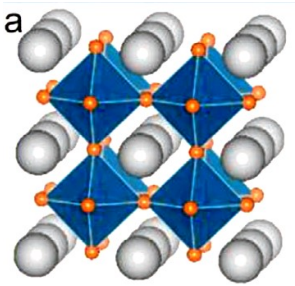
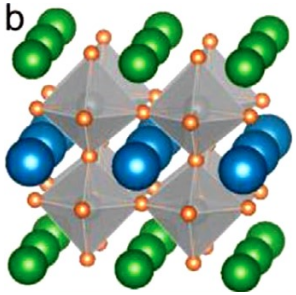
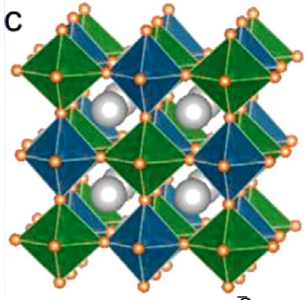
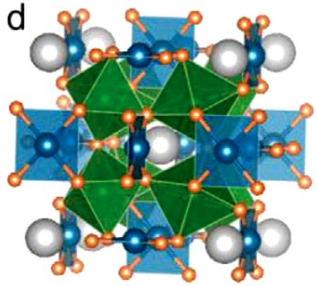
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Table S1. Comparison of single perovskite oxides, double perovskite oxides, and quadruple perovskite oxides from aspects of their crystal structures and physical properties.

	Single perovskite oxides	Double perovskite oxides (DPOs)		A- and B-site-ordered quadruple perovskite oxides
		A-site ordered DPOs	B-site ordered DPOs	
General formula	ABO_3	$A'A''B_2O_6$	$A_2B'B''O_6$	$AA'_3B'_2B''_2O_{12}$
Crystal structure	 Cubic, space group $Pm\bar{3}m$;	 Cubic, space group $R32$ or $Imm2$;	 Cubic, space group $Fm\bar{3}m$ or Monoclinic, space group $P2_1/n$	 Cubic, space group $Pn\bar{3}$
Magnetic interactions	B-B interaction (or B-O-B interaction *via* oxygen ions)	A″-B, A″- A″, B-B interactions	B′-B′, B″-B″, B′-B″ interactions	A′–A′, A′–B′, A′–B″, B′–B″, B′–B′ and B″–B″ interactions
Structural flexibility	In ABO_3 simple perovskite (orthorhombic, *Pnma*) with AO_8 and BO_6 coordination environment, the B–O–B tilt angles are within the range of 140–180°. Random arrangements of the cation distribute along 3D directions.	$A'A''B_2O_6$ double perovskite oxides have a lamella structure with a stacking sequence of –A′O–BO_2–A″O–BO_2–, and A′ and A″ cations are arranged alternatively along the [001] crystallographic axis.	Distorted $A_2B'B''O_6$ double perovskite (monoclinic, $P2_1/n$) exhibits rock-salt ordering B′ and B″ and eight-coordination AO_8. B′ and B″ cations are arranged alternatively along the [111] crystallographic axis.	$AA'_3B'_2B''_2O_{12}$ quadruple perovskite oxides with 1:3 ordering A-site arrangement, have icosahedral AO_{12}, square planar $A'O_4$, and $B'O_6$ and $B''O_6$ octahedra. This special perovskite family is formed in the $a^+a^+a^+$ tilt system with very large B–O–B tilt angles of 140–145°.
Compositional flexibility	There are 32/54 kinds of elements that have been found at the A/B site with diverse oxidation states ranging from 1+ to 7+ and a wide range of ionic radii of 0.76 Å (Li^+)–1.52 Å	Layered ordering of an $A'A''B_2O_6$ perovskite results in $P4/mmm$ space group symmetry. This arrangement leads to three chemically distinct environments	The structure has extremely large tolerance to different elemental combinations of (B′ and B″). To maintain the charge balance, $A_2B'B''O_6$ must satisfy	$AA'_3B'_2B''_2O_{12}$ quadruple perovskite oxides combine the advantages of A- and B-site-ordered quadruple perovskite oxides. Unlike the A-site in the basic ABO_3

	(K^+) for A and 0.45 Å (Be^{2+})–1.52 Å (K^+) for B, exhibiting large flexibility of compositions that can form the crystal structure of perovskites. In theory, there are 2346 kinds of ABO_3 and at least 265 of them have been experimentally synthesized [1].	for the anions a structural instability when the sizes and/or bonding strengths of the A′ and A″ cations are significantly different. Thus, layered ordering of A-site cations only partially alleviates the lattice strains associated with an A′/A″ size mismatch. From an electrostatic point of view rock salt ordering must also be preferable for A-site cations, yet long-range rock salt ordering of A-site cations is very rare [2].	the following equation of $2Q_A + Q_{B'} + Q_{B''} = 12$ [1]. There are thousands of the $A_2B'B''O_6$ DPOs reported in the literature which were synthesized under ambient pressure [3]. Many new DPs were also synthesized at high-pressure.	perovskites, which is usually occupied by alkali-metal, alkaline-earth or rare-earth cations, the A′-site in $AA'_3B'_2B''_2O_{12}$ can accommodate transition metal ions. The introduction of A′-A′, A′-B′ and A′–B″ magnetic interactions in addition to B′–B″, B′–B′ and B″-B″ couplings results in a variety of intriguing properties [4]. A large number of consistent elements can be introduced into A, A′, B′ and B″ -sites by high pressure synthesis method.
Modulation of physical properties	Physical properties of the ABO_3 simple perovskite are controlled by partial or complete substitution of the A-/B-site cations. The B-B interaction is dominantly responsible for the physical properties.	Physical properties of the $A'A''B_2O_6$ double perovskites are not only controlled by the B–B interaction (mainly responsible for the properties of simple perovskites) but also the A″-A″ and A″–B interactions.	Instead of the B−B interaction in a simple ABO_3 perovskite, B′-B″ interaction mainly contributes to the physical properties of $A_2B'B''O_6$ with a rock-salt ordered structure at B-site.	Physical properties of the $AA'_3B'_2B''_2O_{12}$ quadruple perovskite oxides are controlled by the multiple interactions between transition metal ions, i.e., A′-A′, A′-B′, A′-B″, B′-B″, B′-B′ and B″-B″ interactions, which are complete each other.
Magnetic transition temperature (T_C)	Simple ABO_3 perovskite compounds, $La_{0.67}Ba_{0.33}Mn_{1-x}Cr_xO_3$ ($0 \le x \le 0.15$), are reported to have T_C values ranging from 275 K to 345 K [5]. The decrease of T_C is mainly interpreted by the decrease of the B-O-B bond angle and the increase of the B-O bond length as the Cr	$A_2B'B''O_6$ DPOs with a 3*d* transition metal ion at the B′-site and a 4*d* or 5*d* transition metal ion at the B″-site, are reported to exhibit magnetic transition temperatures ranging from ~ 200 K to ~ 800 K [6]. For example, Sr-based $Sr_2B'B''O_6$ DPOs such as Sr_2FeReO_6 (T_C = 432 K) [7], Sr_2FeWO_6 ($T_C \approx$ 450 K) [8], Sr_2FeMoO_6 ($T_C \approx$ 420 K) [9], Sr_2CrMoO_6 (T_C = 450 K) [10], Sr_2CrReO_6 (T_C = 635 K) [1q], Sr_2CrWO_6 (T_C = 390 K) [12], and Sr_2CrOsO_6 (T_C = 725 K) [13] are reported.		In the $AA'_3B'_2B''_2O_{12}$ quadruple perovskite oxides with the $Pn\bar{3}$ space group, the A′-A′, A′-B/B′, B/B′-B/B′ interactions can further enhance and/or tune the physical properties. For example, the T_C value of quadruple perovskite oxide $LaCu_3Fe_2Re_2O_{12}$ was

	content increases.		reported to be 710 K due to the strong $Cu^{2+}(\uparrow)$ $Fe^{3+}(\uparrow)$ $Re^{4.5+}(\downarrow)$ spin interactions [14].
Magnetization (μ_B/f.u.)	Simple ABO_3 perovskite compounds, $La_{0.67}Ba_{0.33}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.15$), are reported to have magnetization values ranging from 2.73 to 3.49 μ_B/f.u. [5].	For $A_2B'B''O_6$ DPOs, a fully ordered state in an ideal state will result in a maximum saturation magnetization (M_S). For example, in theory, M_S is 2.0 μ_B/f.u. in fully ordered Bi_2FeCrO_6 and Bi_2NiMnO_6 thin films [15,16], and even higher in fully ordered La_2CoMnO_6 thin films, M_S = 6.0 μ_B/f.u. [17,18]. This value can be used to estimate the degree of "magnetic" ordering.	Quadruple perovskite oxide $LaCu_3Fe_2Re_2O_{12}$ has a large saturation magnetization (M_S) of 8.7 μ_B/f.u., which is considerably enhanced compared with those observed in A_2FeReO_6 (A = Ca, Sr and Ba) DPOs [19-21].

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Table S2. Summaries of quadruple perovskite oxides synthesized by different methods and their crystal structures and physical properties

Synthesized methods	Quadruple perovskite oxides	Crystal structures	Physical properties	Reference
Solid-state reaction (SSR) method	**A-site ordered perovskite $AA'_3B_4O_{12}$**			
	$CaCu_3Ti_4O_{12}$	Cubic, $Im\bar{3}$	AFM, $T_N \approx 25$ K, $M_s = 0.56\ \mu_B$/f.u., ε_r~10286, tan δ~0.067	1-3
	$ACu_3Ru_4O_{12}$ (A = Ca, La, and Nd)			
	$CaCu_3Ru_4O_{12}$ $LaCu_3Ru_4O_{12}$ $NdCu_3Ru_4O_{12}$	Cubic, $Im\bar{3}$	PM, $M_s = 0.32\ \mu_B$/f.u., $\rho_{0\ (1.5\ K)} = 0.110$ mΩ·cm $\rho_{0\ (1.5\ K)} = 0.313$ mΩ·cm, $\rho_{300\ K}$=1.28 mΩ·cm, Θ = 390 K $\rho_{0\ (1.5\ K)} = 0.474$ mΩ·cm, Θ = 390 K	4,5 6,7 6
	A-site columnar-ordered perovskite $A_2A'A''B_4O_{12}$			
	$CaMnTi_2O_6$ (HT-HP)	Tetragonal, $P4_2mc$	T_c= 630 K, P=24 μC/cm^2, P_r=3.5 μC/cm^2, E_c=53 kV/cm	8
	$CaFeTi_2O_6$ (HT-HP)	Tetragonal, $P4_2/nmc$	-	9
	$MnLaMnSbO_6$ $MnPrMnSbO_6$ $MnNdMnSbO_6$ $MnSmMnSbO_6$ (HT-HP)	Tetragonal, $P4_2/n$	T_c=48 K, μ_{th}=8.37 μ_B/f.u. T_c=89 K, T_{N2}=75 K, μ_{th}=9.12 μ_B/f.u. T_c=76 K, T_{N2}=42 K, μ_{th}=9.14 μ_B/f.u., μ_{exp}=8.9 μ_B/f.u. T_c =48 K, T_{N2}=39 K, μ_{th}=8.5 μ_B/f.u., μ_{exp}=8.3 μ_B/f.u.	10
	$SmMnGaTiO_6$ $GdMnGaTiO_6$(HT-HP)	Tetragonal, $P4_2/nmc$	μ_{eff}=6.21 μ_B/f.u., M_s=2.5 μ_B/f.u., C=4.82 emu K, T_N=3 K μ_{eff}=9.75 μ_B/f.u., M_s =11 μ_B/f.u., C=11.88 emu K, T_N=3 K	11
Solid-state reaction (SSR) method	$RMnMn_2O_6$ (R=Gd-Tm and Y) (HTHP) $Tm_{0.88}Mn_3O_{5.82}$ $Er_{0.88}Mn_3O_{5.82}$ $Ho_{0.9}Mn_3O_{5.85}$ $Y_{0.9}Mn_3O_{5.85}$ $DyMn_3O_6$ $GdMn_{2.833}O_{5.75}$	Orthorhombic, $Pmmn$	μ_{eff}=10.608 μ_B/f.u, M_s=6.4 μ_B/f.u., T_{N1}=75 K, T_{N2}=20 K μ_{eff}=12.318 μ_B/f.u, M_s=6.97 μ_B/f.u., T_{N1}=68 K, T_{N2}=21 K μ_{eff}=12.917 μ_B/f.u, M_s=6.89 μ_B/f.u., T_{N1a}=69 K, T_{N1b}=65 K μ_{eff}=8.027 μ_B/f.u, M_s =3.05 μ_B/f.u., T_{N1a}=69 K, T_{N1b}=65 K μ_{eff}=13.444 μ_B/f.u, M_s =7.18 μ_B/f.u., T_{N1}=58 K, T_{N2}=46 K μ_{eff}=11.095 μ_B/f.u, M_s =6.39 μ_B/f.u., T_N=87 K	12

	$CaMnMnReO_6$ (HT-HP) $Ca(Mn_{0.5}Cu_{0.5})FeReO_6$	Tetragonal, $P4_2/n$	T_{N1}=100 K, T_{N2}=120 K, M_s=3.4 μ_B/f.u. T_{N1}=160 K, T_{N2}=560 K, M_s=4.8 μ_B/f.u.	13
	A- and B-site multiply ordered perovskite $AA'_3B_2B'_2O_{12}$			
	$LaCu_3Fe_2TiSbO_{12}$	Cubic, $Im\bar{3}$	AFM, T_{N1}=60 K, T_{N2}=160 K, M_s =1.2 μ_B/f.u.	14
	Hexagonal quadruple perovskite oxides			
	$Ba_4BiIr_3O_{12}$	Hexagonal, $C2/m$	T_N=215 K, μ_{eff}=0.22 μ_B/Ir.	15
	$Ba_4EuRu_3O_{12}$ $Ba_4EuIr_3O_{12}$	Hexagonal, $C2/m$	AFM, T_N=4 K, μ_{eff}=1.18 μ_B/f.u., E_a=0.18 eV PM, E_a=0.22 eV, Θ_p = -0.773K	16
	$Ba_4LuRu_3O_{12}$ $Ba_4NdRu_3O_{12}$	Hexagonal, R-3m Hexagonal, $C2/m$	AFM, μ_{eff}=2.86 μ_B/f.u., T_N=8 K FiM, μ_{eff}=4.7 μ_B/f.u., T_N=11.5 K	17
	$Ba_4CuNb_3O_{12}$	Hexagonal, $P6_3/mmc$	-	18
Sol-gel method	**A-site ordered perovskite $AA'_3B_4O_{12}$**			
	$CaCu_2MnTi_3MnO_{12}$	Cubic, $Im\bar{3}$	AFM, μ_{eff}=3.85 μ_B/f.u., ε_r~2040	19
	$CdCu_3Fe_4O_{12}$	Cubic, $Im\bar{3}$	FM/AFM, T_c = 190 K, T_N=170 K, M_s =1.6 μ_B/f.u.	20
	$LaCu_3Mn_3TiO_{12}$ $LaCu_3Mn_{3.5}Ti_{0.5}O_{12}$ $LaCu_2Mn_4TiO_{12}$	Cubic, $Im\bar{3}$	AFM, T_c=230 K, M_s =8.6 μ_B/f.u., M_{cal}=7 μ_B/f.u. AFM, T_c=235 K, M_s=10.4 μ_B/f.u., M_{cal}=8.5 μ_B/f.u. AFM, T_c=225 K, M_s=10.82 μ_B/f.u., M_{cal}=9 μ_B/f.u.	21
	A- and B-site multiply ordered perovskite $AA'_3B_2B'_2O_{12}$			
	$CaCu_3Fe_2Sb_2O_{12}$	Cubic, $Pn\bar{3}$	AFM, T_N=160 K, M_s =5.35 μ_B/f.u., ρ>10^7 Ω	22
	A-site columnar-ordered perovskite $A_2A'A''B_4O_{12}$			
	$Y_2CuMnMn_4O_{12}$	$Pmmn$	PM, T_N=175K/159K	26

High temperature and high pressure	$Ho_2MnGaMn_4O_{12}$	$P4_2/nmc$	μ_{eff}=18.428 μ_B/f.u., Θ_p = −21.5(3) K	27
	$Dy_2CuMnMn_4O_{12}$	*Pmmn*	T_{N1}=160 K, T_{N2}=125 K, T_{N3}=21 K	27
	$Y_2CuMnMn_4O_{12}$	*Pmmn*	PM, T_N=175K/159K	26
	A- and B-site multiply ordered perovskite $AA'_3B_2B'_2O_{12}$			
	$CaCu_3Co_2Re_2O_{12}$	Cubic, $Pn\bar{3}$	FiM/FM, μ_{eff}=10.09 μ_B/f.u., M_s=4 μ_B/f.u., T_c=20 K, T_N=28 K, C=12.1 emu K Oe^{-1} mol^{-1}	28
	$CaCu_3Fe_2Re_2O_{12}$	Cubic, $Pn\bar{3}$	FiM, M_s=8.7 μ_B/f.u., T_c = 560 K, T_N= 28 K, ρ=10 mΩ·cm	29
	$LaMn_3Ni_2Mn_2O_{12}$	Cubic, $Pn\bar{3}$	FM, M_s=6.6 μ_B/f.u., T_c=34 K, T_N= 46 K	30
	$NaCu_3Fe_2Os_2O_{12}$	Cubic, $Pn\bar{3}$	FiM, T_c=380 K, M_s=5.5 μ_B/f.u.	31

FM: Ferromagnetic; AFM: Antiferromagnetic; PM: Paramagnetic; FiM Ferrimagnetic, T_N: Neel temperature; T_c: Curie temperatures; ρ: Electrical resistivity; ρ_0: Residual resistivity; Θ: Einstein temperature; E_c: Coercive field; P: Spontaneous Polarization; μ_{eff}: Effective moment; μ_{th}: Theoretical moment; μ_{exp}: Experimental moments; C: Curie constants; E_a: Activation energies; Θ_p: Curie-Weiss temperature; M_{cal}: Calculated magnetization; M_s:Saturation magnetization; ε_r: Dielectric constant; tan δ: Dielectric loss.

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