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Influence of Ternary and Quaternary Inclusion on Bandgap Tuning of CaTe: Prediction of Potential Thermoelectric Materials

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The structural, optoelectronic, and thermoelectric properties of CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys are studied using the full-potential linearized augmented plane wave method within the framework of density functional theory. The calculated ground-state properties agree well with available data. The electronic and bonding behavior of the materials is studied and further verified by electron density contours. Additionally, mechanical stability is confirmed by calculating the shear modulus, Young's modulus, bulk modulus, and hardness values. From the brittle/ductile analysis, the newly predicted compounds are found to be less brittle (more ductile) than the parent CaTe compound. The valence band maxima and the conduction band minima (CBM) of the $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys are located at the Γ point, resulting in a direct bandgap. The optical properties of the materials are calculated for the energy range of 0–13.5 eV. As expected, the highest Seebeck coefficient value is observed as 245.8 $\mu\text{V/K}$ and 248.6 $\mu\text{V/K}$ for $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys, respectively, at 300 K. The present work exhibits the optoelectronic and thermoelectric properties, but the available material flexibility has various other applications.

Key words: Ab initio, mechanical properties, optical properties, semiconductors, thermoelectric properties

INTRODUCTION

One of the most significant and exciting aspects of research is bandgap engineering in semiconducting materials, as it determines various characteristics such as structural, electronic, thermal, and optical

properties. Over the past decade, possibilities have emerged for potential applications in II-VI chalcogenides, calcium chalcogenides,¹ strontium chalcogenides,² and beryllium chalcogenides.³ At ambient conditions, the alkaline earth chalcogenides form a closed-shell ionic system, crystallizing in a NaCl-type structure (B1).^{4,5} Recent studies have reported rare earth chalcogenides as essential materials for application in optoelectronic^{6–8} and thermoelectric devices.⁹

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Group II-VI semiconductors and their heterostructures are well known to form ternary alloys with a direct bandgap and high absorption coefficients.¹⁰ The energy gaps of ternary II-VI semiconductor alloys can absorb broad spectra, and lattice parameters can be tailored independently to fabricate high-efficiency photovoltaic devices.^{11–15} These semiconductors are considered as potential materials for fabricating thin-film heterojunction photovoltaic devices. Among all alkaline earth chalcogenides, calcium chalcogenides seem to be the most interesting, as they have a high cation-anion radius ratio, resulting in high phase transition pressures.

Several experimental and theoretical studies have been performed to describe the structural, electronic, elastic, optical, and thermodynamic properties at ambient conditions and under high pressure. Zimmer et al.¹⁶ investigated the X-ray diffraction of structural and pressure volume relationships in CaTe and SrTe at high pressure. Cartona et al.¹⁷ reported the cohesive properties of CaX compounds under pressure. The elastic constants were studied using pseudopotential¹⁸ and tight-binding theory.¹⁹ Arya et al.²⁰ investigated high-pressure structural and elastic properties, and the linear optical properties of these compounds were reported using the full-potential linearized augmented plane wave (FP-LAPW) method.²¹ Ab initio investigations of calcium chalcogenides were conducted by Slimani et al.²² The structural phase transition and related properties of calcium chalcogenides were reported by Bhardwaj et al.²³ Charifi et al.²⁴ discussed the structural and electronic properties of calcium chalcogenides under high pressure.

The purpose of the present work is to investigate the structural, electronic, elastic, mechanical, optical, and thermoelectric properties of barium- and selenium-doped CaTe semiconductors. A phase transition is found to occur from a NaCl-type B1 structure to a cubic 227 (Fd3m) structure in ternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$. The essential characteristics of the absorber material in a solar cell are direct bandgap in the range of 1.0–1.7 eV and a high absorption coefficient. The parent binary CaTe alloy has an indirect bandgap, and its energy gap value is 1.587 eV,^{25,26} whereas the Ba-doped CaTe (ternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$), Se-doped CaTe (ternary $\text{CaTe}_{0.5}\text{Se}_{0.5}$), and both Ba- and Se-doped CaTe (quaternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$) alloys have direct bandgaps with energy gap values of 1.693 eV, 1.779 eV, and 1.859 eV, respectively; these values are close to the optical energy gap of solar cell absorbers. Hence, ternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ and $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and quaternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ have triggered immense interest for the potential application as solar cell absorbers. The

thermoelectric properties of materials have always attracted great interest due to their practical applications in coolers and generators.²⁷ To develop an efficient thermoelectric material, which typically demands direct conversion of heat to electricity, high-performance materials are needed.^{28–31} Direct heat to electricity conversion has a vital role in future energy production, conversion, utilization, etc. Since wide-energy-bandgap semiconductors have promising applications in the field of thermoelectric materials, the present study focuses on bandgap tuning by both doping and co-doping. The effect of doping is to reduce the thermal conductivity and thereby increase the figure of merit.

CALCULATION METHOD

In order to calculate the structural, electronic, mechanical, elastic, and optical properties of CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys, the FP-LAPW method is used to solve the Kohn–Sham equations. All the calculations are carried out using the WIEN2k code³² within the framework of density functional theory (DFT). The generalized gradient approximation (GGA) as parameterized by Perdew et al.³³ is employed for the exchange–correlation potentials. The l_{max} value for the wave function expansions inside spheres is confined to $l_{\text{max}} = 10$. The $R_{\text{MT}} \times K_{\text{max}} = 7$ and $G_{\text{max}} = 12$ are chosen for the plane wave expansions in the interstitial region and charge density Fourier expansion, respectively. The muffin-tin radius R_{MT} is assumed to be 2.5, 2.5, 2.5, and 2.08 for Ca, Ba, Se, and Te atoms, respectively. For k-space summation, $10 \times 10 \times 10$ k-points are used. The self-consistent calculations are iterated until the total energy converges to < 0.0001 Ry and charge converges to less than 0.001 eV. In order to model the $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ alloy, we employ a 16-atom supercell of the type $2 \times 2 \times 2$. The lattice structure of $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ ($\text{CaTe}_{0.5}\text{Se}_{0.5}$) is obtained by replacing four Ca (Te) atoms with an equal number of Ba (Se) atoms in the crystal lattice of CaTe, whereas in the case of $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$, Ca is replaced by Ba atoms and Te is replaced by Se atoms simultaneously.

RESULTS AND DISCUSSION

Structural Properties

The structural properties of the II-VI binary compound CaTe and its ternary alloy $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ is investigated at ambient conditions using a GGA scheme. CaTe crystallizes in a NaCl-type B1 structure with the space group 225, whereas $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ crystallizes in a cubic structure with space group 227. The constituent Ca atom is positioned at (0, 0, 0), and the Te atom is positioned at (0.5, 0.5, 0.5). Ba-doped CaTe (ternary

$\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ is found to undergo a phase transformation from Fm3m (225) to Fd3m (227) structure. Ternary $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and quaternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys undergo a phase change from a cubic-type structure with space group Fm3m to another cubic-type structure with space group Fd3m (227) and F43m (216), respectively, and the crystal structure of the alloys is shown in Fig. 1. The lattice constant a_0 , bulk modulus B , and pressure derivative of bulk modulus B' are obtained by fitting the total energy versus volume according to the Birch–Murnaghan equation of state.³⁴ The atomic positions (Table I) and structural properties calculated for CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys are presented in Table II. The calculated results of the parent compound CaTe are in good agreement with the available experimental and theoretical values.^{35,36}

Electronic Properties

Density of States

The density of states (DOS) and band structure are calculated using the FP-LAPW method within GGA and presented in Figs. 2 and 3. The DOS below the Fermi level (0 eV) is the valence band due to the completely filled states, whereas the DOS above 0 eV is the conduction band due to the unoccupied states. In the binary CaTe alloy (Fig. 2a), the DOS below the Fermi level is mainly due to the Te-5s and 5p states, and above the Fermi level is mainly due to the Ca-4s and 3d states, whereas in the ternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ alloy (Fig. 2b), the DOS below the Fermi level is mainly due to the Te-5s and 5p states, with a small contribution from Ba-p and d states, and above the Fermi level is due to Ca-d and Ba-d states. From Fig. 2a, it can be observed that there is

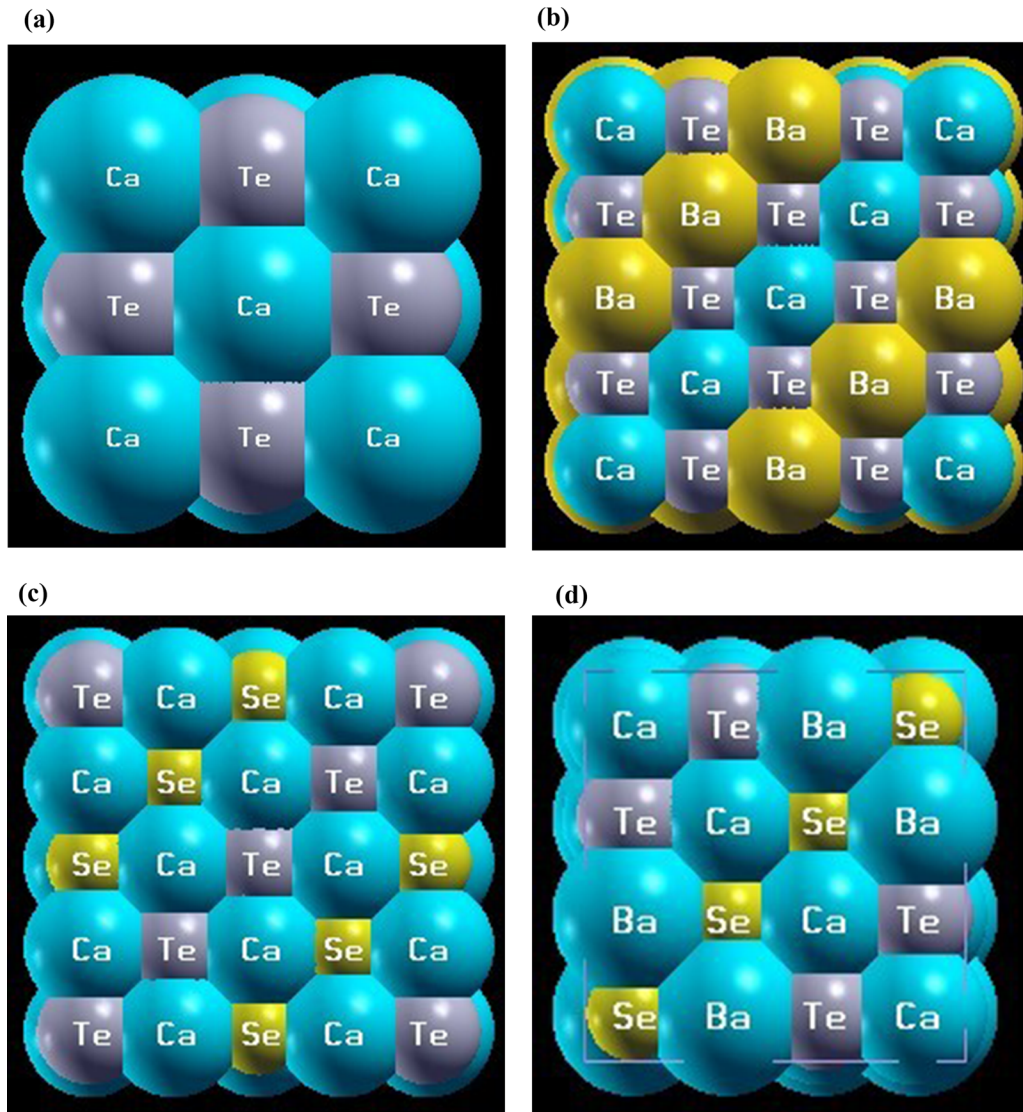


Fig. 1. Graphical representation of the relaxed structure of (a) CaTe, (b) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, (c) $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and (d) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$.

Table I. Atomic positions of CaTe, Ca_{0.5}Ba_{0.5}Te, CaTe_{0.5}Se_{0.5}, and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5}

Alloy	Atom	Atomic positions
CaTe	Ca	(0, 0, 0)
	Te	(0.5, 0.5, 0.5)
Ca _{0.5} Ba _{0.5} Te	Ca	(0, 0, 0) (0.25, 0.25, 0) (0.25, 0, 0.25) (0, 0.25, 0.25)
	Ba	(0.5, 0, 0) (0.75, 0.25, 0) (0.75, 0, 0.25) (0.5, 0.25, 0.25)
	Te	(0.25, 0.25, 0.25) (0.75, 0.25, 0.25) (0, 0, 0.25) (0.5, 0, 0.25)
		(0, 0.25, 0) (0.5, 0.25, 0) (0.25, 0, 0) (0.75, 0, 0)
CaTe _{0.5} Se _{0.5}	Ca	(0.25, 0.25, 0.75) (0.75, 0.75, 0.25) (0.75, 0.5, 0) (0.25, 0, 0.5)
	Te	(0, 0, 0.75) (0.5, 0.5, 0.25) (0.5, 0.75, 0) (0, 0.25, 0.5)
	Se	(0, 0, 0) (0, 0.25, 0.25) (0.25, 0.25, 0) (0.25, 0, 0.25)
		(0, 0, 0.5) (0, 0.25, 0.75) (0.25, 0.25, 0.5) (0.25, 0, 0.75)
Ca _{0.5} Ba _{0.5} Te _{0.5} Se _{0.5}	Ca	(0.125, 0.125, 0.125) (0.125, 0.875, 0.875)
		(0.875, 0.875, 0.125) (0.875, 0.125, 0.875)
	Ba	(0.125, 0.125, 0.625) (0.125, 0.875, 0.325)
		(0.875, 0.875, 0.625) (0.875, 0.125, 0.375)
	Te	(0.375, 0.375, 0.375) (0.375, 0.625, 0.625)
		(0.625, 0.625, 0.375) (0.625, 0.375, 0.625)
	Se	(0.375, 0.375, 0.875) (0.375, 0.625, 0.125)
		(0.625, 0.625, 0.875) (0.625, 0.375, 0.125)

Table II. Equilibrium lattice constant a_0 (Å), bulk modulus B (GPa), pressure derivative bulk modulus B' , total energy (Ry), and bandgap E_g (eV) for CaTe, Ca_{0.5}Ba_{0.5}Te, CaTe_{0.5}Se_{0.5}, and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} alloys

Parameter	CaTe			Ca _{0.5} Ba _{0.5} Te	CaTe _{0.5} Se _{0.5}	Ca _{0.5} Ba _{0.5} Te _{0.5} Se _{0.5}
	Present work	Experimental work	Other work			
a_0 (Å)	6.398	6.348 [18]	6.396 [1] 6.396 [22]	6.774	6.2019	6.5808
B (GPa)	35.689	41.8 [18]	39.6 [1] 38.7 [22]	32.221	41.301	35.4736
B'	5.3675			4.0746	4.122	4.2154
E (Ry)	-14954.853315			-179310.710207	-84705.622191	-144377.281647
E_g (eV)	1.587		1.53 [1] 1.578 [22]	1.693	1.779	1.859

strong hybridization between Ca- d and d - t_{2g} states and Te- p and d states, indicating the covalent bonding nature of the atoms. It can be observed from Fig. 2b that the charge sharing between the Ca atom and Ba atom at the Fermi level indicates the covalent nature of the atoms. In the CaTe_{0.5}Se_{0.5} combination, it is observed from Fig. 2c that the DOS below the Fermi level is due to Te- s, p states and Se- p states, and above the Fermi level is contributed mainly by Ca- d states, and there is a small contribution of Te- p, d and Se- p, d states. In addition, hybridization is observed between Te- p and Se- p states below the Fermi level, and between Te- p, d and Se- p, d states above the Fermi level. The Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} DOS histogram shows that the DOS below the Fermi level originates from Te- s, p states and Se- s, p states, and above the Fermi level from Ca- d and Ba- d states, respectively. From Fig. 2d, it can be clearly seen that a similar

hybridization occurs in Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} as in CaTe_{0.5}Se_{0.5}.

Band Structure

The self-consistent scalar relativistic bandgaps of CaTe, Ca_{0.5}Ba_{0.5}Te, CaTe_{0.5}Se_{0.5}, and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} alloys are calculated and presented in Table II, and are compared with the theoretical values and the available experimental data. The lowest sharp band in the conduction band is due to the electron effective mass, whereas along the same symmetry, the maximum of the valence band is a hybrid of flat and sharp bands. The combination of flat and sharp bands enhances the electron transport, as the flat band is responsible for the higher value of electron electrical conductivity. Thus, the hybrid band is more effective for solar cell materials. The valence band maxima (VBM) and the

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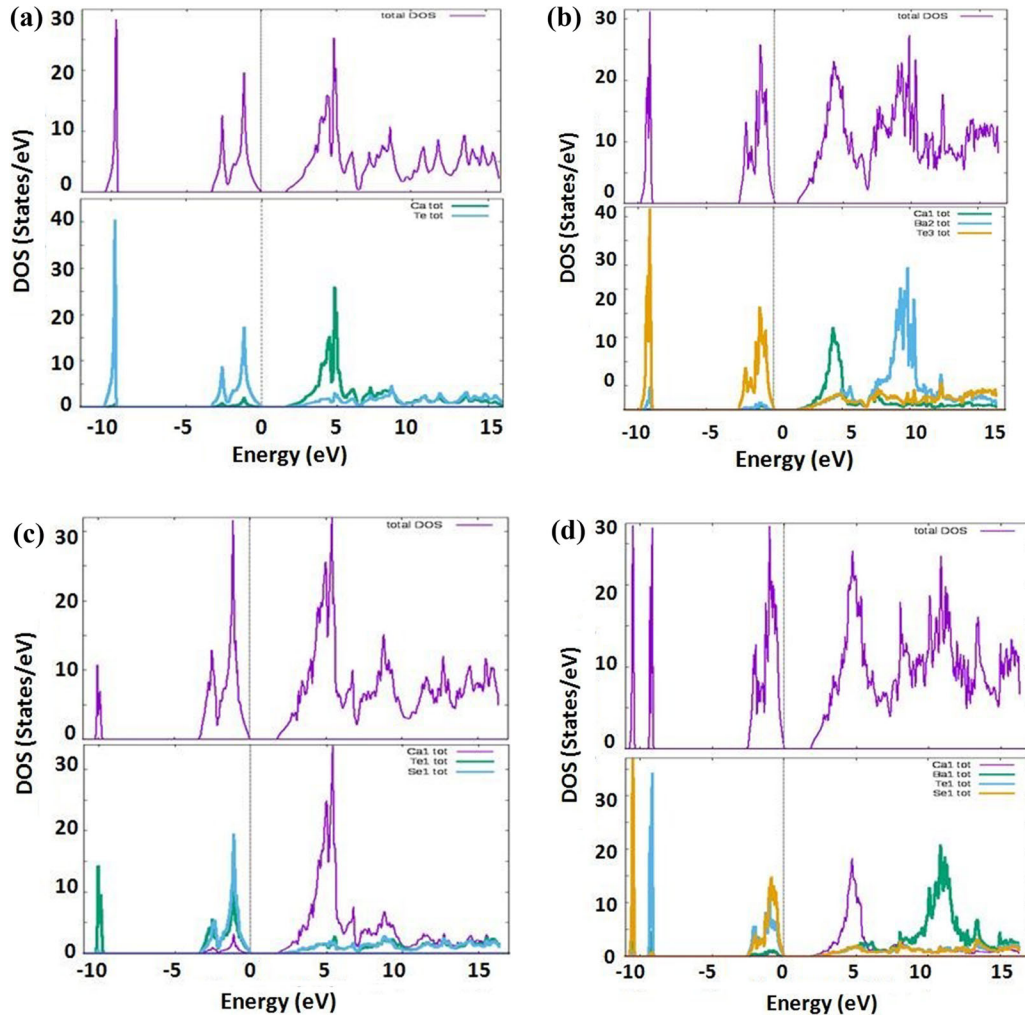


Fig. 2. Total density of states of (a) CaTe, (b) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, (c) $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and (d) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$.

conduction band minima (CBM) of $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ ($\text{CaTe}_{0.5}\text{Se}_{0.5}/\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$) alloy is located at the Γ point, resulting in a direct bandgap, whereas in the case of the parent compound CaTe, the nature of the bandgap is indirect such that the VBM lies at the Γ point and the CBM at the X point of the Brillouin zone. Figure 3e, f, g, and h shows that the fat band structure of Ca- d , Ca- d - t_{2g} , Te- p , and Te- d states confirms the hybridization between Ca- d and d - t_{2g} states, and Te- p and d states indicate the covalent bonding nature of the atoms.

Charge Density Plot

In order to understand the nature of chemical bonding, charge density plots are drawn for CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys, as shown in Fig. 4. From Fig. 4a, it can be observed that the directional charge density contour that encloses the Ca and Te atoms indicates the strong hybridization between Ca- d and d - t_{2g} and Te- p and d states. It can be attributed to the covalent nature of the material.^{37,38} In Fig. 4b, it is clearly seen that the covalent interaction occurs

between Ca and Ba atoms, due to charge sharing between Ca and Ba atoms. At the same time, Ba doping breaks the covalent bonding between Ca and Te atoms. The near-spherical charge distribution around Te indicates the bond between Ca and Te is ionic, with no charge sharing between the atoms. In Fig. 4c and d, it is observed that the Se atoms are doped at the Te site (Ba atom in the Ca site), hence it decreases the covalent bonding nature of CaTe, but the presence of bonding charge is evident for mixing of ionic and weak covalent bonding of the material.

Optical properties

The optical properties, namely complex dielectric function, absorption coefficient, optical conductivity, energy loss function, and reflectivity, are calculated for CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys and are shown in Fig. 5. All calculations are performed with no intra-band contributions added. The complex dielectric function $\epsilon(\omega)$ ³⁹ is determined by the transition between the valence and conduction bands and is given by:

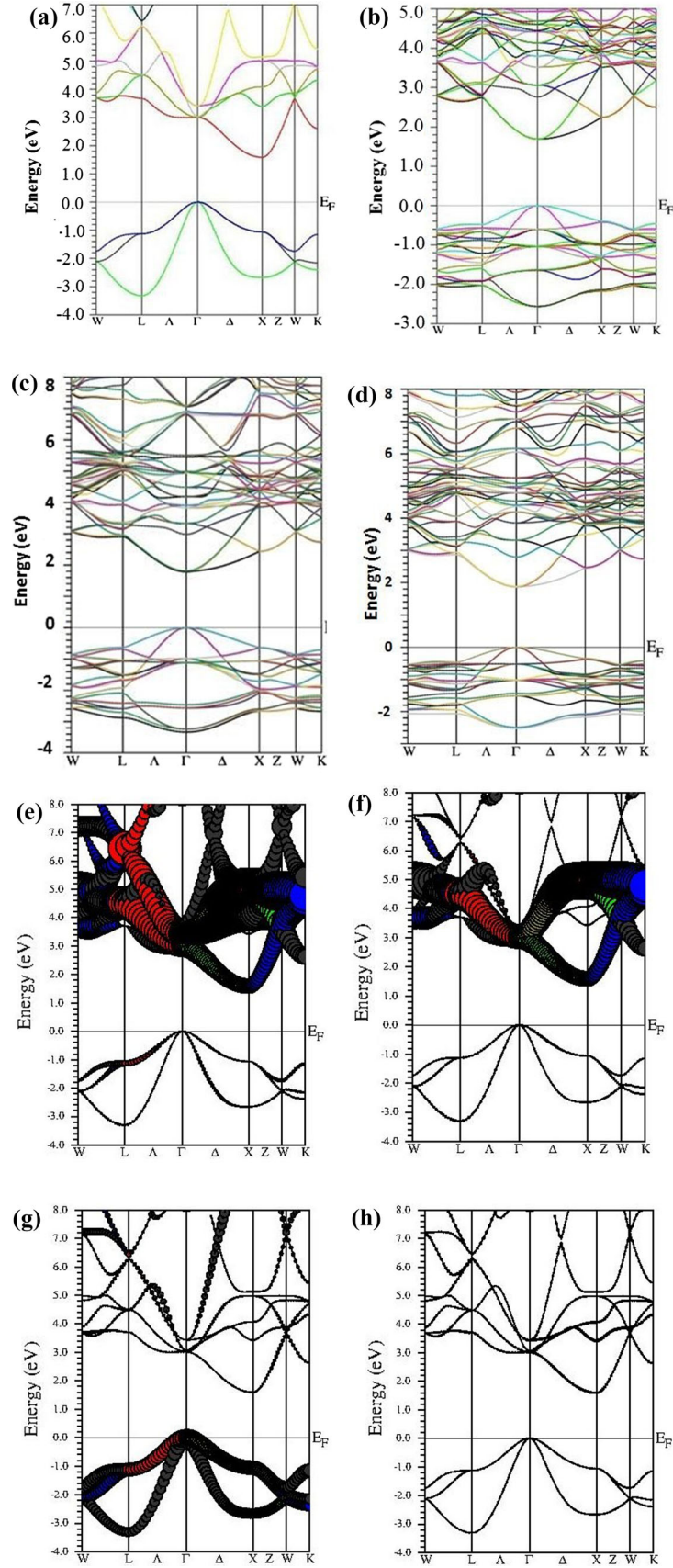


Fig. 3. Band structure of (a) CaTe, (b) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, (c) $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and (d) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$, and fat band structure of (e) Ca-*d*, (f) Ca-*d*-*t*_{2g}, (g) Te-*p*, and (h) Te-*d* states.

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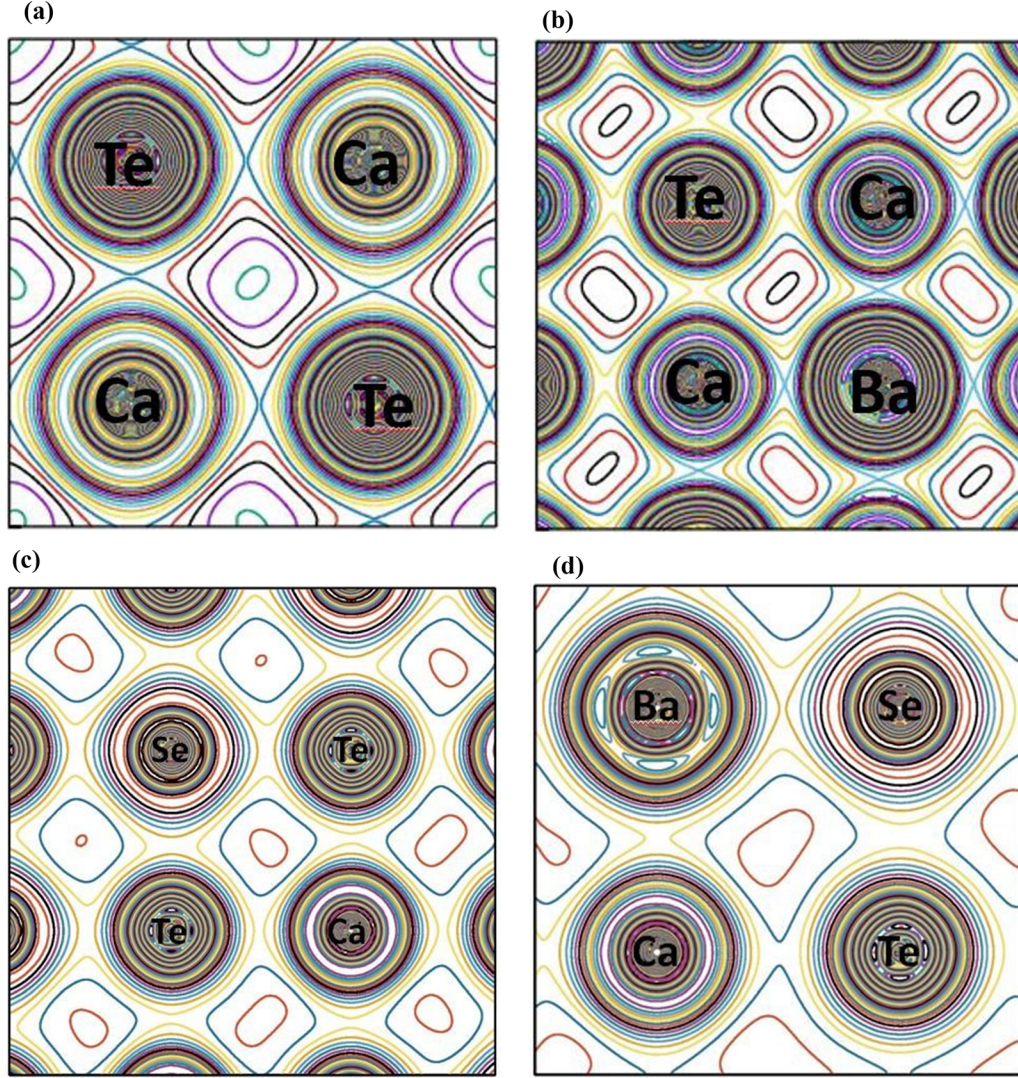


Fig. 4. Charge density plot of (a) CaTe, (b) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, (c) $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and (d) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$.

$\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega)$. The real and imaginary parts of the dielectric function correspond to the dispersive and absorptive behavior of the material, respectively. The static dielectric constant is the most important quantity in the real part of the dielectric function, which strongly depends on the energy gap, and it is given (Fig. 5a) as 6.8, 6.5, 6.2, and 6.0 for the CaTe , $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys, respectively. The absorption coefficient determines the ability of the material to absorb the incident photon of specific frequency.⁴⁰ It can be seen from Fig. 5c that the absorption part of binary CaTe and ternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ and $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and quaternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ spectra starts with nearly 1.8 eV, 2.1 eV, 2.2 eV, and 2.0 eV, respectively. In binary CaTe , $E_0 = 1.58$ eV, the first peak appears for 4.5 eV, and the optical conductivity has a maximum value of 7500 [$1/(\Omega \text{ cm})$], whereas in $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $(\text{CaTe}_{0.5}\text{Se}_{0.5}/\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5})$ $E_0 = 1.69$ eV (2.1 eV/2.0 eV), the first peak appears

for 4.7 eV (4.2 eV/4.6 eV) (Fig. 5d), and the optical conductivity has a maximum value of 6800 (6600/6400) [$1/(\Omega \text{ cm})$] corresponding to the visible region of the electromagnetic spectrum.

The energy loss spectrum describes the energy loss of a fast electron traversing in the material.⁴⁰ Its main peak is defined as the bulk plasma frequency, which occurs where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ reach the zero point and the reflectivity spectrum attains a minimum. From Fig. 5e, the main peak of the energy loss spectrum of CaTe , $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ is roughly located at 13 eV, 11.5 eV, 12.6 eV, and 12.0 eV, respectively. The value of reflectivity at zero frequency is known as the static reflectivity (R_0). From Fig. 5f, it can be observed that, depending on the energy value, the reflectivity has many peaks. For CaTe , $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys, $R_0 = 0.2$, 0.19, 0.18, and 0.17 (from Fig. 5f), respectively. The reflectivity has a maximum value $R_{\text{max}} = 0.58$ (0.53/0.51/0.49) at energy of

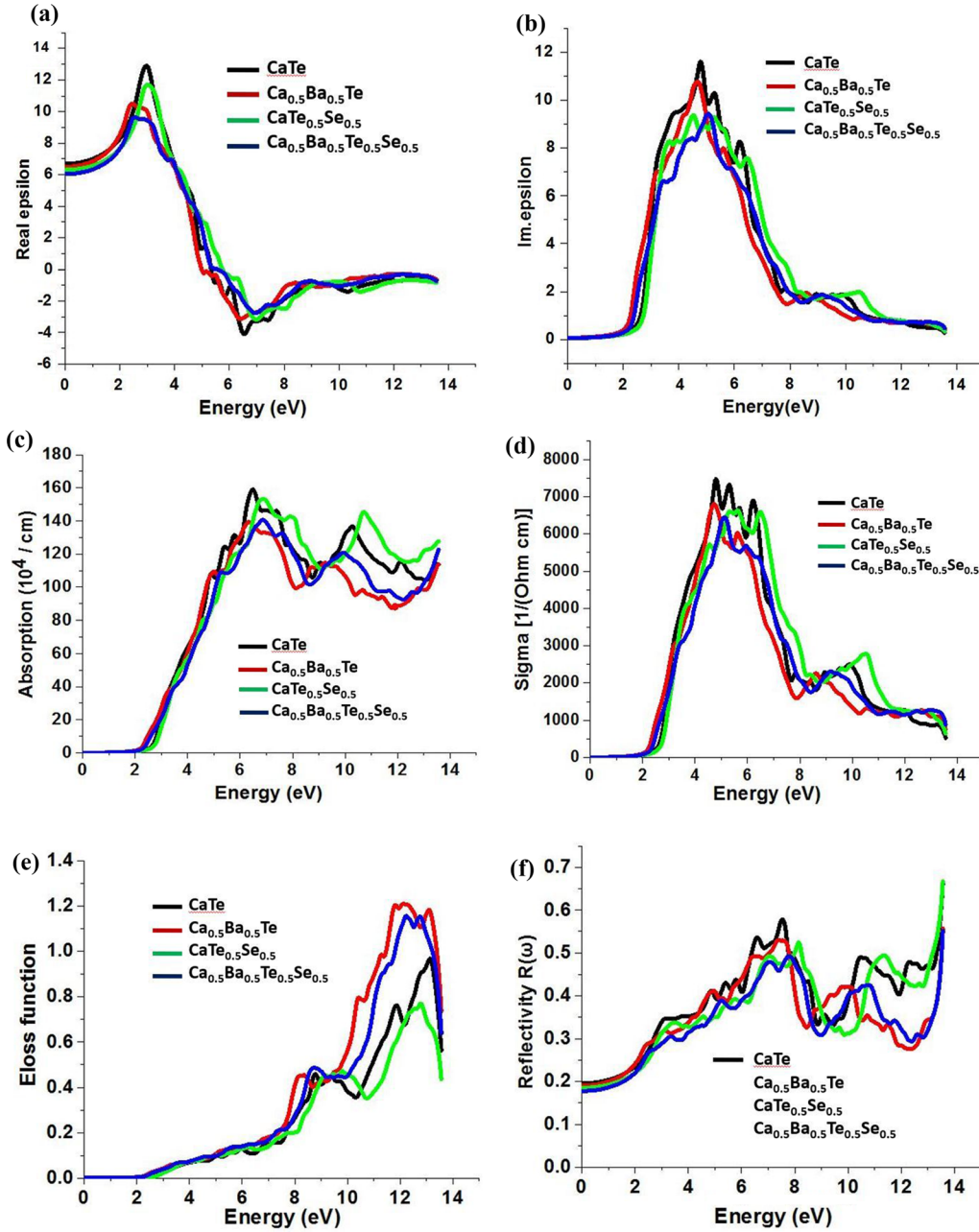


Fig. 5. Optical properties of (a) CaTe, (b) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, (c) $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and (d) $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$.

7.5 eV (7.2 eV/8.1 eV/7.5 eV) and a minimum value $R_{\min} = 0.38$ (0.33/0.3/0.29) at 8.8 eV (8.2 eV/9.9 eV/8.9 eV) for CaTe ($\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ / $\text{CaTe}_{0.5}\text{Se}_{0.5}$ / $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$).

Mechanical and Elastic Properties

Elastic constants of solids give important information such as interatomic bonding characteristic between adjacent atomic planes, equations of state, and phonon spectra. To study the stability of the considered alloys, we have calculated the three independent elastic constants, namely C_{11} , C_{12} , and C_{44} . The calculated elastic constants satisfy the

stability criteria.⁴¹ Using elastic constants,⁴² one can determine the mechanical properties such as shear modulus (G), Young's modulus (E), Cauchy pressure ($C_{12}-C_{44}$), Poisson's ratio (ν), and hardness (H_V),^{43,44} and the computed values for the alloys are given in Table III. The larger value of shear modulus indicates the pronounced directional bonding (covalent bonding) between atoms,⁴¹ and it describes the material's response to shearing strain. Covalent materials have a high shear modulus, and the shear modulus can provide better correlation with hardness than the bulk modulus. The high value of shear modulus represents that the material is hard. Bulk modulus⁴⁵ is defined as the ratio of

Table III. Calculated elastic and mechanical properties of CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$

Parameter	CaTe		$\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$	$\text{CaTe}_{0.5}\text{Se}_{0.5}$	$\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$
	Present work	Other work			
C_{11} (GPa)	92.28	89.26 [¹]	72.62	93.25	81.32
C_{12} (GPa)	10.73	14.77 [¹]	11.38	15.54	13.46
C_{44} (GPa)	27.84	18.52 [¹]	13.84	22.91	17.38
G (GPa)	32.45		19.14	28.35	22.79
E (GPa)	75.75		47.82	69.26	56.49
$C_{12}-C_{44}$ (GPa)	-17.10		-2.46	-7.38	-3.92
G/B	0.86		0.60	0.68	0.63
N	0.17		0.25	0.22	0.24
H_V	9.10		3.18	5.29	3.96

volume stress to volume strain, and it measures the resistance to volume by applied pressure. Young's modulus is a measure of the stiffness of the solid, defining the relationship between stress and strain in a material in the linear elasticity regime of a uniaxial deformation, and it has an impact on the ductility. From Table III, it can be noted that the stiffness of the material decreases in the following order: $\text{CaTe}_{0.5}\text{Se}_{0.5}$ (69.26 GPa)– $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ (56.49 GPa)– $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ (47.82 GPa). A similar trend is observed for shear modulus, bulk modulus, and hardness values. From the analysis of shear modulus, bulk modulus, and hardness values, we can state that the strength of covalent bond, binding energy, and hardness of the considered alloys are decreased.

The ductile/brittle analysis is conducted using Cauchy's pressure, G/B ratio,^{46–48} and Poisson's ratio,^{49,50} and the calculated values are shown in Table III.

- Cauchy's pressure values are negative; the material exhibits brittle nature.
- G/B ratio is greater than 0.57; the material exhibits brittle behavior.
- Poisson's ratio is less than 0.3; the materials are of brittle nature.

From the calculated Cauchy's pressure ($C_{12}-C_{44}$) and G/B ratio (in Table III), the trend of diminishing brittleness follows the order of $\text{CaTe}_{0.5}\text{Se}_{0.5}$ (–7.38 GPa and 0.68)– $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ (–3.92 GPa and 0.63)– $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ (–2.46 GPa and 0.60). From the above study, it can be revealed that the Ba and Se doping in CaTe decreases the brittle nature (improves ductile nature) of the material.

Thermal properties

The sound velocities for longitudinal and shear waves (V_L and V_S), Debye average velocity (V_m),

Debye temperature (θ_D),^{51–53} melting temperature (T_m),⁴⁵ and Grüneisen parameter (ζ)^{54,55} have been calculated for CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys and presented in Table - IV. Debye temperature is correlated to the strength of covalent bonds, and it is used to measure the thermal conductivity of materials. Debye temperature (θ_D) is directly related to average sound velocity, indicating that the greater the average sound velocity, the greater the Debye temperature. The Grüneisen parameter (ζ) is defined as the measure of the anharmonicity of the crystal, and it depends on elastic moduli through sound velocities. The calculated Debye temperature and the corresponding Grüneisen parameter (in Table IV) values follow the order as $\text{CaTe}_{0.5}\text{Se}_{0.5}$ (205 K and 1.368)– $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ (180 K and 1.432)– $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ (144 K and 1.497). Hence, the lower Debye temperature (θ_D) and large value of Grüneisen parameter (ζ) indicate the soft bonding nature of the given crystal. The melting temperatures⁵³ of the materials are calculated from the elastic constants and modulus values, where the elastic constants and moduli are in GPa and are discussed in our previous studies.

Thermoelectric properties

Using BoltzTraP code, the thermoelectric properties such as thermal conductivity (κ), electrical conductivity (σ), Seebeck coefficient (S), power factor, and figure of merit (ZT) are studied for the considered compounds. The values of electrical conductivity (σ), Seebeck coefficient (S), and power factor are calculated for the temperature range from 100 K to 1000 K at Fermi energy. Graphs are plotted between S versus T , σ/τ versus T , and $S^2\sigma/\tau$ versus T and presented in Fig. 6. The power factor was calculated by using the formula $S^2\sigma$. The figure of merit (ZT) at temperature T (K) of a material is as follows: $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ thermal conductivity, and T is the absolute

Table IV. Calculated sound velocities for longitudinal and shear waves (V_L and V_S), Debye average velocity (V_m), Debye temperature (Θ_D), melting temperature (T_m), and Grüneisen parameter (ζ) of CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$

Parameter	CaTe	$\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$	$\text{CaTe}_{0.5}\text{Se}_{0.5}$	$\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$
V_L (10^3 m/s)	8.741	2.228	2.816	2.427
V_S (10^3 m/s)	5.525	1.287	1.686	1.427
V_m (10^3 m/s)	6.079	1.429	1.865	1.582
Θ_D (K)	568	144	205	180
T_m (K)	1398	1282	1404	1333
ζ	1.168	1.497	1.368	1.432

temperature of the material. The calculated values of S , σ/τ , $S^2\sigma/\tau$, and power factor at Fermi energy for room temperature are presented in Table V.

The Seebeck coefficient is also known as thermoelectric power, and the convention of the Seebeck coefficient depends on the majority of charge carriers. The Seebeck coefficient⁵⁶ is considered positive for a material which possesses a majority of charge carriers as holes, whereas it is considered negative for electrons. In the present study, the considered calcium chalcogenides are found with holes as the majority charge carriers, and therefore the Seebeck coefficients become positive, as shown in Fig. 6a and b, and the values are given in Table V. This suggests the possibility that the CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys are p -type semiconductors.

From Fig. 6a it is observed that the value of Seebeck coefficient (S) starts to increase at low temperature and then decreases at high temperature for CaTe and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ alloys; a similar trend was observed in PbTe alloys.⁵⁷ At room temperature, the value of S for CaTe is 44.547 ($\mu\text{V/K}$), which is in agreement with the values reported for PbTe and PbSe.⁵⁷ When Ca is doped with Ba, the Seebeck coefficient value decreases to a very low value of 4 ($\mu\text{V/K}$); this can be attributed to a shift in the Fermi energy level and also a change in the direct-bandgap energy. Thus, doping Ca with Ba does not enhance the Seebeck coefficient, which is an essential parameter in utilizing the material for thermoelectric energy conversion of heat into electricity. When Te is doped with Se, the Seebeck coefficient value increases to 246 ($\mu\text{V/K}$) and 249 ($\mu\text{V/K}$), and decreases with an increase in temperature for $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys (shown in Fig. 6b); a similar trend was observed and explained by Singh⁵⁸ for a CaSe alloy. The reason for the high Seebeck coefficient is the location of hole pockets near the Fermi energy level in these two alloys. This high value makes these two alloys suitable material for thermoelectric applications.

In general, electrical conductivity is a measure of a material's capability to move electric charge carriers throughout the material. It depends on the type of material, stress states, and the chemical

composition, and it provides information about the current flow and energy required to traverse the energy gaps. From Fig. 6c, the value of electrical conductivity first increases and then decreases with respect to temperature for CaTe and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ alloys, whereas in $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ combinations, it increases with respect to temperature, as shown in Fig. 6d. The electrical conductivity values for $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys are of the order of 10^{18} , which is in excellent agreement with values reported by Subramanian⁵⁹ for efficient thermoelectric materials. The corresponding electrical conductivity (σ/τ in $1/\Omega\text{ ms}$) values of CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys at 300 K are 2.2968×10^{23} , 1.9706×10^{23} , 1.1157×10^{18} , and 1.3423×10^{18} , respectively.

The electronic contribution to thermal conductivity, that is κ_E/τ values (W/m Ks), for CaTe, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys at 300 K is 1.6181×10^{18} , 1.362×10^{18} , 2.6545×10^{13} , and 3.2673×10^{13} , respectively. In the present study, it is observed that the thermal conductivity increases as the temperature increases. Considering relaxation time of 1×10^{-14} s, at 300 K the electronic thermal conductivity (W/m/K) is 1.6181×10^4 , 1.362×10^4 , 0.2654, and 0.3267 for $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, $\text{CaTe}_{0.5}\text{Se}_{0.5}$, and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys, respectively.

The maximum value of the Seebeck coefficient and the corresponding electrical conductivity are used to calculate $S^2\sigma/\tau$. In the case of CaTe (Fig. 6e) and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$ (Fig. 6f), the value of $S^2\sigma/\tau$ is very high due to the very high value of σ/τ . In the case of $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys, $S^2\sigma/\tau$ decreases with increasing temperature (Fig. 6g), due to the similar trend exhibited by S and σ/τ . If the value of $S^2\sigma/\tau$ is multiplied by τ , the power factor is obtained.

The figure of merit (ZT)⁶⁰ is the most significant factor for investigating the quality of a material for its possible use in thermoelectric applications, and is dependent on the Seebeck coefficient, electrical conductivity, thermal conductivity, and temperature. For a good thermoelectric material, the material should have a high Seebeck coefficient and electrical conductivity and low thermal

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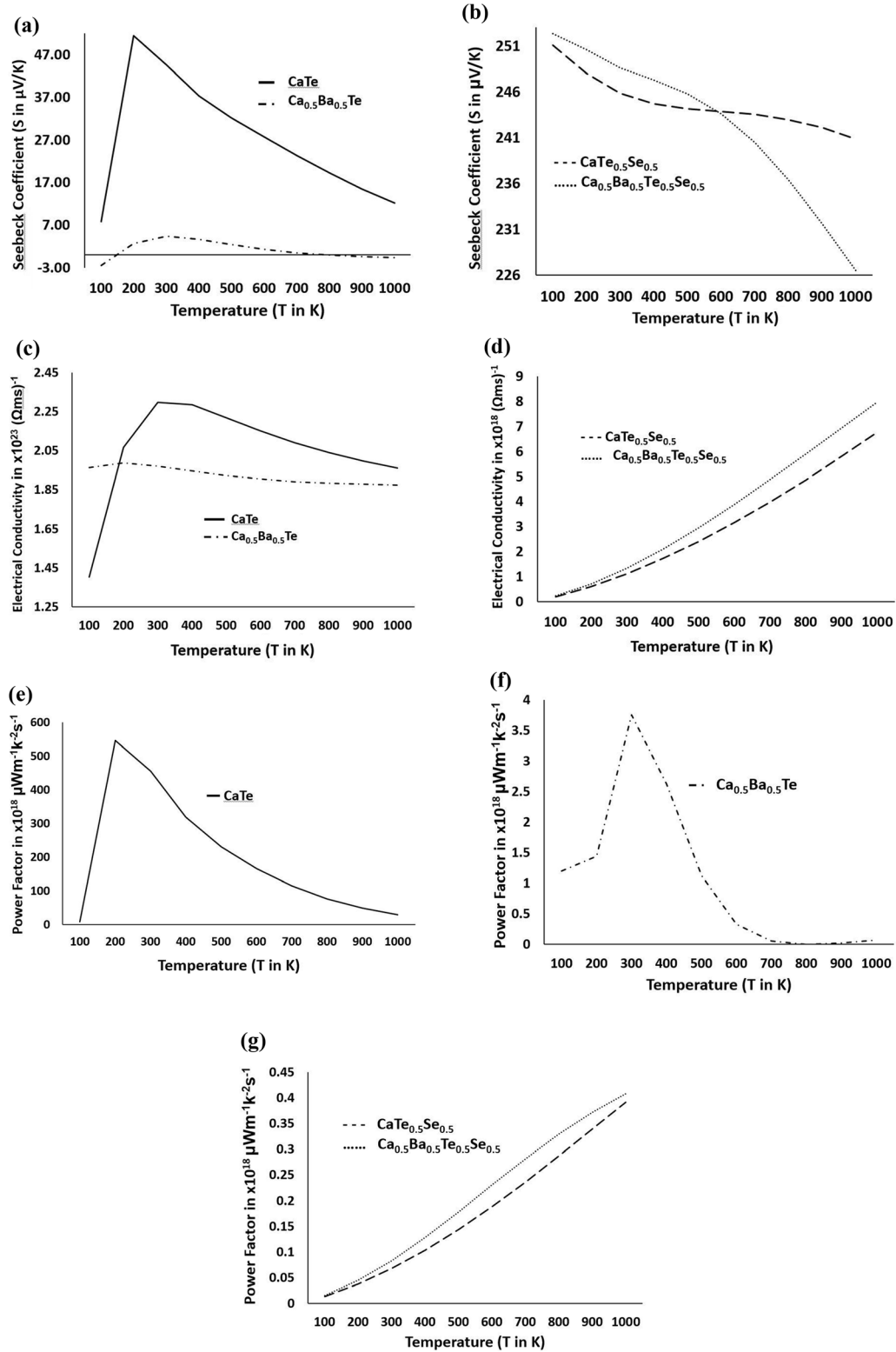


Fig. 6. The thermoelectric properties of (a) Seebeck coefficient versus temperature of CaTe and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, (b) Seebeck coefficient versus temperature of $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$, (c) electrical conductivity versus temperature of CaTe and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, (d) electrical conductivity versus temperature of $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$, (e) power factor versus temperature of CaTe, (f) power factor versus temperature of $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}$, and (g) power factor versus temperature of $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$.

conductivity. From this study, among the four studied alloys, the ternary $\text{CaTe}_{0.5}\text{Se}_{0.5}$ and quaternary $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5}$ alloys are identified as

good thermoelectric materials, having high Seebeck coefficients and corresponding electrical conductivity and low thermal conductivity.

Table V. Thermoelectric properties of CaTe, Ca_{0.5}Ba_{0.5}Te, CaTe_{0.5}Se_{0.5}, and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} at 300 K for Fermi energy

Parameter	CaTe	Ca _{0.5} Ba _{0.5} Te	CaTe _{0.5} Se _{0.5}	Ca _{0.5} Ba _{0.5} Te _{0.5} Se _{0.5}
Seebeck coefficient (S) ($\mu\text{V/K}$)	44.547	4.3646	246	249
σ/τ [$1/(\Omega \text{ m s})$]	2.2968×10^{23}	1.9706×10^{23}	1.1157×10^{18}	1.3423×10^{18}
$S^2 \sigma/\tau$ 10^{14} [$\text{W}/(\text{cm K}^2 \text{ s})$]	4.55	0.0375	0.00067	0.00083
Power factor 10^{20} [$\mu\text{W}/(\text{cm K}^2 \text{ s})$]	4.55	0.0375	0.00067	0.00083

CONCLUSIONS

The structural, electronic, optical, mechanical, elastic, and thermal properties of CaTe, Ca_{0.5}Ba_{0.5}Te, CaTe_{0.5}Se_{0.5}, and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} alloys are investigated using the full-potential linearized augmented plane wave (FP-LAPW) method based on DFT within generalized gradient approximation (GGA). From the results of DOS and band calculations, we can conclude that the considered alloys are direct-bandgap semiconductors with a covalent bonding nature. Because of the band matching with the incident photon energy, the direct bandgap has technological importance, and the presence of the lowest sharp band in the conduction region and the maximum hybrid band in the valence region enhances the electron transport. To determine the optical properties of the alloys, the optical parameters dielectric constants, absorption coefficient, optical conductivity, and energy loss function are calculated for radiation up to 13.5 eV. The other important features of Ca_{0.5}Ba_{0.5}Te, CaTe_{0.5}Se_{0.5}, and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} alloys are the maximum Sigma (electrical conductivity) at lower photon energy and the maximum electron E_{loss} at higher energy. Hence, the calculated electronic and optical properties of Ca_{0.5}Ba_{0.5}Te, CaTe_{0.5}Se_{0.5}, and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} alloys show that the studied alloys are better candidates for electronic devices, optical devices, and solar cell applications. Out of the four studied alloys, the two Ca chalcogenides CaTe_{0.5}Se_{0.5} and Ca_{0.5}Ba_{0.5}Te_{0.5}Se_{0.5} are found to display good thermoelectric behavior, having a larger Seebeck coefficient (thermoelectric power) and lower thermal conductivity. In order to understand the effect of doping, calculations are performed for both ternary addition in cation and anion sites separately, and quaternary addition in both sites parallelly. Due to the presence of Te-*p* and Se-*p* states hybridization (below the Fermi level) and Te-*p,d* and Se-*p,d* states hybridization (above the Fermi level), selenium in co-doping yields better results than the other systems.

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CONFLICT OF INTEREST

All authors declare that they have no conflict of interest.

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