



OPEN The nanosized structure and relative paramagnetic properties of ZnFe_2O_4 by the polyol processes and the heat treatment processes

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The controlled synthesis and paramagnetic properties of nanosized Zn–Fe–O oxides have been researched by the polyol and the heat treatment processes designed according to drying, annealing, and sintering from low to high temperatures. The structural changes have led to change weak superparamagnetism of nanosized Zn–Fe–O oxides in the forms of hybrid nanosized ZnO/ ZnFe_2O_4 oxides into paramagnetism of nanosized ZnFe_2O_4 when the as-prepared samples of both ZnO and ZnFe_2O_4 oxides were isothermally annealed and sintered from low temperature at about 60 °C to high temperature at 950 °C for 2 h during their structural phase transitions in all the measurements of x-ray diffraction (XRD), vibrating sample magnetometer (VSM), scanning electron microscopy (SEM) and SEM/energy dispersive X-ray spectroscopy (EDX) combined methods. Interestingly, it is experimentally confirmed that one original paramagnetic hysteresis consists of paramagnetic segments and closed curves. Both normal and abnormal paramagnetic properties of ZnFe_2O_4 were carefully investigated.

Keywords The polyol processes, Heat treatment processes, Sintering, ZnO, ZnFe_2O_4 , Paramagnetism

In recent years, the synthesis, fabrication, structural characterization, and investigation of the physical properties of magnetic micro- and nanomaterials with spinel-type crystal structures have garnered significant attention. This growing interest arises from the fact that these materials exhibit unique physicochemical characteristics and tunable functionalities at the nanoscale, making them promising candidates for a wide range of advanced engineering and technological applications^{1–4}. Among them, zinc ferrite (ZnFe_2O_4) is well known to adopt a spinel-type crystal structure, which plays a crucial role in determining its magnetic and physicochemical properties^{5,6}. Consequently, ZnFe_2O_4 and related spinel ferrites have attracted increasing attention due to their versatile applications in electronics, telecommunications, magnetism, electromagnetics, catalysis, energy conversion and storage, as well as environmental remediation^{7–14}. To realize these applications, a wide range of chemical and physical synthesis techniques have been employed for the preparation of spinel-type ZnFe_2O_4 (AB_2O_4 , a generalized original structure) and related ferrite oxides. These include sol-gel methods, coprecipitation, hydrothermal and solvothermal synthesis, combustion processes, as well as solid-state reactions, each offering distinct advantages in terms of particle size control, crystallinity, and morphology^{15–25}. To meet the growing demand for magnetic micro- and nanosized powders, researchers have developed polyol-based synthesis routes for Co-, Ni-, and Fe-based magnetic ferrites, as well as Sr- and Ba-based hexaferrites. These processes often utilize sodium borohydride (NaBH_4) or potassium borohydride (KBH_4) as reducing agents, followed by heat treatment, annealing, and sintering to achieve desired crystallinity and magnetic properties^{26–31}. The development of next-generation ferrites and hexaferrites is expected to be driven by the incorporation and doping of cobalt (Co) as a key functional element^{27,28}. Currently, polyol-based synthesis routes are widely recognized for their significant advantages and cost-effectiveness in the fabrication of magnetic nanoparticles. This is largely

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attributed to the inherent limitations and the complexity associated with conventional chemical and physical methods. These polyol processes provide better control over particle size, morphology, and dispersion, thereby offering a promising alternative for the scalable production of magnetic nanomaterials^{27,28}. Moreover, the increasing popularity of polyol processes can be attributed to their inherent technological advantages, primarily arising from the superior solubility and effective dissolution of precursors in glycols, including ethylene glycol (EG), polyethylene glycol (PEG), and similar solvents. Furthermore, a wide range of nanosized ZnFe₂O₄ ferrites have found the applications in sensing and photocatalysis^{22,32,33}. In the near future, new and advanced electrode materials, utilizing nanosized mixed ferrites, are anticipated to play a significant role in applications related to environmental management, catalysis, energy storage, and the conversion, especially for next-generation batteries and capacitors^{34–49}. Therefore, the heating and firing technologies necessitate precise and optimal experimental conditions to effectively synthesize engineered nanosized magnetic powders.

In this study, nanosized Zn–Fe–O oxides, including ZnO and ZnFe₂O₄, were synthesized through polyol processes and heat treatment processes at low and intermediate temperatures ranging from 60 to 700 °C. Subsequently, the crystal structure of the Zn–Fe–O oxides was transformed into a single crystal structure of ZnFe₂O₄ through annealing and sintering at temperatures between 800 °C and 950 °C. Moreover, the structures and properties of the nanosized Zn–Fe–O oxides, including ZnO and ZnFe₂O₄, were determined using XRD, VSM, and SEM measurements, in accordance with the engineered processes. In addition, the paramagnetic properties of all samples of nanosized Zn–Fe–O oxides were also discussed and analyzed in detail. Specifically, it was found that the single crystal structure of ZnFe₂O₄ was formed at high temperatures of 800 °C, 900 °C, and 950 °C. Finally, the exciting zigzag paramagnetic properties of nanosized Franklinite ZnFe₂O₄ oxides were also addressed.

Experimental

In the typical polyol processes, precursor chemicals used for synthesis were FeCl₃ (0.0625 M) (China, AR, CAS:10025-77-1; characteristic: yellow-brown crystals. Readily deliquescent in air), ZnCl₂ (China, AR, CAS: 7646-85-7; characteristic: white powder or powder. Strongly hygroscopic), NaOH (0.0625 M) (China, AR, CAS: 1370-73-2; characteristic: white uniform granular or flaky solid), EG (China, AR, CAS: 107-21-1), PVP (0.375 M) (China, AR; or Sigma-Aldrich), NaBH₄ (China, AR, CAS: 16940-66-2; appearance: white powder) purchased from industrial chemicals, following laboratory and industrial manufacturing approach. In the experiments, FeCl₃ (0.0625 M) and ZnCl₂ (0.0625 M) can be used for synthesis (or FeCl₃ (0.0625 M) can be replaced by FeCl₂ (0.0625 M)) (or both FeCl₂ and FeCl₃ were used) according to the lab skills and experiences of the experimenters, and the designed polyol processes^{27–31}. We did not need to present the detailed experiment here. The key idea was that the molar ratio for chemical synthetic reaction between FeCl₃ and ZnCl₂ must be carefully adjusted in 2.0,^{30,31} in comparison with the original chemical equation for synthesis of Fe₃O₄ oxides by scientists^{40,41,44}. To investigate the kinds of as-prepared nanosized Zn–Fe–O oxides, the most typical samples selected were used, which were prepared by heat processes and isothermally heated from low to high temperatures in air.

The annealing temperature points used were at about 60, 100, 200, 300, 400, 500, 600, 650, 700, 800, 900, and 950 °C for preparing the magnetic powder samples in a period of 2 h. Additionally, XRD, SEM (SEM/EDX), and VSM measurements were performed at room temperature in order to determine the crystal structures and related magnetic properties, respectively. Typically, the features of magnetism and hysteresis loops of M–H of nanosized Zn–Fe–O oxide powders were measured using a VSM, EZ9 vibrating sample magnetometer (VSM, MicroSense, LLC Corporation, USA), and demagnetization field (H_c) in the range of –1500 to +1500 Oe. The crystal structures of the as-prepared samples (magnetic Zn–Fe–O powder samples) were investigated using XRD from 5 to 80° (Empyrean PANalytical diffractometer, USA). In particle size analysis and image data, the as-prepared Zn–Fe–O oxide powders were primarily investigated using ultrahigh-resolution scanning electron microscopy (FESEM, S-4800, Japan) to study their sizes, shapes, and compositions. In addition, SEM (Tescan Mira, Czech Republic) was used with an FEG Schottky electron emission source combined with SEM imaging and live elemental composition analysis. The high resolution for imaging and EDX analysis was maintained to investigate the as-prepared nanosized Zn–Fe–O oxide powders.

Results and discussion

XRD: structure of nanosized ZnFe₂O₄ oxides

In X-ray diffraction, Fig. 1 shows the XRD diagrams of Zn–Fe–O oxides that were isothermally heated at different temperatures, providing sufficient detail for understanding their crystallization. In the range of annealing temperatures of 60–950 °C for the samples for 2 h, the identified crystal parameters of two phases of ZnO and ZnFe₂O₄ oxides in the as-prepared Zn–Fe–O oxides exhibited the values of 2θ(°) or Two-Theta (deg), d(Å), I(%), and a set of (hkl) planes, i.e. Miller indices in the typical diagrams of XRD. See supplementary data file (see supplementary Fig. S1 (XRD of all of samples)), and (supplementary Fig. S2 (XRD of ZnFe₂O₄ samples heated at 800, 900, and 950 °C, in respect with as-prepared samples in Figures: S3, S4, S5, S6, S7, and S8)). It is emphasized that the XRD data and results of the as-prepared samples of the major phase of nanosized ZnFe₂O₄ oxides coincided with the standard pattern of PDF#74-2397, with 18 lines (Franklinite, syn, ZnFe₂O₄, cubic structure, Fd-3 m (227)) using λ radiation (CuKα1, λ = 1.5406 Å) in the primary crystal characteristics. Therefore, the crystal phases of nanosized ZnFe₂O₄ oxides show the cubic structure in a cell (a, b, c (Å): 8.4432, 8.4432, 8.4432; α, β, γ (°): 90.0, 90.0, 90.0). All the samples show the 13 strong lines, and the strongest intensity, i.e. I(%) of (311) plane is 100% of intensity. The most typical values of 2θ (18.184, 29.908, 35.225, 36.846, 42.806, 53.059, 56.595, 62.139, 65.330, 70.479, 73.488, 74.480, and 78.450 (°), respectively), d (4.8747, 2.9851, 2.5457, 2.4373, 2.1108, 1.7235, 1.6249, 1.4926, and 1.4272 Å), respectively), I(4.2, 32.2, 100, 7.6, 17.5, 14.9, 45.7, 55.9, 0.9, 5.7, 12.7, 5.2, and 2.7%, respectively), and the Miller index, i.e. a set of (hkl) ((111), (220), (311), (222), (400),

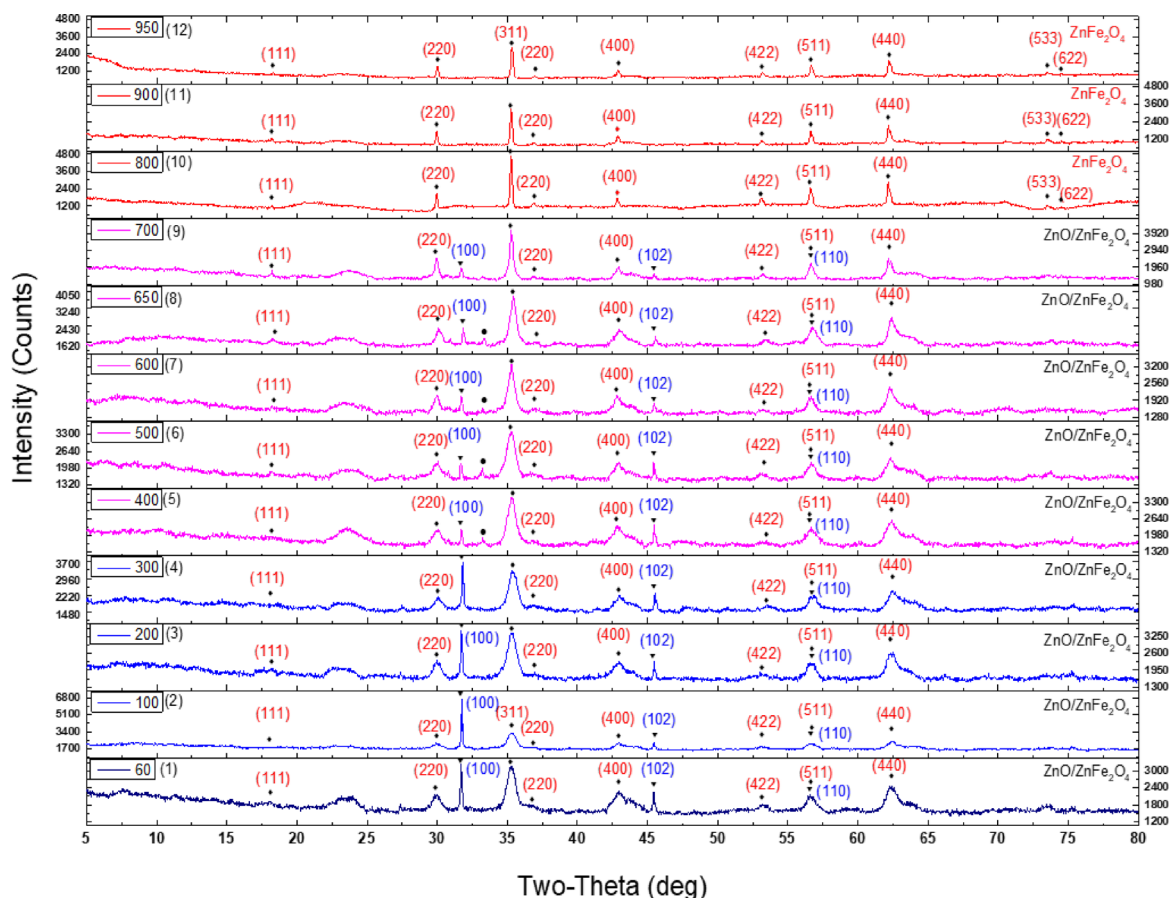


Fig. 1. XRD diagrams of samples of spinel-type nanosized Zn-Fe-O oxides were isothermally heated at (1) 60, (2) 100, (3) 200, (4) 300, (5) 400, (6) 500, (7) 600, (8) 650, (9) 700, (10) 800, (11) 900, and (12) 950 °C for 2 h.

(422), (511), (440), (531), (620), (533), (622), and (444), respectively are shown. The unnecessary minor lines can be ignored in XRD data and analysis. The appearance and disappearance of the lines located at $2\theta = 31.8^\circ$, $d = 2.8135 \text{ \AA}$, and $I = 1682$ counts were observed in the temperature range of 400–650 °C. It should be noted that XRD data and results of the as-prepared samples of the nanosized ZnO phase coincide with the standard pattern of PDF#74–0534, which contains with 11 lines (Zinc oxide, ZnO, Hexagonal, P63mc(186)). This phase exhibited the crystal parameters of $2\theta^\circ$ (31.768, 34.421, 47.538, 56.594, 66.374, 67.946, 72.566, and 76.958, respectively), $d(\text{\AA})$ (2.8145, 2.6033, 1.9111, 1.6249, 1.4072, 1.3785, 1.3017, and 1.2379, respectively), $I(\%)$ (100, 19.8, 55.5, 22.9, 13.8, 19.4, 1.5, and 13.2, respectively), and (hkl), i.e. Miller index ((100), (002), (102), (110), (200), (112), (004), and (202), respectively). Therefore, the crystal phases of nanosized ZnO show the cubic structure in a cell (a, b, c (Å): 3.24986, 3.24986, 5.20662; α, β, γ (°): 90.0, 90.0, 120.0). It is evidenced that there was a significant change of a mixed structure of mixed ZnO-ZnFe₂O₄ converted into a single ZnFe₂O₄ structure in the range of annealing temperatures of 700–800 °C, which was due to the good incorporation of Zn into the ZnFe₂O₄ lattice. In the most important range of annealing temperatures of 800–950 °C, which was critical for the magnetic powder samples annealed for 2 h, the final products were nanosized ZnFe₂O₄ oxides formed in a single ZnFe₂O₄ phase, consistent with the standard of their crystallization (Franklinite, syn, cubic structure, Fd-3 m(227)). In the present research, the crystal phases and structures of large nanosized ZnFe₂O₄ oxide particles were formed by isothermally heated processes from 800, 900, and 950 °C for 2 h, respectively. The Scherrer equation $D = K\lambda / (\text{FWHM} \times \cos\theta)$ for one single crystal phase was used to estimate the crystallite sizes of Zn-Fe-O samples based on XRD data. K is the shape factor of the average crystallite ($K = 0.89 - 0.94$, typically taken as 0.9; $\lambda = 1.5406 \text{ \AA}$). The FWHM (Full Width at Half Maximum) was calculated at specific 2θ angles. The obtained values D_1 and D_2 of crystallite sizes of ZnO/ZnFe₂O₄ heated from 60 to 700 °C, and those of ZnFe₂O₄ (D_1) heated from 800 to 950 °C were listed in Table 1 using pattern simulation with pseudo-Voigt function.

The crystallite sizes of ZnFe₂O₄ (D_1) were determined to be 11 nm (60 °C), 10 nm (100 °C), 11 nm (200 °C), 12 nm (300 °C), 12 nm (400 °C), 12 nm (500 °C), 16 nm (600 °C), 15 nm (650 °C), 26 nm (700 °C), 63 nm (800 °C), 61 nm (900 °C), and 52 nm (950 °C), respectively. In hybrid ZnO/ZnFe₂O₄ samples heated in a range of 60–700 °C, the crystallite sizes of ZnO (D_2) were calculated to be 69 nm (60 °C), 75 nm (100 °C), 67 nm (200 °C), 55 nm (300 °C), 85 nm (400 °C), 56 nm (500 °C), 44 nm (600 °C), 48 nm (650 °C), and 23 nm (700 °C), respectively.

Samples	Temp. (°C)	Structure	D ₁ (nm)	D ₂ (nm)
1	60	ZnO/ZnFe ₂ O ₄	11.0 nm	69.0 nm
2	100	ZnO/ZnFe ₂ O ₄	10.0 nm	75.0 nm
3	200	ZnO/ZnFe ₂ O ₄	11.0 nm	67.0 nm
4	300	ZnO/ZnFe ₂ O ₄	12.0 nm	55.0 nm
5	400	ZnO/ZnFe ₂ O ₄	14.0 nm	85.0 nm
6	500	ZnO/ZnFe ₂ O ₄	12.0 nm	56.0 nm
7	600	ZnO/ZnFe ₂ O ₄	16.0 nm	44.0 nm
8	650	ZnO/ZnFe ₂ O ₄	15.0 nm	48.0 nm
9	700	ZnO/ZnFe ₂ O ₄	26.0 nm	23.0 nm
10	800	ZnFe ₂ O ₄	63.0 nm	0.0
11	900	ZnFe ₂ O ₄	61.0 nm	0.0
12	950	ZnFe ₂ O ₄	52.0 nm	0.0

Table 1. The crystallite sizes of ZnO/ZnFe₂O₄ and ZnFe₂O₄.

VSM: zigzag paramagnetism of nanosized ZnFe₂O₄ oxides

It is confirmed that all the as-prepared samples of nanosized Zn–Fe–O oxides exhibit the typical paramagnetic properties of magnetization curves (H_c , M_s , M_r , and χ), and very small remanent magnetic properties observed during the measured hysteresis cycles (Figs. 2 and 3). Refer to online supplementary material: supplementary Figures: S9, S10, S11, S12, S13, S14, S15, S16, S17, S18, S19, S20, S21, and S22 as well as S37 to S48 (original data). Refer to online supplementary material: supplementary Figures from S23 to S34. As shown in Figs. 2 and 3, the key paramagnetic parameters have been identified in the hysteresis loops with the upward and downward parts in the change of magnetization M dependent on external magnetic field H . The coercive field shows the applied field at which M/H changes sign, which leads the averaged values of H_c . Here, M_r means remanent magnetization of M at $H=0$. Additionally, saturation M (M_s) is observed when H increases or changes sign. Figure 3 shows the VSM measurements of nanosized Zn–Fe–O oxides, and the typical samples of nanosized Zn–Fe–O oxides by the polyol process, and the samples isothermally heated at 60, 100, 200, 300, 400, 500, 600, and 700 °C. These samples consisted of nanosized mixed ZnO and ZnFe₂O₄ oxides in the two crystal phases, with the corresponding magnetic parameters given in Tables 1 and 2. Figures 2, 3 and 4 also shows the VSM measurements of nanosized Zn–Fe–O oxides by the polyol process, and the samples isothermally heated at 800, 900, and 950 °C for 2 h, which displayed the very special forms of nanosized ZnFe₂O₄ oxides in the only crystal phase and structure (Franklinite, syn, ZnFe₂O₄, cubic structure, Fd-3 m(227)). There are the similar shapes of hysteresis loops of four samples (60, 100, 200, and 300 °C), four samples (400, 500, 600, and 650 °C), one sample (700 °C), three samples (800, 900, and 950 °C) in the four similar stages of hysteresis, which are typically paramagnetic properties, which can be ideally estimated and allowed in order to study and investigate three samples isothermally heated at 800, 900, and 950 °C, measured in the different ranges, respectively. The experimental values of calculated magnetic susceptibility (χ ; $\chi = M/H$ or linear fit of M according to H) of the Zn–Fe–O nanomaterials fabricated in this present study are positive but very small values. They have they magnitudes of 10^{-4} or 10^{-5} , as calculated in Table 2. This is good agreement with other works [49,50], which could be due to the interesting super-exchange interaction for superparamagnetic/paramagnetic behaviour responsible for all the as-prepared samples, especially for one typical sample heated at 400 °C for 2 h because of a new line appeared around at $2\theta = 31.8^\circ$ in XRD data of crystal structure of hybrid ZnO/ZnFe₂O₄. It is suggested that quantum-mechanical calculations by density functional theory (DFT) for understanding the magnetic behaviour of ZnFe₂O₄ with the most typical [ZnO₄] and [FeO₆] models in a normal spinel structure or strongly correlated hybrid magnetic materials^{48,49}. These particular interactions need to be studied further. This led to M_r of sample heated at 400 °C exhibiting the highest value among the mentioned samples as well as ZnFe₂O₄ by other methods^{1,2}.

It is noted that very weak superparamagnetism of nanosized Zn–Fe–O oxide samples isothermally heated at 60, 100, 200, 300, 400, and 700 °C was transformed into specific paramagnetism of nanosized Zn–Fe–O samples isothermally heated at 500, 600, 650, 800, 900, and 950 °C, respectively. Therefore, the magnetic characteristics consist of confirmed superparamagnetic and paramagnetic types in hybrid ZnO/ZnFe₂O₄ oxides, and in ZnFe₂O₄ oxides.

It is experimentally evidenced that nanosized mixed ZnO–ZnFe₂O₄-type Zn–Fe–O oxides have small values of M_s , ranging from 3.737 to 7.259 emu/g (Table 2) in respect with samples isothermally heated at 60, 100, 200, 300, 400, 500, 600, and 700 °C for 2 h. Here, the results show that nanosized mixed ZnFe₂O₄-type Zn–Fe–O oxides have M_s from 1.399 to 1.89 emu/g for samples heated at 800, 900, and 950 °C, respectively. The important variation of structure from nanosized mixed ZnO–ZnFe₂O₄-type Zn–Fe–O oxides formed in a temperature range of 60–700 °C into ZnFe₂O₄ was observed in a temperature range from 800, 900, and 950 °C, respectively.

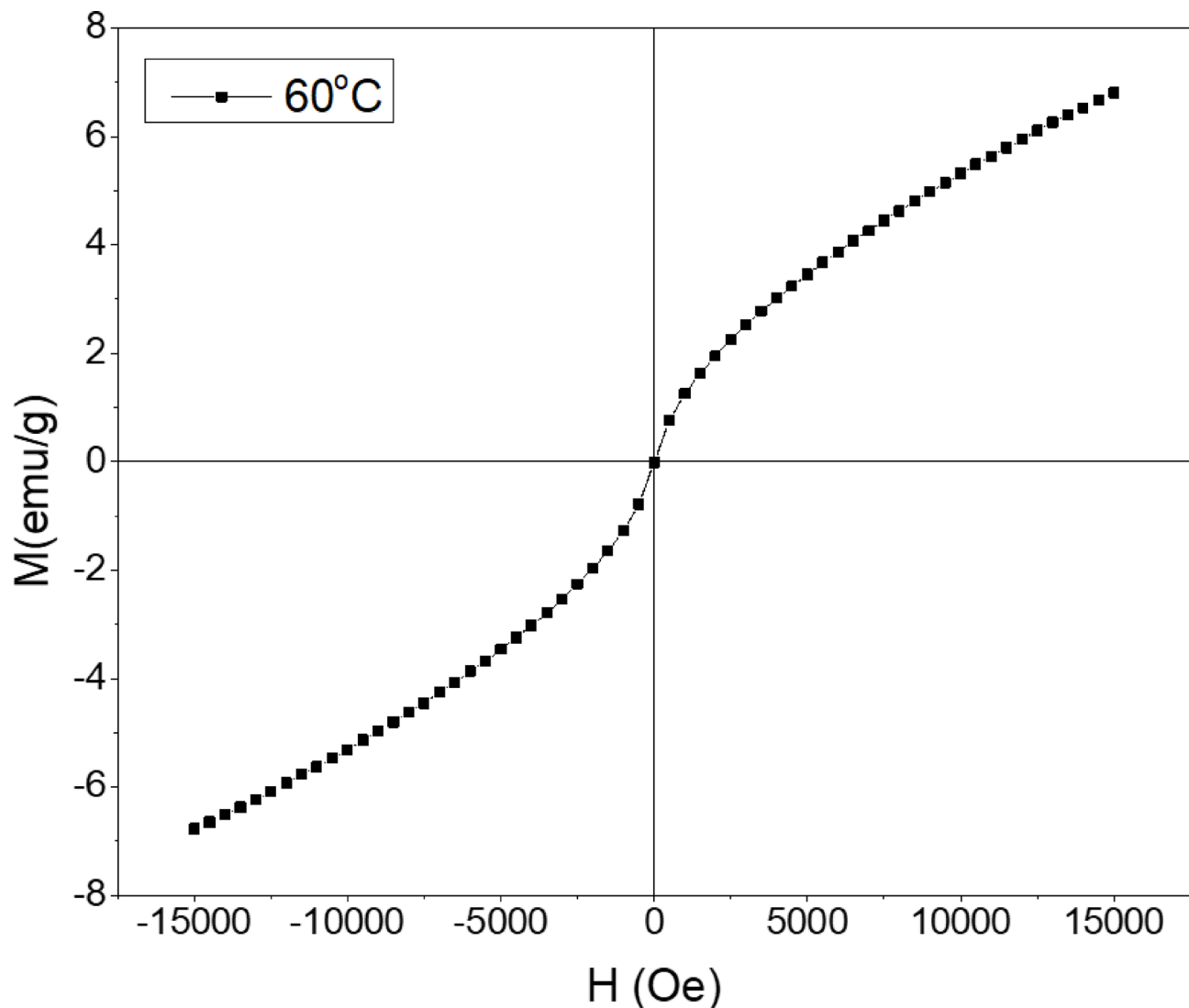


Fig. 2. Spinel-type nanosized Zn–Fe–O oxides isothermally heated at 60 °C for 2 h.

It is suggested that this led to the high stability of Zn^{2+} and Fe^{3+} cations at tetrahedral sites (T) and octahedral sites (O) in the theoretical defined crystal structure of ZnFe_2O_4 was relatively achieved through their balanced valences and cation distribution^{30,31}.

It is observed that the variations of magnetic parameters of nanosized paramagnetic Zn–Fe–O oxide materials (Fig. 5) according to the calcination temperatures of the heat treatment process, including the average values of H_c , M_r , M_s , and χ as shown in Table 2, respectively. The values of H_c and M_r are relatively small in hysteresis loops. M_r tended to be proved in the up-part directions of hysteresis loops, which are negative values ($-M_r$) (see supplementary Figure S14). Here, ZnFe_2O_4 calcined at 800–950 °C for 2 h has high averaged value of H_c . The function of linear fit of M can be used in the case that is $M = a + bH$ (emu/g) consistent with the mathematical estimation based on empirical data, meaning that the small value of $M = b \times H$ (emu/g) with $a = 0$ and $b = 9.84 \times 10^{-5}$ for a sample isothermally heated at 950 °C for a period of 2 h. Magnetic properties are related to each other, depending on the degree and nature of their structure and their interaction with external magnetic field³⁶. For magnetic nanomaterials, common types are ferromagnetic, ferrimagnetic, paramagnetic and superparamagnetic, diamagnetic, and ideal diamagnetic (superconducting). In nature, the magnetic properties of atoms or magnetic moment of atoms led different magnetic materials. One of the properties of magnetic ferri-, ferro-materials is that the degree of M depends complexly on H due to magnetic anisotropy and domains. However, paramagnetism and diamagnetism are approximately linearly proportional to H . To explain paramagnetism, researchers used classical Langevin theory or quantum theory of paramagnetism explained

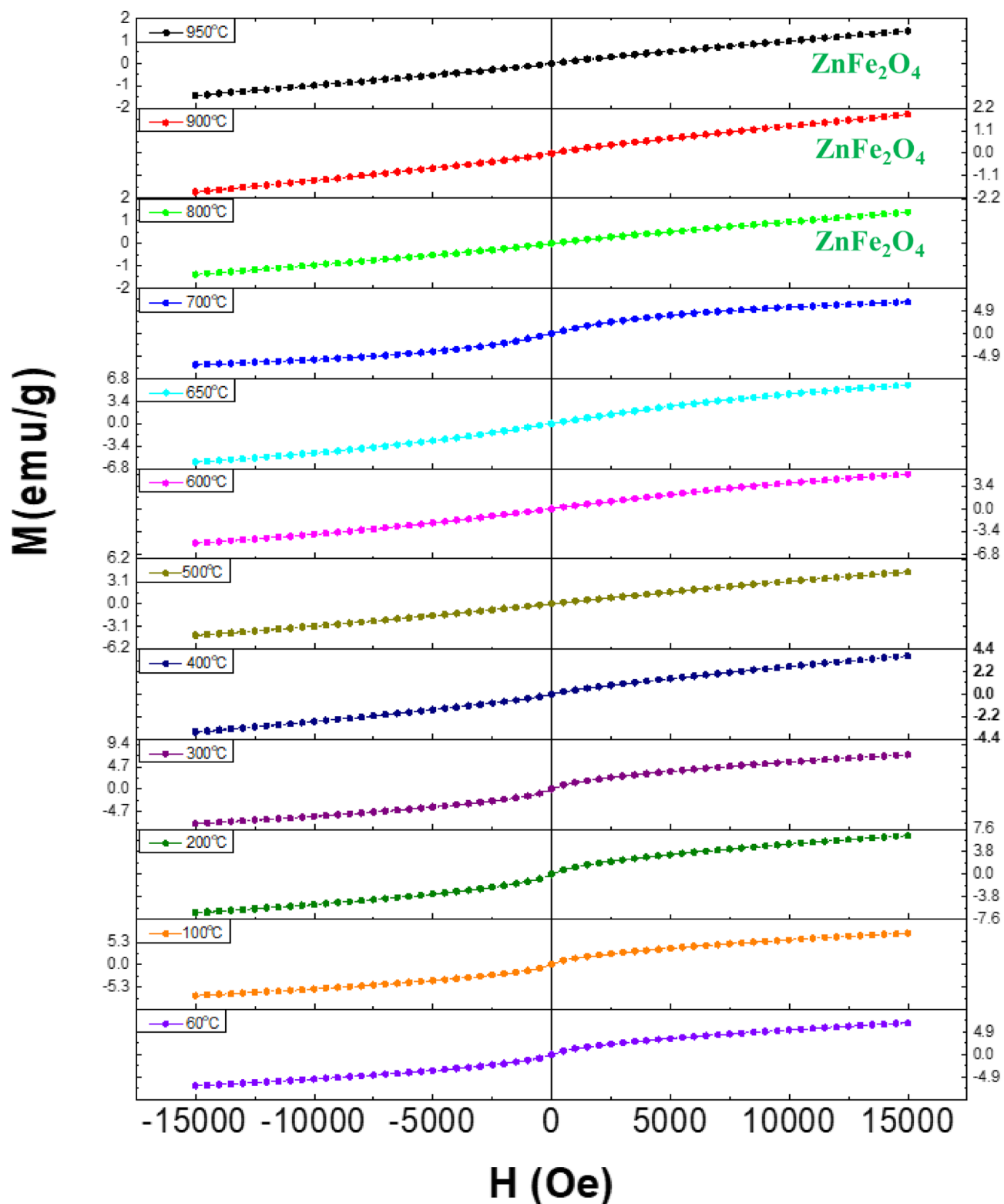


Fig. 3. Hysteresis loops of samples of spinel-type nanosized Zn–Fe–O oxides isothermally heated at (1) 60, (2) 100, (3) 200, (4) 300, (5) 400, (6) 500, (7) 600, (8) 650, (9) 700, (10) 800, (11) 900, and (12) 950 °C for 2 h.

Temp. (°C)	Hc (Oe)	Mr (emu/g)	Ms (emu/g)	χ
60	5.985	0.0092993	6.799290	0.000519
100	4.925	0.0088498	7.259640	0.000558
200	4.829	0.0074320	6.527320	0.000497
300	4.831	0.0084485	7.249210	0.000557
400	0.021	0.4224227	3.737310	0.000265
500	0.023	0.0000083	4.392395	0.000305
600	0.027	0.0000123	5.171620	0.000374
650	0.025	0.0000139	5.813330	0.000430
700	0.021	0.0000238	6.797285	0.000545
800	62.525	0.0080471	1.399680	0.000097
900	22.752	0.0046301	1.896400	0.000132
950	50.028	0.0046268	1.438070	0.000098

Table 2. The averaged values of magnetic parameters of ZnO/ZnFe₂O₄ and ZnFe₂O₄.

by Brillouin functions when taking into account magnetic quantization,³⁷ which had clarified various kinds of nanosized ferrites^{38,39}, as well as nanosized Fe-, Ni-, and Co-based ferrites as well as Ba- and Sr-based hexaferrites prepared by the polyol processes in experimental evidences and data²⁷. Here, ZnFe₂O₄ (or CdFe₂O₄) was a kind of normal-spinel ferrite with all Zn²⁺ (or Cd²⁺) cations at tetrahedral sites in the form of Zn²⁺[Fe₂³⁺]O₄²⁻ that was different from inverse-spinel ferrite, i.e. M²⁺ cations stably located at octahedral sites (M: Co, Ni) in the form of Fe³⁺[M²⁺Fe³⁺]O₄²⁻. It is suggested that the small contents of Zn element can change magnetic properties of NiFe₂O₄ or CoFe₂O₄ from ferrimagnetism into paramagnetism or superparamagnetism when Zn cations are well integrated into the inverse structures to form the various kinds of nanosized mixed spinel ferrites in the various mixed forms of M²⁺_(1-x)Fe_x³⁺[M_x²⁺Fe_(2-x)³⁺]O₄²⁻ (0 ≤ x ≤ 1), i.e. M²⁺ and Fe³⁺ possibly located in both tetrahedral sites and octahedral sites that leads the kinds of new high entropy ferrites³⁸. It is usually understood that the surveys of mixed normal and inverse spinel ferrites were identified in comparison with emphasizing and addressing the problems of magnetic structures and properties among them,^{39,45} as well as other catalytic and electronic properties. In this case, it was believed that there is a complex dependence of M on H for the as-fabricated ZnFe₂O₄ materials (Fig. 4) from segments from (1) to (11) (See supplementary data file: Figures from S23 to S34). It is suggested that the magnetic phenomenon that there are many typical minor hysteresis loops (finely minor hysteresis loops) located on the main original loop of paramagnetic hysteresis. In typical paramagnetic behavior, the original paramagnetic hysteresis shows many short segments and lines, and other closed hysteresis loops of ZnFe₂O₄ that are paramagnetic and very small and weak ferromagnetic. In up and down parts of hysteresis, M-H loops appears the matching paramagnetic segments and lines (straight segments and lines (1a), 2(a), 9(a), 10(a), 11(a), and others), and extremely small ferromagnetic lines (closed curves), such as (2), (3), (4), (5), (6), (7), (8), (9), (10), and (11) belonging to original paramagnetic hysteresis of well-sintered nanosized ZnFe₂O₄ (Figs. 4 and 7). Similarly, it is noted that the segments and lines (3) and (10), (6) and (4) have the same shapes.

In terms of intrinsic property, the segments of original hysteresis correspond to paramagnetic phenomena (the zig-zag line: a segment and a line). In addition, very small ferromagnetism is observed on the original paramagnetic hysteresis. Such magnetic order requires further understanding and research. In our highlights, it is certain that the prepared samples also demonstrated that high paramagnetic nanosized ZnFe₂O₄ oxides were finally heated and formed in the different stages of the crystal growth and stability through annealing and sintering.

SEM: nanosized ZnFe₂O₄

Typically, Figs. 6 and 7 show the interesting SEM and SEM/EDX results of nanosized Zn-Fe-O oxide particles isothermally heated at 60 °C in the initial stage for ZnO/ZnFe₂O₄, and 950 °C for 2 h in the end stage for ZnFe₂O₄, which are novel nanosized structures. See supplementary data file: Figures S35 and S36.

It is evidenced that the issues of size, shape, and morphology of nanosized Zn-Fe-O oxide particles are studied when heated at 60 and 950 °C for 2 h. In these cases, the kinds of new, large, and special micro/nanotextures of magnetic ZnO/ZnFe₂O₄ particles (sample isothermally heated at 60 °C), and ZnFe₂O₄ oxide particles (sample isothermally heated at 950 °C, respectively) were adequately formed in the evolution from self-assembly of magnetic nanosized oxide particles or nanotextured particles by heat treatment at low and high temperatures. Furthermore, the role of shape-oriented nanoparticles in magnetic properties demonstrated in nanotextured ZnFe₂O₄ particles by various heat treatment processes. Finally, it is clear that elements were

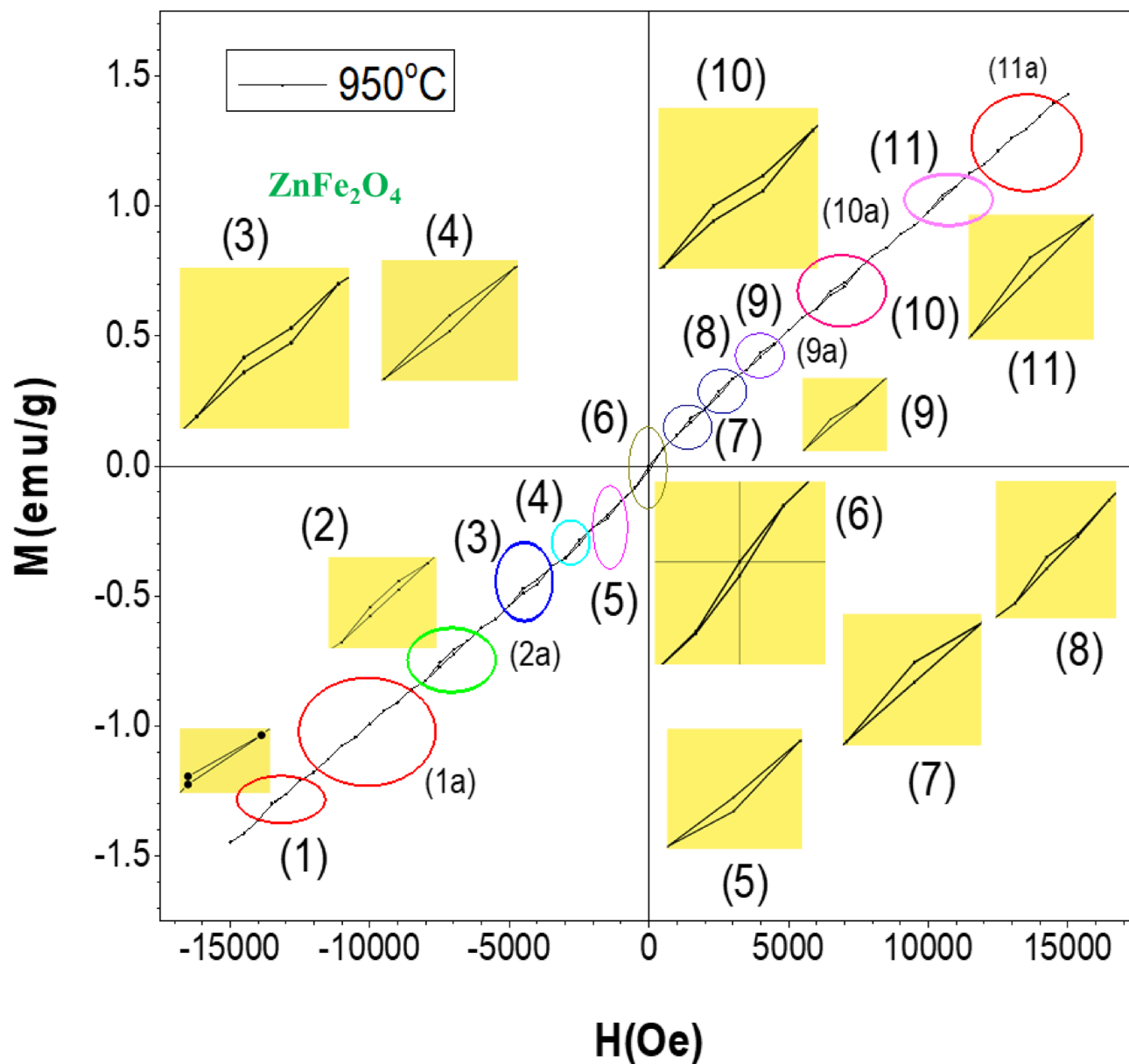


Fig. 4. Spinel-type nanosized Zn-Fe-O oxides isothermally heated at about 950 °C for 2 h. The phenomena of partial hysteresis (closed curves) and linear hysteresis (linear segments) of down and up magnetization process.

experimentally found in SEM/EDX data and results for two samples sintered at 60 °C and 950 °C as shown in Figs. 6 and 7 including Fe(L), O(K), and Zn(L), respectively.

In this comparison, the evidence of elements (Fe, Zn, and O) is in agreement with the XRD measurements addressing the crystal phase formation of ZnFe_2O_4 in two samples isothermally heated at 60 °C and 950 °C for 2 h. Figure 7a,b,c, and e show the large nanosized textures of ZnFe_2O_4 particles, consisting of numerous small ZnFe_2O_4 particles assembled together. Figure 7a,b,c,d, and e typically show polyhedral ZnFe_2O_4 particles with very high and stable crystallinity. Specifically, this indicates a successful synthesis of nanosized spinel-type ZnFe_2O_4 and other ferrites with desirable shapes and morphology^{40–48}. To enable further investigation, conventional ultrasonic sources, without the use of lasers, may be employed to disintegrate the nanosized particles. A diversity of sizes, shapes, and morphologies of nanosized spinel-type ZnFe_2O_4 particles was observed. These particles exhibited a wide range of paramagnetic nanosized complex architectures, as revealed by our XRD and VSM results. Recently, nanosized ZnFe_2O_4 has been used as a promising anode material in advanced lithium-ion batteries^{43,44}.

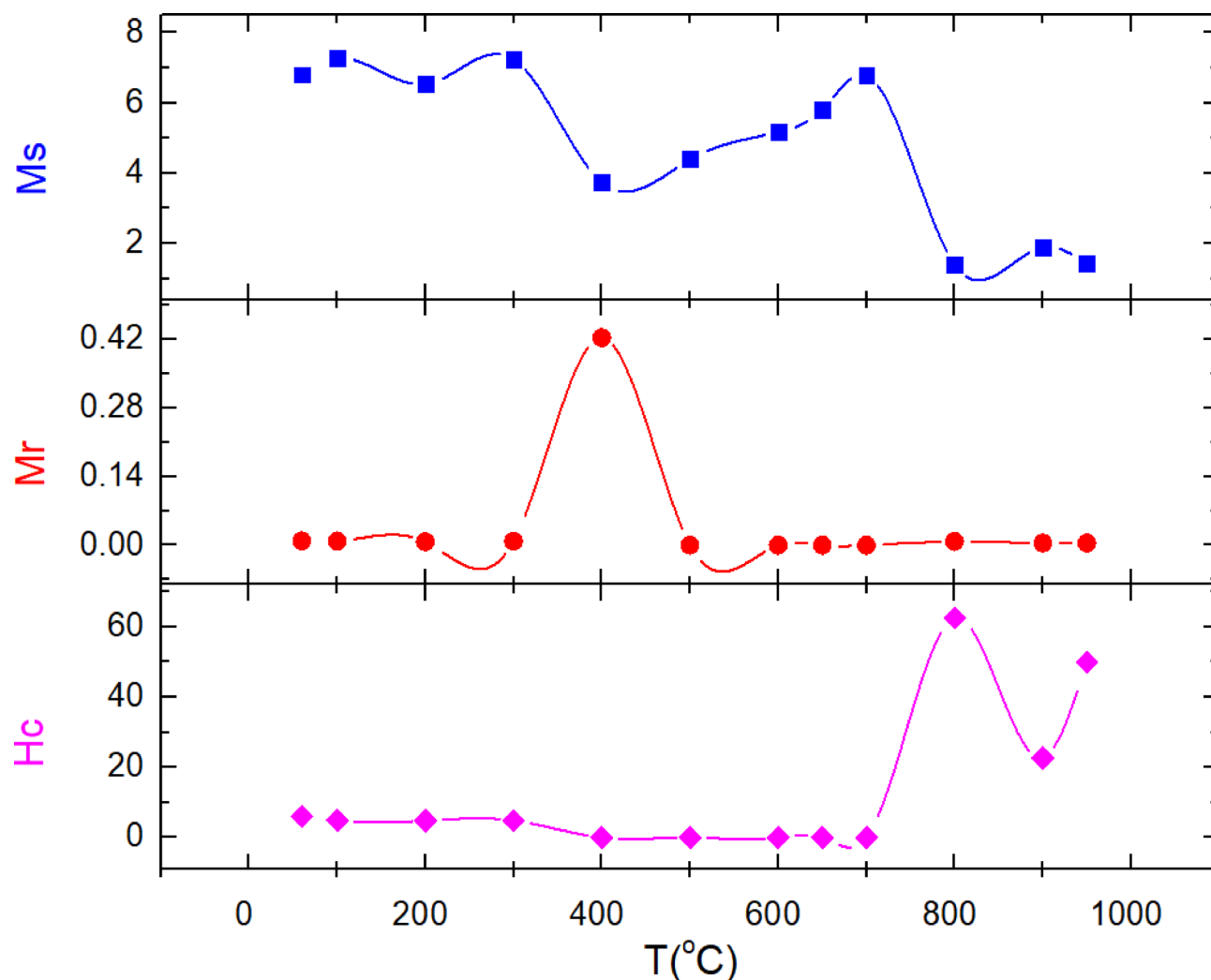


Fig. 5. Magnetic parameters of hysteresis loops of samples of spinel-type nanosized Zn–Fe–O oxides isothermally heated at about (1) 60, (2) 100, (3) 200, (4) 300, (5) 400, (6) 500, (7) 600, (8) 650, (9) 700, (10) 800, (11) 900, and (12) 950 °C for 2 h.

Conclusion

In this work, the paramagnetic properties of nanosized Zn–Fe–O oxides, including ZnO/ZnFe₂O₄ and ZnFe₂O₄, were studied in relation to their magnetic crystal structures. The effects of temperature and synthesis conditions on the paramagnetic behavior of these oxides were confirmed, particularly for nanosized ZnFe₂O₄ ferrites subjected to isothermal heat treatment at 800, 900, and 950 °C for 2 h in the stability of micro/nanoscale structures. A distinctive zigzag magnetic behavior was observed during the synthesis of ZnFe₂O₄. Several samples containing ZnFe₂O₄ were prepared, each undergoing different polyol and heat treatment conditions, allowing for a comprehensive comparison of their magnetic properties. The polyol and heat treatment processes were optimized through systematic experimentation, where variables such as temperature, reaction time, and precursor concentrations were adjusted to achieve optimal nanosized textures and enhanced paramagnetic properties. These findings suggest that the optimized polyol synthesis and heat treatment techniques can be effectively applied for the production of high-entropy ferrites based on Co, Fe, and Ni, as well as Ba- and Sr-based hexaferrites.

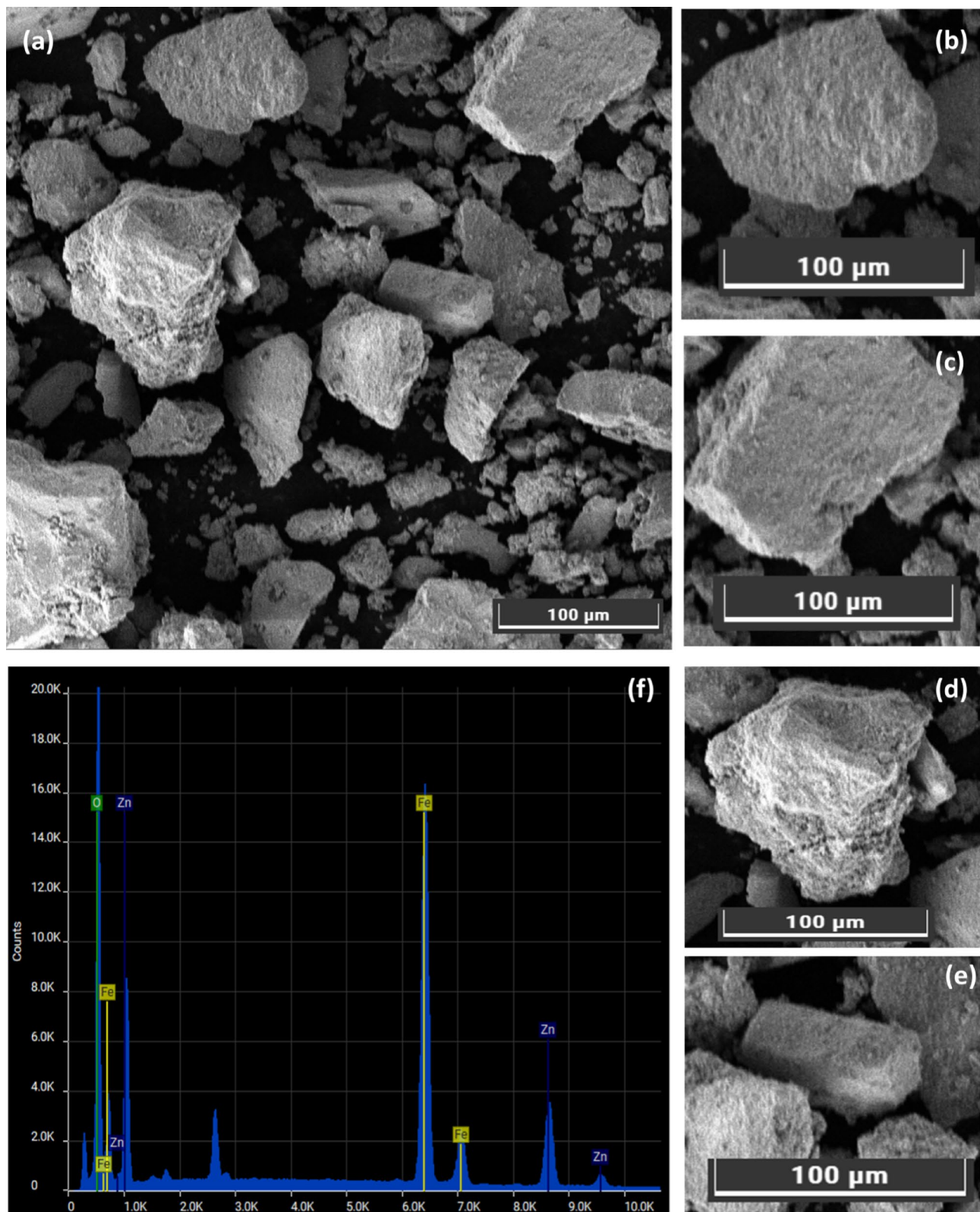


Fig. 6. Nanosized Zn–Fe–O oxide particles heated at about 60 °C for 2 h observed by SEM/ EDX (Scale bar: 100 μm).

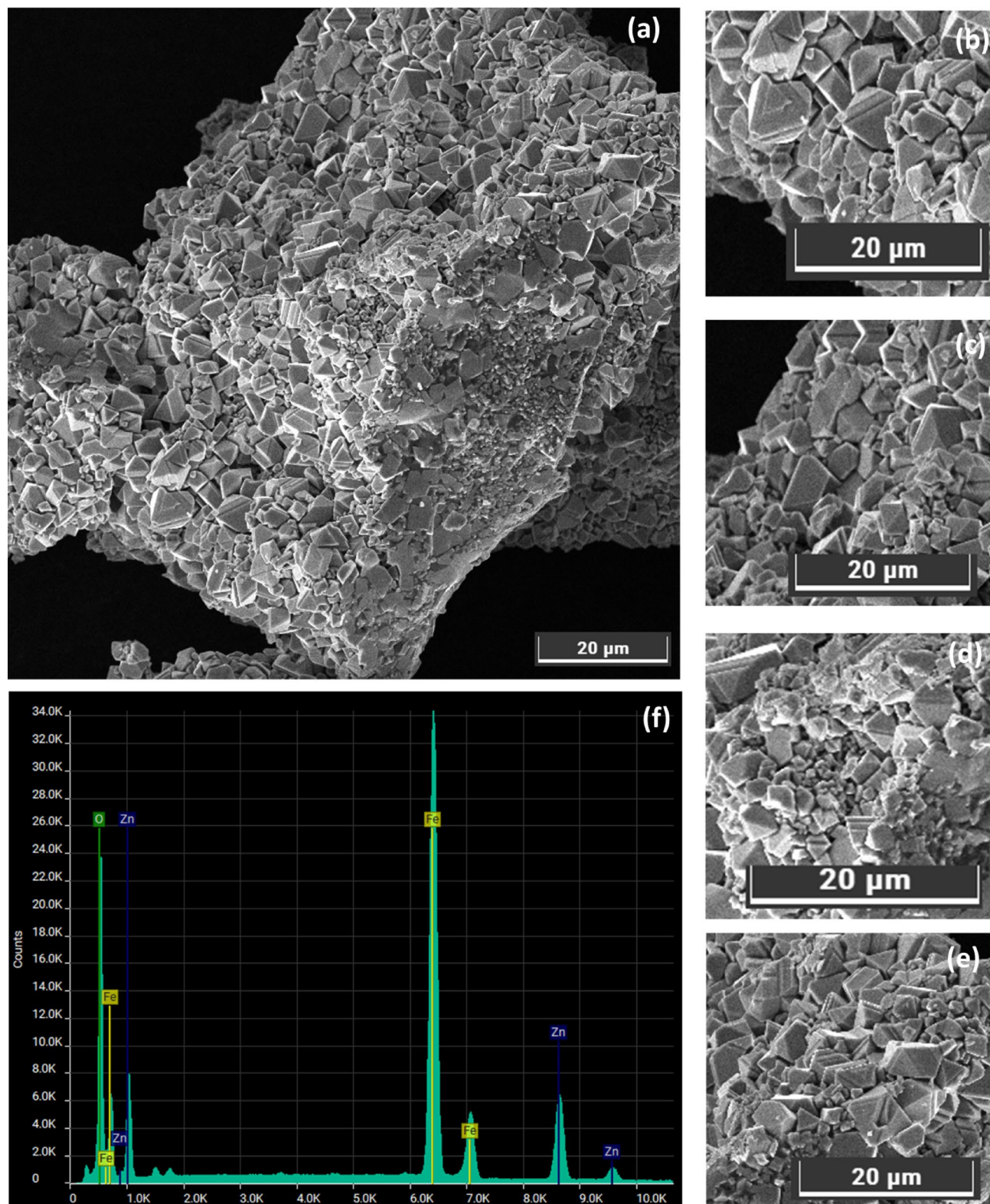


Fig. 7. Nanosized ZnFe_2O_4 oxide particles isothermally heated at about 950 $^{\circ}\text{C}$ for 2 h observed by SEM, SEM/EDX methods (Scale bar: 20 μm).

Data availability

Data will be available from the corresponding author upon request.

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Author contributions

Nguyen Viet Long conducted the experiments, collected the data and results, wrote the entire original manuscript, and evaluated and discussed the results and insights into the polyol processes for synthesis of micro/nanosized iron oxides, ferrites and hexaferrites oxides. Nguyen Thi Nhat Hang, Yong Yang, Le Hong Phuc, Nguyen Quan Hien, Ho Van Cuu, Nguyen Huu Tri, Nguyen Xuan Hoang, Masayuki Nogami, and Nguyen Viet Long reviewed and discussed experimental data and research results. All the authors have read and agreed to the published version of the manuscript. This study is original and novel experimental study that complements the theory and experiment of magnetization, demagnetization field, zigzag paramagnetism of nanosized ZnFe_2O_4 oxides. This manuscript is the authors' original work and has not been published nor has it been submitted simultaneously elsewhere. All authors have checked the manuscript and have agreed to the submission.

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Declarations

Competing interests

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Ethical approval

The data presented in our research do not involve animal or human health data as well as human tissue engineering.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-025-19772-3>.

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