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Physical properties of vacancy-ordered double perovskites K_2TcZ_6 ($Z = Cl, Br$) for spintronics applications: DFT calculations

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Vacancy-ordered double perovskites (DPs) are emerging materials for spintronics due to their stable structures and non-toxic properties. In this study, we conducted a comprehensive investigation into the role of 4d electrons in Tc to understand their impact on the ferromagnetic properties of K_2TcY_6 ($Y = Cl, Br$). We have employed a modified Back and Johnson potential to assess electronic and magnetic characteristics and utilized the BoltzTraP code to investigate thermoelectric effects. Experimental lattice constants confirmed the presence of stable structures and formation energy estimates affirmed their thermodynamic stability. The Heisenberg model and density of electron states (DOS) at the Fermi level provides insights into Curie temperature and spin polarization. The presence of ferromagnetism is evident in the density of states, reflecting the transition of electron spins that support the exchange mechanism. The study delves into how electron functionality influences the control of ferromagnetism, considering exchange constants, exchange energies, hybridization process and the crystal field energies. Moreover, the exploitation of magnetic moments from Tc to K and Cl/Br sites takes precedence in driving ferromagnetism by exchanging electron spins rather than forming magnetic clusters. Additionally, to explore the optical characteristics of the compounds, we investigated their optical absorption, dielectric constants and refractive index within the energy range of 0–10 eV, ensuring absorption across both the visible and ultraviolet regions. Finally, we delve into the impact of the thermoelectric effect on both thermoelectric performance and spin functionality, taking into account factors such as the Seebeck coefficient, power factor, and electronic conductivity.

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1. Introduction

Over the last two decades, there has been significant research interest in the field of room temperature ferromagnetism in semiconductors, primarily because of its potential applications in non-volatile memory, quantum computing and spintronics.^{1–5} Ferromagnetism in semiconductors holds the promise of facilitating the transmission of spin-polarized electrons, a crucial requirement in spintronics.⁶ Initial reports suggesting the possibility of a Curie temperature above room temperature in materials like GaN and ZnO⁷ led to several experimental studies claiming the existence of room temperature ferromagnetism.^{8–11} Furthermore, ferromagnetism has

been identified in a range of non-magnetic semiconductor samples through the introduction of the creation of atomic defects and non-magnetic elements.^{12–21} This phenomenon is commonly referred to as d^0 ferromagnetism.²² In such cases, the source of magnetism is distinct from the partially filled 4d or f-orbital electrons. The investigation of ferromagnetic characteristics has become a technological necessity for future advancements, given that spin-polarized currents have the ability to flow, unlike the unpolarized currents found in traditional electronic devices. As a result, researchers have reported the presence of ferromagnetic characteristics in perovskite materials.²³ However, the applicability of perovskites on a broader scale is hindered by the presence of toxic constituent elements and stability concerns.²⁴

To address these limitations, researchers have undertaken studies on ferromagnetism in various $A_2BB'X_6$ type double perovskites (DPs).^{25–27} The half-metallic DP Sr_2FeMoO_6 has demonstrated a magnetic transition at temperature 410 K, as reported in ref. 28. This finding highlights the potential of such materials to unveil magnetic characteristics at higher temperatures.²⁸ In a more recent experimental study of Pr_2FeCrO_6 , researchers observed a magnetic transition occurring at 550 K. This finding was supported by the observed changes in

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magnetic susceptibility, dielectric constant and resistivity as a function of temperature.^{29,30} Double perovskite materials have been extensively explored for their magnetic and thermoelectric characteristics using a Density Functional Theory (DFT) approach, including compounds like Ba₂FeMoO₆ and Dy₂-CoMnO₆.^{31,32} Double perovskite structures with a vacancy ordering are created by replicating the conventional ABX₃ perovskite configuration and subsequently eliminating half of the B-type cations.³³ These DPs are appealing because of their resemblance to perovskites in terms of structure and their impressive material characteristics, stemming from their broad range of constituent ion compositions and the potential for tilting in the [BX₆]²⁻ octahedra.³⁴⁻³⁶ Recently, DPs with cubic vacancy ordering in the A₂BX₆ structure have been employed in light absorption applications.³⁷

Researchers are also engaged in theoretical investigations of these vacancy-ordered DPs to explore their half-metallic ferromagnetic characteristics.³⁸ Moreover, vacancy-ordered DPs with ferromagnetic properties are worth exploring for potential applications in thermoelectric systems.³⁹ Using DFT calculations, spin dependent DPs Rb₂(Tc,Mo)X₆ (X = Cl, Br) are investigated for spintronic applications due to the role of Mo/Tc atom 4d electrons and show all DPs ferromagnetic characteristics.⁴⁰ Mustafa *et al.*,⁴¹ systematically explored the ferromagnetic characteristics in DPs Rb₂(Os/Ir)Cl/Br₆ using density functional theory. Their analysis of the computations shows that electron spin causes ferromagnetism to be induced by crystal field energy. The structural formula of K₂TcY₆ (Y = Cl or Br) suggests the potential for ferromagnetism in these vacancy-ordered DPs. These investigated DPs are gaining prominence as novel materials in the realm of spintronic applications, including the realization of phenomena such as dynamic random-access memories (DRAM), swift quantum computing, spin valves, magnetic switches and the giant magnetoresistance effect (GMR). In such devices, properties are controlled by manipulating the spin of electrons rather than altering their charge, making these materials faster and more versatile. Additionally, these materials find use in power-harvesting tools such as thermoelectric generators.

The investigation of these DPs is motivated by their full spin polarization, substantial magnetic coupling and enduring ferromagnetism, making them promising candidates for spintronic devices. Particularly, these DPs present the intriguing feature of maintaining ferromagnetic properties at temperatures exceeding room temperature, while simultaneously exhibiting ultralow thermal conductivity.^{42,43} Moreover, Cs₂-AgFeCl₆ is subjected to magnetic and transport analysis employing the TB-mBJ potential, and its thermoelectric features are elucidated through a figure of merit scale.^{44,45} This study includes the comprehensive first-principles calculations to explore the magnetic characteristics within the DPs K₂TcY₆ (Y = Cl, Br). Experimental findings⁴⁶ regarding K₂TcY₆ suggest that the Tc atom is a promising candidate for generating a substantial magnetic moment and ferromagnetic spin ordering in initially non-magnetic materials. Consequently, the K₂TcY₆ (Y = Cl, Br) DPs may exhibit intriguing electronic properties, which could play a crucial role in advancing the field of spintronics

within these direct bandgap semiconductors. We have further examined the impact of their ferromagnetic nature on the thermoelectric properties by analyzing key thermoelectric parameters computed using the BoltzTraP code.⁴⁷ Moreover, our results clearly demonstrate semiconducting ferromagnetic nature of these compounds and ultralow values of κ_e that can prove useful for application of these materials in spintronic and thermoelectric devices.

2. Method of calculations

The DFT gives the absolute information of the compounds' properties before recognizing them for being utilized in useful manufacturing of various devices. BoltzTraP codes were brought into use for thermoelectric analysis whereas the Wien2k code⁴⁸ was employed for the evaluation of the structural, magnetic and spin-polarized electronic features. The optimization for AFM and FM states along with structural properties were conducted by PBESol in the FP-LAPW method.⁴⁹ Although the PBESol accurately determines the lattice parameters as well as the energies of the system, it is unable to evaluate their band gaps and electronic behavior. For that reason, TB-mBJ potential were employed as an entire package for the improvement of band gap on which the compounds' physical features relies.⁵⁰ In the whole potential method, the electronic gap system was divided into interstitial regions and muffin-tin corresponding to the plane wave and spherical harmonic solutions. In addition, $R_{MT} \times K_{max} = 8.0$ was set by holding the radius of the muffin tin sphere as well as the wave vector in the opposite lattice. A k -mesh of $20 \times 20 \times 20$ was employed for the iterative energy conversion approach within the first Brillouin zone. The above-mentioned k -mesh performed the convergence of the whole observed system. As a default setup, the other two fundamental factors such as angular momentum $\ell_{max} = 10$ and Gaussian factor $G_{max} = 16$. The convergence of energy was the sequence of 10^{-4} Ry. The charge convergence obtained from TB-mBJ, alongside the ground state energy, serves as the input for the BoltzTraP code, a classical transport theory-based tool for studying transport properties.

3. Results and discussion

3.1 Structural properties

Fig. 1 shows the structural nature of the observed compounds ($Fm\bar{3}m$ (225)) in cubic phase. The left part in the Fig. 1 presents the polyhedral form whereas the right one displays ball format. The geometric and atomic configurations are ensured by the unit cell. Amongst the octahedral of M(Cl/Br)₆, the K atoms are located. The octahedral form for every atom is kept by the 12-fold composition order of Cl/Br atoms. The Tc atoms lie in the middle position of every octahedron of Cl/Br atoms. Further, the Wyckoff positions for Tc, Cl/Br and K are 4a (0, 0, 0), 24e (0.20, 0, 0), and 8c (0.25, 0.25, 0.25), respectively. The obtained values of the lattice constants (a_0) determined through Murnaghan equation of state and found comparable to experimental lattice constant.⁴⁶ From Table 1, it is clear when the ionic radius increases, the a_0 also starts increasing from Cl to Br containing



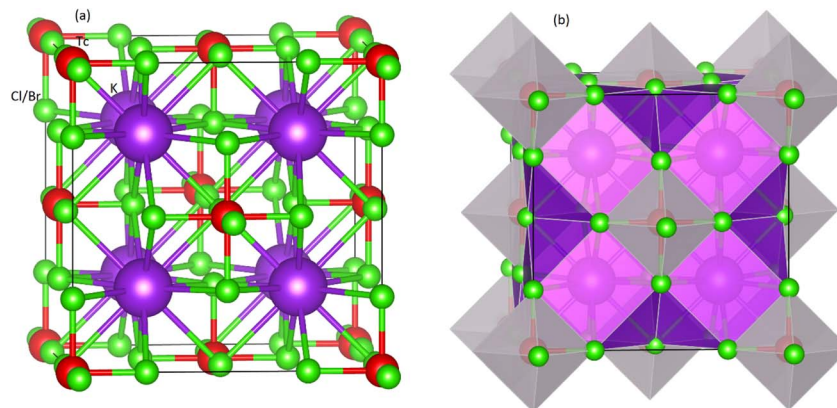


Fig. 1 Unit cell of double perovskites K_2TcX_6 ($X = Cl, Br$) (a) ball format and (b) polyhedral format. Purple, red and green spheres show K, Tc, and X atoms, respectively.

Table 1 The calculated lattice constant (a_0 (Å)), bulk modulus (B_0 (GPa)), formation energy and Curie temperature T_c (K) for DPs K_2TcX_6 ($X = Cl, Br$)

| Parameters | K_2TcCl_6 | K_2TcBr_6 |
|--------------|-------------------|-------------|
| a_0 | 9.84 | 10.46 |
| Exp. work | 9.83 ^a | |
| B_0 | 43.68 | 35.04 |
| ΔH_f | -1.43 | -1.28 |
| T_c | 545 | 505 |

^a Ref. 46.

compound. On the other hand, it is also evident from Table 1 that the larger electronegativity value of Cl causes it to have large value of formation energy compared to K_2TcBr_6 . As the increasing values of a_0 reduces the density of the structures, the bulk modulus (B_0), quite contrary to a_0 , starts decreasing from Cl to Br.

3.2 Curie temperature and structural stability

The graphs of the volume and augmented energy in anti-ferromagnetic (AFM) and in ferromagnetic (FM) states have been plotted in Fig. 2a–c. The estimation and comparison of the

energies affirmed in Rydberg for AFM and FM states was done from the bottom. For FM, the highest omission of energy was observed as compared with AFM states. Thus, more suitability in the FM state is believed for the K_2TcX_6 ($X = Cl, Br$).

Further, formation energy helped illustrating the thermodynamic behavior while employing a reasonable chemical relation:⁵⁰

$$\Delta H_f = E_{\text{total}}(K_aTc_bX_c) - aE_K - bE_{Tc} - cE_X \quad (1)$$

where E_K , E_{Tc} , E_X , are the energies of K, Tc, X atoms and $E_{\text{total}}(K_aTc_bX_c)$ are the energies of K_2TcX_6 ($X = Cl, Br$). The major contribution of atoms towards the computation remained from the a -Rb, b -Tc, and n -X. In FM state, the obtained values of ΔH_f for K_2TcCl_6 and K_2TcBr_6 are listed in Table 1. The energy exhausted is symbolized by the negative sign during the compound formation ensuring the thermodynamic stability of the observed compounds. Further, Br based DPs discharge less energy than that of the Cl based DP. After evaluating thermodynamic stability, it is very important to observe low Curie temperature (T_c) of the compounds. In this regard, Heisenberg model through the equation $T_c = 2\Delta E/3xK_B$, was brought into use where K_B represents the Boltzmann constant, x symbolizes the percentage of Tc and $\Delta E = E_{AFM} - E_{FM}$ shows the lowest amount of energy in the compounds. The noted values of T_c for

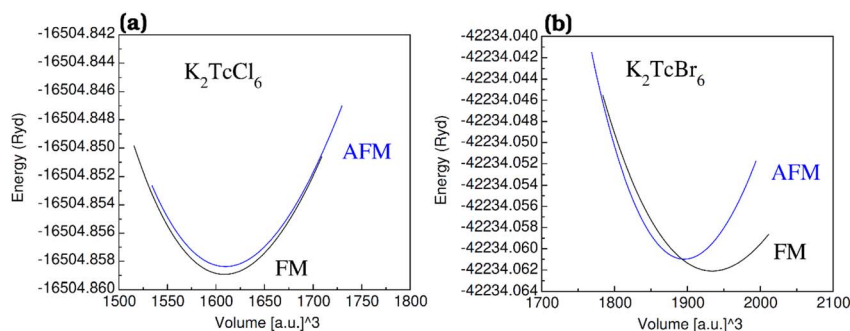


Fig. 2 The energy (in term of Ryd) vs. volume (in term of $[a.u.]^3$) plots of double perovskites (a) K_2TcCl_6 and (b) K_2TcBr_6 in ferromagnetic (FM) and anti-ferromagnetic (AFM) phases.



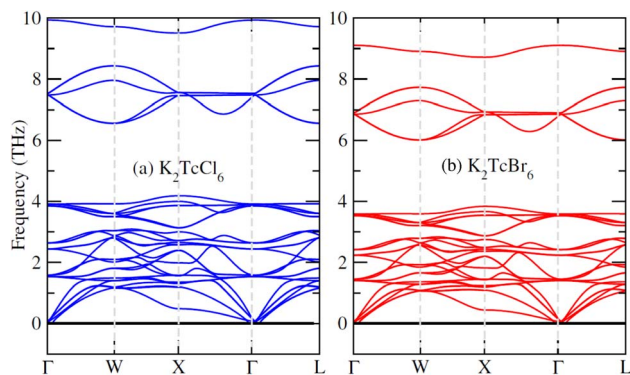


Fig. 3 Calculated phonon band structures for DP (a) K_2TcCl_6 and (b) K_2TcBr_6 .

K_2TcCl_6 and K_2TcBr_6 are 545 K and 505 K. These values confirm the higher-temperature ferromagnetism for the observed compounds. The Curie temperature of $Cs_2Re(Cl/Br)_6$ and $Sr_2Cr(Re/Os)O_6$ are mentioned as 635/725 K in ref. 34. We conducted calculations on phonon band structure and thermal stability for both DP Cs_2TcCl_6 and Cs_2TcBr_6 to assess their stability. The phonon band structures for both compounds are computed and illustrated in Fig. 3a and b. The supercell approach, implemented in the PHONOPY package,⁵¹ was utilized for these analyses. Analyzing the phonon dispersion provides insights into the phonon spectrum's band gaps. Imaginary modes in the phonon spectra signify structural dynamical instability. If the frequencies gained from the phonon spectra are imaginary, the perovskite structure is deemed unstable. In a structurally stable crystal, the absence of imaginary phonon frequencies and continuous phonon dispersion curves without gaps between optical phonon branches are expected. Gaps in these curves suggest an unstable crystal structure, indicating the existence of unrealizable vibrational modes. Such gaps often occur near the zone boundaries in the Brillouin zone and are associated with soft modes, indicating structural instabilities that can lead to phase transitions. The phonon frequencies are significantly influenced by the mass difference between atoms in a crystal lattice, as well as the force constants between the lattice structure and atoms.

3.3 Spin polarized electronic properties and magnetic behavior

The band structure (BS) for spin-down (\downarrow) as well as spin-up (\uparrow) orientations were computed using TB-mBJ potential for illustrating the ferromagnetism and spin polarization for DP K_2TcCl_6 and K_2TcBr_6 (see Fig. 4a and b). Fermi-level (E_F) remains within the insulating region between conduction band (CB) and valence band (VB) of for spin-down (\downarrow) for both DP. On the other hand, the states stay at E_F for K_2TcCl_6/Br_6 in spin-up (\uparrow). Resultantly, our compounds exhibited semiconducting ferromagnetic DP that is assumed a necessary factor in spintronics. Spin-up (\uparrow) channel indicate direct bandgap nature having bandgap values are 3.3 eV and 2.7 eV for K_2TcCl_6 and

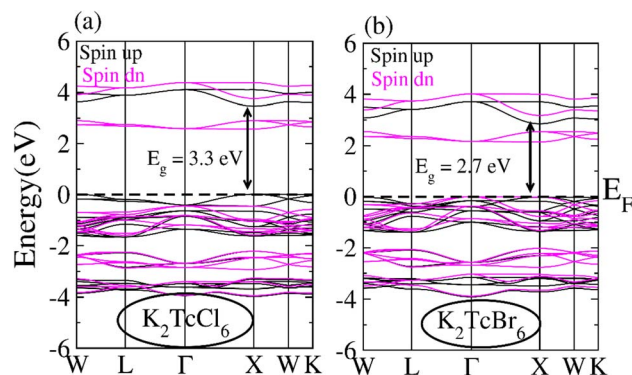


Fig. 4 Band structures calculated for (a) K_2TcCl_6 and (b) K_2TcBr_6 for spin up (black line) and spin down (pink line) using mBJ potential.

K_2TcBr_6 respectively. Both double perovskites studied in this work have earlier been studied with theoretical calculations and have been shown to have band gaps above 1 eV. However, accurate determination of band gap with TB-mBJ functional has not been reported which we have done for the first time. Although no experimental data is available for comparison, our calculated values of band gaps for the two systems are better than those reported by Berri *et al.*,⁵² and materials project database.⁵³ The larger exchange interaction value causes the larger semiconducting gap that ensures the larger ferromagnetism.

Total density of states (TDOS) along with partial density of states of Tc, K and Cl/Br atoms are calculated and represented in Fig. 5 and 6. TDOS also represent the semiconducting ferromagnetic behavior according to spin down (\downarrow) and spin up (\uparrow) calculated DOS. From PDOS, we see a major role of the burly hybridization of 3p/4p-Cl/Br electrons with 4-d states electrons of Tc in justifying the ferromagnetic interface [see Fig. 5 and 6].

The 4d states of Tc are sum of 4d- t_{2g} and 4d- e_g states. The black color from 4d states overlapped by the red and blue color in the plot of the 4d- t_{2g} and 4d- e_g states from which it is confirmed the complete division of the 4d states into degenerated states. The 4d-Tc states are separated in five degenerated states. Three states (d_{zx} , d_{yz} and d_{xy}) out of five degenerate states recombined to triplet- t_{2g} -states. On the other hand, the rest of the two states (d_{z^2} and $d_{x^2-y^2}$) recombined to doublet- e_g -states and lie at the highest energy-states. The hybridization of t_{2g} states with 3p/4p-Cl/Br is found to observe at E_F level in spin-up (\uparrow). While at -3.2 eV, the hybridization of t_{2g} and e_g states was noted with p states of Cl/Br atom both (\downarrow) and (\uparrow) channels. However, the t_{2g} significantly contribute to hybridization with p from -0.4 eV at E_F . Further, there was interaction between t_{2g} states and p states of Cl/Br in (\downarrow), which generated exchange energies ($\Delta(d)$, $\Delta(pd)$) and crystal field energy (Δ_{CF}). The limitations of the studied compounds for ferromagnetism are also known through these energies. The calculation of the Δ_{CF} was performed of the energy differences among degenerated states of Tc by the equation; $\Delta_{CF} = t_{2g} - e_g$. Nevertheless, $\Delta(d)$ was estimated from differences of 4d states of (\downarrow) and (\uparrow) for Tc. The same ($\Delta(d)$) also ensured the existence of ferromagnetism. $\Delta(d)$



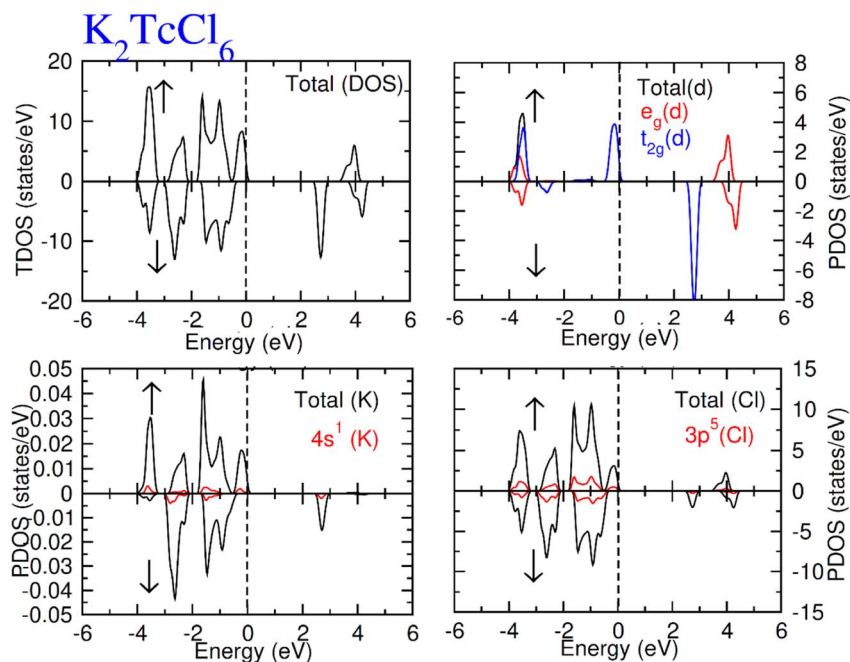


Fig. 5 Total DOS and partial DOS for DP K_2TcCl_6 with K, Tc and Cl atoms in spin up (\uparrow) and spin down (\downarrow).

holding larger value than that of Δ_{CF} (see Table 2) confirms the ferromagnetism in the compounds in hand. The stable ferromagnetism is vilified by the negative value of $\Delta(pd)$, due to lower energy operating through energy forbidden region in (\downarrow).⁵⁴

The major contribution of the partial sub states 3p/4p of Cl/Br, 4d of Tc, and 4s of K is confirmed by the electronic arrangements of Br [Ar] $4s^23d^{10}4p^5$, Cl [Ne] $3s^23p^5$, Tc [Kr]

$4d^55s^2$, and K [Ar] $4s^1$. The band edge splitting at CB and VB caused by the mentioned partially filled states are represented as exchange constants ($N_o\beta$ and $N_o\alpha$). The p-d interactions are attributed to $N_o\beta$ whereas s-d states interactions are related to $N_o\alpha$ by the relation as under:

$$N_o\alpha = \frac{\Delta E_C}{x\langle S \rangle} \quad (2)$$

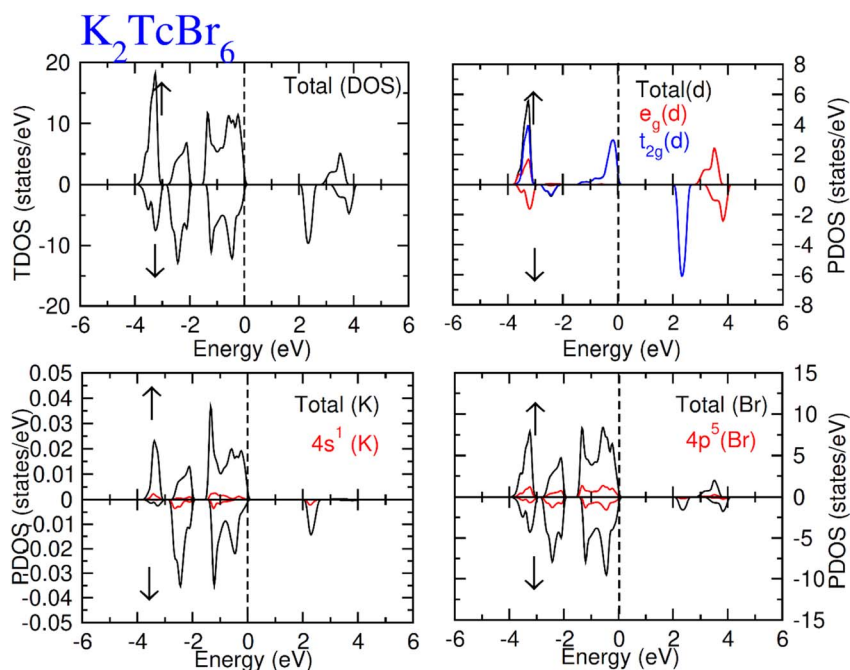


Fig. 6 Total DOS and partial DOS for DP K_2TcBr_6 with K, Tc and Br atoms in spin up (\uparrow) and spin down (\downarrow).



Table 2 Computed crystal field energy, exchange splitting $\Delta_x(d)$, p-d exchange constant ($N_o\beta$) and s-d exchange-constant ($N_o\alpha$) for DPs K_2TcX_6 ($X = Cl, Br$)

| Parameters | K_2TcCl_6 | K_2TcBr_6 |
|------------------|-------------|-------------|
| ΔE_{cry} | 3.2 | 2.9 |
| $\Delta_x(d)$ | 5.4 | 5.0 |
| $\Delta_x(pd)$ | -0.6 | -0.4 |
| $N_o\alpha$ | -0.39 | -0.33 |
| $N_o\beta$ | -0.53 | -0.38 |

$$N_o\beta = \frac{\Delta E_V}{x\langle S \rangle} \quad (3)$$

The ΔE_V is the valence band edge (VBE) difference whereas ΔE_C is the conduction band edge (CBE) difference for (\downarrow) and (\uparrow) channels. x represents the concentration of Tc and $\langle S \rangle$ is symbolized for the value of magnetic moment.^{55,56} $N_o\beta$ remains negative whereas $N_o\alpha$ stays positive for normal wave functions that become just like stationary waves afterwards, which reverts the sign of $N_o\alpha$, by being trapped into deep potential through quantum confinement effect, (see Table 2). The exchange mechanism helps lowering the energy of the compounds while stabilizing the ferromagnetism; hence, the $N_o\beta$ becomes more outstanding for ferromagnetism. Our results show that exchange mechanism is responsible for ferromagnetic interaction for the two double perovskites. This is based on the computed s-d exchange-constant ($N_o\alpha$), p-d exchange constant ($N_o\beta$), exchange splitting $\Delta_x(d)$ and crystal field energy for DPs K_2TcX_6 ($X = Cl, Br$) reported in Table 2.

The role electronic spins in magnetic moment (MM) along FM for K_2TcCl_6 and K_2TcBr_6 is explained in Table 3. The absolute polarization is shown by the integer values of MM. Further, the exchange of electrons spin is confirmed by the electronic shift from Tc to K, Cl/Br. In addition, Tc and MM is increased by the empty places at Tc, which becomes their outstanding properties for spintronics. The solitude electrons configuration along with MM connects neighboring polarized atoms, increasing broad-range FM through RKKY exchange model.⁵⁷ The shift of MM towards nonmagnetic sites (Rb, Cl/Br) from magnetic elements (Tc) is generated by the hybridization between 3p/4p-Cl/Br and 4d-Tc. The ferromagnetism is shown for Cs_2MoCl_6 along with node ring electrons in BS.⁵⁸ The potency of spin-orbit coupling of A_2TaCl_6 because of octahedral of halogen ions and substantial ionicity, $J_{eff} = 3/2$ of 5d was

Table 3 The calculated values of magnetic moments, M for DPs K_2TcX_6 ($X = Cl, Br$)

| Parameters | K_2TcCl_6 | K_2TcBr_6 |
|---------------------|-------------|-------------|
| $M_{tot} (\mu_B)$ | 2.999 | 2.999 |
| $M_K (\mu_B)$ | 0.006 | 0.008 |
| $M_{Tc} (\mu_B)$ | 2.259 | 2.215 |
| $M_{Cl/Br} (\mu_B)$ | 0.061 | 0.056 |
| $M_{Int} (\mu_B)$ | 0.373 | 0.442 |

studied by Ishikawa *et al.*⁵⁹ Consequently, 100% spin polarization is exhibited by the integer values of MM, which is the major contribution of Tc (see Table 3).

3.4 Optical properties

Fig. 7a-f show the elaboration of the optical parameters, which depend on bandgap (BG). These compounds become very imperative for being utilized in optoelectronics just because of having direct BG of ferromagnetic DPs K_2TcX_6 as it limits the de-excitation along with direct electronic transition to CB from VB. In addition, changeability in band gap further formulates them for being employed in a range of other device applications. K_2TcBr_6 and K_2TcCl_6 possessing the values of absorption of light energy 2.7 eV and 3.3 eV for BGs goes down in UV and visible spectrum.^{60,61} The optical parameters have been analyzed in the form of real as well as imaginary parts of dielectric constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$. The polarization and dispersion of light is symbolically and quantitatively measured by $\epsilon_1(\omega)$. Fig. 7a clearly displays its observed value $\epsilon_1(\omega)$ at $\omega = 0$, reaching at 3.9 after increasing from 3.2 when Cl was changed to Br. The increasing value of $\epsilon_1(0)$ due to changing the halide ions causes the reduction in BG from 3.3 to 2.7 exactly satisfying the Penn's model $\epsilon_1(0) \approx 1 + (\hbar\omega_p/E_g)^2$.⁶² The polarization and dispersion of light energy becomes comparatively high due to resonance peaks of the $\epsilon_1(\omega)$ that have different peak sets, as at 4.3/3.0 eV and at 2.5/1.0 eV. The variation in refractive index $n(\omega)$ also changes the speed decay of light while passing through compounds. The behavior of $\epsilon_1(\omega)$ and $n(\omega)$ has also been proven to be alike (see Fig. 7b). The $n(0)$ has been observed through the equation $n(0) = (\epsilon_1(0))^{1/2}$, (see Table 1). The change of anions enhances the values of $n(0)$, however, largely the relation with $\epsilon_1(0)$ remains secured. Further, Krammer-Kronge formulism was used to determine $\epsilon_2(\omega)$ from $\epsilon_1(\omega)$.⁶³ The absorbed light energy in a compound is symbolized by $\epsilon_2(\omega)$. Therefore, its higher value due to huge absorption is believed to be incredible for optoelectronic applications. It obtained value has been displayed in Fig. 7c. Its critical values were recorded as 2.2 eV and 3.2 eV showing the band gap of K_2TcBr_6 and K_2TcCl_6 correspondingly. Similarly, the absorption bands observed for K_2TcBr_6 and K_2TcCl_6 are 2.5 to 3.5 eV and 4.0 to 4.5 eV accordingly. K_2TcBr_6 is certified by the recorded bands for visible regions and K_2TcCl_6 for UV as well. The absorption bands were also formed by the electronic transitions at 3.8 eV onwards, 3.0 to 4.0 eV and 4.2 to 4.8 eV. However, generally the first absorption bands are strongly preferred for optoelectronics.

Fig. 7d shows the recorded values of absorption coefficient $\alpha(\omega)$. A similar trend of $\alpha(\omega)$ as that of $\epsilon_2(\omega)$ was found to observe. It was so because the both ($\alpha(\omega)$ and $\epsilon_2(\omega)$) have representation of absorption of light. There is also a bit over-estimation in the obtained values of absorptions and optical bands gap due to DFT. When Cl is replaced by Br, the absorption bands move towards lower energy. The modeling of band gap causes this shift towards lower values. The $k(\omega)$ represents to be the fictional of refraction as $\epsilon_2(\omega)$. It represents the decayed part of light energy (see Fig. 7d). In addition, it has two



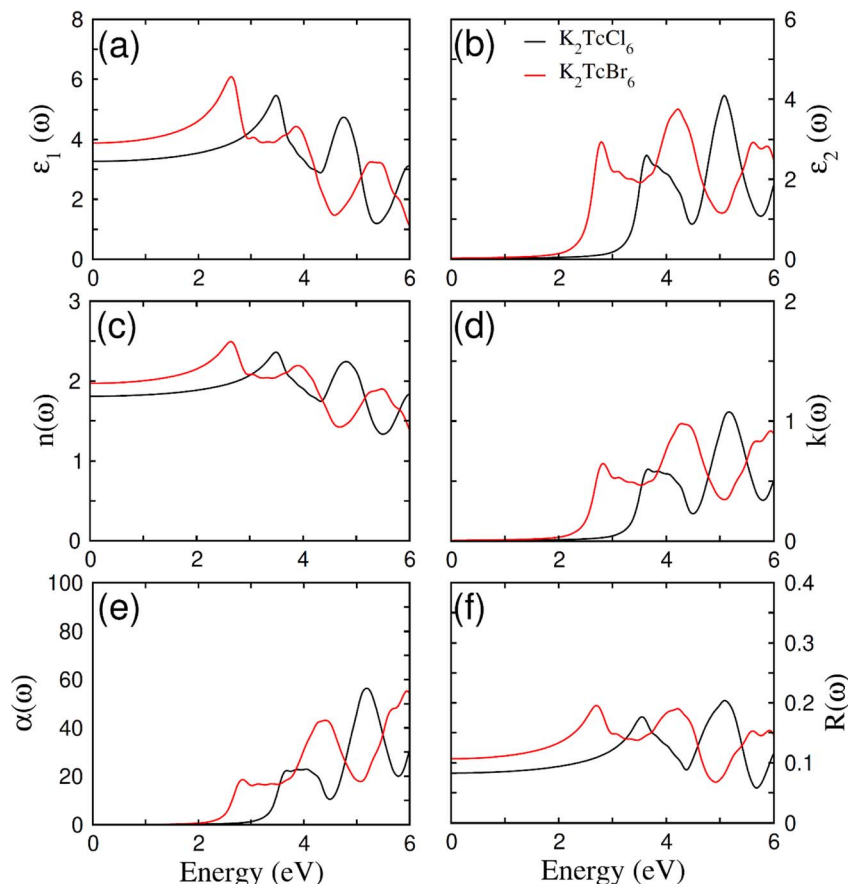


Fig. 7 The calculated (a) real part $\varepsilon_1(\omega)$, (b) imaginary part $\varepsilon_2(\omega)$, (c) refraction $n(\omega)$, (d) extinction co-efficient $k(\omega)$, (e) absorption $\alpha(\omega)$, (f) reflectivity $R(\omega)$ of DPs K_2TcCl_6 and K_2TcBr_6 .

consecutive sets of peaks; the first one at 2.8/4.4 and the second one at 3.6/5.2 for Br/Cl correspondingly. The obtained values proved to be in accordance with $\varepsilon_2(\omega)$ and $\alpha(\omega)$.⁶⁴ The reflected part of energy from the surface of the compound is known as reflectivity $R(\omega)$. Its frequency dependent value and static value $R(0)$ have been expressed in Fig. 7f. Its static value $R(0)$ started increasing by replacing the Cl with Br. The uppermost peak value of $R(\omega)$ remained below 0.21 that was much smaller as compared with the absorption of light energy in the compounds.

3.5 Thermoelectric properties

Thermoelectric features are generally investigated for the better understanding of their effects on thermoelectric performance and electronic spin in specific compounds. Any thermoelectric compound is believed to possess heavier elements to restrain the phonons transport.^{65,66} The ideal thermoelectric compounds also possess ultralow thermal conductivity (κ_e), electric conductivity (σ), and extensive Seebeck coefficient (S). The temperature limit for the computed parameters is from 200 K to 800 K. In this regard, power factor (σS^2) was computed to assay the performance of DPs K_2TcCl_6 and K_2TcBr_6 . In accordance with the classical Boltzmann theory, the collision rate of time for electronic gas was set as 10^{-14} s. Thus, the division of

the κ_e and the σ was taken in terms of 10^{-14} s [see Fig. 8a–f]. The combination of all three parameters (κ_e , σ , S) for (\downarrow) and (\uparrow) is taken by the following equation:⁴⁷

$$\kappa = \kappa(\uparrow) + \kappa(\downarrow)/2 \quad (4)$$

$$S = S(\uparrow)\sigma(\uparrow) + S(\downarrow)\sigma(\downarrow)/\sigma(\uparrow) + \sigma(\downarrow) \quad (5)$$

The above written relation shows the means of the both spin formations. Fig. 8a shows the computed values of σ . There is a difference between the thermoelectric factors of Tc based double perovskites as Tc possesses the electrons in odd numbers (5) in 4d orbitals. Its values increases at 200 K and 800 K from $0.6/0.3 \times 10^{19}$ ($\Omega^{-1} \text{ m}^{-1} \text{ s}^{-1}$) to $0.9/1.6 \times 10^{19}$ ($\Omega^{-1} \text{ m}^{-1} \text{ s}^{-1}$) respectively. The values of σ are more for Br based DPs than that of Cl based DPs at 400–800 K. It is so because the free carriers are increased in numbers by increasing the size of ions. Quite contrary to the values of σ , the κ_e starts increasing at 200 K to 800 K from $0.4/0.5 \times 10^{14}$ $\text{W m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$ to $1.9/5.5 \times 10^{14}$ $\text{W m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$ for $\text{K}_2\text{Tc}(\text{Cl}/\text{Br})_6$. It is so because the lattice disturbance and the flow of carriers is increased by thermal effect (see Fig. 8c). Here, due to the restrictions of classical theory of Boltzmann, the merely electronic contribution to thermal conductivity was investigated whereas we could not



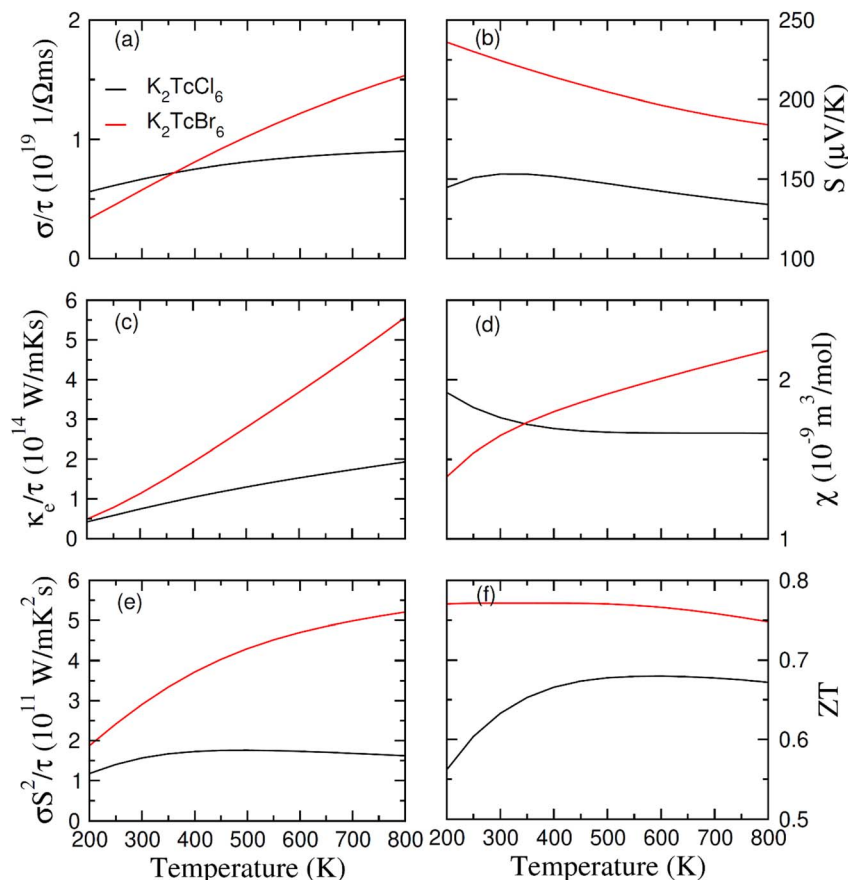


Fig. 8 The computed (a) electrical conductivity (σ/τ), (b) thermal conductivity (k_e/τ), (c) Seebeck coefficients (S), (d) specific heat capacity (C_v), (e) power factor and (f) figure of merit against temperature for DPs K_2TcCl_6 and K_2TcBr_6 .

touch the lattice disturbance. The comparison of σ and κ_e was performed through the κ/σ that is set as 10^{-6} in order to evaluate the relative effect.⁶⁷ The ultralow values of κ_e provide the room for the compounds to be the best for spintronic and thermoelectric projects.

The potential gradient for thermoelectric measured through S is presented in Fig. 8b. The value of S became positive for $K_2Tc(Cl/Br)_6$ at 200–800 K, showing the p-type character. With increasing temperature from 200 K to 800 K, the values of S reduced from 148/230 mV K⁻¹ to 130/180 mV K⁻¹ for $K_2Tc(Cl/Br)_6$. The variation of the susceptibility of $K_2Tc(Cl/Br)_6$ as depicted in Fig. 8d, manifest an opposite trend. For K_2TcCl_6 , the value of χ decreases up to 400 K then becomes constant to reach approximately value of $1.6 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ at 800 K. For K_2TcBr_6 , the value of χ increases steadily up to 800 K then attains almost a steady approximately value of $2.3 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$.

From the analysis of the computed values of power factor (PF) (see Fig. 8e), it is clear that its values are lowest for K_2TcCl_6 and highest for K_2TcBr_6 . Therefore, Br based DP is believed to be more suitable for being used in thermoelectric device applications as compared with the Cl based DP. Additionally, the PF, mathematically equivalent to σS^2 , is calculated consequently, by utilizing these Seebeck coefficients in conjunction

with the structural factor, one can determine the figure of merit, which fundamentally characterizes the efficacy of any thermoelectric material. When calculating the thermal efficiency (ZT) (see Fig. 8f), it exhibited a pattern similar to that of PF, for both studied DPs. This underscores the potential of both DPs as promising thermoelectric materials for a wide array of thermoelectric purposes.

4. Conclusion

To sum up, we have conducted a systematic evaluation of ferromagnetism and its impact on the functionality of electrons in the double perovskites (DPs) K_2TcY_6 ($Y = Cl, Br$) with the aim of exploring their potential applications in energy harvesting and spintronic devices. Primarily, our examination of cubic spinel structures of the investigated double perovskites in both ferromagnetic (FM) and antiferromagnetic (AFM) states has affirmed that with higher energy release the FM states are more energetically stable. Their structural and thermodynamic stability in FM states has also been corroborated by the tolerance factor and formation energy assessment. Moreover, the Heisenberg model corroborates that Tc remains above room temperature, while the larger exchange-energies in comparison to crystal field energy, coupled with the double exchange model,



point towards the presence of ferromagnetism resulting from spin functionality and hybridization, as opposed to clustering. The prevailing negative exchange-constants exert a significant influence through the quantum confinement effect, effectively confining the electron wavefunction within a deep potential well. This negative pd exchange-interaction, coupled with the shift of magnetic moments from Tc to the K and Cl/Br sites, is a result of exchange mechanism that reduces the system's energy and bolsters the stability of ferromagnetism. From our results it can be seen that the band gaps of K_2TcBr_6 and K_2TcCl_6 are 2.2 eV and 3.2 eV, respectively. Since these values are in the UV region, one can expect these materials to be suitable for optical devices operating in UV region of electromagnetic spectrum. Absorption spectra have been observed in both the UV and visible regions for double perovskites containing Cl and Br anions. Furthermore, the presence of unpaired electrons in Tc enhances electrical conductivity and the performance of K_2TcBr_6 -based double perovskites surpasses that of K_2TcCl_6 -based DP. Moreover, our computed properties exhibit semi-conducting ferromagnetic DPs that is assumed a necessary factor in spintronics devices.

Conflicts of interest

There are no conflicts to declare.

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