Double perovskites with 3d and 4d/5d transition metals: compounds with promises

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Abstract

Double perovskites, which can host two different transition metal cations at the B-sites of its perovskite derived structure, provide the possibility to explore the interplay of localized 3d transition metals and the relatively delocalized 4d or 5d transition metals within the same structure. This interplay gives rise to extraordinary magnetic properties. In this overview article, we summarize our recent computational efforts in understanding the curious properties of magnetic double perovskites with 3d and 4d/5d transition metal ions, make predictions on new functionalities in known compounds of this family, engineering functionalities via chemical modifications/doping and prediction on a new set of magnetic 3d-4d/5d double perovskite compounds, which may be synthesized to explore and expand further this interesting family.

1. Introduction

Double perovskite compounds in the recent time, have attracted an increasing amount of attention due to their fascinating properties and possible applications [1, 2]. Double perovskite structures can be derived out of simple perovskite structure of general formula ABO$_3$, which is well known for exhibiting wide range of interesting properties. Due to the structural and compositional flexibility of the perovskite structure, perovskites can accommodate almost all of the elements of the periodic table [3]. With an aim to tailor properties further, one of the common route is cation substitution. Double perovskite structure is formed when exactly half of B site cations is replaced by another B' cation, and a rock salt ordering between these two is achieved [4]. As schematically shown in figure 1, this results in doubling of the formula unit of perovskite structure, making it A$_2$B$_2$O$_6$, where one of the B in the formula is replaced by B', giving rise to the A$_2$BB'O$_6$ formula. Double perovskite compounds with possible presence of two different transition metal (TM) elements at B sites (B, B') and possible presence of even two different rare-earth and alkaline earth elements at A sites, offer even better flexibility and degrees of freedom to play around, compared to simple perovskite structure with one A cation and one B cation sites [2]. A large number of studies exist in literature consisting of double perovskite halides, nitrides, sulfides and hydroxides [3]. Also, as mentioned above, even the A site can host two different A-site cations, with the formula AA'BB'O$_6$, named as doubly ordered perovskite [5], or double-double perovskite. Other than 1:1 ordering, one may even have 3:1 ordering giving rise to quadrupolar perovskite structure [6]. Even restricting only to double perovskite structures of formula A$_2$BB'O$_6$, as clearly understood, several different cation combinations are possible. So far, about a thousand double perovskite compounds have been synthesized, with A site being occupied divalent cations like Sr, Ca or Ba (some rare cases of Pb or Cd) and trivalent cations like La [2]. This leaves a large choices also at B site, with an average oxidation state of 4+ at B site for choice of divalent A cation and average oxidation state of 3+ at B site for choice of trivalent A cation. This basically covers all the cations in the periodic table as a possible candidate for B site in a double perovskite structure. For a concise review, see [2].

Within the limited scope of the present review, we restrict ourselves to A$_2$BBO$_6$ double perovskites with choice of divalent cations Sr, Ca, and Ba at A site, and 3d and 4d or 5d transition metals ions at B and B' sites, respectively. We discuss the theoretical attempts within the framework of ab-initio density functional theory,
coupled with solution of model Hamiltonian derived based on \textit{ab-initio} inputs, applied to understanding and predictions on these magnetic compounds. The primary goal in these studies was to understand and tailor the fascinating magnetic properties of these compound. With this goal in mind, we start with discussions on the mechanisms of the magnetism that is found to be operative in a large class of 3\textit{d}-4\textit{d}/5\textit{d} double perovskites [8, 9]. Following this, we discuss the predictions on applicability of these compounds as promising candidate materials for magneto-optic applications [10]. We further show, starting from already synthesized double perovskite compounds, reported in literature, by substitution of divalent A cation by trivalent or monovalent A cations, it is possible to drive novel magnetic states like antiferromagnetic metallic state [11], or high T\textsubscript{c} half-metallic state [12]. We also show that replacement of divalent A cations by combination a monovalent and trivalent A cations in AA\textsuperscript{'}BB\textsuperscript{'}O\textsubscript{6} double double perovskite structure, it may be possible to achieve room temperature multiferroicity [13]. We also discuss the possible impact of disorder, namely the anti-site disorder in the interesting magnetic properties of these compounds, as all sythesized compounds are subject to such disorder [14]. Finally using multi-pronged tools of machine learning combined with genetic algorithm and density functional theory, we make prediction on synthesis, and properties of 3\textit{d}-4\textit{d}/5\textit{d} double perovskite compounds, which are yet-to-be synthesized [15]. We do hope that review of these theoretical reports will motivate future experimental studies in terms of synthesize of new magnetic double perovskites, tailoring of properties of known double perovskites, and search of new properties in known compounds.

2. Magnetism in double-perovskites—mechanisms

The mechanism of magnetism in double perovskite (DP) compound was heavily discussed in context of Sr\textsubscript{2}FeMoO\textsubscript{6}, which till date is perhaps the most studied member in the double-perovskite family. This compound shows large magnetoresistance effect with a fairly high ferromagnetic transition temperature of about 410 K [16], opening up the possibility of designing spintronics materials operating at room temperature. Given the fact that in the crystal structure of Sr\textsubscript{2}FeMoO\textsubscript{6}, which consists of corner-shared FeO\textsubscript{6} and MoO\textsubscript{6} octahedra alternating in all three directions, the magnetic ions in the structure, namely Fe ions are separated by essentially non-magnetic MoO\textsubscript{6} units, the observed high magnetic transition temperature of 410 K is unusually high and counter-intuitive. Furthermore, within the conventional super-exchange mechanism between two Fe\textsuperscript{3+} ions in their d\textsuperscript{5} valences via the O-Mo-O path is expected to be antiferromagnetic rather than ferromagnetic. The observed unusual behavior was rationalized [8] in terms of kinetic energy driven mechanism, which induces a negative spin-polarization in otherwise nonmagnetic site, through symmetry and spin-conserved hybridization between the spin-split states of magnetic ion and nonmagnetic ion. This mechanism becomes operative when the energy states of nonmagnetic ion fall within the energy window of the
spin-split levels of magnetic ion, as shown schematically in figure 2(A). This mechanism originally proposed for Sr$_2$FeMoO$_6$ [8], is found to be applicable in a number of other 3d-4d/5d based double perovskites including Sr$_2$CrWO$_6$ [9], Sr$_2$FeReO$_6$ [9], Ba$_2$FeReO$_6$ [17] etc. Figure 2(A) shows the energy levels of Cr and W crystal field and spin-split d orbitals, in absence of hybridization, and the renormalized energy level positions of W t$_{2g}$ states upon switching on the hybridization between Cr and W, for the specific example of Sr$_2$CrWO$_6$. The strong hybridization between Cr and W states, as evidenced in the plot of effective W Wannier function taking into account Cr-W hybridization, pushes the W t$_{2g}$ down spin states down and the W t$_{2g}$ up spin states up, resulting in an effective spin splitting at W site which is oppositely oriented to the intrinsic spin splitting at Cr site. This mechanism can be mathematically formulated in terms of a two sublattice double-exchange model [18], consisting of large core (classical) spin at magnetic site, strong coupling at the magnetic site between the core spin and the itinerant electron, and delocalization of the itinerant electron on the B-B’ network, expressed as,

\[
H = \epsilon_p \sum_{i \in B} f_{i\sigma} f_{i\sigma} + \epsilon_{p'} \sum_{i \in B'} m_{i\sigma} m_{i\sigma} - t_{B B'} \sum_{(ij), \sigma, \alpha} f_{i\sigma, \alpha} m_{j\sigma, \alpha} - t_{B B'} \sum_{(ij), \sigma, \alpha} m_{i\sigma, \alpha} f_{j\sigma, \alpha} + \frac{1}{2} \sum_{i \in B} S_i \sum_{\mu, \nu} \sigma_{i\mu} f_{i\mu} f_{i\nu}
\]

where f’s refer to B sites and m’s refer to B’ sites. $t_{BM}$ represent the nearest neighbor B-B’ hoppings. $\sigma_{\mu}$ is the Pauli spin matrix and $\alpha$ is the orbital index that spans the relevant d manifolds of B and B’. The difference between the levels of B and B’, $\varepsilon_{p} - \varepsilon_{p'}$, denotes the charge transfer energy. $S_i$ are ‘classical’ (large S) core spins at the B site, coupled to the itinerant electrons through a coupling $J \gg t_{BM}$.

This picture gets modified in case of double perovskites like Sr$_2$CrReO$_6$, Sr$_2$CrOsO$_6$ [9], Sr$_2$CrMoO$_6$ [19], for which an intrinsic spin polarization is present at B’ site, which provides an extra super-exchange contribution in addition to above mentioned two sublattice double exchange contribution. As shown schematically in figure 2(D), in these case, even before switching on the hybridization between B and B’ (Cr and Os in the example

\[
\begin{align*}
H &= \epsilon_p \sum_{i \in B} f_{i\sigma} f_{i\sigma} + \epsilon_{p'} \sum_{i \in B'} m_{i\sigma} m_{i\sigma} - t_{B B'} \sum_{(ij), \sigma, \alpha} f_{i\sigma, \alpha} m_{j\sigma, \alpha} - t_{B B'} \sum_{(ij), \sigma, \alpha} m_{i\sigma, \alpha} f_{j\sigma, \alpha} + \frac{1}{2} \sum_{i \in B} S_i \sum_{\mu, \nu} \sigma_{i\mu} f_{i\mu} f_{i\nu} \\
&\quad + \frac{1}{2} \sum_{i \in B'} S_{i'} \sum_{\mu, \nu} \sigma_{i'\mu} f_{i'\mu} f_{i'\nu}
\end{align*}
\]
of Sr$_2$CrOsO$_6$), there exists an intrinsic spin splitting at B’ (Os) site (compare figures 2(A) and (D)) which gets further enhanced upon switching on the hybridization between B and B’. The two scenarios in presence of band structure effect in crystal, which broadens the energy levels into bands with finite band widths, represented schematically as semi circular density of states, are shown in figures 2(C) and (F). Figures 2(B) and (E) show the effective Wannier functions of the renormalized t$_{2g}$ orbitals at B’ site, whose tails are shaped according to hybridizing B site t$_{2g}$ degrees of freedom, the head parts being shaped according to t$_{2g}$ symmetry of B’ site. Comparing figures 2(B) and (E), we find that B-B’ hybridization gets weakened in the situation with intrinsic spin splitting of B’.

The general spin Hamiltonian explaining the mechanism of magnetism in 3d-5d DPs which captures both scenarios can be expressed as,

$$H = \sum_{\langle i,j \rangle, \sigma, \alpha} m_{i\sigma, j\sigma} - t_{BB'} \sum_{\langle \langle i,j \rangle, \sigma, \alpha \rangle} f_{i\sigma, \alpha} f_{j\sigma, \alpha} + J_B \sum_{i \in B} S_i \cdot S_j,$$

where, the last term incorporates the superexchange interaction between the intrinsic spin residing at B’ site and the core spin at B site. While this term is non-zero for compounds like Sr$_2$CrReO$_6$, Sr$_2$CrOsO$_6$ [19], it is zero for compounds like Sr$_2$FeMoO$_6$ [8], or Sr$_2$CrWO$_6$ [9], Ba$_2$FeReO$_6$ [17]. We note the above model Hamiltonian does not take into account the effect of spin-orbit coupling present at 4d/5d TM sites. While spin-orbit is crucially important in explaining the specific properties of these compounds, as is the case discussed for magneto-optic properties in section 3, in explanation of magnetic or conducting properties spin-orbit does not play the vital role, and thus neglected for the model constructed describing magnetic and electronic properties. The discussed compounds are therefore qualitatively different from recently discussed Ir based oxides, in which spin-orbit brings in dramatic change in electronic behavior like driving insulating state [20]. The effect of spin-orbit coupling in the presently discussed metallic systems, except for the case of Sr$_2$CrOsO$_6$ which is a slater insulator, gets strengthened due to the three dimensional connectivity between 3d TM site at B and 4d/5d TM sit at B’. The results are thus found to be qualitatively correct to a first–approximation even without explicit inclusion of spin-orbit term in the model Hamiltonian used in sections 4 or 7.

3. Candidate materials for magneto-optic applications

Magneto–optic Kerr effect (MOKE) is utilized to read digitalized informations stored in magnetic or magnetized materials [21]. This phenomena uses the fact that light can interact with a magnetic material if there is a finite spin–orbit coupling (SOC) inherent in the material [22]. The presence of large spin–orbit coupling at 4d/5d TM site of B’, together with high magnetic transition temperature, thus make 3d-4d/5d DPs as ideal candidates as read heads in optical data storage devices. Motivated by possible interesting magneto–optical properties of 3d-5d DPs with potential technological applicability, the magneto–optic properties of Sr$_2$CrB’O$_6$ (B = W, Re, Os) were explored by computing reflectivity, optical conductivity, magneto-optic spectra like polar Kerr and Faraday spectra [18]. figure 3(A), shows the density of states of Sr$_2$CrB’O$_6$ (B = W, Re, Os) as computed within the choice of generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) [23] formulation for the exchange-correlation within density functional theory along with SOC. The various possible optical transitions have been also marked, which shows low-energy d-d transitions, permitted due to finite d–p hybridization, and d-p transitions at relatively higher energies. The calculated Kerr and Faraday rotations computed for the series (cf figure 3(B)) show that Sr$_2$CrWO$_6$ and Sr$_2$CrReO$_6$ should exhibit large rotations of 2–3 degree in the visible range. Sr$_2$CrOsO$_6$ which shows an optical gap of about 0.6 eV, shows a Faraday rotation of $-0.25 \times 10^6$ degree/cm at about 1 eV. The rather large computed value of Kerr rotation of 2.7 degree in case of Sr$_2$CrWO$_6$, should make them suitable for industrial application in terms of having even better performance compared to predictions made for ferromagnetic Sr$_2$FeMoO$_6$ and antiferromagnetic Sr$_2$FeWO$_6$ [24].

4. Curious case of antiferromagnetic metallic double perovskites

As is conventionally known, ferromagnets are metals and antiferromagnets are insulators. There are exceptions to this conventional knowledge. For example, there are reports of ferromagnetic insulators like EuO [25], CdCr$_2$S$_4$ [26], SeCuO$_2$ [27], La$_2$NiMnO$_4$ [28], La$_2$CoMnO$_4$ [29]. Reports of antiferromagnetic metals are even more rare, apart from some antiferromagnetic elemental metals like Cr, reported primarily in case of compounds, with reduced electronic and structural dimensionality, e.g. (La/Sr)$_2$Mn$_2$O$_7$ or Ca$_2$Ru$_2$O$_7$ [30], and only one in case of three-dimensional transition metal oxide, namely CaCrO$_3$ [31]. The prediction [11] of doping driven transition from ferromagnetic to antiferromagnetic metallic state in La doped Sr$_2$FeMoO$_6$, which
subsequently have been confirmed experimentally through magnetic and spectroscopic measurements, therefore was unexpected [32]. A combination of first-principles density functional calculation and exact diagonalization of low-energy Fe-Mo model Hamiltonian was used to explore the effect of La doping in Sr₂FeMoO₆ [11]. Figure 4(A), shows the stability of the G-type and A-type antiferromagnetic (AFM) alignment of Fe spins with respect to that of ferromagnetic alignment of Fe spins. La doping in place of Sr in Sr₂FeMoO₆ causes electron doping. The undoped Sr₂FeMoO₆, with Mo⁵⁺ in its d¹ valence state has one conduction electron. La doping increases the number of conduction electron, being three in case of fully doped situation of La₂FeMoO₆. As is seen from the plot, beyond a critical concentration of La (estimated to be La fraction of 0.8 at A site, corresponding to conduction electrons ∼2.6) a transition from ferromagnetic to antiferromagnetic state happens. Interestingly, the driving mechanism of magnetism being the hybridization-driven mechanism, as explained in section 2, this antiferromagnetic state is metallic, as opposed to super-exchange driven magnetism which results in insulating solutions. The calculated ferromangetic, and antiferromagnetic transition temperatures are plotted figure 4(B). As is seen, upon La doping the ferromagnetic Tc drops down, and finally becomes zero. The antiferromagnetic Néel temperature, TN, on other hand, rises upon suppression FM Tc, and reaches a maximum for La₂FeMoO₆. A co-existence region is observed around the critical doping region, suggesting complex magnetic behaviour due to competing ferro and antiferro interactions.

This curious behavior can be rationalized in the following manner. Figures 4(C) and (D), show the schematic representation of ferromagnetic and antiferromagnetic density of states, respectively. The ferromagnetic density of states of Sr₂FeMoO₆ shows highly localized Mo t₂g states in the up spin channel, situated above Fermi level (E₀) and separated from the Fe d states (not shown the figure), while in the down spin channel, the Fe t₂g - Mo t₂g strongly hybridized state crosses E₀, resulting in a half-metallic situation. Upon La doping, the Fermi level moves towards higher energy in a rigid band fashion, due to increase in number of conduction electrons, until it hits the localized Mo t₂g states in the up spin channel. Instead of populating the localized Mo t₂g up spin states, it then becomes energetically favorable to become antiferromagnetic, for which the corresponding Fermi level lands in the minimum of its three-peaked structure. Creation of two Fe sublattices in the AFM phase (marked as red and blue in inset of figure 4(D)), restricts the hopping of Mo (sites with empty symbols in the figure) electrons to a reduced dimensionality, as Mo electrons can only hop to Fe’s having their spins oriented to Mo electron spins.
manifested as three-peaked density of states with characteristic features of van Hove singularities. This, however, allows Mo electrons in both spin channels to conduct in the AFM case, as opposed to FM case at critical doping concentration, for which the highly localized up spin state would get populated, resulting in a loss in hybridization energy. The filling driven FM to AFM, thus is a general feature of hybridization-driven mechanism of magnetization, as has been established in several model calculations \[33\]. Following, this expectation in recent time metallic antiferromagnetism has been predicted in yet-to-be synthesized Sr$_2$FeRhO$_6$ and Ca$_2$FeRhO$_6$ \[34\].

5. engineered half-metallicity with high $T_c$

For practical usage, it is desirable to have magnetic materials operational at room temperature. However, the demagnetization effect can restrict the usage of even magnetic materials having transition temperatures around room temperature. One should thus look for magnetic materials with technologically important properties.
having transition temperatures much higher than room temperatures. One such class of technologically important magnetic materials is that of half-metals with conducting electrons in one spin channel and insulating in the other, which have been heavily discussed for spintronics applications. With a goal to achieve high temperature half metals having $T_c$ much higher than room temperature, La and No doping of $\text{Sr}_2\text{CrOsO}_6$ double perovskites were proposed. $\text{Sr}_2\text{CrOsO}_6$ is a ferrimagnetic insulator with transition temperature of 725 K, one of very high ones ever known among the perovskite oxides. Na and La doping in $\text{Sr}_2\text{CrOsO}_6$ cause hole and electron doping of the Os t$_{2g}$ states, respectively, as shown in figures 5(A) and 5(B), respectively. As a result of that, starting from the insulating, compensated ferrimagnetic solution in absence of SOC, of undoped $\text{Sr}_2\text{CrOsO}_6$, the down spin Os t$_{2g}$ states gets depopulated from its t$_{2g}$ occupancy upon Na doping, resulting into partially filled bands in down spin channel, with empty Os t$_{2g}$ states in up spin channel, Cr t$_{2g}$ states being filled and empty in up and down spin channels, respectively. Similarly, La doping populates the empty Os t$_{2g}$ states in the up spin channel, giving rise to conducting states in the up spin channel, while the down spin channel remains insulating with filled Os t$_{2g}$ states. Both La and Na caused increase in net moment (cf figures 5(C) and 5(D)), with a maximum value of 1 $\mu_B$ and 0.7 $\mu_B$ for 18.75% of Na and 18.75% of La doping, respectively, the maximum doping value of Na and La that were considered in the study. The calculations carried out including spin-orbit coupling, showed that the qualitative results including the half-metallicity achieved by Na/La doping remained intact. The tiny orbital moment (M$_{z}$) developed at Cr site, remained more or less unchanged upon doping of Na or La. The orbital moment was found to point oppositely to spin moment (M$_{s}$) for the parent as well as Na doped compounds, with nominal filling of Os being t$_{2g}$ or less. On the other hand, La doping makes

**Figure 5.** The change of electronic valences of Cr and Os upon Na [(A)] and La doping [(B)] of $\text{Sr}_2\text{CrOsO}_6$ double perovskite. The small arrows denote partial occupancies at Os sites. [(C)-(D)] The net magnetic moment of Na and La doped $\text{Sr}_2\text{CrOsO}_6$. The filling at Os site decreases from 3 upon Na doping and increases from 3 upon La doping. The moment of the undoped compound is shown with a red circle. The energy difference between the ferromagnetic and paramagnetic alignment of Cr spins [(E)] and calculated spin-polarization for different dopings of Na and La [(F)]. Different doping concentrations of Na and La doping have been marked with vertical lines. Reproduced from [12]. CC BY 4.0.
nominal filling of Os larger than $t_{2g}$ with orbital moment at Os site pointing in the same direction as the spin moment. Interestingly, the ratio $M_s/L_s$ which is considered to be a maker for importance of spin-orbit coupling was found to be much less than 1 at Os site, stressing once more the spin-orbit though non-negligible is not the deciding factor for the description of the physical/chemical properties of the compounds.

The computed $T_c$ obtained from the energy difference between paramagnetic and ferromagnetic alignment of Cr spins, calculated by solving the Cr-Os model Hamiltonian using exact diagonalization (cf figure 5(E)) showed that doped compounds are expected to retain the high $T_c$ property of the undoped Sr$_2$CrOsO$_6$, estimated to be 87 to 99% of $T_c$ of the undoped compound. The calculated degree of spin polarized also turned out to be high, as shown in figure 5(F), enforcing the possible potential use of these doped double perovskites as high $T_c$ half-metals.

6. Designing of multi-ferroicity in double perovskites

Multiferroics with co-existing ferromagnetic and ferroelectric long range order are materials of high technological importance [36]. In spite of a huge surge of activity in this field, the number of materials that are useful from technological point of view are still limited. This is primarily due to scarcity of compounds that can act as possible candidates for search of multiferroics. These materials should be ferro or ferrimagnetic insulators with appreciable value of uncompensated moment exhibiting high transition temperature.

Double perovskite compounds hold promise as starting materials for such exploration, as many of the members in this family show high magnetic transition temperature. Specifically, as discussed above, Sr$_2$CrOsO$_6$ is a ferrimagnetic insulator with $T_c ∼ 725$ K [34] which is the highest $T_c$ magnetic insulator with uncompensated spin moment, known so far. This is remarkable as most known ferromagnetic insulators like EuO, CdCr$_2$S$_4$, SeCuO$_3$ are low $T_c$ [25–27]. It will be of great technological advancement, if this compound can be made ferroelectric as well. Along this line of thought, theoretical study has been carried out [37], on computer designed double perovskites, consisting of 3d-5d B-B’ combination like MnRe or NiRe to achieve high-temperature magnetism combined with insulating behavior and introducing lone-pair active cations like Bi on the A sites to induce polarizability. However, the constructed structures were found to be antipolar with net zero polarization [38].

In another possible route, a coupling between polarization and rotational modes of BO$_6$ octahedra has been proposed [39], where ferroelectricity can develop from the combination of two lattice rotations, neither of which produces ferroelectric properties individually and this mechanism has been defined as ‘Hybrid improper ferroelectricity’ (HIF). Following this proposal, the double perovskite compound, NaLaMnWO$_6$ was synthesized and calculations [40, 41] established that while the common tilting instabilities of MnO$_6$ and WO$_6$ octahedra yield non-polar phases, the additional presence of the Na and La ordering is sufficient to make these rigid unit modes as a source of the ferroelectricity. However, NaLaMnWO$_6$ is an antiferromagnet with rather low $T_c$ of ∼10 K and therefore, not of much technological significance.

Study by Das et al [13] showed that considering Sr$_2$CrOsO$_6$, through a choice of combination of (A/A’) cations in place of Sr, it is possible to achieve materials with robust insulating properties, uncompensated sizable moment and switchable polarization, keeping the good magnetic transition temperature properties of the pristine compound intact.

There are three known patterns of ordering between A and A’ cations that are possible in a AA’BB’O$_6$ double perovskite with rock-salt ordering at B-site, namely layered, columnar and rock-salt, as shown in figure 6(A). The $a - a - c +$ type rotations of B-site octahedra was shown to induce polarization in layer and rock-salt AA’ arrangements, while the columnar phase was predicted to centro-symmetric. Graham King et al [41] proposed an electronic route to stabilize the layered phase, in presence of second order Jahn–Teller (JT) active d$^3$ ions at one of the B-sites, which was demonstrated in NaLaMnWO$_6$ (L = La, Nd, Tb) systems, where W is in $6^+$ oxidation state, thus has 5d$^3$ valence [38]. The d$^3$ electronic structure of W$^{6+}$ however reduces the strength of magnetic interactions between Mn$^{2+}$ ions, which in turn decreases the magnitude of the magnetic transition temperature. Therefore development of alternate route to stabilize the layered phase is the key to design new high-temperature bulk double ferroptics multiferrics.

With the above view in mind, starting from Sr$_2$CrOsO$_6$, a set of A-A’ combinations were considered with choice of monovalent ion at A site and trivalent ion at A’ site, so as to maintain the average divalent configuration at A-site [13]. This would guarantee that the valences and the electronic/magnetic properties at B sublattice will remain intact as in parent compound, Sr$_2$CrOsO$_6$. Figure 6(B) shows the energy comparison for a number of A-A’ combinations, considering the choice of Na or K at A site and a range of trivalent rare-earth cations at A’ site. As is seen, depending of the ionic radius difference between A and A’, and the tolerance factor, one is able to stabilize the layered ordering of A-A’ and a non-centrosymmetric polar space group for A-A’ combinations of K-Sm, K-Gd, K-Dy, K-Y, K-Tm. The calculated total uncompensated moment, polarization, and the energy...
shown in case of ordered domains or patches of situation gets further complicated by the fact that such anti-site disorder can be of correlated nature, in which generating defect pairs of B-B and B′-B′ perovskites is anti-site disorder. In case of anti-site disorder, the position of B and B′ natural to occur during the synthesis. The most prevalent defect or disorder that happens in case of double perovskites is antisite disorder with formation of patchy structure. The strongly suppressed magnetic behavior (mechanism for compounds driven by hybridization mechanism of magnetism, like Sr₂FeMoO₆, Sr₂CrWO₆, Ca₂CrWO₆, Sr₂CrMoO₆, the magnetic Tₛ, as well as saturation magnetization gets much less affected compared to Sr₂CrReO₆ or Sr₂CrOsO₆ for which magnetism is driven by combined hybridization and superexchange, the disorder kills magnetism for large strength of it, as seen in the figure in terms of vanishing Tₛ and zero magnetization. This situation changes dramatically upon consideration of correlated nature of antisite disorder with formation of patchy structure. The strongly suppressed magnetic behavior considering uncorrelated or random nature of disorder, regains almost the magnetic behavior of fully ordered compounds upon consideration of correlated nature of the disorder, as shown in figure 7(C). This general

7. Effect of disorder in properties of double perovskites

All the discussions so far were restricted to perfectly ordered double perovskites. However, defects are most natural to occur during the synthesis. The most prevalent defect or disorder that happens in case of double perovskites is anti-site disorder. In case of anti-site disorder, the position of B and B′ site gets switched, thus generating defect pairs of B-B and B′-B′ instead of B-B′ pairs, as shown schematically in figure 7(A). The situation gets further complicated by the fact that such anti-site disorder can be of correlated nature, in which case ordered domains or patches of ...B-B′-B′-B′. appear separated by antiphase boundaries, as shown in figure 7(A). Spectroscopic [42] as well as microscopic [43] studies on Sr₂FeMoO₆ support formation of such correlated anti-site disorders. It is crucial to understand how much the fascinating magnetic properties discussed in the above gets effected by antisite disorder, as it is unavoidable in any synthesis. In order to answer this, first principles calculations in combination with model Hamiltonian study was conducted considering seven different double perovskites [14]. It gave rise to results that were surprising in many ways. First of all, the antisite disorder was found to effect the magnetic properties of double perovskites, depending on whether the magnetism is hybridization driven, or combined hybridization-superexchange driven, as discussed in section 2. For compounds driven by hybridization mechanism of magnetism, like Sr₂FeMoO₆, Sr₂CrWO₆, Ca₂CrWO₆, Sr₂CrMoO₆, the magnetic Tₛ, as well as saturation magnetization gets much less affected compared to Sr₂CrReO₆ or Sr₂CrOsO₆ for which magnetism is driven by combined hybridization and superexchange mechanism (cf figure 7(B)). For double perovskites with magnetism driven by combined effect of hybridization and superexchange, the disorder kills magnetism for large strength of it, as seen in the figure in terms of vanishing Tₛ and zero magnetization. This situation changes dramatically upon consideration of correlated nature of antisite disorder with formation of patchy structure. The strongly suppressed magnetic behavior considering uncorrelated or random nature of disorder, regains almost the magnetic behavior of fully ordered compounds upon consideration of correlated nature of the disorder, as shown in figure 7(C). This general

Figure 6. (A): Possible ordering of A and A′ ions in a AA′BB′O₆ double perovskite, namely layered (left), columnar (middle) and rock salt (right). A and A′ ions are marked as large balls colored as cyan and green, respectively, while the BO₆, and B′O₆ octahedra are colored differently as grey and blue with oxygen atoms shown as small, blue balls. (B): The energy of rock salt (blue symbols) and columnar (black symbols) arrangement of A and A′ ions measured with respect to that of layered, plotted as a function of ionic radii difference of A and A′ ions, in Na₃A′CrO₆ and K₃A′CrO₆ (A′ = La, Ce, Pr, Nd, Sm, Gd, Dy, Y, Tm) compounds. Shown are the tolerance factor of the each compounds within bracket. The open symbols indicate the cases for which layered arrangement of A and A′ gives rise to non polar space group. (C): The spin magnetic (Mₛ) and orbital magnetic (Mₗ) moments (top), polarization (middle) and the energy barrier (bottom) for switching of polarization in polar KA′CrOsO₆ (A′ = Sm, Gd, Dy, Y, Tm) compounds. For the energy barrier, the results for three possible paths are shown.
finding is expected to solve the puzzling report [44] of magnetic ordering in apparently fully disordered sample of SrCr0.5Ru0.5O3. The microscopic analysis of the magnetic properties of the compound [14] showed that the magnetism in this material is governed by combined effect of hybridization and superexchange, as in case of Sr2CrReO6 or Sr2CrOsO6. Therefore, possibly the disorder present in SrCr0.5Ru0.5O3, which was measured in a site insensitive x-ray typediffraction (XRD) probe, was of correlated type, thus retaining the magnetic properties of the fully ordered compound.

8. Prediction of new double perovskites

The screening of materials with targeted properties has become a topic of great interest, from basic science to application point of view. Two conventional ways of fulfilling such a purpose are experimental investigation and computational study. However, the list of all possible materials for such scrutiny is immense. Machine learning (ML) guides in narrowing down the search on which further experimentation or computational study can be made [45]. It helps to find patterns (linear or non-linear) and building up models from a given dataset which can be used for prediction. In a recent work [15], combination of machine learning technique with quantum-chemical calculations have been used with a goal of discovering new magnetic DPs.

Specifically, a dataset was constructed considering all known double perovskite compounds from literature having divalent A cations, Ca, Sr and Ba. Each of these known compounds (termed as instance in language of ML) was labeled with a set of characteristics, built from the knowledge of structure and chemical compositions (known as attribute in language of ML). Following the setting up of the dataset, the pre-processing of data set was carried out in terms of normalization of the data sets, elimination of redundant attributes through examination of correlations via the so-called heatmap, and removal of outliers from the dataset. Subsequently, pattern recognition learning from the constructed dataset was obtained through a tree-based model (the random tree model in the specific example). Finally, the trained model was applied on a new set of yet-to-be synthesized B-B’ compositions, with B from 3d series and B’ from 4d or 5d series in order to ascertain the possible formation of stable DPs with those chosen B-B’ combinations (cf figure 8(A) for the steps followed in ML). Out of more than 400 number of such possible B-B’ combinations, 33 were predicted to be formed in stable DP structure with more than 80% confidence level.
In the next stage, out of 33 screened B-B’ combinations by ML, 25 compounds were picked up for characterization of their crystal structure, electronic and magnetic properties by applying state-of-art genetic algorithm for crystal structure determination \[46\] and rigorous first-principles calculations. The application of genetic algorithm resulted in 7 different crystal structures, with predicted crystal structures in conformity with the expectation based on the tolerance factor, defined as \( t = \frac{(r_A + r_O)}{\sqrt{(r_B + r_{B’})/2 + r_O}} \), where \( r_A, r_B, r_{B’}, r_O \) define the radii of A, B, B’, and O, respectively. Based on the density functional theory calculations within the framework of generalized gradient approximation (GGA) + U + spin-orbit coupling (SOC) of the predicted 25 compounds in their genetic algorithm predicted crystal structures, it was found that the predicted compounds can be grouped into six different classes, depending on their electronic and magnetic properties, as shown in figure 8(B). The different predicted classes spanned a wide range, from the largest group of ferromagnetic half-metal, followed by ferrimagnetic insulator, to antiferromagnetic insulator, ferromagnetic metals, and rare case of antiferromagnetic metal. Four of the compounds were also predicted to nonmagnetic metal. This provided a rather large landscape with a possibility of achieving technologically important materials like insulators with net uncompensated moment, or ferromagnetic half metals with reasonably high magnetic transition temperatures. This possibly also paves a new way to computer guided search for new DPs.

9. Conclusion and outlook

In this review, we attempted to provide a brief overview of some of the computational studies carried out on double perovskites with 3d TM ions at B site and 4d/5d TM ions at B’ site. In this context, we started the review with discussion on the microscopic understanding of the driving mechanism of fascinating magnetic properties of the double perovskite compounds, which turned out to be a novel mechanism of hybridization-driven mechanism, distinct from commonly known super-exchange mechanism. The cases of 3d-4d/5d DPs having a combined source of magnetism from hybridization-driven and super-exchange driven has been also discussed. Based on this understanding, tailoring of their magnetic/electronic properties have been proposed, which
resulted in prediction of antiferromagnetic metallic state in La doped Sr$_2$FeMoO$_6$ [11] and prediction of half-metallic ferromagnetic with high T$_c$ in Na and La doped Sr$_2$CrOsO$_6$ [12]. While the former computational prediction has been verified experimentally [32], the later is yet to be taken up by the experimentalists.

Prediction of yet-to-explored properties has been made in Sr$_2$CrWO$_6$ and Sr$_2$CrReO$_6$, in terms of calculated values of large magneto-optic Kerr signals of 2–3 degree in visible light range [10], which to our opinion, needs to be pursued experimentally. Similarly prediction of high temperature multiferroicity with large uncompensated magnetic moment, reasonably large switchable polarization on a series AA’CrOsO6 double perovskites with layered ordering of A and A’ cations [13], should motivate the solid state chemists to synthesize these double perovskite compounds. The practical issue of antisite disorder, which is prevalent in real samples of DPs, and its computational modeling has been discussed [14]. This computational study highlighted that the correlated nature of antisite disorder, may make the double perovskite compounds behave magnetically much like the perfectly ordered counterparts, even though from global crystallographic viewpoint, as probed through XRD, they may appear to be disordered [43]. The review ended with a new direction of computational study on DPs, in which combination of machine learning, genetic algorithm and first-principles calculations has been employed in prediction of new, yet-to-be synthesized double perovskites, with interesting magnetic properties [15].

This review thus, makes a number of prediction of unexplored properties in known double perovskites, either in their pristine form, or obtained through doping, and/or chemical modifications of A-site cations, as well as prediction of new yet-to-be synthesized double perovskite compounds with specified properties. We hope that some of the theoretical proposals discussed in this review will be taken by the solid-state chemists in terms of making these samples, and physicists to make measurements and validate the exciting properties predicted through computation. We strongly believe that such a feedback loop will be extremely helpful to make significant advancement in the fascinating field of double perovskites.

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