

Supplementary Information

Iron deficiency strategy toward single-phase high-entropy M-type ferrites for broadband millimeter-wave absorption with low thickness

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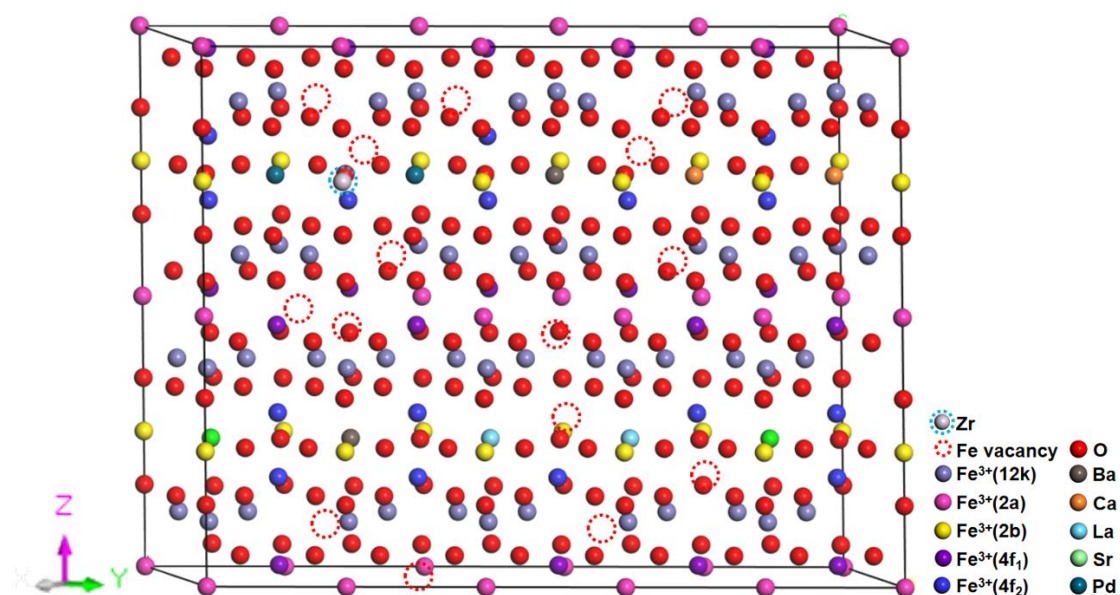
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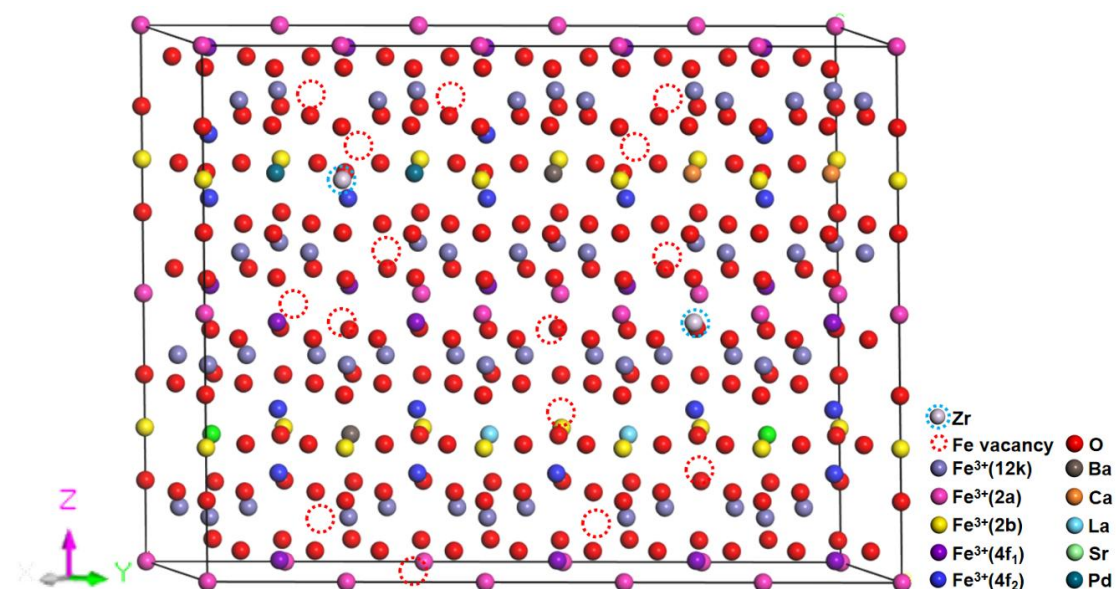
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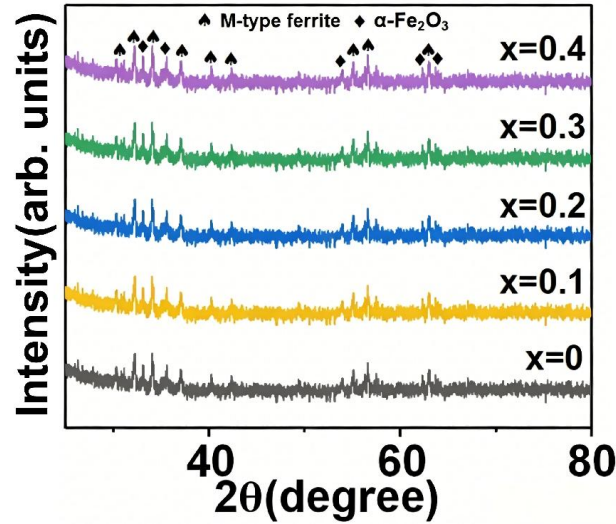
Supplementary Figures:



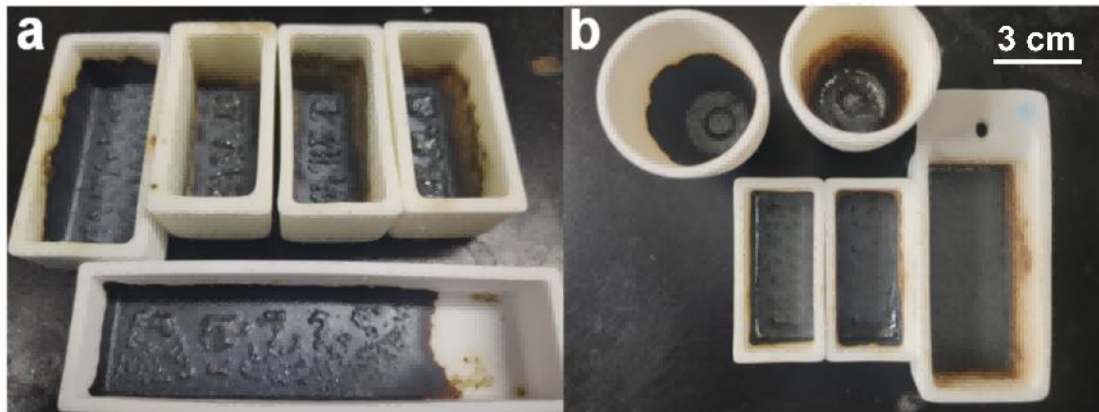
Supplementary Fig. 1 | The 3D unitcell diagram of the high-entropy iron-deficient M-type ferrites with stoichiometric ratio of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$, where $x=0.1$. The sites of blue balls indicate the lattice positions preferentially occupied by Zr^{4+} ions.



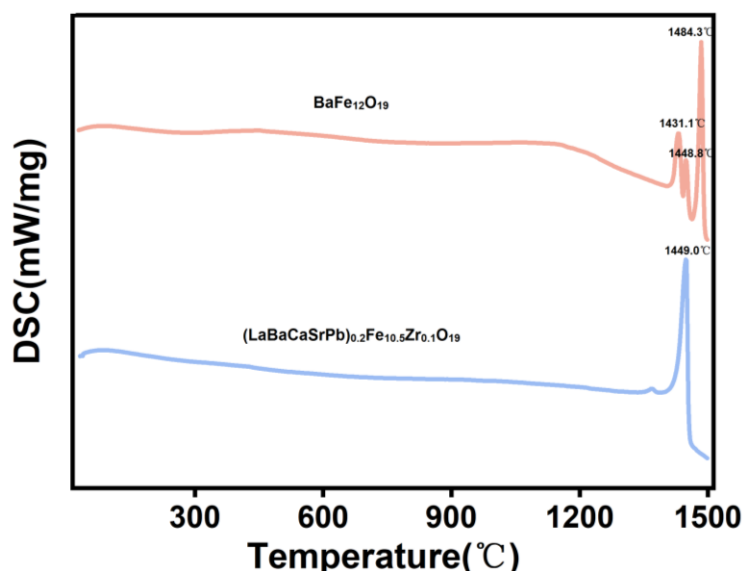
Supplementary Fig. 2 | The 3D unitcell diagram of the high-entropy iron-deficient M-type ferrites with stoichiometric ratio of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$, where $x=0.2$. The sites of blue balls indicate the lattice positions preferentially occupied by Zr^{4+} ions.



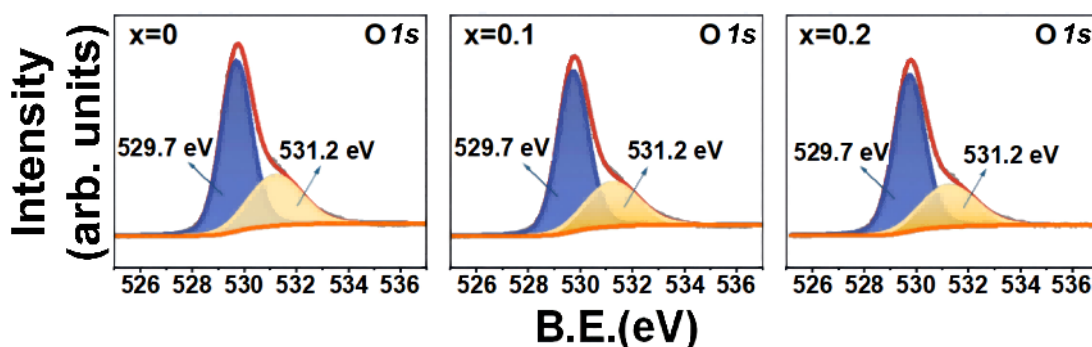
Supplementary Fig. 3 | The XRD patterns of the high-entropy ferrites with stoichiometric ratio of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{12-x}\text{Zr}_x\text{O}_{19}$ ($x=0-0.4$) sintered at 1400°C for 3 h. The diffraction peaks belong to $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS NO.33-0664) are observed for all the samples, indicating that components in stoichiometric proportions with no iron deficiency are not favorable for obtaining single-phase M-type ferrite under identical preparation conditions.



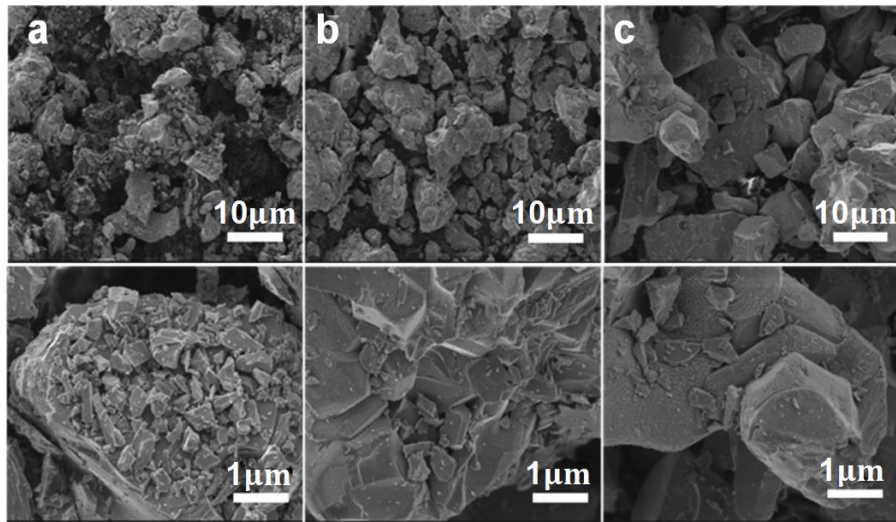
Supplementary Fig. 4 | The digital photos of the high-entropy ferrites with stoichiometric ratio of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{12}\text{Zr}_x\text{O}_{19}$ ($x=0-0.4$) sintered at (a) 1450°C and (b) 1500°C for 3 h. When the sintering temperature is increased to 1450°C - 1500°C , the sample adheres firmly to the crucible instead of remaining as fine and uniform powders, which demonstrates that further increasing the sintering temperature to reduce impurity content is not a suitable approach.



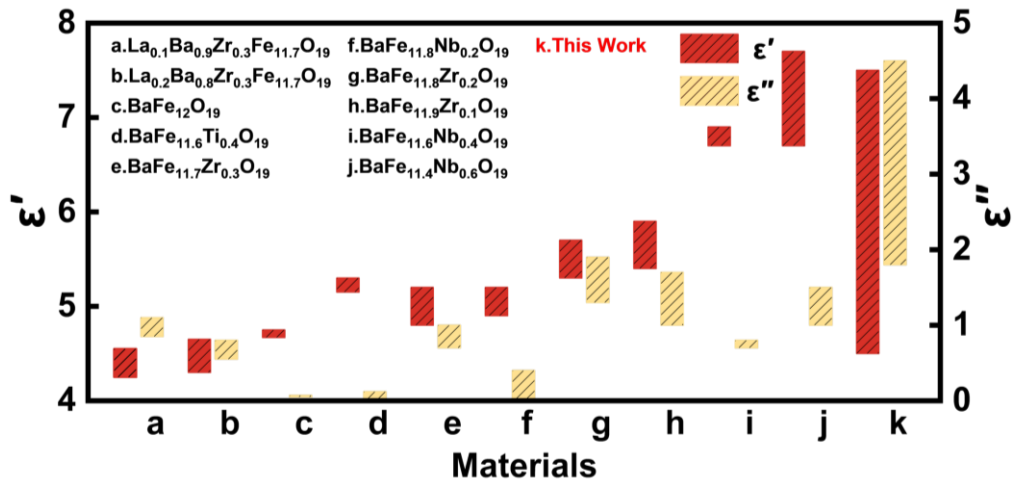
Supplementary Fig. 5 | The DSC curves of the commercial M-type barium ferrite and the Zr^{4+} doped high-entropy M-type ferrite with $x=0.1$. Both M-type barium ferrite and high-entropy M-type ferrite exhibit no obvious thermal reaction below 1400 °C. The former undergoes significant thermal decomposition at multiple temperatures, beginning at 1431.1 °C and proceeding at 1448.8 °C and 1484.3 °C, whereas the latter exhibits significant thermal decomposition at a higher temperature of 1449 °C.



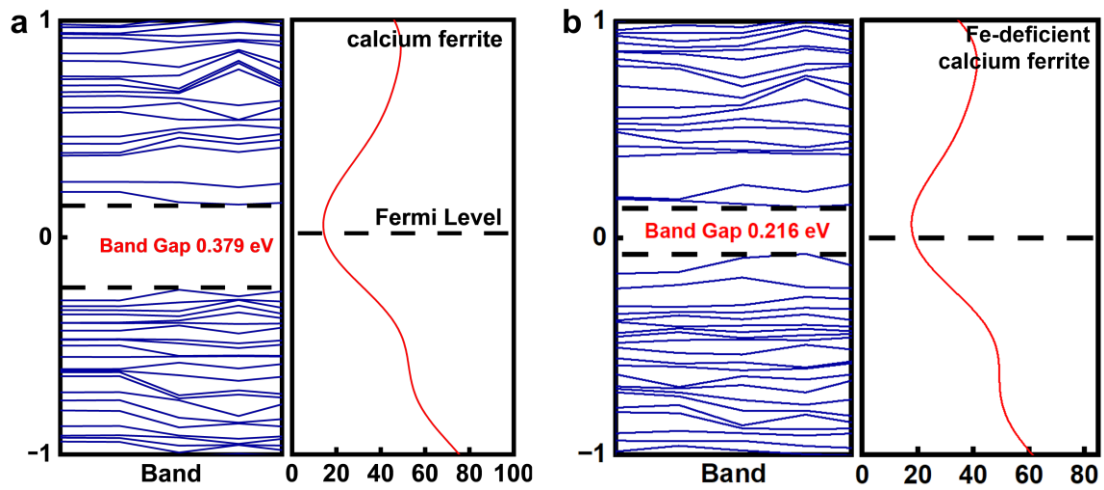
Supplementary Fig. 6 | The XPS $\text{O}1s$ spectra of the iron-deficient high-entropy M-type ferrites with composition of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ ($x=0, 0.1, 0.2$) sintered at 1400°C for 3 h. The $\text{O}1s$ spectra are resolved into dual peaks at 529.7 eV and 531.2 eV, indicating the existence of both lattice oxygen and oxygen vacancies for all the samples.



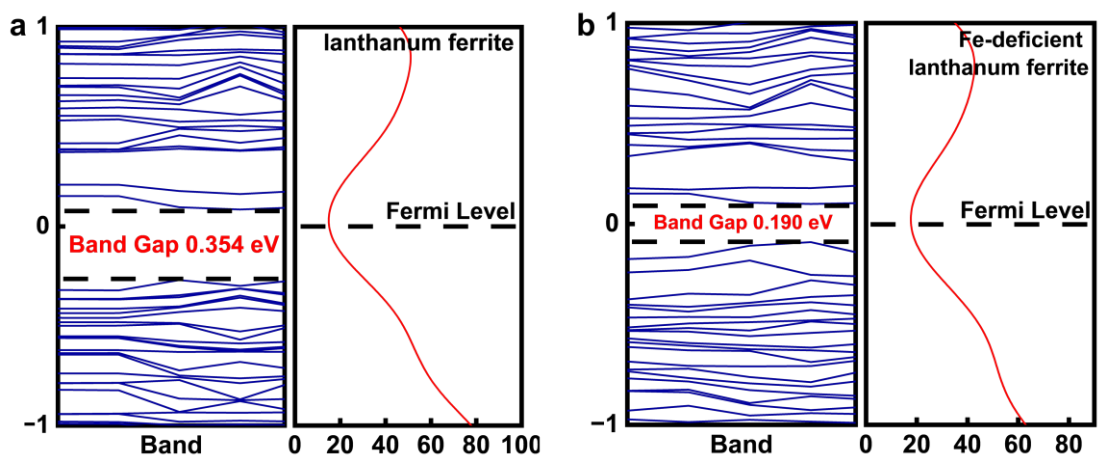
Supplementary Fig. 7 | SEM images of the iron-deficient high-entropy M-type ferrites with composition of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ (a) $x=0$, (b) $x=0.1$ and (c) $x=0.2$ sintered at 1400°C for 3 h. The particle size is seen to grow larger gradually with the increasing Zr^{4+} doping content. It is because that an increase in the doping level may lower the grain boundary energy, thereby accelerating grain boundary migration to achieve energy optimization.



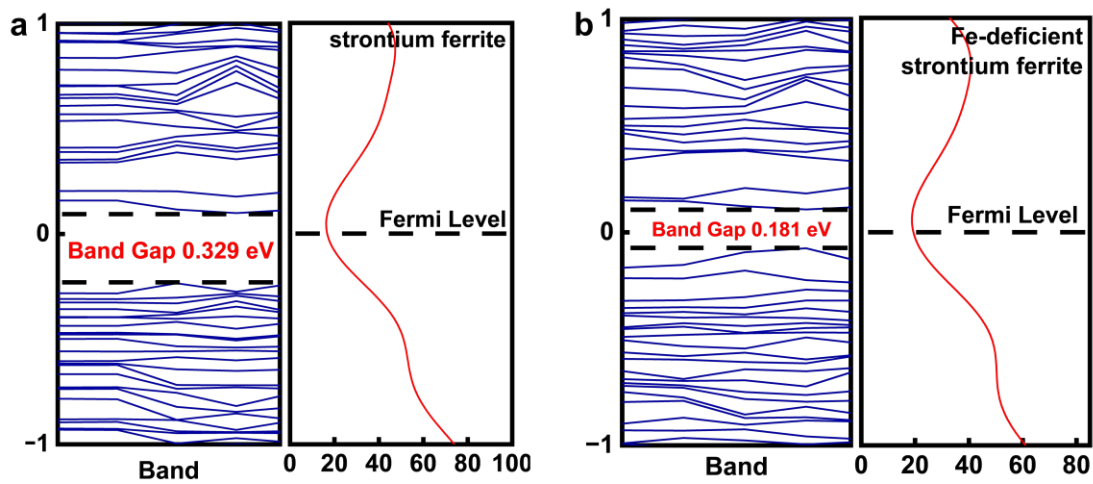
Supplementary Fig. 8 | The ϵ' and ϵ'' ranges of the M-type barium ferrite doped with Ti^{4+} , Zr^{4+} , Nb^{5+} ions and $\text{La}^{3+}\text{-Zr}^{4+}$ and the as-prepared iron-deficient high-entropy M-type ferrites in this work. By comparison, the complex permittivity, particularly its imaginary component, of high-entropy iron-deficient M-type ferrite is markedly higher than that of other M-type ferrites.



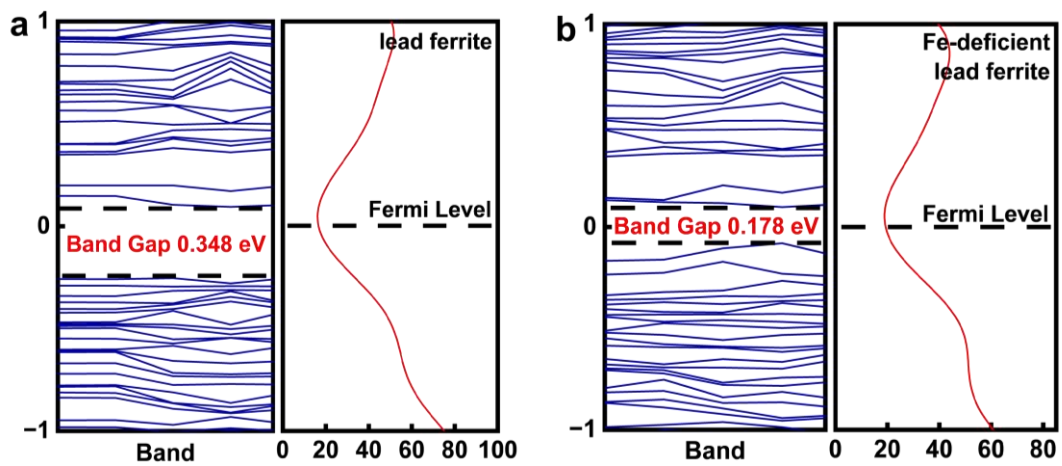
Supplementary Fig. 9 | Electronic band structure of the M-type (a) calcium ferrite and (b) iron-deficient calcium ferrite. The band gap of M-type calcium ferrite decreases from 0.379 eV to 0.216 eV by iron-deficient strategy.



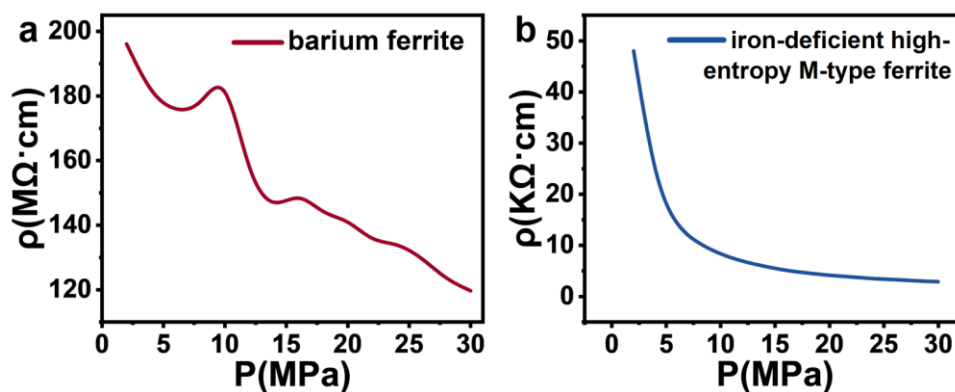
Supplementary Fig. 10 | Electronic band structure of the M-type (a) lanthanum ferrite and (b) iron-deficient lanthanum ferrite. The band gap of M-type lanthanum ferrite decreases from 0.354 eV to 0.190 eV by iron-deficient strategy.



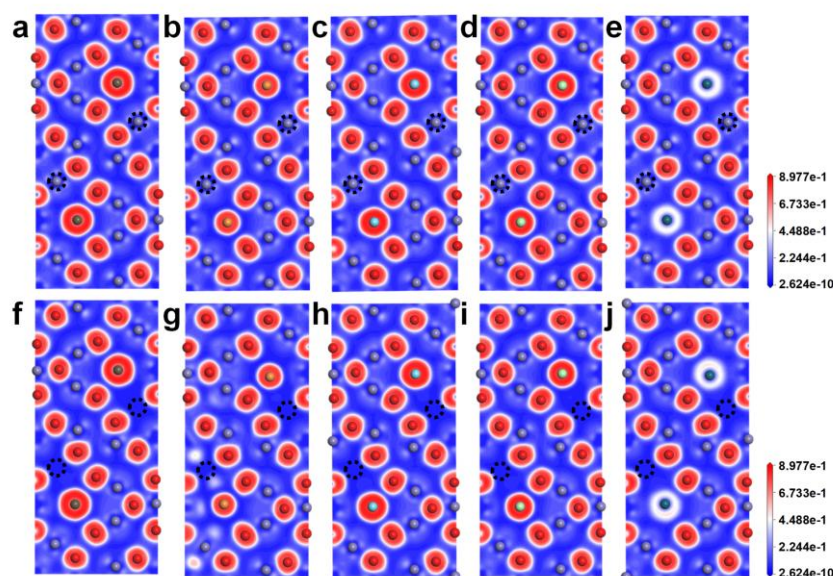
Supplementary Fig. 11 | Electronic band structure of the M-type (a) strontium ferrite and (b) iron-deficient strontium ferrite. The band gap of M-type strontium ferrite decreases from 0.329 eV to 0.181 eV by iron-deficient strategy.



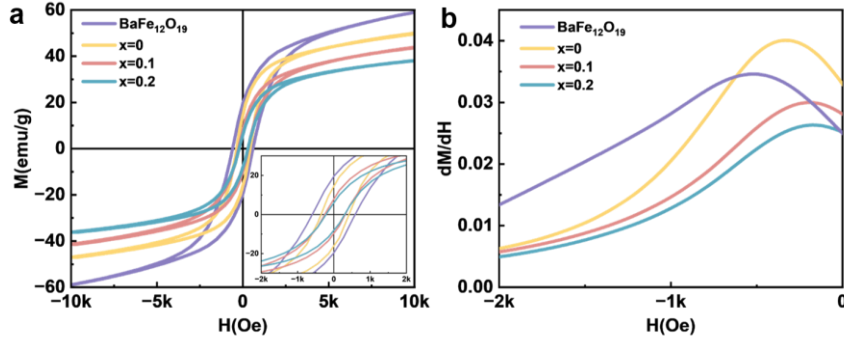
Supplementary Fig. 12 | Electronic band structure of the M-type (a) lead ferrite and (b) iron-deficient lead ferrite. The band gap of M-type lead ferrite decreases from 0.348 eV to 0.178 eV by iron-deficient strategy.



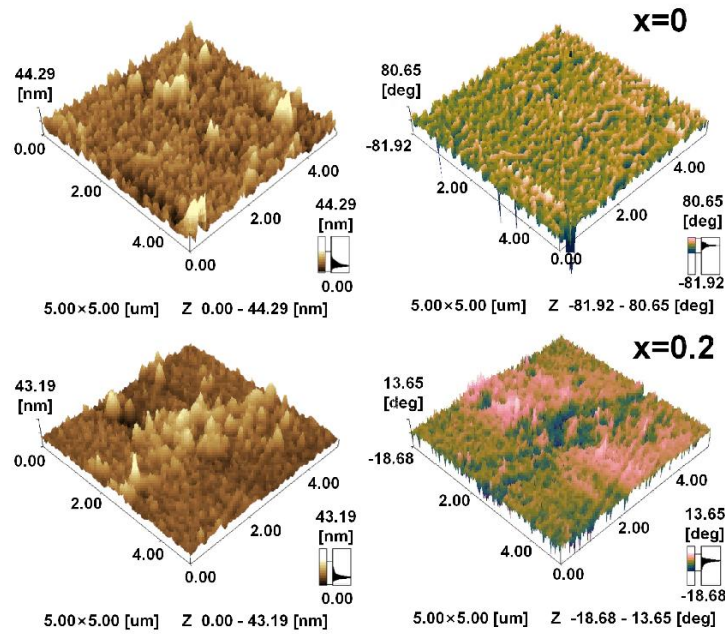
Supplementary Fig. 13 | Room-temperature DC resistivity of M-type (a) barium ferrite and (b) iron-deficient high-entropy ferrite with Zr^{4+} doping content of $x=0.1$ powders. The DC resistive values of iron-deficient high-entropy Zr^{4+} doped M-type ferrite powders have decreased by 3 to 4 orders of magnitude, consistent with the DFT calculation results that electronic band structure changing from semiconductor to conductor properties.



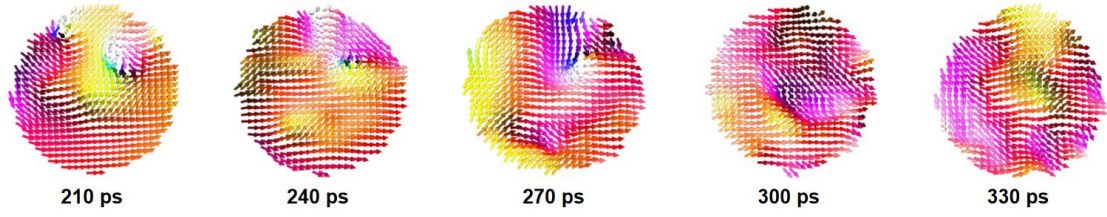
Supplementary Fig. 14 | Differential charge density maps of (a) $\text{BaFe}_{12}\text{O}_{19}$, (b) $\text{CaFe}_{12}\text{O}_{19}$, (c) $\text{LaFe}_{12}\text{O}_{19}$, (d) $\text{SrFe}_{12}\text{O}_{19}$, (e) $\text{PbFe}_{12}\text{O}_{19}$, (f) $\text{BaFe}_{11}\text{O}_{19}$, (g) $\text{CaFe}_{11}\text{O}_{19}$, (h) $\text{LaFe}_{11}\text{O}_{19}$, (i) $\text{SrFe}_{11}\text{O}_{19}$ and (j) $\text{PbFe}_{11}\text{O}_{19}$. Through comparison, it is found that the electron clouds of the ions near the iron vacancy have undergone obvious distortion for all the M-type ferrites. Blue and red regions represent electron depletion and accumulation, respectively.



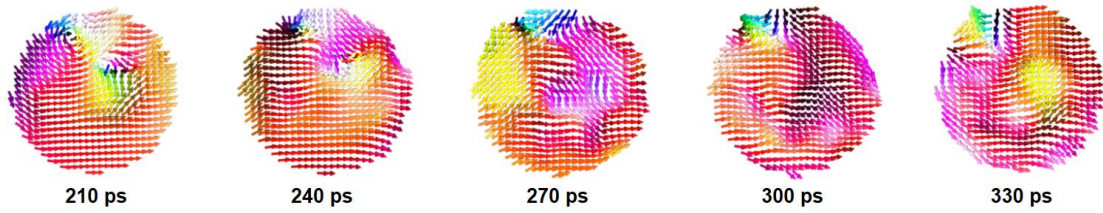
Supplementary Fig. 15 | (a) Hysteresis loops and (b) dM/dH - H plots of the M-type ferrites with composition of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ ($x=0, 0.1, 0.2$) and $\text{BaFe}_{12}\text{O}_{19}$ sintered at 1400°C for 3 h. The saturation magnetization and coercivity of the designed sample with $x=0$ is significant smaller than the M-type barium ferrite. Besides, both saturation magnetization and coercivity decrease with the increase of Zr^{4+} doping amount, indicating a deteriorated permanent magnetic performance.



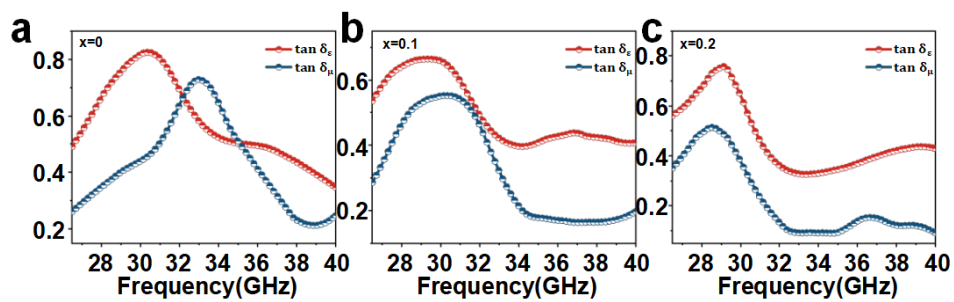
Supplementary Fig. 16 | Magnetic force microscopy images (3D) of the $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ with $x=0$ and $x=0.2$. It clearly shows the uniformity of particle size has deteriorated while the magnetic domain size has increased by Zr^{4+} doping.



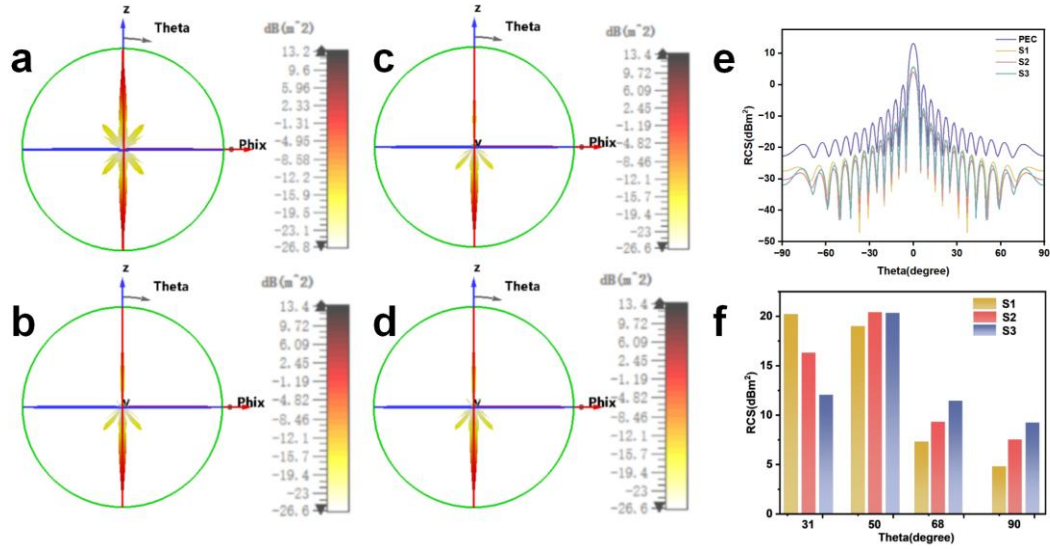
Supplementary Fig. 17 | Micromagnetic simulations of the pristine M-type barium ferrite. The shift, vanishment and reappearance of magnetic vortices subsequently occur under the influence of the external electromagnetic field for pure M-type barium ferrite.



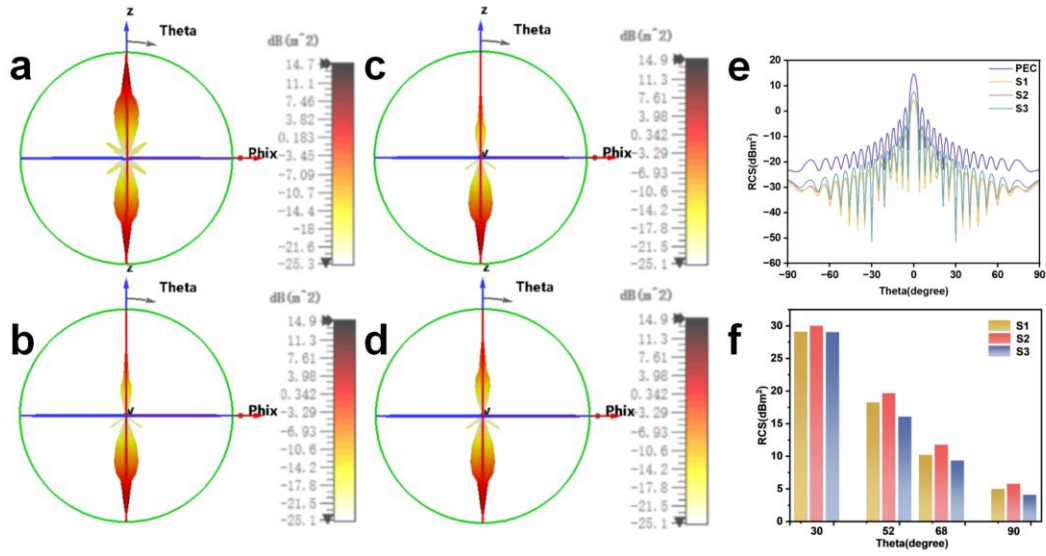
Supplementary Fig. 18 | Micromagnetic simulations of the high-entropy M-type ferrite. The more pronounced magnetic vortices are formed in the high-entropy M-type ferrites compared with the pure M-type barium ferrite, identified by the distinct color differences in magnetic moment directions.



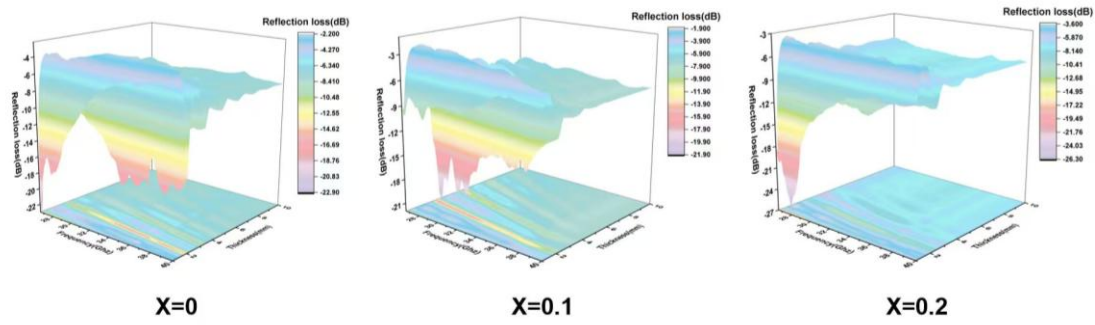
Supplementary Fig. 19 | Dielectric loss tangent ($\tan\delta_\epsilon$) and magnetic loss tangent ($\tan\delta_\mu$) of the M-type ferrites with composition of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ (a) $x=0$, (b) $x=0.1$ and (c) $x=0.2$ sintered at 1400°C for 3 h. Both large dielectric loss tangent and magnetic loss tangent are achieved for all the samples, and the peak in magnetic loss tangent shifts toward lower frequency range with increasing Zr^{4+} doping.



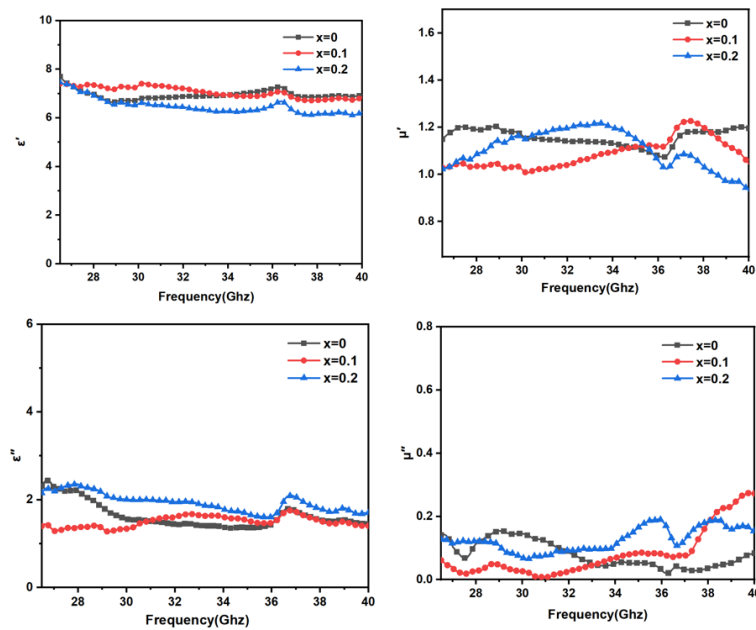
Supplementary Fig. 20 | The RCS values of the PEC plate simulated by CST at 32 GHz (a) without covering absorbing materials, covered by $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ with (b) $x=0$, (c) $x=0.1$ and (d) $x=0.2$; (e) 2D RCS curves and of the pure PEC plate, and the PEC plate covered by $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ with $x=0$ (S1), $x=0.1$ (S2) and $x=0.2$ (S3); (f) Relative RCS reduction values of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ with $x=0-0.2$ at specific angles. As the detection angle deviates gradually toward 90° and -90° , the RCS value decreases progressively and undergoes multiple fluctuations. The absorbing material-coated planes demonstrate weaker scattered signals in comparison with the original PEC plate.



Supplementary Fig. 21 | The RCS values of the PEC plate simulated by CST at 38 GHz (a) without covering absorbing materials, covered by $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ with (b) $x=0$, (c) $x=0.1$ and (d) $x=0.2$; (e) 2D RCS curves and of the pure PEC plate, and the PEC plate covered by $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ with $x=0$ (S1), $x=0.1$ (S2) and $x=0.2$ (S3); (f) Relative RCS reduction values of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ with $x=0-0.2$ at specific angles. As the detection angle deviates gradually toward 90° and -90° , the RCS value decreases progressively and undergoes multiple fluctuations. The absorbing material-coated planes demonstrate weaker scattered signals in comparison with the original PEC plate.



Supplementary Fig. 22 | The 3D RL values of the high-entropy ferrites with stoichiometric ratio of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{12-x}\text{Zr}_x\text{O}_{19}$ ($x=0-0.2$) sintered at 1400°C for 3 h. The samples with $x=0$, 0.1 and 0.2 reveal a deteriorated millimeter-wave absorption performance for the 35 GHz window with maximum absorption bandwidth of 5.15 GHz, 4.21 GHz and 6.63 GHz at matching thickness of 2.7mm, 2.8 mm and 1 mm, respectively.



Supplementary Fig. 23 | The electromagnetic parameters of the high-entropy ferrites with stoichiometric ratio of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{12-x}\text{Zr}_x\text{O}_{19}$ ($x=0-0.2$) sintered at 1400°C for 3 h. Compared with the high-entropy iron-deficient M-type ferrites, the samples without an iron-deficient design exhibit lower dielectric loss values in the range of 1.3-2.5, and the magnetic resonance peak is also reduced to merely 0.2-0.3 in magnitude.

Supplementary Tables:

Supplementary Table 1. The elemental mass content and molar content of the iron-deficient high-entropy M-type ferrites. The molar ratios of (Fe+Zr)/(Ba+La+Ca+Sr+Pb) in these samples are all obviously lower than that in the standard stoichiometric ratio M-type ferrite ($\text{MFe}_{12}\text{O}_{19}$, Fe:M=12:1).

test element	x=0		x=0.1		x=0.2	
	mass	molar	mass	molar	mass	molar
	content	content	content	content	content	content
	W (%)	W/M	W (%)	W/M	W (%)	W/M
Ba	2.843	0.0207	2.8283	0.0206	2.8694	0.0209
Ca	0.8271	0.0206	0.8166	0.0204	0.8153	0.0203
La	2.731	0.0197	2.7476	0.0198	2.7834	0.0200
Sr	1.8565	0.0212	1.8581	0.0212	1.8468	0.0211
Pb	4.1862	0.0202	4.1638	0.0201	4.1650	0.0201
Zr	0	0	0.9222	0.0101	1.8100	0.0198
Fe	62.6959	1.1226	62.6102	1.1210	62.5803	1.1206
Molar ratio (Fe+Zr)/ (Ba+La+Ca +Sr+Pb)	10.96:1		11.08:1		11.13:1	

Supplementary Table 2. The oxygen vacancy concentration of the iron-deficient high-entropy M-type ferrites with composition of $(\text{LaBaCaSrPb})_{0.2}\text{Fe}_{10.5}\text{Zr}_x\text{O}_{19}$ (x=0, 0.1, 0.2) sintered at 1400°C for 3 h. The content of oxygen vacancy is calculated to decrease gradually from 31.86% to 29.59% with Zr^{4+} content increasing from x=0 to x=0.2.

x	c (OV)
0	31.86%
0.1	30.14%
0.2	29.59%

Supplementary Table 3. Mössbauer parameters of the iron-deficient high-entropy M-type ferrite without Zr^{4+} doping sintered at 1400°C for 3 h. The distribution proportions of five Fe^{3+} sextets (12k, 4f₁, 4f₂, 2a, 2b) are identified to be close to the theoretical ratio of 50:17:17:8:8.

Position	IS(mm/s)	QS(mm/s)	H(T)	Γ (mm/s)	Area(%)
4f ₂	0.21	0.20	50.03	0.41	18.50
4f ₁	0.46	0.35	50.87	0.37	19.20
12k	0.36	0.36	42.29	0.41	46.20
2a	0.20	-0.32	50.27	0.28	8.60
2b	0.24	0.05	32.64	0.65	7.50

Supplementary Table 4. Mössbauer parameters of the iron-deficient high-entropy M-type ferrite with Zr^{4+} doping ratio of x=0.2 sintered at 1400°C for 3 h. The distribution proportions of trigonal site (2b) and tetrahedral site (4f₁) to octahedral sites (12k, 4f₂, and 2a) decrease obviously upon Zr^{4+} doping.

Position	IS(mm/s)	QS(mm/s)	H(T)	Γ (mm/s)	Area(%)
4f ₂	0.29	0.23	48.16	0.48	24.40
4f ₁	0.40	0.30	50.59	0.36	15.60
12k	0.35	0.36	41.57	0.50	45.10
2a	0.10	-0.30	48.88	0.49	8.10
2b	0.19	0.36	32.85	0.59	6.80