECs and TOECs [21]:

$$\phi_{\mu\nu}(r) = \phi_{\mu\nu}^C(r) + \phi_{\mu\nu}^{BM}(r)$$  \hspace{1cm} (1)

$$\phi_{\mu\nu}(r) = \pm \frac{e^2}{r} + A^0 \exp \left(-\frac{r}{b}\right),$$  \hspace{1cm} (2)

where $e, r, A^0$ and $b$ are the electrostatic charge, nearest-neighbour distance, strength parameter and hardness parameter, respectively. The elastic strain energy density of a crystal is the sum of the internal energy (at 0 K) and the vibrational free energy density. So we can write the elastic constants $C_{pqr...}$ as

$$C_{pqr...} = C_{pqr...}^s + C_{pqr...}^v$$  \hspace{1cm} (3)

where the superscripts $s$ and $v$ represent the static (at 0 K) and vibrational (at the preferred temperature) contributions of the elastic constants, respectively. The formulations used in the static parts of the SOECs and TOECs are as follows:

$$C_{111}^s = \frac{3e^2}{2r_0^4} \ell(2) + \frac{1}{b} \left( \frac{1}{r_0} + \frac{1}{b} \right) \phi(r_0)$$

$$+ \frac{1}{b} \left( \frac{\sqrt{2}}{r_0} + \frac{2}{b} \right) \phi(\sqrt{2}r_0)$$  \hspace{1cm} (4)

$$C_{12}^s = C_{44}^s = \frac{3e^2}{2r_0^4} \ell^{(1,1)} + \frac{1}{2b} \left( \frac{\sqrt{2}}{r_0} + \frac{2}{b} \right) \phi(\sqrt{2}r_0)$$  \hspace{1cm} (5)

$$C_{112}^s = C_{166}^s = -\frac{15e^2}{2r_0^4} \ell^{(2,1)}$$

$$- \frac{1}{4b} \left( \frac{3\sqrt{2}}{r_0^2} + \frac{6}{b} + \frac{2\sqrt{2}}{b^2} \right) \phi(\sqrt{2}r_0)$$

$$C_{123}^s = C_{44}^s = C_{456}^s = -\frac{15e^2}{2r_0^4} \ell^{(1,1,1)}$$

where $r_0$ is the short-range distance, $\phi(r_0)$ and $\phi(\sqrt{2}r_0)$ are the inter-ionic Born–Mayer potentials given in the second term of eq. (1) and $A^0$ is the strength parameter [21,22] given by

$$A^0 = -3b\ell^{(1)} \frac{e^2}{r_0^2}$$

$$\times \left[ 6 \exp(-d_0) + 12\sqrt{2} \exp(-d_0\sqrt{2}) \right]^{-1},$$  \hspace{1cm} (6)

where $d_0 = r_0/b$. 
The numerical values of the lattice sum are
\[ \ell_1 = -0.58252, \ell_2 = -1.04622, \ell_5 = 0.23185, \]
\[ \ell_3 = -1.36852, \ell_7 = 0.16115, \]
\[ \ell_7^{(1,1)} = -0.09045. \]

The vibrational terms of the SOECs and TOECs are given as
\[
\begin{align*}
C_{11}^v &= g^{(1,1)} G_1^2 + g^{(2)} G_2 \quad (11) \\
C_{12}^v &= g^{(1,1)} G_1^2 + g^{(2)} G_{1,1} \quad (12) \\
C_{14}^v &= g^{(2)} G_{1,1} \\
C_{12}^v &= g^{(1,1,1)} G_1^{3} + g^{(2)} G_{1,1} + g^{(3)} G_{2,1} \\
C_{123}^v &= g^{(1,1,1)} G_1^{3} + 3g^{(2,1)} G_1 G_{1,1} \\
C_{144}^v &= g^{(2,1)} G_1 G_{1,1} + g^{(3)} G_{1,1,1} \\
C_{166}^v &= g^{(2,1)} G_1 G_{1,1} + g^{(3)} G_{2,1} \\
C_{456}^v &= g^{(3)} G_{1,1,1} \\
\end{align*}
\]
where the expressions of \(g^{(n)}\) and \(G_n\) are
\[
\begin{align*}
g^{(2)} &= g^{(3)} = \frac{\hbar \omega_0}{8r_0^3} \coth x; \\
g^{(1,1)} &= g^{(2,1)} = \frac{-\hbar \omega_0}{96r_0^3} \left( \frac{\hbar \omega_0}{2k_b T \sinh^2 x} + \coth x \right), \\
g^{(1,1,1)} &= \frac{\hbar \omega_0}{384r_0^3} \left( \frac{\hbar \omega_0}{6k_b T \sinh^2 x} \coth x + \frac{\hbar \omega_0}{2k_b T \sinh x} + \coth x \right),
\end{align*}
\]
where \(x = \hbar \omega_0/2k_b T\), \(k_B\) is the Boltzmann’s constant, \(T\) is the temperature in Kelvin, \(\hbar\) is the reduced Planck’s constant \((\hbar = h/2\pi)\) and \(\omega_0\) is the angular frequency, which is expressed as follows:
\[
\omega_0^2 = \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \frac{1}{br_0} \left\{ \frac{r_0}{b} - 2 \right\} \phi(r_0) + 2 \left\{ \frac{r_0}{b} - \sqrt{2} \right\} \phi(\sqrt{2}r_0),
\]
where \(M_1\) and \(M_2\) are the ionic masses.

\[
\begin{align*}
G_1 &= 2 \left( 2 + 2d_0 - d_0^2 \right) \phi(r_0) + 2 \left( \sqrt{2} + 2d_0 - \sqrt{2d_0^2} \right) V(\sqrt{2}r_0) \times H, \\
G_2 &= 2 \left( -6 - 6d_0 - d_0^2 + d_0^3 \right) \phi(r_0) + \left( -3\sqrt{2} + 6d_0 - \sqrt{2d_0^3} + 2d_0^3 \right) \phi(\sqrt{2}r_0) \times H, \\
G_3 &= 2 \left\{ (30 + 30d_0 + 9d_0^2 - d_0^3 - d_0^4) \phi(r_0) + \left( (15/2) \sqrt{2} + 15d_0 (9/2) \sqrt{2d_0^3} - d_0^3 - \sqrt{2d_0^3} \right) \phi(\sqrt{2}r_0) \right\} H,
\end{align*}
\]
where
\[
\begin{align*}
G_{1,1} &= \left\{ -3\sqrt{2} - 6d_0 - \sqrt{2d_0^2} + 2d_0^3 \right\} \phi(\sqrt{2}r_0) H, \\
G_{2,1} &= \left\{ (15/2) \sqrt{2} + 15d_0 \right\} \phi(\sqrt{2}r_0) H, \\
G_{1,1,1} &= 0,
\end{align*}
\]
where
\[
\begin{align*}
H &= \left\{ (d_0 - 2) \phi(r_0) + 2(d_0 - \sqrt{2}) \phi(\sqrt{2}r_0) \right\}^{-1}.
\end{align*}
\]

In a cubic crystal, the total free energy must be minimum at equilibrium and the required condition is given by
\[
\begin{align*}
-\frac{e^2}{r_0} \ell_3 &= \frac{2r_0}{b} \phi(r_0) - 4 \frac{\sqrt{2}r_0}{b} \phi(\sqrt{2}r_0) \times \frac{\hbar \omega_0}{4} G_1 \coth x = 0.
\end{align*}
\]

The value of \(b\) that fulfils the criterion given above and also minimises \(\sum (C_{pq}^{\text{cal}} - C_{pq}^{\text{exp}})^2\) is treated as the most likely set parameter. \(C_{pq}^{\text{exp}}\) and \(C_{pq}^{\text{cal}}\) are the SOECs determined experimentally and based on calculations, respectively. It is assumed that \(b\) does not depend on the temperature.

### 2.2 Mechanical properties

The stability, microhardness, strength and nature of the divalent metal fluorides were analysed by evaluating mechanical parameters such as Young’s modulus, shear modulus, bulk modulus, Poisson’s ratio, Pugh’s ratio and Vicker’s hardness. We used the calculated values of SOECs and TOECs for the evaluation of these parameters under the Voigt–Reuss–Hill approximation (VRH). The expressions for these mechanical parameters under the VRH approximation are given as \cite{21}

\[
\begin{align*}
B_V &= B_R = \frac{C_{11} + 2C_{12}}{3}; \quad B = \frac{B_V + B_R}{2} \\
p &= \frac{B}{G}; \quad P_C = C_{12} - C_{44} \\
G_V &= \frac{C_{11} - C_{12} + 3C_{44}}{5} \\
G_R &= \frac{5(C_{11} - C_{12})C_{44}}{4[C_{44} + 3(C_{11} - C_{12})]} = \frac{G_V + G_R}{2}; \\
H_v &= 2 \left( \frac{G}{p^2} \right)^{0.585} = 3; \quad Y = \frac{9GB}{G + 3B} \\
\sigma &= \frac{3B - 2G}{6B + 2G},
\end{align*}
\]
2.3 Thermophysical and ultrasonic properties

The approach proposed by Mason and Bateman [22–24] has been applied to compute the ultrasonic attenuation over the frequency square \((\alpha/f^2)\) in the divalent metal fluorides. These are the most widely accepted methods for studying the anharmonicity of the lattice because they incorporate the acoustic coupling constant \((D)\) directly in the computation of the ultrasonic attenuation. At higher temperatures \((T > 100\,\text{K})\), the dominant causes of ultrasonic attenuation are the Akhieser loss (phonon–phonon interaction/phonon viscosity mechanism) and thermoelastic loss. The ultrasonic attenuation coefficient over frequency square \((\alpha/f^2)_{\text{Akh}}\) due to Akhieser loss is given by the following equation:

\[
\left( \frac{\alpha}{f^2} \right)_{\text{Akh}} = \frac{2\pi^2 \tau_0 D_S E_0}{3\rho V^3_S} \left\{ \begin{array}{l} \left( \frac{\alpha}{f^2} \right)_{S} = \frac{2\pi^2 \tau_0 D_S E_0}{3\rho V^3_S} \\ \left( \frac{\alpha}{f^2} \right)_{L} = \frac{2\pi^2 \tau_0 D_L E_0}{3\rho V^3_L} \end{array} \right. \tag{14}
\]

where \((\alpha/f^2)_{L}\) and \((\alpha/f^2)_{S}\) are the longitudinal and shear components of the Akhieser loss, \(E_0\), \(\rho\) and \(\tau_0\) are the thermal energy density, density and thermal relaxation time, respectively, \(V_L\) and \(V_S\) are the longitudinal and shear components of the ultrasonic velocity, \(D_L\) and \(D_S\) are the longitudinal and shear components of \(D\) calculated using the Grüneisen number \(\gamma\), and \(i\) and \(j\) are the mode and the direction of propagation.

\[
D = 9\langle \gamma_{ij}^3 \rangle^2 - 3\langle \gamma_{ij}^2 \rangle^2 \frac{C_V T}{E_0}
= \frac{3\alpha C}{E_0}, \tag{15}
\]

where \(C_V\) denotes the specific heat per unit volume. The values of \(E_0\) and \(C_V\) were taken from the Debye temperature \((\theta_D/T)\) table in the AIP handbook [25]. The expression for the ultrasonic attenuation due to the thermoelastic mechanism [26,27] is

\[
(\alpha/f^2)_{\text{Th}} = 4\pi^2 \langle \gamma_{ij}^2 \rangle^2 \kappa T / 2\rho V^5_L. \tag{16}
\]

Here, \(\kappa\) is the lattice thermal conductivity. \(V_D\) provides information about the crystallographic texture and various lattice thermal phenomena. It has been calculated with formulations given elsewhere [27]. The lattice thermal conductivity was computed using the method described by Slack [28] and Berman [29]. The total ultrasonic attenuation over frequency square at a temperature greater than 100 K is the sum of attenuation due to thermoelastic loss \((\alpha/f^2)_{\text{Th}}\) and Akhieser loss \((\alpha/f^2)_{\text{Akh}}\), and given as follows:

\[
(\alpha/f^2)_{\text{Total}} = (\alpha/f^2)_{\text{Th}} + (\alpha/f^2)_{\text{Akh}}. \tag{17}
\]

3. Results and discussion

3.1 SOECs and TOECs

The second and third-order elastic constants for divalent metal fluorides XF\(_2\) \((X = \text{Ca, Sr, Cd, Ba})\) have been calculated following the methodology described in §2.1. The values of lattice parameters for CaF\(_2\), SrF\(_2\), CdF\(_2\) and BaF\(_2\) are 2.73 Å, 2.89 Å, 2.69 Å and 3.10 Å, respectively, and have been taken from [30]. The value of the hardness/nonlinearity parameter \((b)\) has been determined under minimum energy conditions and is found equal to 0.303 Å for all divalent metal fluorides. The calculated values of higher-order elastic constants for XF\(_2\) in the temperature range 100–300 K are presented in table 1.

It is obvious from table 1 that the calculated values of \(C_{11}, C_{112}\) and \(C_{144}\) enhance whereas \(C_{12}, C_{111}, C_{123}\) and \(C_{166}\) decay with the temperature. The shear constant \(C_{44}\) remains almost constant while \(C_{456}\) remains unchanged with the temperature for all XF\(_2\). Among the chosen divalent metal fluorides, the value of \(C_{11}\) is maximum for CdF\(_2\), indicating that its mechanical behaviour is superior to the other materials of the same group. The change in stiffness constant with temperature is due to the alteration in interatomic distances or lattice parameters of the material with the temperature. The temperature-dependent elastic constants are essential for understanding and predicting the effects of temperature on the stiffness and mechanical strength of materials, as well as to diagnose the behaviour of interatomic forces within the adjacent atomic plane to the crystals. As the SOECs are found to hold Born’s stability criteria (eq. (18)) for these crystals [31], the chosen materials shall be mechanically stable.

\[
\frac{C_{11} + 2C_{12}}{3} > 0; \quad \frac{C_{11} - C_{12}}{3} > 0; \quad C_{44} > 0. \tag{18}
\]

The interactions of acoustical and thermal phonons related to anharmonic properties have been analysed using TOECs. It is obvious from table 1 that the value of \(C_{166}\) has been large among the other TOECs and is maximum for CdF\(_2\) in comparison to other divalent metal fluorides at a temperature range of 100–300 K. Among the other TOECs, \(C_{123}\) showed the maximum variation with temperature whereas \(C_{456}\) remain unchanged due to the vanishing of the vibrational part of \(C_{456}\). It is also obvious from table 1 that the calculated values of \(C_{12}\) and \(C_{44}\) are nearly equal at 100 K. Similarly, the values of \(C_{112}\) and \(C_{166}, C_{456}\) and \(C_{144}\) are nearly equal at 100 K. All these values of higher-order elastic constants validate the Cauchy relations [32] at 100 K. As temperature increases, the Cauchy
The mechanical constants such as bulk modulus \((B)\), shear modulus \((G)\), Young’s modulus \((Y)\), Poisson’s ratio \((\sigma)\), Pugh’s ratio \((p)\), Vicker’s hardness \((H_v)\) and Cauchy’s pressure \((PC)\) have been evaluated following the methodology described in §2.2. The calculated values of SOECs have been used for the evaluation of the temperature-dependent mechanical constants and are presented in table 2.

It is obvious from table 2 that the evaluated values of the bulk modulus are almost constant within the chosen temperature range. The almost constant and highest value of bulk modulus for CdF\(_2\) confirms its good mechanical strength and stability than the other investigated divalent metal fluorides. Due to greater mechanical capacity, CdF\(_2\) can resist deformation in terms of the volume strain (bond length) under an applied pressure. The results also indicate that CdF\(_2\) is stiffest among CaF\(_2\), SrF\(_2\) and BaF\(_2\). The shear modulus is also a vital mechanical constant for examining the changes in shape (angle-bond) under transverse internal forces (plastic deformation). The evaluated values of shear modulus are the highest for CdF\(_2\) and positively dependent on temperature (between 100 and 300 K). Young’s modulus is a valid index for analysing the mechanical properties and is found to exhibit similar behaviour as the shear modulus with temperature for all the divalent metal fluorides.

Pugh’s ratio \((p)\) and Poisson’s ratio \((\sigma)\) define the brittleness and ductility of a solid. A solid is usually brittle with \(\sigma \leq 0.26\) and \(p \leq 1.75\); otherwise it is ductile [33]. In our evaluation, the lower values of Poisson’s and Pugh’s ratio with respect to their critical values indicate that all the chosen divalent metal fluorides are brittle in the temperature regime 100–300 K. The Poisson’s ratio also represents the degree of directionality of covalent bonding and helps to determine the hardness of materials. For a covalent compound, the value of \(\sigma\) will be just equal to 0.1, whereas it will be between 0.28 and 0.42 for metallic compounds [12,34]. It is also obvious from table 2 that the evaluated values of \(\sigma\) lie between 0.23 and 0.25 and these values are negatively dependent on the temperature. Thus, the degree of directional covalent bonding of all the chosen divalent metal fluorides increases with temperature. These findings also indicate the non-central nature of the interatomic forces. The hardness is a vital parameter for a crystal and it describes the resistance against the localised deformation under applied abrasion. In this evaluation, we have used Vicker’s hardness constant to assess the hardness of the chosen divalent metal fluorides. The evaluated value of hardness constant \((H_v)\) of CdF\(_2\) is higher than other divalent metal fluorides of the same group. Thus, CdF\(_2\) is a comparatively harder material than other divalent metal fluorides in the temperature

### Table 1. The SOECs (in GPa) and TOECs (in GPa) of divalent metal fluorides XF\(_2\) (X = Ca, Sr, Cd and Ba) in the temperature range 100–300 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>(T) (K)</th>
<th>(C_{11})</th>
<th>(C_{12})</th>
<th>(C_{44})</th>
<th>(C_{111})</th>
<th>(C_{112})</th>
<th>(C_{123})</th>
<th>(C_{144})</th>
<th>(C_{166})</th>
<th>(C_{456})</th>
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<tbody>
<tr>
<td>CaF(_2)</td>
<td>100</td>
<td>151.2</td>
<td>71.3</td>
<td>73.4</td>
<td>−220.0</td>
<td>−292.6</td>
<td>104.9</td>
<td>113.0</td>
<td>−299.5</td>
<td>112.3</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>152.6</td>
<td>70.4</td>
<td>73.3</td>
<td>−220.1</td>
<td>−290.5</td>
<td>101.2</td>
<td>113.2</td>
<td>−299.7</td>
<td>112.3</td>
</tr>
<tr>
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<td>200</td>
<td>154.0</td>
<td>69.7</td>
<td>73.2</td>
<td>−220.4</td>
<td>−288.1</td>
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<td>113.5</td>
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<td></td>
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<td>155.3</td>
<td>68.6</td>
<td>73.1</td>
<td>−220.9</td>
<td>−285.6</td>
<td>93.7</td>
<td>113.8</td>
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<td>157.1</td>
<td>67.8</td>
<td>73.0</td>
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<td>90.4</td>
<td>114.2</td>
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<td>56.5</td>
<td>57.6</td>
<td>−169.4</td>
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<td>55.4</td>
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<td>57.0</td>
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<td>88.4</td>
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<td>CdF(_2)</td>
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<td>−293.8</td>
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<td>70.4</td>
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regime 100–300 K. It is also obvious from table 2 that as the temperature increases, the values of $H_v$ increase whereas the values of the Poisson’s ratio decrease. Thus, the evaluated values of Vicker’s hardness constant exhibited inverse behaviour with respect to Poisson’s ratio. At 300 K, the value of $H_v$ is the highest for CdF$_2$ (10.50 GPa) and the lowest for BaF$_2$ (5.94 GPa). Negative values of Cauchy’s pressure confirm the brittle nature of all the chosen divalent metal fluorides. Therefore, these metal fluorides will be mechanically stable and brittle owing to the good mechanical strength, least alteration in bulk modulus and enhancement in Young’s/shear modulus.

### 3.3 Thermophysical and ultrasonic properties

The densities ($\rho$), longitudinal and shear components of ultrasonic velocities ($V_L$ and $V_S$), Grüneisen parameters and acoustic coupling constants ($D_L$ and $D_S$) have been also evaluated for XF$_2$. These ultrasonic and thermophysical parameters in the temperature range 100–300 K are presented in table 3.

It is obvious from table 3 that the densities of all the chosen divalent metal fluorides decreases when temperature increases. As the temperature increases, the velocities of longitudinal as well as shear waves also increase for all the chosen divalent metal fluorides. The increase in ultrasonic velocity with temperature is prominently influenced by elastic constants. These longitudinal and shear ultrasonic velocities have been used for evaluating Debye average velocities ($V_D$). Therefore, $V_D$ shows the combined effect of these velocities. The Debye average velocities are shown in figure 1.

It is obvious from figure 1 that the Debye average velocity varies in an almost linear manner with the temperature in all the chosen divalent metal fluorides. To the best of the authors’ knowledge, no previous theoretical, as well as experimental data, are available for comparing these parameters for the chosen divalent metal fluorides. The anharmonic properties of the crystalline material can be understood by knowing the Grüneisen parameter. It is the measurement of change in the vibrational frequency of atoms of crystalline materials with a change in its volume. This parameter is directly proportional to SOECs and TOECs while inversely proportional to the specific heat and density of the material. We have computed the Grüneisen parameters following the procedure used in our previous work [35]. It is obvious from table 3 that the values of Grüneisen’s parameter decay gradually with temperature. The nominal variation in Grüneisen’s parameter reveals that the anharmonicity in the chosen divalent metal fluorides is approximately constant within the selected range of temperature. This parameter is useful for estimating thermal conductivity as well as ultrasonic attenuation.

When the ultrasonic wave propagates through a crystal, the equilibrium distributions of phonon have been disturbed. The specific time for the re-establishment of the equilibrium is called the thermal relaxation time ($\tau$). The combined effect of the average thermal conductivity, Debye velocity and specific heat can

### Table 2. B (in GPa), G (in GPa), Y (in GPa), $\sigma$, $\rho$, $H_v$ (in GPa) and $P_C$ (in GPa), for divalent metal fluorides XF$_2$ (X = Ca, Sr, Cd and Ba) in the temperature range 100–300 K.

<table>
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<th>Material</th>
<th>$T$ (K)</th>
<th>$B$</th>
<th>$G$</th>
<th>$Y$</th>
<th>$\sigma$</th>
<th>$\rho$</th>
<th>$H_v$</th>
<th>$P_C$</th>
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</thead>
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<tr>
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<td>150</td>
<td>97.8</td>
<td>58.1</td>
<td>145.5</td>
<td>0.252</td>
<td>1.68</td>
<td>8.71</td>
<td>-2.9</td>
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Table 3. $\rho(\times 10^3 \text{ kg m}^{-3})$, ultrasonic velocities \((\times 10^3 \text{ m s}^{-1})\), Grüneisen parameters, $D_L$ and $D_S$ for XF$_2$ ($X = \text{Ca, Sr, Cd and Ba}$) in the temperature range 100–300 K.

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<th>$V_S$</th>
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<th>$\langle \gamma_i^0 \rangle_L^2$</th>
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<th>$D_L$</th>
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<td>0.19</td>
<td>4.62</td>
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</table>

Figure 1. Debye average velocity vs. temperature for divalent metal fluorides XF$_2$ ($X = \text{Ca, Sr, Cd and Ba}$).

be monitored from the behaviour of $\tau$ [35,36]. The temperature-dependent thermal energy density $E_0$, thermal conductivity $\kappa$, specific heat capacity $C_V$ and thermal relaxation time for the chosen divalent metal fluorides are presented in figures 2a–2d respectively.

The thermal conductivity is inversely proportional to the square of Grüneisen’s parameter and temperature. It is clear from figure 2b that the thermal conductivity of all the chosen divalent metal fluorides decreases with temperature despite a gradual decay in the Grüneisen’s parameter. It reveals that the thermal conduction process is completely governed by three-phonons interaction mechanisms in which the algebraic sum of all phonon wave vectors is zero and is least affected by anharmonicity caused by four-phonons interaction mechanisms. It also indicates that the momentum transferred in the forward direction decreases with an increase in temperature due to scattering of phonons, enhancement in entropy and disorderness in structural inhomogeneity. Thermal conductivity is maximum for CdF$_2$ whereas it is the lowest for CaF$_2$ among the chosen divalent metal fluorides. It is obvious from figure 2d that the thermal relaxation time decreases nonlinearly with the temperature in all the chosen divalent metal fluorides and resembles the same characteristics of thermal conductivity. Therefore, both the thermal conductivity and thermal relaxation time are least affected by the Grüneisen’s parameter or anharmonicity in the chosen divalent metal fluorides in a given temperature range. Similar to other NaCl-type structured crystals, the thermal relaxation for the chosen divalent metal fluorides is of the order of picosecond which is lower than that for metals and higher than that for dielectric materials but is comparable to that for previously reported semiconducting materials [12,36]. As the temperature increases, a significant decrement in the thermal conduction is observed due to the scattering of phonons. The phenomenon is crucial for understanding the reduction of heat transfer in many insulating materials and for determining the
Figure 2. (a) Thermal energy density, (b) thermal conductivity, (c) specific heat capacity and (d) thermal relaxation time vs. temperature for divalent metal fluorides XF₂ (X = Ca, Sr, Cd and Ba).

coefficient of a heat exchanger. The determination of temperature-dependent ultrasonic absorption over the squared frequency, \( \alpha/f^2 \), is an important aspect of our investigation as it relates to several thermophysical properties. The temperature-dependent total ultrasonic attenuations, as well as their components, are presented in figures 3a–3d.

It can be seen from figure 3 that the ultrasonic attenuation over the square frequency for Akhieser loss and thermoelastic loss exhibited an almost similar nature in the temperature range 100–300 K. The trends of ultrasonic attenuation over the squared frequency have similar nature to that of thermal relaxation time for all chosen divalent metal fluorides. Figures 3a–3d show that the thermoelastic loss is trivial compared to the Akhieser loss because of the low values of thermal conductivities for all the chosen divalent metal fluorides. As temperature increases, the Akhieser loss becomes dominant on the total ultrasonic attenuation because the anharmonic interaction between acoustical and thermal phonons increases with temperature. These anharmonic interactions are usually three-phonons process in which two phonons collide and form a third, or a phonon breaks up into two other phonons. As the temperature of the crystal increases, the average energy of the dominant phonons increases and three-phonons processes become more probable. If the temperature reaches maximum value, four-phonons interactions become possible. Thus, Akhieser damping plays a significant role in ultrasonic attenuation. Since the chosen materials are perfect, single-crystalline and non-magnetic, imperfection scattering and magnon-phonon scattering do not play a noteworthy role in total ultrasonic attenuation. Also, the coupling between conducting electrons and acoustical phonons does not occur in the chosen temperature range as mean free paths of electrons and acoustical...
phonons are not comparable. The values of ultrasonic attenuation over the square of frequency are greater for BaF$_2$ and smaller for CdF$_2$. The ultrasonic attenuation of the longitudinal mode is higher than that of the shear mode because the acoustic coupling constant value is larger for the longitudinal mode ($D_L$) than for the shear mode ($D_S$). The nominal value of loss in ultrasonic energy by thermoelastic relaxation and dominance of acoustic coupling constants confirm the prominence of phonon–phonon interaction towards ultrasonic attenuation. Unfortunately, to the best of the authors’ knowledge, no previous experimental or theoretical data regarding the ultrasonic attenuations have been reported previously to allow direct comparisons. Thus, we compared our results with the data of similar FCC structured compounds, recently reported for B$_1$ structured materials such as U, Pu and Am carbides [12] and rare-earth monopricptides [36]. The nature and behaviour of the investigated materials were in satisfactory agreement.

4. Conclusions

The theory based on a simple interaction potential model for the calculation of higher-order elastic constants is supported for FCC structured divalent metal fluorides. At the temperature range 100–300 K, CdF$_2$ shows superior elastic, mechanical and thermophysical properties among CaF$_2$, SrF$_2$ and BaF$_2$, due to larger values of stiffness and elastic constants. The chosen divalent metal fluorides have a higher value of brittleness and hardness. The hardness is directly related to the bond strength and we have predicted that the hardness of CdF$_2$ is greater than that of the other divalent metal fluorides. The thermal relaxation time was of the order of picosecond, which is comparable to that for the previously reported semiconducting materials. In contrast to the thermoelastic loss and electron–phonon interactions, the interaction between acoustic and thermal phonons made the main contribution to the total ultrasonic attenuation. CdF$_2$ shows less loss to ultra-

Figure 3. Components of total ultrasonic attenuation vs. temperature for divalent metal fluorides XF$_2$ (X = Ca, Sr, Cd and Ba).
sonic energy as the re-establishment time for thermal phonons is less than that of the other divalent metal fluorides of the same group. The study may be fruitful for the processing and characterisation of the reported as well as other divalent metal fluorides. These findings will provide a base for further investigation of crucial thermophysical properties in the field of industrial applications.

References