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Research Article

Large terahertz faraday rotation in high entropy M-type hexaferrites

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Abstract

Magneto-optical materials exhibiting strong Faraday rotation are essential for advanced non-reciprocal photonic and electronic devices. Beyond conventional doping, high-entropy design offers a novel paradigm for engineering functional properties by introducing atomic-scale configurational disorder. Here, high-entropy M-type hexaferrite $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{La}_{0.2})\text{Fe}_{12}\text{O}_{19}$ (HEM) ceramics were prepared and characterized systematically. While retaining the hexagonal structure ($P6_3/mmc$), HEM displays significantly enhanced room-temperature magnetic properties ($M_s \approx 53.5$ emu/g) and a giant Faraday rotation angle ($\sim 105^\circ/\text{mm}$) at 0.2 THz. Raman spectroscopy reveals that the elemental high entropy at the *Me*-site modifies the local Fe-O bonding, especially strengthening the Fe-O stretching at the $2b$ site, which may contribute to the enhanced $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ superexchange interactions. Meanwhile, the refined domain structures may be associated with a higher domain wall density and are consistent with the enhanced magnetization under an applied magnetic field. These two contributions synergistically support the simultaneous enhancement of magnetic and magneto-optical responses. This work establishes high-entropy design as a powerful strategy for tailoring the magnetic properties and Faraday effect of M-type hexaferrites, paving the way for further innovations in advanced ferromagnetic materials.

Keywords: High entropy, M-type Hexaferrites, THz spectroscopy, Faraday rotation

Introduction

Ferrites with a hexagonal crystal structure are termed hexaferrites (HFs). These materials are extensively studied due to their high magnetocrystalline anisotropy and excellent magnetic properties, enabling applications in memory devices[1], communication antennas[2], catalysis[3-5], microwave absorbers[6-8], sensors[9] and optical isolators [10], etc. Among all these HFs, M-type subgroup is particularly prominent owing to its relatively simple crystal structure and strong uniaxial magnetic anisotropy along the c -axis. M-type hexaferrites with a general formula $MeFe_{12}O_{19}$ (where Me typically is a divalent cation such as Sr, Ba, Pb, or Ca), exhibit a hexagonal structure with the space group $P6_3/mmc$ at room temperature. The diversity of possible Me cations allows for the synthesis of high-entropy M-type hexaferrites with a stable and single phase structure[11, 12]. The unit cell features a layered structure described by the stacking sequence SRS^*R^* . Here S is the spinel block $(Fe_6O_8)^{2+}$, R represents the hexagonal block $(MeFe_6O_{11})^{2-}$, and asterisk (*) indicates a 180° rotation of the S/R block around the c -axis[13]. Specifically, each unit cell comprises a total of 64 ions, among which 24 iron ions are distributed across five different sites: $2a$, $2b$, $4f1$, $4f2$, and $12k$, as shown in Fig. 1a. Spins at $2a$, $2b$, and $12k$ sites are oriented in the upward direction, while those at $4f1$ and $4f2$ sites are oriented downward. This antiparallel ferrimagnetic spin alignment results in a net magnetic moment of $20 \mu_B$ per formula unit (equivalent to $5 \mu_B$ per Fe^{3+} ions). This room-temperature ferrimagnetic behaviour of M-type subgroup originates from the superexchange interactions between adjacent Fe^{3+} ions mediated by O^{2-} ions [14], as illustrated in Fig. 1b, which also confer a large saturated magnetisation and high coercivity. Moreover, the ferrimagnetism in $LaFe_{12}O_{19}$ system, owing to the presence of Fe^{2+} cations, arises not only from superexchange interactions between Fe^{3+} ions but also from superexchange interactions between Fe^{2+} ions and possible Fe^{3+} - O^{2-} - Fe^{2+} mechanism[15], depicted in Fig. 1b. The combination of strong ferrimagnetism and non-dispersive gyrotropic features makes M-type hexaferrites ideal candidate materials for nonreciprocal devices especially at microwave/terahertz frequencies.

The Faraday rotation effect is a magneto-optical phenomenon in which the polarization plane of a linearly polarized light beam rotates as it propagates through a medium under an applied magnetic field parallel to its direction of propagation[16]. As illustrated in Fig. 1c, this typically results in an elliptically polarized transmitted beam, an outcome known as Faraday rotation[10]. While extensive research on Faraday rotation has been conducted in the microwave and infrared frequencies[16], the terahertz frequencies—which lies between them—has received comparatively little attention. It is therefore essential to extend the study of the Faraday rotation effect to the terahertz frequencies. Such research is crucial for applications like suppressing back-reflected radiation, which enables source protection and noise cancellation[17, 18]. Previously, observing the Faraday effect required the application of an external magnetic field, which was both costly and complicated[19, 20]. Recently, a zero-magnetic field methodology has been developed to measure Faraday rotation of magnetized materials using the modified terahertz time-domain spectroscopy (THz-TDS), as

demonstrated in our previous work[13]. As reported for YIG ferrites, the total non-reciprocal phase rotation (Φ) in the THz region can be calculated as the below equation 1[18]:

$$\Phi = \frac{\beta_+ - \beta_-}{2} z \quad (1)$$

where β_+ and β_- are propagation constants of the right-handed circularly polarized (RCP) and left-handed circularly polarized (LCP) waves, respectively. z is the sample thickness. These two propagation constants can be described by $\beta_+ = \omega n_+/c$ and $\beta_- = \omega n_-/c$, respectively, where ω is the circular frequency of the incident wave, n_+ and n_- are refractive indices for the RCP and LCP eigenwaves, and c is the speed of light ($\approx 3 \times 10^8$ m/s). Substituting these expressions into equation (1) yields:

$$\Phi = \frac{\omega(n_+ - n_-)}{2c} z \quad (2)$$

Though the incident frequency ω of THz waves varies, the intrinsic factors governing Φ are primarily the refractive index difference ($n_+ - n_-$) and sample thickness z [18].

The compositional design via ions doping and solid-solution formation is a prevalent strategy for tuning magnetic properties[21]. This approach works by influencing key electronic and microstructural parameters, including lattice parameters, grain size, content of point defects, indirect exchange interactions between adjacent magnetic ions, etc. For example, introducing magnetic ions with larger magnetic moments into the crystal lattice can directly increase the saturation magnetization[22] and tune microwave dielectric properties [23]. One common methodology involves the partial substitution of host cations (Me^{2+} or Fe^{3+} ions) with dopants of identical valence but differing ionic radii [13, 22, 24-28]. This substitution may induce significant lattice distortion, which can increase the net magnetic moment and strengthen indirect exchange interactions between magnetic ions of mixed valence states or ionic radii. The concept of high entropy (HE), first proposed in the context of alloys[29, 30], has recently gained significant attention across materials science. High entropy alloys (HEAs) are typically defined as single phase materials containing five or more principal elements in near-equimolar ratios at the same lattice point, yielding a configurational entropy exceeding $1.5R$ (where R is the gas constant)[31, 32]. This paradigm has since been extended to numerous material classes, including oxides[31, 33, 34], carbides[35], nitrides[36], silicides[37, 38], which have attracted considerable research interest due to their superior properties.

Though few studies have reported high entropy HFs with compelling magnetic performances[24, 39, 40], this area remains underexplored. In contrast to parent compositions, high-entropy magnetic oxides possess a complex crystal structure. This complexity and crystal heterogeneity manifests as locally disordered magnetic moments and enhanced spin-induced polarization[41], enabling significant tuning of key properties such as saturated magnetization, magneto-optical, magnetoelectric, dielectric and mechanical properties, etc[42]. Despite this potential, research on the Faraday rotation effect in high entropy magnetic oxides is scarce, without reported studies in the THz band. As a result, the current understanding of the magnetic and magneto-optical properties of this novel class of materials remains fundamentally incomplete.

In this work, the composition $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{La}_{0.2})\text{Fe}_{12}\text{O}_{19}$ was designed, whose configurational entropy ($\Delta S_{\text{config}} \approx 1.61 \text{ R}$) exceeds the typical threshold of 1.5R for high entropy materials. The selection of these elements is well-supported in other high-entropy oxides, such as $(\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Pb}_{0.5})\text{Nb}_2\text{O}_7$ [43], $(\text{Li}_{0.2}\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{La}_{0.2})\text{TiO}_3$ [44] and $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{La}_{0.2}\text{Pb}_{0.2})\text{TiO}_3$ [45] ceramics, etc. Furthermore, the feasibility of designing high-entropy M-type hexaferrites using Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , and La^{3+} cations is well supported by reported works in low entropy M-type HFs like $\text{BaFe}_{12}\text{O}_{19}$ [26, 46], $\text{SrFe}_{12}\text{O}_{19}$ [47], $\text{PbFe}_{12}\text{O}_{19}$ [11, 25], and $\text{LaFe}_{12}\text{O}_{19}$ [48]. While ion doping has been shown to enhance the THz Faraday rotation of M-type HFs, for example from 0.75 to 1.30 in Nb doped $\text{SrFe}_{12}\text{O}_{19}$ ceramics[13]. In contrast, this high entropy strategy offers three distinct advantages: (i) severe lattice distortion, (ii) sluggish diffusion, and (iii) the cocktail effect. Nevertheless, the THz Faraday rotation of high entropy HFs has not yet been systematically investigated, and the present study provides the first experimental evidence of entropy-engineered THz Faraday rotation responses in the M-type HFs.

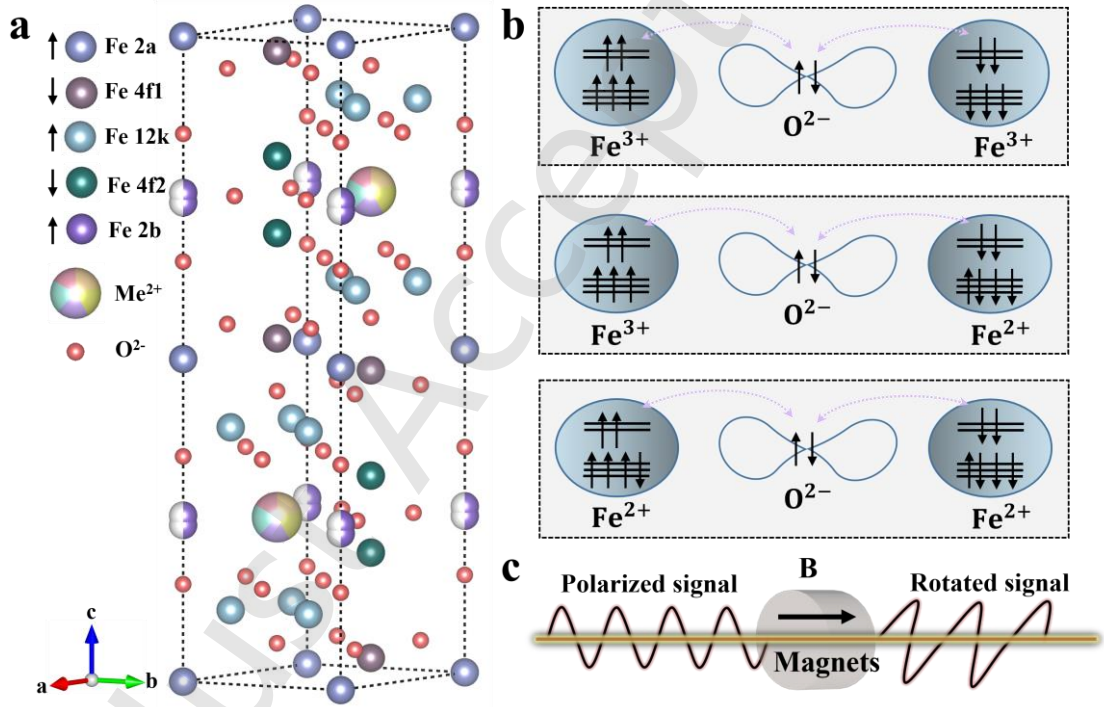


Figure 1. (a) The crystal structure of HEM hexaferrites with space group $P6_3/mmc$. (b) Superexchange interactions between adjacent Fe^{3+} (Fe^{2+}) ions mediated by O^{2-} ions. (c) Schematic of Faraday rotation effect.

2. Materials and methods

High purity powders of CaCO_3 (99.0%, Sigma), SrCO_3 (99.9%, Sigma), BaCO_3 (99.8%, Alfa), PbO (99.9%, Sigma), La_2O_3 (99.9%, Sigma) and Fe_2O_3 (99.945%, Alfa) were used as starting materials to synthesize high-entropy hexaferrites with the chemical formula $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{La}_{0.2})\text{Fe}_{12}\text{O}_{19}$ ceramics, abbreviated as HEM. Prior to weighing, the carbonate precursors (CaCO_3 , SrCO_3 , and BaCO_3) were dried at 200°C for 24 h to remove the absorbed moisture. All starting powders were weighed precisely according to

the stoichiometric ratios and ball-milled in ethanol for 12 hours at 250 rpm using stainless steel balls. The prolonged milling step is crucial for achieving the fine particle size and homogeneity. The resulting slurry was then calcined in air at 1100°C for 6 hours. To ensure microstructural homogeneity, the calcined powder was subjected to a second round of ball-milling under identical conditions. The milled powder was mixed with 10wt% polyvinyl alcohol (PVA) and then heated to 800°C in air for 2 hours. Finally, all ceramic pellets were sintered in an oxygen-rich atmosphere at 1200°C for 6 hours. The density of the ceramics was measured using the Archimedes method.

The crystal structure of sintered $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{La}_{0.2})\text{Fe}_{12}\text{O}_{19}$ ceramics was analyzed by X-ray powder diffraction (XRD) using a Panalytical X'Pert Pro CubiX3 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Data was collected over a 2θ range of 5-120° with a step size of 0.0315°. The morphology and elemental distribution of thermal etched HEM ceramics were studied by scanning electron microscopy (SEM, FEI Inspect-F, Oxford, UK) equipped with an energy-dispersive X-ray spectrometer (EDX, Oxford INCA, UK). Chemical states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) after surface cleaning by Ar^+ ion etching. The Fe 2p and O 1s XPS spectra were deconvoluted using a Shirley background and the Gaussian-Lorentzian product (GLP) function, as reported in previous work[49]. Local Fe-O bonding environments were probed using Raman spectroscopy (Horiba LabRAM HR Evolution). Domain morphologies were imaged by magnetic force microscopy (MFM, Bruker Dimension Icon) at room temperature. High-resolution transmission electron microscopy (HRTEM, FEI Verios G4) was employed to further investigate the micromorphology and lattice spacings of the crushed HEM powder.

For dielectric measurements, HEM ceramics were polished to 0.5 mm thickness and coated with silver paste (Gwent Electronic Materials Ltd., C2011004D5). The temperature dependence of the relative permittivity (ϵ') and loss tangent ($\tan\delta$) was measured from -160°C to 160°C at selected frequencies using an LCR meter (Agilent 4284A) integrated with a computer-controlled furnace. Magnetic hysteresis (M - H) loops, along with zero-field-cooling (ZFC) and field-cooling (FC) magnetization curves, were acquired using a vibrating sample magnetometer integrated with a superconducting quantum interference device (VSM-SQUID, Quantum Design) over a wide range of magnetic fields and temperatures. The Faraday rotation of pre-magnetized HEM ceramics (~0.8 mm thick) in the THz region was characterized using a modified terahertz time-domain spectroscopy system (THz-TDS, Techs Ltd, Canada) in a transmission mode[13]. The complex permittivity and loss tangent in this paper were extracted from the Fourier-transformed THz time-domain spectrum[50].

3. Results and discussion

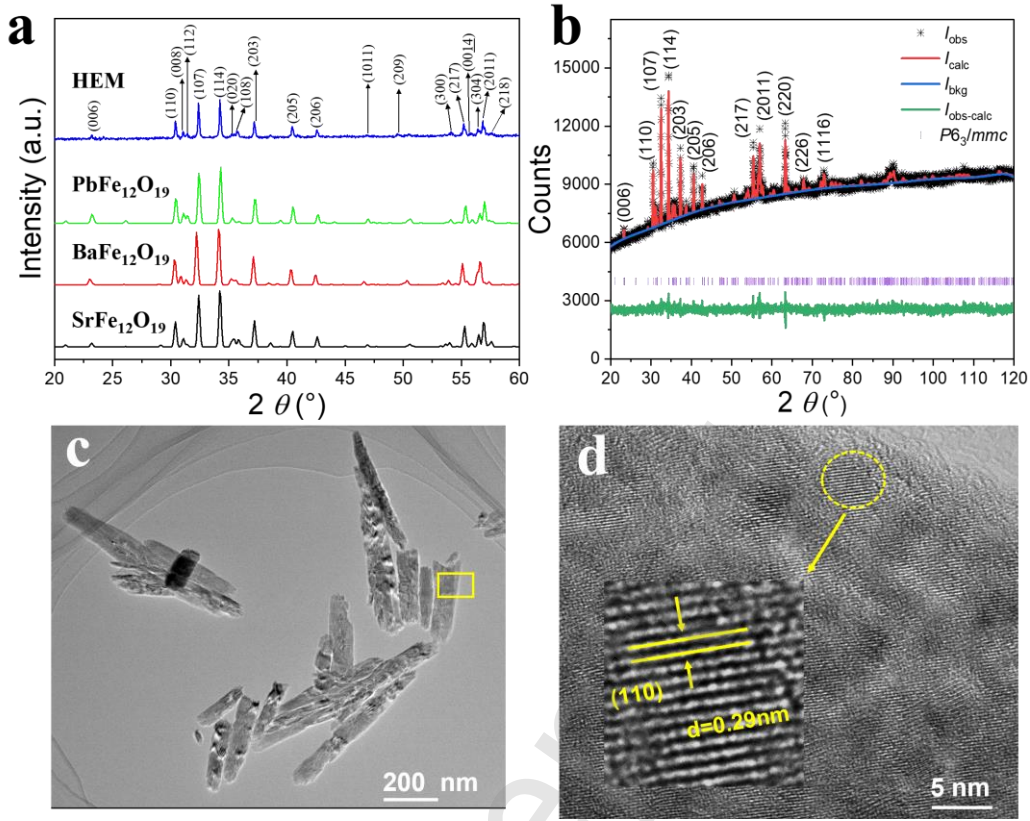


Figure 2. (a) Room temperature XRD pattern of HEM crushed powder with labelled hkl lines, in comparison with standard PDF files for other M-type hexaferrites. (b) Rietveld refinement of HEM XRD pattern. (c) Bright field image and (d) HRTEM image of crushed HEM powder.

All characterized HEM ceramics exhibited dense microstructures, with a relative density of approximately 95%. Figure 2 presents the room-temperature XRD pattern of sintered and crushed $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{La}_{0.2})\text{Fe}_{12}\text{O}_{19}$ powder. All observed diffraction peaks, indexed with their corresponding hkl planes in Fig. 2a, are in good agreement with the standard ICDD Powder Diffraction Files of other M-type hexaferrites (e.g., $\text{SrFe}_{12}\text{O}_{19}$ #33-1340, $\text{BaFe}_{12}\text{O}_{19}$ #43-0002, and $\text{PbFe}_{12}\text{O}_{19}$ #41-1373, $\text{CaFe}_{12}\text{O}_{19}$ #27-1029, and $\text{LaFe}_{12}\text{O}_{19}$ #13-0474). In this regard, HEM hexaferrite ceramics prepared by a conventional solid-state reaction method, crystallizes as a single hexagonal phase with the $P6_3/mmc$ (No. 194) space group, demonstrating the entropy-stabilization effect on the phase structure. The XRD pattern of HEM was refined using the GSAS software, assuming that Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} and La^{3+} cations occupy the same crystallographic site. The refinement converged with good statistics, as evidenced by the low R_p (1.06%), R_{wp} (0.81%), and χ^2 (1.440) values. The refined lattice parameters are summarized in Table S1, with a comparative analysis against other M-type hexaferrites (Table S2). The c/a ratio and lattice volume for HEM is 3.918 and $691.30 \text{ \AA}^3$, respectively, which are comparable to those reported for pure $\text{SrFe}_{12}\text{O}_{19}$ ($c/a = 3.921$, $V = 692.89 \text{ \AA}^3$)[13]. This alignment can be attributed to the similar ionic radii of the constituent cations. The average ionic radius at the A-site is $1.448 \text{ \AA}$ for HEM, which closely matches that of Sr^{2+} ($\sim 1.44 \text{ \AA}$). The microstructure of the synthesized HEM ceramics was further examined by low resolution and high-resolution TEM. Fig. 2c

reveals a bar-shaped crystal, a morphology consistent with the hexagonal crystal structure and indicative of strong crystalline anisotropy at room temperature. A representative HRTEM image taken from the region marked by the yellow rectangle area in Fig. 2c is shown in Fig. 2d. The image displays well-defined lattice fringes with an interplanar spacing of 0.29 nm, corresponding to the (110) crystal plane of HEM ceramics. The SAED pattern of HEM was depicted in Figure S1 and is referenced with Miller indices in the corresponding SAED visual representations. The good agreement between SAED and XRD pattern confirms the structural assignment and single hexagonal phase of HEM sample.

Elemental composition and distribution were analyzed using SEM coupled with EDX. Figure 3 represents the grains' morphology and corresponding EDX mapping images of HEM ceramics after thermal etching. The microstructure consists of densely packed, flake-like grains with average dimensions of approximately $3.2 \pm 0.5 \mu\text{m}$ in diameter and $0.6 \pm 0.2 \mu\text{m}$ in thickness. The dense microstructure with fine grain size can be attributed to the sluggish diffusion inherent to the high-entropy design. In M-type hexaferrites, the *c*-axis represents the preferred growth direction for such platelet morphology. As reported by hexaferrites with layered structures[51], this crystallographic orientation is perpendicular to the easy magnetic axis along *c* axis. The EDX mapping results depicted in Figs. 3a-g demonstrate that constituent elements (Ca, Sr, Ba, Pb, La, Fe and O) are distributed uniformly on the fracture surfaces. Quantitative EDX analysis (Table S3) further verifies that the experimental atomic percentages of all elements align closely with their theoretical stoichiometric values, confirming the successful synthesis of the targeted HEM composition.

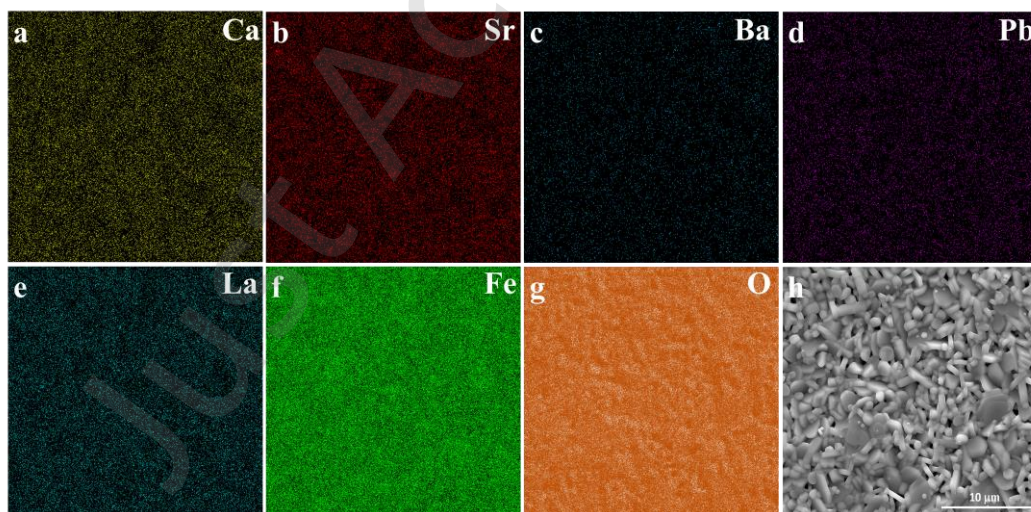


Figure 3. EDX mapping (a-g) and SEM micrograph (h) of HEM hexaferrites after thermal etching.

The chemical states and electronic structures of constituent elements in the HEM sample were analyzed by XPS. The survey spectrum and high-resolution spectra for Ca 2p, Sr 3d, Ba 3d, Pb 4f and La 3d core levels are presented in Figs. S2a-f, with all binding energies corrected by standard carbon peaks (284.8 eV). As shown in Fig. S2a, from the full survey spectrum of HEM, signals of Ca, Sr, Ba, Pb, La, Fe, and O are easily identified, confirming the designed composition. In the Ca 2p spectra (Fig. S2b), the dominant peaks are located at 350.48 eV and 346.78 eV, corresponding to $\text{Ca}^{2+} 2p_{1/2}$ and $\text{Ca}^{2+} 2p_{3/2}$, respectively. The Sr 3d

spectrum is fitted with spin-orbit doublets at 135.28 eV and 132.98 eV, characteristic of Sr^{2+} . Similarly, the Ba 3d peaks at 794.78 eV and 779.58 eV are assigned to $\text{Ba}^{2+} 3d_{3/2}$ and $\text{Ba}^{2+} 3d_{5/2}$. The asymmetric Pb 4f peaks at approximately 137.7 eV and 142.5 eV align with $\text{Pb}^{2+} 4f_{7/2}$ and $\text{Pb}^{2+} 4f_{5/2}$, consistent with previous studies of PbO[52]. As illustrated in Fig. S2f, the characteristic peaks of La 3d are located at 834.9, 838.8, 851.8 and 855.6 eV, corresponding to the +3 state of La ions. The asymmetric Fe 2p spectrum (depicted in Fig. 4a) was deconvoluted to reveal the coexistence of Fe^{2+} and Fe^{3+} cations. The corresponding binding energies for $\text{Fe}^{3+} 2p_{3/2}$ and $\text{Fe}^{2+} 2p_{3/2}$ are summarized in Table S4. The partial reduction of Fe^{3+} is attributed to the charge compensation upon La^{3+} incorporation, as well as the oxygen vacancy formation during high sintering temperature. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio for HEM was quantitatively derived from the area ratio of the $\text{Fe}^{2+} 2p_{3/2}$ and $\text{Fe}^{3+} 2p_{3/2}$ peaks in the deconvoluted XPS spectra, consistent with previous work. The calculated ratio is 0.23(2) for HEM, much lower than that of pure SrM[13]. According to charge neutrality considerations, the reduction of Fe^{3+} is intrinsically coupled with the generation of oxygen vacancies. This is further supported by the deconvolution of the O 1s spectrum (Fig. 4b), which reveals three components at 533.58 eV (adsorbed oxygen), 531.58 eV (oxygen in the reduced state), and 530.28 eV (lattice oxygen)[53, 54]. Given that magnetic properties can be tuned by Fe^{2+} ions and oxygen vacancies (defect chemistry), it is compulsory to distinguish the individual contributions of each defect species. In conventional La^{3+} doped M-type HFs[15, 48, 55], the substitution of divalent cations by La^{3+} is known to induce partial Fe^{3+} reduction for charge compensation. However, although the present HEM composition also contains a substantial amount of La^{3+} , the significantly lower $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio indicates that the high-entropy design effectively suppresses Fe^{3+} reduction. Therefore, changes of magnetic/dielectric properties of HEM cannot be attributed to the presence of La^{3+} substitution, but rather originates from the collective high-entropy effect.

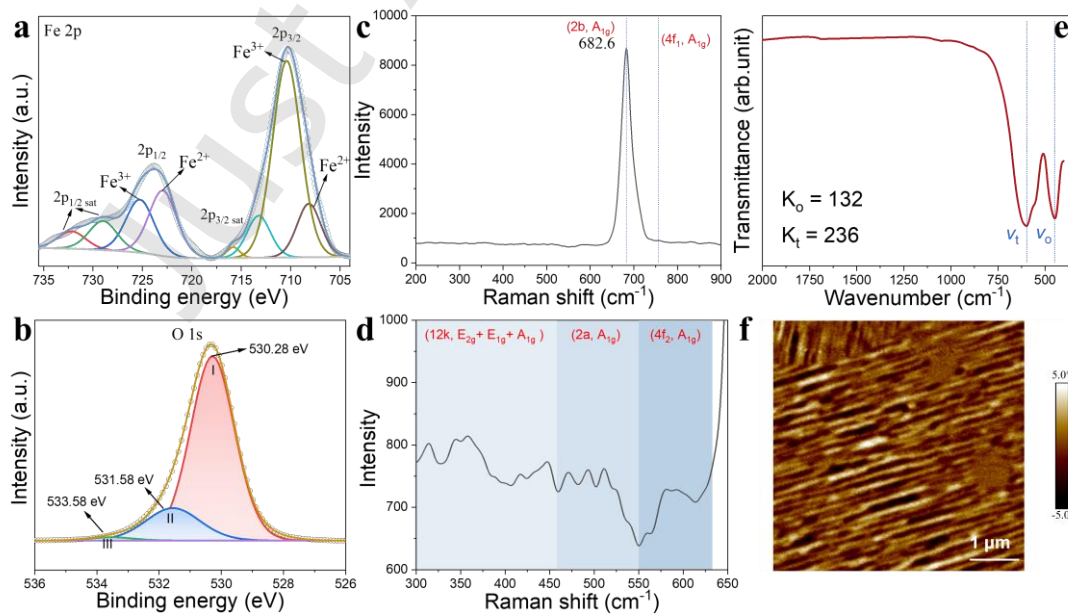


Figure 4. Deconvoluted Fe 2p (a), and O 1s (b) high resolution XPS spectra of HEM pellets. (c) Raman spectra of crushed HEM powder within 200-900 cm^{-1} . (d) Enlarged view of Raman spectra from 300 to 650

cm⁻¹. (e) FTIR spectra measured at room temperature from 2000 to 400 cm⁻¹. (f) The MFM phase image of polished HEM ceramics.

Raman spectroscopy was employed to probe the local structural environment and potential lattice disorder in the HEM ceramics. Group theory predicts 42 Raman-active modes (11 A_{1g} + 14 E_{1g} + 17 E_{2g})[56, 57] in SrFe₁₂O₁₉ and BaFe₁₂O₁₉ ferrites. Room-temperature Raman data was presented in Figs. 4c, d, with frequencies of major peaks corresponding to Fe–O vibrations summarized in Table S5. Based on earlier established assignments for M-type hexaferrites[57], the Raman peak at 682.6 cm⁻¹ (Fig. 4c) with the most intense response is attributed to the stretching vibration of Fe–O bonds at the 2b site[58]. This greatly enhanced Fe (2b)-O bonding may contribute to, though does not directly prove, an enhancement of the Fe³⁺(2b)–O²⁻–Fe³⁺(2b) superexchange interaction. While other weaker Raman features (Fig. 4d) originate from symmetric stretching modes associated with Fe–O bonds at the 2a, 12k sites and 4f₂ site[58-60].

Fig. 4e represents the FTIR spectrum of HEM hexaferrite. Two characteristic absorption bands are observed at approximately 448 cm⁻¹ (ν_o) and 599.27 cm⁻¹ (ν_t), corresponding to the stretching vibrations of Fe–O bonds at octahedral (2a, 12k) and tetrahedral sites (4f₂), respectively[58, 61]. The force constant for tetrahedral site (K_t) and octahedral site (K_o) is determined by equations 3 and 4 [58, 61], as given below:

$$K_t = 4\pi^2 c^2 \nu_t^2 \mu \quad (3)$$

$$K_o = 4\pi^2 c^2 \nu_o^2 \mu \quad (4)$$

Where c is the light speed, ν_t corresponds to the wavenumber of tetrahedral sites, while ν_o corresponds to the wavenumber of octahedral sites, and $\mu (= \frac{M_o \times M_{Fe}}{M_o + M_{Fe}})$ is the reduced mass of the Fe³⁺(Fe²⁺) and O²⁻ ions ($\sim 1.85 \times 10^{-26}$ kg). Based on the measured wavenumbers, the calculated force constants are $K_o \approx 132$ N/m and $K_t \approx 236$ N/m. The comparison of wavenumbers and force constants with those of BaM and SrM hexaferrites is summarized in Table S6. Evidently, both the K_o and K_t values of HEM are smaller than those of BaM but larger than those of SrM. Since the force constant K serves as a symbol of the Fe-O bonding strength and stiffness, a shorter bond length and stronger bonding manifest as larger K values. Such structural modifications may further impact magnetic properties of the design hexaferrites.

The MFM measurements were performed on a well-polished pellet with a surface roughness below 20 nm to ensure reliable phase contrast. The corresponding MFM phase image is shown in Fig. 4f, covering a scan area of 5 $\mu\text{m} \times 5 \mu\text{m}$. The alternating dark and bright contrast within the MFM phase image correspond to domains with different out-of-plane magnetization orientations. Well-defined stripe magnetic domains are clearly observed, with an average width of $0.23 \pm 0.05 \mu\text{m}$ and a length of $2.15 \pm 0.60 \mu\text{m}$. These magnetic domains with slight angular variation caused by high configurational entropy design may be associated with high domain wall mobility, thereby enabling an enhanced magnetization under an applied magnetic field. The presence of such stripe domains, which are analogous to those reported in other uniaxial hexaferrites[62],

provides direct evidence for the magnetocrystalline anisotropy inherent to the layered structure of HEM compositions.

As shown in Fig. 5a, the permittivity increases monotonically over the entire temperature range. The increase in permittivity at high temperatures is mainly caused by thermally excited polarization and defects (vacancies, defect pairs and domain walls)[63]. A prominent, frequency-dependent relaxation peak is observed in the loss tangent. The peak temperature shifts from 280 K at 1 kHz to 395 K at 100 kHz, indicating a thermally activated relaxation behaviour. This relaxation behaviour can be attributed to combined effects of the electron hopping process ($d-d$ transitions) and point defects (*e.g.*, oxygen vacancies), consistent with previous reports on M-type hexaferrites[13, 64]. This relaxation behaviour should follow the Arrhenius law:

$$f = f_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (5)$$

where f is the measurement frequency, f_0 is the frequency constant, E_a is the activation energy of charge carriers, k_B is Boltzmann's constant, and T is the temperature corresponding to the loss tangent. As highlighted in Fig. 5b, the activation energy E_a (0.43 eV) and characteristic relaxation frequency f_0 (1.69×10^{10} Hz) are typical values for oxygen vacancy migration in M-type HFs[13]. Furthermore, room-temperature permittivity decreases significantly with increasing frequency, following the Koop's phenomenological theory[55]. At higher frequencies, the space charge polarization and electron hopping between defect sites cannot follow the rapidly oscillating electric field, leading to a reduced dielectric response.

Temperature dependent dielectric properties for HEM from RT to 350°C are shown in Figure S3. Two distinct anomalies are observed in both relative permittivity and loss tangent across the measured temperature range. The first anomaly, centered at approximately 300°C, exhibits strong frequency dispersion, with the peak position shifting toward higher temperatures with decreasing frequency. This behaviour is characteristic of a relaxor-like phase transition, consistent with the ferrimagnetic to paramagnetic transition commonly observed in M-type hexaferrites[13]. The frequency dependent relaxation near this transition arises from the critical slowing down of spin dynamics or concomitant fluctuation of local magnetic moments ($\text{Fe}^{2+}/\text{Fe}^{3+}$). Moreover, the ϵ_m' decreases with the measured increasing frequency, because the electron hopping fails to follow the rapidly alternating electric field, resulting in a frequency-dependent reduction in polarization until it stabilizes[4]. The second anomaly, located at approximately 200°C, also displays frequency dependent characteristics. This feature is tentatively attributed to magnetic structural transitions associated with domain wall motion. However, the precise microscopic origin of this anomaly: whether dominated by domain wall relaxation, dipolar effects, or electron hopping between Fe^{2+} and Fe^{3+} remains to be clarified. Further investigations, including temperature dependent magnetic and structural characterizations, are required to unambiguously resolve the critical behaviour of HEM at high temperatures.

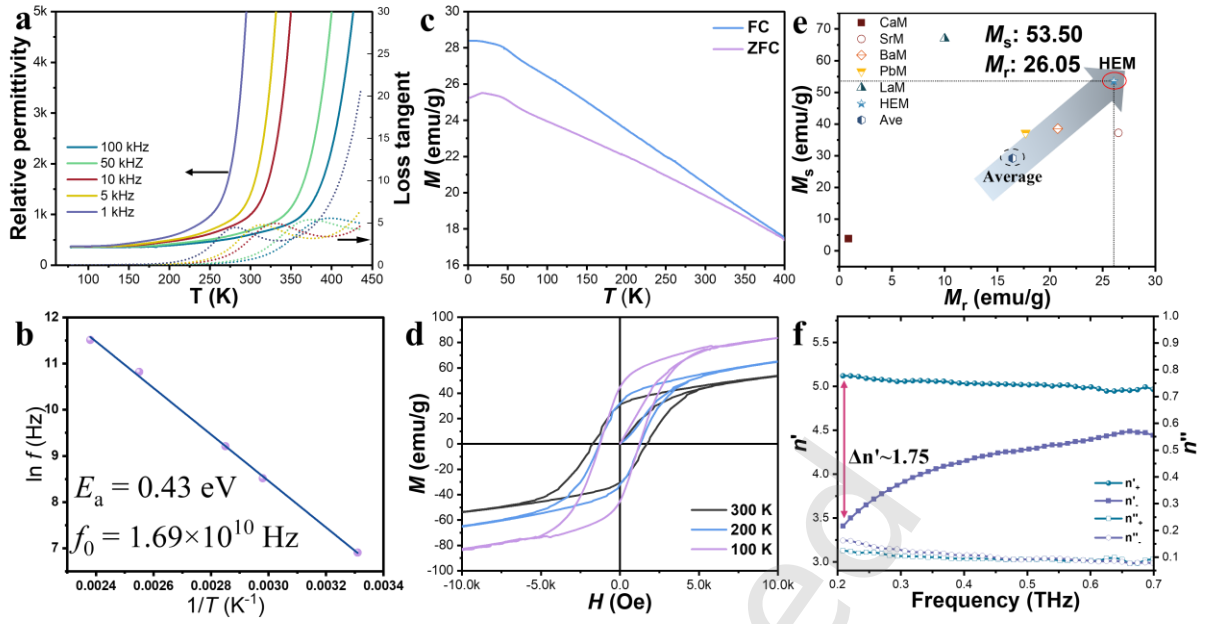


Fig 5. (a) Temperature dependence of relative permittivity and loss tangent of HEM ceramics. (b) Arrhenius law fitting of loss tangent data. (c) ZFC and FC curves of HEM ceramics measured within 1.8 K to 400 K. (d) Variation temperature M - H loops of HEM ceramics within ± 10 kOe. (e) A comparison of the M_s and M_r of prepared HEM ceramics and the state-of-the-art low entropy M type HFs[11, 48, 65]. Here, CaM, SrM, BaM, PbM, and LaM represent $\text{CaFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$, $\text{BaFe}_{12}\text{O}_{19}$, $\text{PbFe}_{12}\text{O}_{19}$, and $\text{LaFe}_{12}\text{O}_{19}$, respectively. (f) Faraday rotation of HEM ceramics after magnetizing in the THz band.

The magnetic properties of HEM ceramics were characterized by temperature-dependent magnetization measurements. Fig. 5c presents the FC and ZFC magnetization curves, while Fig. 5d shows M - H hysteresis loops measured at various temperatures under an applied field of ± 10 kOe. HEM exhibits typical hard ferrimagnetic behaviour across the entire temperature range. The saturated magnetization (M_s) increases significantly at cryogenic temperatures, a trend consistent with the FC/ZFC data and attributable to reduced thermal perturbation of spins. Conversely, the coercive field (H_c) decreases with lowering temperature, which can be understood within the framework of multidomain theory[66], where $H_c \propto \frac{\sqrt{AH_A}}{M_s D}$. Here, A is the exchange stiffness, H_A is the magneto-crystalline anisotropy, M_s is the saturated magnetization and D indicates the grain size factor. The observed decrement in H_c VS. measured temperature thus suggests a dominant influence from the rising M_s at low temperatures. Moreover, the M - H loops reveal a pronounced decrease in the coercivity for HEM samples (~ 1850 Oe), in contrast to pure SrM (~ 4200 Oe)[13]. This lower coercivity implies a reduced resistance to magnetization reversal, consistent with enhanced domain-wall mobility under an external field[12].

A comparison of M_s and M_r between HEM and conventional M-type hexaferrites is summarized in Fig. 5e. Among them, the HEM ceramic exhibits superior magnetic properties, featuring both a high M_s (53.5 ± 0.5 emu/g) and M_r (26.3 ± 0.3 emu/g). The squareness ratio, M_r/M_s , a key indicator of magnetic domain configuration, is determined to be 0.49 for HEM. This ratio is slightly below the 0.5 threshold, indicating a

multidomain magnetic structure of HEM, in agreement with the behaviour reported for previously reported low entropy M-type HFs[5, 8, 64]. Clarifying the magnetic mechanism requires understanding both the site occupancy and the role of Fe^{2+} . In La doped SrM HFs, Fe^{2+} ions preferentially occupy the $2a$ site (octahedral, spin-up)[15]. Although replacing Fe^{3+} (5 μB) with Fe^{2+} (4 μB) tends to decrease the net magnetization, the presence of Fe^{2+} at the octahedral site can induce local lattice distortion, releasing the orbital magnetic moment[67], and can also induce the Fe^{2+} ($2a$)- O^{2-} - Fe^{3+} ($2b$) superexchange interaction within the sublattice[15]. The interplay of these competing effects contributes to the magnetic performances. In addition, the simultaneous occupation of the Me site by five cations (Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , and La^{3+}) with different ionic radii introduces local lattice distortions that alter the Fe–O–Fe bonding geometry along the superexchange pathways. Notably, this Me site is located in close proximity to both the spin-up Fe^{3+} ($2b$) and spin-down Fe^{3+} ($4f_2$) sites in M-type HFs[68]. Such local structural complexity is a key factor in enhancing magnetic properties, as it strengthens the Fe^{3+} ($2b$)- O^{2-} - Fe^{3+} ($2b$) superexchange interaction, evidenced by Raman spectroscopy discussed above. While the most intense Raman peak (located at 682.6 cm^{-1}) corresponds to Fe–O bonding at the $2b$ site, the direct verification of site-specific occupancy and its influence on magnetic exchange would require complementary techniques such as Mössbauer spectroscopy or neutron diffraction. Nevertheless, the observed correlation between the structural modifications at the $2b$ site and the enhanced magnetic properties underscores the effectiveness of high-entropy design in regulating the spin configuration and net magnetization of hexaferrites.

To evaluate its potential for magneto-optical applications, the Faraday rotation effect was investigated. Fig. 5f displays the complex refractive indices for right-handed and left-handed circularly polarized light. A pronounced difference ($\Delta n' = n'_+ - n'_-$) between the two indices is observed, directly reflecting the strength of the Faraday rotation effect as depicted in equation 2 and previous work[13, 16]. Meanwhile, three low-entropy M-type hexaferrites ($\text{SrFe}_{12}\text{O}_{19}$, $\text{SrFe}_{11.99}\text{Nb}_{0.01}\text{O}_{19}$, and $\text{SrFe}_{11.97}\text{Nb}_{0.03}\text{O}_{19}$) were prepared under the identical processing conditions for comparison. The THz Faraday rotation properties of these compositions were systematically measured, and the results are presented in Figure S4. All three reference samples exhibit substantially smaller $\Delta n'$ values than HEM, confirming the pronounced enhancement of the Faraday rotation in HEM. However, since these reference samples do not contain La^{3+} and differ from HEM in oxygen stoichiometry and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, they do not fully decouple the contribution of configurational disorder from those associated with La incorporation, oxygen non-stoichiometry or coexistence of Fe^{2+} and Fe^{3+} . A compositionally relevant La-containing control would allow a more direct separation of these contributions. While such a control is beyond the scope of this work, future studies employing a systematic series of La-substituted M-type HFs would be valuable to quantify the individual contributions.

The $\Delta n'$ for HEM is around 1.75 at 0.2 THz, about 2.5 times greater than that of $\text{SrFe}_{12}\text{O}_{19}$ (0.75), even exceeds that of SFN3O with an optimized value of 1.30, and 4 times larger than that of a doped silicon wafer under a 3T magnetic field applied (0.4)[16]. The $\Delta n'$ values at 0.2 THz were repeatedly measured on

independently prepared HEM ceramics, yielding a mean value of 1.75 with a standard error of ± 0.04 . This variation is within the typical uncertainty range of THz time-domain spectroscopy measurements, confirming the reliability of the observed enhancement. The total non-reciprocal phase retardation is further calculated to be $\Phi \approx 2.93$ rad for the 0.8 mm thick HEM sample using the equation (2). In other words, fully magnetised HEM samples can induce non-reciprocal polarization angle, up to $105^\circ/\text{mm}$. Moreover, a comprehensive comparison between HEM and reported THz magneto-optical materials is listed in the Table S7. Clearly, the Faraday rotation angle of HEM substantially exceeds that of $\text{SrFe}_{12}\text{O}_{19}$ ($\sim 45^\circ/\text{mm}$), as well as those of other conventional magneto-optical materials such as doped silicon ($48\sim 60^\circ/\text{mm}$)[16], Bi:RIG ($8\sim 18.5^\circ/\text{mm}$)[69] and La:YIG ($\sim 14^\circ/\text{mm}$)[70]. This giant polarization rotation angle of the HEM ceramics, makes them promising candidates for next-generation THz magneto-optical devices. Nevertheless, further reduction of insertion losses and broadening of the response bandwidth in the THz range are still required for practical applications.

Previous studies have shown that the Faraday rotation effect can be enhanced by higher saturation magnetization and lower coercivity[13]. In the present work, the significantly improved magneto-optical response was primarily attributed to the high-entropy effect. The high-entropy approach simultaneously introduces multiple cations with distinct ionic radii and magnetic moments into the same sublattice. This creates severe lattice distortion, fluctuating exchange pathways, and configurational entropy stabilization, which collectively suppress long-range magnetic ordering while promoting short-range correlated spin structures and enhanced domain wall mobility. As illustrated in reported work, the *Me* site is located in close proximity to Fe^{3+} at the $2b$ (spin-up) and $4f_2$ (spin-down) sites in M-type HFs[68, 71]. Consequently, the superexchange interactions between $2b$ or $4f_2$ Fe^{3+} cations are influenced directly by the high-entropy design. Additionally, the Raman spectroscopy confirms that this high-entropy configuration significantly strengthens the super exchange interaction, particularly along the $\text{Fe}^{3+}(2b) - \text{O}^{2-} - \text{Fe}^{3+}(2b)$ pathway, supporting the above interpretation. It should be noted, however, that when La doping is involved, charge compensation leads to the partial conversion of Fe^{3+} ions (5 μB) at the spin-up $2a$ site into Fe^{2+} ions (4 μB), which tends to reduce M_s [15]. Taking these factors into account, the enhancement of Faraday rotation in HEM can be attributed to the following contributions: i) the strengthened superexchange interaction through the $\text{Fe}^{3+}(2b) - \text{O}^{2-} - \text{Fe}^{3+}(2b)$ pathway; ii) the sluggish diffusion effect of high entropy at the *Me* site, which results in reduced domain size together with increased domain wall density, as well as enhanced domain wall mobility.

4. Conclusions

In summary, this work demonstrates that the “entropy engineering” strategy, applied to the *Me* site of M-type hexaferrites, is an effective approach for simultaneously enhancing magnetic and magneto-optical properties. The *Me*-site atomic-scale complexity in $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{La}_{0.2})\text{Fe}_{12}\text{O}_{19}$ induces local lattice distortions and modifies adjacent Fe-O bonding, especially the $\text{Fe}^{3+}(2b) - \text{O}^{2-} - \text{Fe}^{3+}(2b)$ bonds, indirectly evidenced by XRD refinement and Raman data. While the exact site occupancy distribution remains to be

determined by future studies employing Mössbauer spectroscopy or neutron diffraction. Meanwhile, the sluggish diffusion effect leads to nanometer-sized domains observed by MFM images, which may contribute to enhanced domain wall mobility. These combined structural changes lead to a large Faraday rotation angle ($\sim 105^\circ/\text{mm}$ at 0.2 THz) for HEM ceramics. Beyond this specific material system, this work demonstrates that high-entropy design, with four core effects, is a powerful strategy to tune superior magnetic and magneto-optical properties of ferrites, further for a new generation of magnetic sensors and optical isolators.

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References

- [1] K. Zhai, D.S. Shang, Y.S. Chai, G. Li, J.W. Cai, B.G. Shen, Y. Sun, Room-temperature nonvolatile memory based on a single-phase multiferroic hexaferrite, *Adv. Funct. Mater.* 28(9) (2018) 1705771.
- [2] P. Yang, Z. Liu, H. Qi, X. Fu, Z. Peng, Significantly improved near-field communication antennas based on novel Ho^{3+} and Co^{2+} ions co-doped Ni–Zn ferrites, *J. Adv. Ceram.* 13(3) (2024) 293-309.
- [3] D.A. Vinnik, A.V. Trukhanov, F.V. Podgornov, E.A. Trofimov, V.E. Zhivulin, A.Y. Starikov, O.V. Zaitseva, S.A. Gudkova, A.A. Kirsanova, S.V. Taskaev, D.A. Uchaev, S.V. Trukhanov, M.A. Almessiere, Y. Slimani, A. Baykal, Correlation between entropy state, crystal structure, magnetic and electrical properties in M-type Ba-hexaferrites, *J. Eur. Ceram. Soc.* 40(12) (2020) 4022-4028.
- [4] V.C. Pujari, P.D. Mhase, S.D. Balgude, S.S. Jadhav, S.J. Gilani, P.S. More, S.E. Shirsath, S.F. Shaikh, S.M. Patange, Eco-friendly synthesis, comprehensive characterization and photocatalytic efficiency of rare earth-substituted M-type hexaferrites for visible-light-driven dye degradation, *Ceram. Int.* 51(23, Part B) (2025) 39866-39885.
- [5] V.C. Pujari, P.D. Mhase, S. Balgude, P. More, S.S. Jadhav, S.M. Patange, Energy band gap tuning of Ba-Ca hexagonal ferrite by Dy^{3+} ion substitution ($0 \leq x \leq 0.2$) to improve spectral, structural, dielectric and photocatalytic properties, *Ceram. Int.* 50(24) (2024) 53351-53361.
- [6] V.G. Harris, Z. Chen, Y. Chen, S. Yoon, T. Sakai, A. Gieler, A. Yang, Y. He, K.S. Ziemer, N.X. Sun, C. Vittoria, Ba-hexaferrite films for next generation microwave devices (invited), *J. Appl. Phys.* 99(8) (2006) 08M911.
- [7] A.V. Trukhanov, S.V. Trukhanov, V.G. Kostishyn, L.V. Panina, V.V. Korovushkin, V.A. Turchenko, D.A. Vinnik, E.S. Yakovenko, V.V. Zagorodnii, V.L. Launetz, V.V. Oliynyk, T.I. Zubar, D.I. Tishkevich, E.L. Trukhanova, Correlation of the atomic structure, magnetic properties and microwave characteristics in substituted hexagonal ferrites, *J. Magn. Magn. Mater.* 462 (2018) 127-135.
- [8] V.C. Pujari, P.D. Mhase, S.M. Patange, P.S. More, S.S. Meena, S.F. Shaikh, A.M. Al-Enizi, S.S. Jadhav, Influence of Dy^{3+} doping on Mossbauer, magnetic and microwave absorption properties of M-type $\text{Ba}_{0.5}\text{Ca}_{0.5}\text{Dy}_x\text{Fe}_{12-x}\text{O}_{19}$ hexaferrites, *J. Magn. Magn. Mater.* 610 (2024) 172555.
- [9] J. Chen, J. Li, Y. Liu, An integrated flexible sensor for decoupled omnidirectional strain and human motion monitoring, *Materials Today Advances* 28 (2025) 100641.
- [10] A.N. Grebenchukov, V.I. Ivanova, G.I. Kropotov, M.K. Khodzitsky, Terahertz Faraday rotation of aluminum-substituted barium hexaferrite, *Appl. Phys. Lett.* 118(19) (2021) 191104.
- [11] M. Amini, A. Gholizadeh, Shape control and associated magnetic and dielectric properties of $\text{MFe}_{12}\text{O}_{19}$ (M = Ba, Pb, Sr) hexaferrites, *J. Phys. Chem. Solids* 147 (2020) 109660.
- [12] V.C. Pujari, P.D. Mhase, S.S. Meena, S.S. Jadhav, S.E. Shirsath, A.M. Al-Enizi, S.M. Patange, Tailoring structural and magnetic properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ru}_x\text{Fe}_{12-x}\text{O}_{19}$ hexaferrites with Ru^{3+} substitution, *Ceram. Int.* 51(16) (2025) 22129-22141.
- [13] Z. Hu, G.B.G. Stenning, V. Koval, J. Wu, B. Yang, A. Leavesley, R. Wylde, M.J. Reece, C. Jia, H. Yan, Terahertz faraday rotation of $\text{SrFe}_{12}\text{O}_{19}$ hexaferrites enhanced by Nb doping, *ACS Appl. Mater. Interfaces* 14(41) (2022) 46738-46747.

- [14] F. Farshidfar, A. Fattahi, R. Brüning, D.H. Ryan, K. Ghandi, A creative method to tune Fe–O interaction in ferrites, *J. Adv. Ceram.* 12(8) (2023) 1612-1624.
- [15] M. Küpferling, R. Grössinger, M.W. Pieper, G. Wiesinger, H. Michor, C. Ritter, F. Kubel, Structural phase transition and magnetic anisotropy of La-substituted M-type Sr hexaferrite, *Physical Review B* 73(14) (2006) 144408.
- [16] O. Morikawa, A. Quema, S. Nashima, H. Sumikura, T. Nagashima, M. Hangyo, Faraday ellipticity and Faraday rotation of a doped-silicon wafer studied by terahertz time-domain spectroscopy, *J. Appl. Phys.* 100(3) (2006) 033105.
- [17] W. Luo, S. Wang, S. Zheng, J. Li, M. Wang, Y. Wen, L. Li, J. Zhou, Dielectric response of ANb₂O₆ (A = Zn, Co, Mn, Ni) columbite niobates: From microwave to terahertz, *J. Adv. Ceram.* 13(8) (2024) 1189-1197.
- [18] T.-F. Li, Y.-L. Li, Z.-Y. Zhang, Q.-H. Yang, F. Fan, Q.-Y. Wen, S.-J. Chang, Terahertz faraday rotation of magneto-optical films enhanced by helical metasurface, *Appl. Phys. Lett.* 116(25) (2020) 251102.
- [19] M. Gu, K.A. Michalski, Giant THz Faraday rotation with stacked magnetized graphene, *J. Appl. Phys.* 129(18) (2021) 183103.
- [20] G.X. Ni, A.S. McLeod, Z. Sun, L. Wang, L. Xiong, K.W. Post, S.S. Sunku, B.Y. Jiang, J. Hone, C.R. Dean, M.M. Fogler, D.N. Basov, Fundamental limits to graphene plasmonics, *Nature* 557(7706) (2018) 530-533.
- [21] R. Chang, F. Wang, Z. Yan, P. Lei, C. Fang, G. Bai, X. Liu, Y. Hong, P. Ping, Z. Nie, L. Zhao, X. Zhang, Y. Zhao, X. Xu, Minimal Dy/Tb competitive lattice diffusion engineering for ultrahigh-coercivity sintered NdFeB magnets, *J. Mater. Sci. Technol.* 274 (2026) 235-244.
- [22] H.M. Umair, I. Bibi, F. Majid, S. Kamal, N. Alwadai, M.I. Arshad, A. Ali, S. Nouren, M. Al Huwayz, M. Iqbal, Ferroelectric, dielectric, magnetic and photocatalytic properties of Mn doped Ca-hexaferrite prepared via microemulsion route, *Mater. Chem. Phys.* 307 (2023) 128152.
- [23] R. Vinaykumar, J. Bera, Characterizations of low-temperature sintered BaCo_{1.3}Ti_{1.3}Fe_{9.4}O₁₉ M-type ferrite for high-frequency antenna application, *J. Magn. Magn. Mater.* 451 (2018) 614-619.
- [24] D.A. Vinnik, E.A. Trofimov, V.E. Zhivulin, O.V. Zaitseva, D.A. Zherebtsov, A.Y. Starikov, D.P. Sherstyuk, S.A. Gudkova, S.V. Taskaev, The new extremely substituted high entropy (Ba,Sr,Ca,La)Fe_{6-x}(Al,Ti,Cr,Ga, In,Cu,W)_xO₁₉ microcrystals with magnetoplumbite structure, *Ceram. Int.* 46(7) (2020) 9656-9660.
- [25] S. Prathap, W. Madhuri, S.S. Meena, Multiferroic properties and Mössbauer Study of M-type hexaferrite PbFe₁₂O₁₉ synthesized by the high energy ball milling, *Mater. Charact.* 177 (2021) 111168.
- [26] A.V. Trukhanov, K.A. Astapovich, M.A. Almessiere, V.A. Turchenko, E.L. Trukhanova, V.V. Korovushkin, A.A. Amirov, M.A. Darwish, D.V. Karpinsky, D.A. Vinnik, D.S. Klygach, M.G. Vakhitov, M.V. Zdorovets, A.L. Kozlovskiy, S.V. Trukhanov, Peculiarities of the magnetic structure and microwave properties in Ba(Fe_{1-x}Sc_x)(₁₂)O-19 ($x < 0.1$) hexaferrites, *J. Alloys Compd.* 822 (2020) 153575.
- [27] N.A. Cherkasova, V.E. Zhivulin, E.A. Trofimov, O.V. Zaitseva, D.E. Zhivulin, S.V. Taskaev, A.R. Zykova, D.A. Vinnik, Synthesis and structure of bulky single crystals of high-entropy ferrites BaFe_{12-x}(Ti, Mn, In, Ga)_xO₁₉, *J. Struct. Chem.* 64(5) (2023) 757-765.
- [28] H. Nikmanesh, S. Hoghoghifard, B. Hadi-Sichani, Study of the structural, magnetic, and microwave absorption properties of the simultaneous substitution of several cations in the barium hexaferrite structure, *J. Alloys Compd.* 775 (2019) 1101-1108.
- [29] J. Dabrowa, M. Stygar, A. Mikula, A. Knapik, K. Mroczka, W. Teichman, M. Danielewski, M. Martin, Synthesis and microstructure of the (Co,Cr,Fe,Mn,Ni)₃O-4 high entropy oxide characterized by spinel structure, *Mater. Lett.* 216 (2018) 32-36.
- [30] R. Djenadic, A. Sarkar, O. Clemens, C. Loho, M. Botros, V.S.K. Chakravadhanula, C. Kubel, S.S. Bhattacharya, A.S. Gandhif, H. Hahn, Multicomponent equiatomic rare earth oxides, *Mater. Res. Lett.* 5(2) (2017) 102-109.
- [31] C.M. Rost, E. Sachet, T. Borman, A. Moballeggh, E.C. Dickey, D. Hou, J.L. Jones, S. Curtarolo, J.-P. Maria, Entropy-stabilized oxides, *Nat. Commun.* 6(1) (2015) 8485.
- [32] R. Nie, J. Tan, Y. Li, X. Liu, C. Qian, Tribological properties of non-equiatomic FeCoCrNiMn high entropy alloys: Molecular dynamics simulations and machine learning predictions, *Tribology International* 217 (2026) 111656.
- [33] X. Chen, L. Yan, H. Zhang, Y. Tong, W. Sang, H. Zhang, Z. Liu, D. Zhang, M. Zhang, Thermophysical and mechanical performances of (Nd_{0.2}Sm_{0.2}Gd_{0.2}Yb_{0.2}Y_{0.2})₃TaO₇ and (Nd_{0.2}Sm_{0.2}Gd_{0.2}Yb_{0.2}Y_{0.2})₃Ta_{0.5}Nb_{0.5}O₇ high-entropy compounds, *J. Alloys Compd.* 1039 (2025) 183097.
- [34] Z. Zhang, H. Zhang, C. Liu, P. Zhang, J. Li, L. Dong, P. Li, L. Wu, X. Qi, Tungsten bronze oxide ceramics for energy storage: Characterization, synthesis, and performance, *Journal of Energy Storage* 161 (2026) 121965.
- [35] Y. Wang, T. Csanádi, H. Zhang, J. Dusza, M.J. Reece, Synthesis, microstructure, and mechanical properties of novel high entropy carbonitrides, *Acta Mater.* 231 (2022) 117887.

- [36] D. Moskovskikh, S. Vorotilo, V. Buinevich, A. Sedegov, K. Kuskov, A. Khort, C. Shuck, M. Zhukovskiy, A. Mukasyan, Extremely hard and tough high entropy nitride ceramics, *Sci. Rep.* 10(1) (2020) 19874.
- [37] H. Chen, H.M. Xiang, F.Z. Dai, J.C. Liu, Y.C. Zhou, High entropy (Yb_{0.25}Y_{0.25}Lu_{0.25}Er_{0.25})(₂)SiO₅ with strong anisotropy in thermal expansion, *J. Mater. Sci. Technol.* 36 (2020) 134-139.
- [38] C. Oses, C. Toher, S. Curtarolo, High-entropy ceramics, *Nat. Rev. Mater.* 5(4) (2020) 295-309.
- [39] A.Q. Mao, H.Z. Xiang, Z.G. Zhang, K. Kuramoto, H. Zhang, Y.G. Jia, A new class of spinel high-entropy oxides with controllable magnetic properties, *J. Magn. Magn. Mater.* 497 (2020) 165884.
- [40] J. Ma, B. Zhao, H. Xiang, F.-Z. Dai, Y. Liu, R. Zhang, Y. Zhou, High-entropy spinel ferrites MFe₂O₄ (M = Mg, Mn, Fe, Co, Ni, Cu, Zn) with tunable electromagnetic properties and strong microwave absorption, *J. Adv. Ceram.* 11(5) (2022) 754-768.
- [41] B. Ni, A. Bao, Y. Gu, X. Zhang, X. Qi, High-entropy enhanced room-temperature ferroelectricity in rare-earth orthoferrites, *J. Adv. Ceram.* 12(4) (2023) 724-733.
- [42] A. Sarkar, R. Kruk, H. Hahn, Magnetic properties of high entropy oxides, *Dalton Transactions* 50(6) (2021) 1973-1982.
- [43] Z. Hu, H. Zhang, M.J. Reece, G. Viola, H. Yan, Relaxor ferroelectric behaviour observed in (Ca_{0.55}Sr_{0.5}Ba_{0.5}Pb_{0.5})Nb₂O₇ perovskite layered structure ceramics, *J. Eur. Ceram. Soc.* 43(1) (2023) 177-182.
- [44] X. Zhu, S. Xiong, G. Zhu, D. Chen, Z. Wang, X. Lei, L. Liu, C. Li, Dielectric properties and excellent energy storage density under low electric fields for high entropy relaxor ferroelectric (Li_{0.2}Ca_{0.2}Sr_{0.2}Ba_{0.2}La_{0.2})TiO₃ ceramic, *J. Alloys Compd.* 984 (2024) 173987.
- [45] P. Zhang, Z. Lou, M. Qin, J. Xu, J. Zhu, Z. Shi, Q. Chen, M.J. Reece, H. Yan, F. Gao, High-entropy (Ca_{0.2}Sr_{0.2}Ba_{0.2}La_{0.2}Pb_{0.2})TiO₃ perovskite ceramics with A-site short-range disorder for thermoelectric applications, *J. Mater. Sci. Technol.* 97 (2022) 182-189.
- [46] S.V. Trukhanov, A.V. Trukhanov, V.A. Turchenko, V.G. Kostishin, L.V. Panina, I.S. Kazakevich, A.M. Balagurov, Crystal structure and magnetic properties of the BaFe₁₂-xIn_xO₁₉ (x=0.1-1.2) solid solutions, *J. Magn. Magn. Mater.* 417 (2016) 130-136.
- [47] S. Zhang, C. Cao, S. Su, A. Xia, H. Zhang, H. Li, Z. Liu, C. Jin, Anisotropic exchange coupling interaction between hard-hard magnetic grains in sintered SrFe₁₂O₁₉ ferrites, *J. Adv. Ceram.* 12(4) (2023) 815-821.
- [48] M. K pferling, V. Corral Flores, R. Gr ssinger, J. Matutes Aquino, Preparation and characterization of LaFe₁₂O₁₉ hexaferrite, *J. Magn. Magn. Mater.* 290-291 (2005) 1255-1258.
- [49] V. Jain, M.C. Biesinger, M.R. Linford, The Gaussian-Lorentzian sum, product, and convolution (Voigt) functions in the context of peak fitting X-ray photoelectron spectroscopy (XPS) narrow scans, *Appl. Surf. Sci.* 447 (2018) 548-553.
- [50] B. Yang, R.S. Donnan, Enhanced rapid and accurate Sub-THz magneto-optical characterization of hexaferrite ceramics, *J. Magn. Magn. Mater.* 323(15) (2011) 1992-1997.
- [51] R.C. Pullar, Hexagonal ferrites: A Review of the Synthesis, Properties and Applications of Hexaferrite Ceramics, *Prog. Mater. Sci.* 57(7) (2012) 1191-1334.
- [52] J. Zhang, K. Cao, X. Zhang, Q. Zhang, Se-directed synthesis of polymeric carbon nitride with potential applications in heavy metal-containing industrial sewage treatment, *Appl. Organomet. Chem.* 34(2) (2020) e5377.
- [53] S.J. Park, J.P. Lee, J.S. Jang, H. Rhu, H. Yu, B.Y. You, C.S. Kim, K.J. Kim, Y.J. Cho, S. Baik, W. Lee, In situ control of oxygen vacancies in TiO(₂) by atomic layer deposition for resistive switching devices, *Nanotechnology* 24(29) (2013) 295202.
- [54] Z. Hu, V. Koval, Y. Yue, M. Zhang, C. Jia, I. Abrahams, H. Yan, Structural evolution and coexistence of ferroelectricity and antiferromagnetism in Fe, Nb co-doped BaTiO₃ ceramics, *J. Eur. Ceram. Soc.* 43 (2023) 2460-2468.
- [55] P. Kaur, V. Kaur, S. Kaur, R. Kaur, M. Sandhu, H. Sarangal, N. Aggarwal, S.B. Narang, Enhanced dielectric properties of co-substituted M-type Sr-La hexaferrite synthesized by citrate auto-combustion method, *Mater. Today: Proc.* In Press (2024).
- [56] M.S. Chen, Z.X. Shen, X.Y. Liu, J. Wang, Raman and magnetization studies of barium ferrite powder prepared by water-in-oil microemulsion, *J. Mater. Res.* 15(2) (2000) 483-487.
- [57] J. Kreisel, G. Lucazeau, H. Vincent, Raman Spectra and Vibrational Analysis of BaFe₁₂O₁₉ Hexagonal Ferrite, *J. Solid State Chem.* 137(1) (1998) 127-137.
- [58] J. Li, J. Feng, D. Guo, X. Fan, Effect of Sm substitution on the structural and magnetic properties of barium hexaferrites, *Ceram. Int.* 52 (8) (2026) 10339-10349.

- [59] M.A.P. Buzinaro, B.F.O. Costa, M.S. Ivanov, G.C. Cunha, M.A. Macêdo, R.S. Angélica, N.S. Ferreira, Investigations on the structural and magnetic properties of Ba_{1-x}GdxFe₁₂O₁₉ ($0 \leq x \leq 0.15$) nanoparticles, *J. Magn. Magn. Mater.* 555 (2022) 169340.
- [60] S.N. Rout, M.K. Manglam, J. Mallick, S. Datta, M. Kar, Magnetic anisotropy and (BH) max studies in microwave sintered Al-substituted strontium hexaferrite, *Physica B: Condensed Matter* 666 (2023) 415134.
- [61] M. Hashim, S.J. Salih, M.M. Ismail, A. Ahmed, S.S. Meena, A.A. Gaikwad, R.B. Jotania, S. Kumar, D. Ravinder, R. Kumar, Effect of lightly substituted samarium ions on the structural, optical, magnetic and dielectric properties of the sonochemically synthesized M-type Sr-hexaferrite nanoparticles, *Physica B: Condensed Matter* 681 (2024) 415840.
- [62] L. Qin, H. Verweij, Magnetic force microscopy study of domain walls in Co₂Z ferrite, *Mater. Res. Bull.* 51 (2014) 109-111.
- [63] S.-P. Shen, Y.-S. Chai, J.-Z. Cong, P.-J. Sun, J. Lu, L.-Q. Yan, S.-G. Wang, Y. Sun, Magnetic-ion-induced displacive electric polarization in FeO₅ bipyramidal units of (Ba,Sr)Fe₁₂O₁₉ hexaferrites, *Physical Review B* 90(18) (2014) 180404.
- [64] P.D. Mhase, V.C. Pujari, S.E. Shirsath, S.S. Jadhav, P.S. More, S.F. Shaikh, S.M. Patange, Synergistic magnetoelectric enhancement in lead-free dual-phase hexaferrite–perovskite multiferroic ceramics for advanced functional devices, *J. Alloys Compd.* 1064 (2026) 187959.
- [65] G. Venkatesh, R. Subramanian, T. Satish Kumar, J. Abuthakir, L. John Berchmans, K. Sethupathi, Investigation on structural and magnetic properties of Al³⁺ and Ce³⁺ doped hexaferrites, *Mater. Today: Proc.* 28 (2020) 440-449.
- [66] J.M. Coey, *Magnetism and Magnetic Materials*, Cambridge university press 2010.
- [67] C. Jacquiod, D. Autissier, Rare-earth substitutions in Z-type hexaferrites, *J. Magn. Magn. Mater.* 104 (1992) 419-420.
- [68] R. Lamouri, K. Daoudi, H. Absike, O. Mounkachi, E. Salmani, M. Hamedoun, A. Benyoussef, H. Ez-Zahraouy, Structural, electronic and magnetic properties of Co-substituted SrFe₁₂O₁₉: A DFT study, *Mater. Today. Commun.* 28 (2021) 102589.
- [69] Y.-L. Li, D. Zhang, M. Luo, Q. Yang, F. Fan, S. Chang, Q. Wen, Terahertz magneto-optical response of bismuth-gadolinium-substituted rare-earth garnet film, *Opt. Express* 29 15 (2021) 23540-23548.
- [70] Y.-L. Li, T.-F. Li, Q.-Y. Wen, F. Fan, Q.-H. Yang, S.-J. Chang, Terahertz magneto-optical effect of wafer-scale La: yttrium iron garnet single-crystal film with low loss and high permittivity, *Opt. Express* 28(14) (2020) 21062-21071.
- [71] J. Muller, A. Collomb, A new representation of the bipyramidal site in the SrFe₁₂O₁₉ M-type hexagonal ferrite between 4.6 and 295 K, *J. Magn. Magn. Mater.* 103(1) (1992) 194-203.