Comparative studies on the room-temperature ferrielectric and ferrimagnetic Ni₃TeO₆-type A₂FeMoO₆ compounds (A = Sc, Lu)

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First-principles calculations have been carried out to study the structural, electric, and magnetic properties of Ni₃TeO₆-type A₂FeMoO₆ compounds (A = Sc, Lu). Their electric and magnetic properties behave like room-temperature ferrielectric and ferrimagnetic insulators where polarization comes from the un-cancelled antiparallel dipoles of (A1), Fe³⁺ and (A2), Mo³⁺) ion groups, and magnetization from un-cancelled antiparallel moments of Fe³⁺ (d⁵) and Mo³⁺ (d⁵) ions. The net polarization increases with A’s ionic radius and is 7.1 and 8.7 μCm⁻² for Sc₂FeMoO₆ and Lu₂FeMoO₆, respectively. The net magnetic moment is 2μB per formula unit. The magnetic transition temperature is estimated well above room-temperature due to the strong antiferromagnetic superexchange coupling among Fe³⁺ and Mo³⁺ spins. The estimated paraelectric to ferrielectric transition temperature is also well above room-temperature. Moreover, strong magnetoelastic coupling is also anticipated because the magnetic ions are involved both in polarization and magnetization. The fully relaxed Ni₃TeO₆-type A₂FeMoO₆ structures are free from soft-phonon modes and correspond to stable structures. As a result, Ni₃TeO₆-type A₂FeMoO₆ compounds are possible candidates for room-temperature multiferroics with large magnetization and polarization.

Single phase polar materials with ferromagnetic (ferri)magnetic properties have drawn much attention recently due to their applications in developing spintronic devices for nonvolatile memories and in achieving electric-field control of magnetization in realistic information storage. Therefore, searching for multiferroic materials becomes an important research direction in material physics. Up to now, various mechanisms have been proposed to explain the electric polarization in magnetic compounds. Among others, the off-center displacement of lone-pairs, the chiral spin-density-wave driven polarization, the charge ordering, and the strain-induced polarization are mechanisms being discussed most. Although great progresses have been made in developing single phase multiferroic materials, many important issues remain unsolved. For example, the ferro(ferr)imagnetic transition temperatures are usually below room temperature and restricted their applications; even if the requirements of large magnetization and polarization are fulfilled, enhancing magnetoelastic coupling is still a big challenge.

In order to meet these crucial requirements, searching for the multiferroics which have magnetic ions contributing simultaneously to electric polarization can be a good choice. Thus in this report, we have analyzed the structural, electric, and magnetic properties of two corundum-derived oxides A₁FeMoO₆ (A = Sc, Lu), all of them are found to be multiferroic materials and have the same polar structure as Ni₃TeO₆, ZnTiO₃, and FeTiO₃. The general crystal structure displayed in Fig. 1(a) is described by a chemical formula A₁BB'O₆ (B = B' for Ni₃TeO₆, type; B = B' for LiNbO₃ or FeTiO₃, type). The structural advantage is its ability to incorporate different magnetic transition-metal ions on all cation sites for realizing magnetoelastic coupling. The common feature of the structures is the small A-site cation in six oxygen coordination, such as Sc³⁺ (0.69 Å) and Lu³⁺ (0.745 Å), in comparison with the large alkaline earth cation in twelve oxygen coordination, such as Ca²⁺ (1.34 Å), Sr²⁺ (1.44 Å), and Ba²⁺ (1.61 Å). The distortion of the structure can be estimated by a similar tolerance factor defined for a perovskite compound, t = \( \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}} \) where \( r_A \), \( r_B \), and \( r_O \) are the ionic radii of A-site ion, B-site ion (in...
′AB O

rB

is an averaged radius of B- and B′-site ions)22, and O ions, respectively. As found in most systems, for 
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, the cubic perovskite changes its symmetry by the BO6 octahedral rotation or tilting or Jahn-Teller distor-

tion. Good examples are the Ni3TeO6 (Ni2NiTeO6) compound with nonhysteretic colossal magnetoelectricity 3,

ScFeO3 (Fe takes both the B- and B′-sites)23,24 and Mn2FeMO6 (M = Nb, Ta, Mo, and W)25–27 compounds with

polar structure and antiferromagnetic or ferrimagnetic structure. Due to the strong antiferromagnetic superex-

change coupling between nearest neighbors Fe3+ (d5)

in ScFeO3, the Néel temperature is well above

room-temperature (545 K). To improve the net magnetization of ScFeO3, constructing ferrimagnetic structure by

replacing one of the B-site Fe3+ by a

dn (n < 5) ion is a possible way, which was done in the synthesized Bi2FeCrO6 (Cr3+: d3 compound28,29).

Results

To accomplish this goal, we have carried out comprehensive first-principles study on Ni3TeO6–type A2FeMoO6

compounds (A = Sc, Lu) where one of the B-site Fe3+ is replaced by Mo3+ (d3). The structural, electric, and mag-

netic properties of Ni3TeO6–type A2FeMoO6 have been systematically analyzed as a function of A-site cation

radius. We found that the ferrimagnetic state is indeed the ground-state with net magnetic moment of 2 μB

forming between the antiparallel Fe3+ (5 μB) and Mo3+ (3 μB) ions. The polarization increases with A’s ionic radius

and is 7.1 and 8.7 μCcm−2 for Sc2FeMoO6 and Lu2FeMoO6, respectively. Moreover, strong magnetoelectric cou-

pling is achieved since the electric polarization comes partly from the same magnetic ions. The robust antiferro-

magnetic coupling is sustained, ensuring a Néel temperature well above room temperature. The structural

analyses suggest that Ni3TeO6–type A2FeMoO6 compounds are free from soft-phonon modes and correspond to

stable structures.

Discussion

Let us start with the Ni3TeO6–type structures of A2FeMoO6 compounds as shown in Fig. 1(a). The structures are

obtained after the full relaxation of lattice parameters and atomic positions with effective on-site Coulomb repul-

sion Ueff = 4.0, 1.0, and 5.0 eV for Fe-3d, Mo-4d and Lu-5f electrons, respectively. The structures can be con-

structed in two steps: (1) (A(1)O6, FeO6) (Fig. 1(b)) and (A(2)O6, MoO6) (Fig. 1(c)) octahedral pairs form

face-sharing structures along c-axis; (2) the two face-sharing structures then form zigzag chains by edge-sharing

A(1)O6/FeO6 and A(2)O6/MoO6 octahedral pairs in the ab-plane. Due to the strong electrostatic repulsion among

the neighboring cations in the centers of the face-shared octahedral pairs, large antiferro-polar displacements

take place along c-axis for (A(1), Fe), and (A(2), Mo) ion pairs (see Fig. 1(b,c)). Thus, antiparallel electric

moments are formed for each face-sharing A(1)O6/FeO6 and A(2)O6/MoO6 octahedral pairs, and ferrielectric

polarization is generated along c-axis. The fully optimized structural parameters and atomic positions of ferrim-

agmatic Ni3TeO6–type A2FeMoO6 are listed in Table 1 together with those of antiferromagnetic ScFeO3 as a re-

dence. In Table 1, the lattice parameters, atomic positions, and bond angles are highly accurate. A relative error less
The spin exchange energy is about 2.90 eV for Fe and 1.32 eV for Mo. The total magnetic moment per formula unit is 2 μB in the ferrimagnetically ordered state. For ferromagnetically ordered state, the total magnetic moment property, but also significantly enhanced the polarization of A2FeMoO6 regarding the reference compound ScFeO3. The incompatibility between ferroelectricity and ferromagnetism gets nicely reconciled in the ferrite and ferrimagnetic A2FeMoO6. In addition, strong magnetoelectric coupling between the polarization and magnetization is also intrinsically embedded in the structures.

Having investigated the structural and electric properties of Ni3TeO6-type A2FeMoO6 compounds, we are now in position to discuss their electronic and magnetic properties. For Ni3TeO6-type A2FeMoO6, the orbital configurations of Fe 3d (d) and Mo 5d (d′) are similar to those of LaFeCrO4 according to previous studies. The schematic diagram for the relevant atomic energy levels is illustrated in Fig. 2. The spin-up and spin-down d-orbitals are separated by spin exchange energy Δσ, d(eg) and d(t2g) orbitals are separated by a crystal-field-splitting energy 10Dq. The nature of the superexchange coupling between Fe 3d (d) and Mo 5d (d′) ions is quite complicated because of the orbital degeneracy and two possible hybridization schemes. pdσ hopping favors ferromagnetic superexchange coupling while pdπ hopping favors antiferromagnetic superexchange coupling. The subtle competition between the two determines the magnetic ordering of ground state. Our first-principles calculations show that the ferrimagnetically ordered state is consistently lower in energy than that of the ferromagnetically ordered state in Ni3TeO6-type A2FeMoO6. Thus the polar state with ferrimagnetic ordering can be the favored ground state.

To have an overall picture of the electronic and magnetic properties of A2FeMoO6, the spin-resolved partial densities of states (DOS) are plotted in Fig. 3 for both ferromagnetically and ferrimagnetically ordered structures. To distinguish between the two types of transition-metal ions associated with A1O6/FeO6 and A2O6/MoO6 octahedral pairs, the DOSs of Fe and Mo are represented by solid (black) and dashed (red) lines, respectively. As shown in Fig. 3, the positions of extended eg orbitals are in accord with the atomic level scheme. In agreement with previous studies, the ScFeO3 demonstrates large band gap for both the ferromagnetically and ferrimagnetically ordered states. For antiferromagnetically ordered state, the total magnetic moment per formula unit is 2 μB in the ferrimagnetically ordered state. For ferromagnetically ordered state, the total magnetic

|                | ScFeMoO6 (Theory) | Lu2FeMoO6 (Theory) | ScFeO3 (Theory) | ScFeO3 (Experiment) |
|----------------|-------------------|-------------------|-----------------|---------------------|
| d/A            | 5.053             | 5.391             | 5.219           | 5.197               |
| c/A            | 13.511            | 14.330            | 14.027          | 13.936              |
| z/Å             | 0.1528            | 0.1220            | 0.1216          | 0.1228              |
| xO             | 0.2887            | 0.2853            | 0.2882          | 0.2895              |
| yO             | 0.0000            | 0.0000            | 0.0000          | 0.0000              |
| zO             | 0.1595            | 0.1604            | 0.1664          | 0.1667              |
| xFe            | 0.3317            | 0.3073            | 0.3169          | 0.3172              |
| yFe            | 0.3562            | 0.3534            | 0.3581          | 0.3555              |
| zFe            | 0.0629            | 0.0638            | 0.0627          | 0.0622              |
| xMo            | 0.3692            | 0.3805            | 0.3745          | 0.3716              |
| yMo            | 0.0288            | 0.0262            | 0.0247          | 0.0221              |
| zMo            | 0.2301            | 0.2309            | 0.2293          | 0.2288              |
| Fe-O-Mo°       | 135.17            | 137.82            | 135.71          | 135.13              |
| dA(1)/Å        | 0.348             | 0.411             | 0.315           | 0.336               |
| dA(2)/Å        | 0.294             | 0.357             | 0.315           | 0.336               |
| dFe/Å          | 0.276             | 0.277             | 0.261           | 0.314               |
| dMo/Å          | 0.183             | 0.187             | 0.261           | 0.314               |

Table 1. The structural parameters and atomic positions for the ferrimagnetic state of Ni3TeO6-type A2FeMoO6 (space group: R3) and the antiferromagnetic state of ScFeO3 (space group: R3c) calculated with Ueff = 4 eV, Ueff = 1 eV, and Ueff = 5 eV. The last column lists the available experimental data. a and c are the lattice constants in the hexagonal setting, whereas, x, y, and z are the reduced internal atomic positions of A(1) (0, 0, z), A(2) (0, 0, z), Fe (0, 0, z), Mo (0, 0, z), and O (x, y, z). Fe-O-Mo is the Fe-O-Mo angle. dA(1), dA(2), dFe, and dMo refer to the atomic displacements with respect to neutral planes in Fig. 1(b,c).
moment per formula unit is $8\mu_B$. The projected magnetic moments on Fe and Mo are 4.06, 2.15 $\mu_B$ and 4.06, 2.20 $\mu_B$ for Sc$_2$FeMoO$_6$ and Lu$_2$FeMoO$_6$, respectively. These values are consistent with the high-spin configuration of Fe$^{3+}$ and Mo$^{3+}$. The projected magnetic moment on Fe in ScFeO$_3$ is 4.15 $\mu_B$, slightly larger than the value 3.71 $\mu_B$ measured experimentally.

The electronic structural patterns can be understood from the level scheme of Fig. 2 together with hybridization processes. In particular, the valence and conduction bands near the Fermi energy is mainly resulted from the $t_{2g}$ orbitals of Fe and Mo. For the ferromagnetically ordered state, the up-spin $d(t_{2g})$ orbitals form the Fe and Mo dominated valence bands while the down-spin $d(t_{2g})$ orbitals form the Fe and Mo dominated conduction bands. The hybridization with oxygen orbitals pushes the Mo dominated $d(t_{2g})$ valence band edge upwards and pulls the Fe dominated $d(t_{2g})$ conduction band edge downwards. This makes the ferromagnetic band-gap extremely small. For the ferrimagnetically ordered state, the band structure in the vicinity of the Fermi energy is mainly determined by down-spin $d(t_{2g})$ orbitals of Fe and Mo across the Fermi energy. The difference in energy level essentially determines the band-gap between Fermi conduction band and Mo dominated valence band. This also explains why the overall features of DOSs for A$_2$FeMoO$_6$ (A = Sc, Lu) look rather similar. In addition, above discussion suggests that ferrimagnetically ordered state mainly involves hybridizing down-spin $t_{2g}$ orbitals of Fe and Mo across the Fermi energy. The resulting band splitting, thus, can significantly lower the binding energy. This is also the basic mechanism dictating the ferrimagnetically ordered ground state. The similar scenario also takes place in the double perovskite La$_2$FeCrO$_6$ as proved by the GGA electronic structure calculation.

It is known that the choice of the Coulomb interaction $U_{\text{eff}}$ has a notable impact on the electronic structure, and thus affects the relative stability of different magnetically ordered states. To investigate such effect, we have also performed GGA + $U$ simulations for other $U_{\text{eff}}^{Fe} = 3$, 4, 5 eV and $U_{\text{eff}}^{Mo} = 1$, 2, 3 eV while keeping $U_{\text{eff}}^{\text{Cu}} = 5$ eV. The choice of parameter values are based on the fact that the Coulomb interaction is typically weaker for spatially more extended 4$d$ electrons than for more localized 3$d$ electrons. The computed energy difference $\Delta E = E_{\text{Ferromagnetic}} - E_{\text{Ferri}}$ between the ferromagnetically and ferrimagnetically ordered states are shown in Fig. 4 as functions of $U_{\text{eff}}^{Fe}$ and $U_{\text{eff}}^{Mo}$. It has been found that $\Delta E$ is a monotonic decreasing function with increasing $U_{\text{eff}}^{Fe}$ or $U_{\text{eff}}^{Mo}$, which varies from 0.65 to 0.3 eV, but the ferrimagnetically ordered state is consistently lower than that of the ferromagnetically ordered state. The monotonic decreasing behavior of energy difference originates from the superexchange interaction, $1/U_{\text{eff}}$, for ferrimagnetic state since the ferromagnetic state is less sensitive to $U_{\text{eff}}$.

The energy difference decreases slightly as A’s ionic radius increases, because large A’s ionic radius reduces the effective hopping integral between Fe and Mo ions and so is that of the antiferromagnetic superexchange coupling. However, large A’s ionic radius expands the oxygen octahedra and favors the polar distortion. To estimate the magnetic transition temperature for A$_2$FeMoO$_6$ and ScFeO$_3$, we adopt the single parameter Heisenberg spin model $H = -\frac{1}{2}\sum_{ij} g_{ij} S_i \cdot S_j$, by assuming the same exchange parameter for all the nearest-neighbor couplings. Using $S = 5/2$ for Fe$^{3+}$ and $S = 3/2$ for Mo$^{3+}$, one can determine the exchange coupling $J$ by matching the energy differences obtained from the Heisenberg model and first-principles calculations. Then magnetic transition temperature $T_C$ is related to the energy difference $\Delta E$ by $T_C = \frac{1}{k_B} \frac{1}{J} \Delta E$. For $U_{\text{eff}}^{Fe} = 4$ eV, $U_{\text{eff}}^{Mo} = 1$ eV, and $U_{\text{eff}}^{\text{Cu}} = 5$ eV which best reproduced the experimentally observed lattice parameters, $T_C$ of ScFeO$_3$ is 661 K. The mean-field estimated $T_C$ is higher than the measured value 545 K since the spin fluctuation effect is not accounted for. Similar estimates yield $T_C = 1119$ K for Sc$_2$FeMoO$_6$ and $T_C = 1086$ K for Lu$_2$FeMoO$_6$, all above room-temperature. More practical estimate of $T_C$ can be made by scaling the energy difference with respect to

![Figure 2. Schematic diagram for the atomic energy levels of Fe-d, Mo-d and O-p orbitals.](image-url)
that of ScFeO₃, which gives \( T_C = 923 \text{ K} \) for Sc₂FeMoO₆ and \( T_C = 895 \text{ K} \) for Lu₂FeMoO₆. This is consistent with Lu's results on AlScFeMoO₆ (space group: \( R3 \))\(^3\). Therefore, we have shown that the \( A_2\)FeMoO₆ not only have large magnetization and polarization, but also possess room-temperature magnetic transition temperature \( T_C \). These encouraging properties make \( A_2\)FeMoO₆ a promising candidate for future multistate memory applications.

It remains to be verified that the structure of ferrielectric and ferrimagnetic Ni₃TeO₆-type \( A_2\)FeMoO₆ (\( A = \text{Sc, Lu} \)) insulators are robust structures and can be prepared by the usual laboratory method. Therefore, the phonon dispersion spectra are calculated using the frozen-phonon method. The calculated phonon dispersions are plotted in Fig. 5 for both the reference compound ScFeO₃ and Ni₃TeO₆-type \( A_2\)FeMoO₆ (\( A = \text{Sc, Lu} \)). The overall dispersion curves are quite similar for the three compounds except that the phonon frequency scales with the inverse square root of transition metal ion mass. It is clear that the soft-phonon modes are absent in the entire Brillouin Zone, which indicates that the Ni₃TeO₆-type \( A_2\)FeMoO₆ structure does correspond to stable structures.

To further check the stability of Ni₃TeO₆-type \( A_2\)FeMoO₆ (\( A = \text{Sc, Lu} \)) \( R3 \) structure against other common structures, we have also considered \( R5, P21/c \), and \( C2 \) structures. After the full structural relaxation with respect to the atomic positions and lattice constants, the initial trial \( C2 \) structure may converge either to \( C2/m, C2, C2/c \), or \( Imma \) structure depending on the material composition. The calculated energies of different structures are summarized in Table 2. Only those of ferrimagnetic (antiferromagnetic) states are shown because they always have lower energy than those of ferromagnetic state. One finds that Ni₃TeO₆-type \( A_2\)FeMoO₆ \( R3 \) structure consistently has lower energy than other structures. However, for large ionic radius of \( Y \) atom, the stable structure of \( Y_2\)FeMoO₆ takes \( P21/c \) space group rather than the \( R3 \) space group. This suggests that Ni₃TeO₆-type \( A_2\)FeMoO₆ is stable with respect to \( P21/c \) structure only for small ionic radius of \( A \) atoms (see Supplementary Information Table S4). The paraelectric to ferrielectric transition temperature can also be estimated from the energy difference between the structurally connected polar \( R3 \) and nonpolar \( R3 \) structures. As shown in Table 2, the energy difference is 1.378 eV/2f.u. for ScFeO₃, 0.408 and 0.542 eV/2f.u. for Sc₂FeMoO₆ and Lu₂FeMoO₆, respectively. Scaling the energy with that of ScFeO₃ and considering its polar structure being stable above 1400 K\(^1,^2\) yield a paraelectric-ferrielectric transition temperature \( T_C > 410 \text{ K} \) for Sc₂FeMoO₆ and \( T_C > 550 \text{ K} \) for Lu₂FeMoO₆. Both of them are well above room-temperature.

Figure 3. The spin and atom (Fe, Mo) projected densities of states of ScFeO₃ and \( A_2\)FeMoO₆ with \( U_{eff}^{Fe} = 4 \text{ eV}, U_{eff}^{Mo} = 1 \text{ eV}, \) and \( U_{eff}^{Lu} = 5 \text{ eV} \). The DOSs for ferromagnetic and ferrimagnetic states are presented as an upper-half and lower-half of each sub-figure. The spin-up and spin-down DOSs are plotted upwards and downwards respectively. The solid and dashed lines refer to the two different sites of transition metal ions (Fe, Fe for ScFeO₃; Fe, Mo for Sc₂FeMoO₆ and Lu₂FeMoO₆). The orbital characters are indicated in the spectra. (a) ScFeO₃, (b) Sc₂FeMoO₆, (c) Lu₂FeMoO₆. The dashed vertical line is the Fermi energy which is set to 0.
Figure 4. The energy difference $\Delta E$ per unit cell between ferromagnetic and ferrimagnetic states as functions of $U_{\text{eff}}^{\text{Fe}}$. The lines denoted by solid squares, circles, and triangles refer to $U_{\text{eff}}^{\text{Mo}} = 1$, 2, 3 eV. $U_{\text{eff}}^{\text{Fe}} = 5$ eV. The unit cell contains two formula units for ScFeO$_3$ and one formula unit for $A_2$FeMoO$_6$.

(a) ScFeO$_3$. (b) Sc$_2$FeMoO$_6$. (c) Lu$_2$FeMoO$_6$.

Figure 5. Phonon dispersion of Ni$_3$TeO$_6$-type $A_2$FeMoO$_6$ with $U_{\text{eff}}^{\text{Fe}} = 4$ eV, $U_{\text{eff}}^{\text{Mo}} = 1$ eV, and $U_{\text{eff}}^{\text{Lu}} = 5$ eV.

(a) ScFeO$_3$. (b) Sc$_2$FeMoO$_6$. (c) Lu$_2$FeMoO$_6$. The wave vector takes a path along the high symmetrical points of the Brillouin Zone: $\Gamma$ (0, 0, 0) $\rightarrow$ K (1/3, 1/3, 0) $\rightarrow$ M (1/2, 0, 0) $\rightarrow$ $\Gamma$ (0, 0, 0) $\rightarrow$ N (0, 0, 1/2) $\rightarrow$ I (1/3, 1/3, 1/2) $\rightarrow$ H (1/2, 0, 1/2) $\rightarrow$ J (0, 0, 1/2).
In the view that ScFeO$_3$, Mn$_2$FeMoO$_6$ ($M=\text{Nb, Ta, Mo, and W}$), and Ni$_2$TeO$_6$, all with smaller A-site ions, can be synthesized under the high temperature and high pressure environment, we expect that the Ni$_2$TeO$_6$-type A$_2$FeMoO$_6$ can also be synthesized under similar conditions. If so, one expects that other room-temperature ferrielectric and ferrimagnetic insulators may also be realized in the corundum-derived transition metal oxides. Through incorporating different magnetic transition metal ions on the cation sites, one can easily tune the super-exchange interaction and polar distortion, so that the polarization, magnetization, magnetoelectric coupling as well as critical temperature can be optimized for potential applications.

In summary, comprehensive first-principles calculations have been carried out for the structural, electronic, and magnetic properties of Ni$_2$TeO$_6$-type A$_2$FeMoO$_6$ ($A=\text{Sc, Lu}$). All of them show the ferrielectric and ferrimagnetic insulator properties with large magnetization ($2\mu_\text{eff}$/f.u.) and polarization ($>7\mu$C cm$^{-2}$). The strong antiferromagnetic superexchange interaction between Fe and Mo yields a mean-field critical temperature above room-temperature. Strong intrinsic magnetoelectric coupling is also ensured because the magnetic ions are involved in both the magnetic moment formation and polarization. The Ni$_2$TeO$_6$-type Sc$_2$FeMoO$_6$ and Lu$_2$FeMoO$_6$ are also proved to be stable structures because they have lower energies than other possible structures. Thus, one expects that these materials and other related ones can be synthesized in experiments.

### Methods

The study has been carried out using the generalized gradient approximation + $U$ (GGA + $U$) method$^{35}$ with Perdew-Becke-Erzenhof exchange-correlation functional$^{36}$ as implemented in the Vienna $ab$ Initio simulation package (VASP)$^{37,38}$. To account for the population imbalance on localized transition metal structures are firstly atomically relaxed with a higher accuracy using the $8 \times 8 \times 8$ supercell composed of ten-atom rhombohedral unit cell. The force constants are calculated by VASP simulations. To account for the population imbalance on localized transition metal structures are firstly atomically relaxed with a higher accuracy using the $8 \times 8 \times 8$ supercell composed of ten-atom rhombohedral unit cell. The force constants are calculated by VASP simulations. To calculate the electric polarization of Ni$_2$TeO$_6$-type A$_2$FeMoO$_6$ ($A=\text{Sc, Lu}$) with space group R3, we choose the structure with space group R3 as a reference state$^{41}$. The R3 structure displayed in Figure S1 has space inversion symmetry. It is a non-polar insulator and has zero electric polarization (see Supplementary Information). Since the electric polarization is along 3-fold rotational axis, a 30-atom hexagonal unit cell is chosen, so that the in-plane polarization is zero. In calculating the electric polarization, a $7 \times 7 \times 7$ Γ-centered $k$-points sampling is used for the self-consistent loop and 14 $k$-points sampling is adopted for parallel direction integration in Berry phase method. As shown in Figure S5, 14 $k$-points sampling is almost convergent for electric polarization calculation.

To calculate the phonon dispersion of Ni$_2$TeO$_6$-type A$_2$FeMoO$_6$ ($A=\text{Sc, Lu}$) and ScFeO$_3$, the structures are firstly atomically relaxed with a higher accuracy using the $8 \times 8 \times 8$ Γ-centered $k$-points sampling and the tolerance force of 0.0001 eV/Å. The phonon dispersion is then calculated using the Phonopy code$^{42}$ with a $2 \times 2 \times 2$ supercell composed of ten-atom rhombohedral unit cell. The force constants are calculated by VASP using a $4 \times 4 \times 4$ Γ-centered $k$-points sampling for the supercell.

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### Table 2. The relative stabilities of various phases of A$_2$FeMoO$_6$ calculated with $U_{eff}^{Fe} = 4$ eV, $U_{eff}^{Mo} = 1$ eV, and $U_{eff}^{energetic} = 5$ eV. The energy is given in unit of eV with R3 phase taken as the reference structure.

| Structure          | R3 | R3 | P21/c | C2  |
|--------------------|----|----|-------|-----|
| Sc$_2$FeMoO$_6$    | 0  | 0.408 | 0.519 | 0.676 (C2/m) |
| Lu$_2$FeMoO$_6$    | 0  | 0.524 | 0.004 | 0.606 (C2)    |
| ScFeO$_3$          | 0  | 1.378 (P6$_3$) | 0.281 (Pmma) | 1.024 (Imma) |
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Author Contributions
W.Y.Z. supervised the work and G.S. carried out the numerical calculations of this work. G.S. and W.Y.Z. both contributed to the analysis and interpretation of results, and the writing of manuscript.

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