

Supporting Information

Critical Control of Highly Stable Nonstoichiometric Mn–Zn Ferrites with Outstanding Magnetic and Electromagnetic Performance for Gigahertz High-Frequency Applications

Yang Yang^{a,*}, Lidong Liu^b, Hangfei Zhu^b, Nina Bao^c, Jun Ding^c, Jing Chen^a, Kuai Yu^{a,*}

^aInstitute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518052, China

^bHeng Dian Group DMEGC Magnetism CO., LTD. Hengdian Industrial Area, Dongyang City, Zhejiang Province, Hengdian 322118, China

^cDepartment of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575, Singapore

Corresponding Author

*Yang Yang. Email: angel2yang@szu.edu.cn.

*Kuai Yu. Email: kyu@szu.edu.cn.

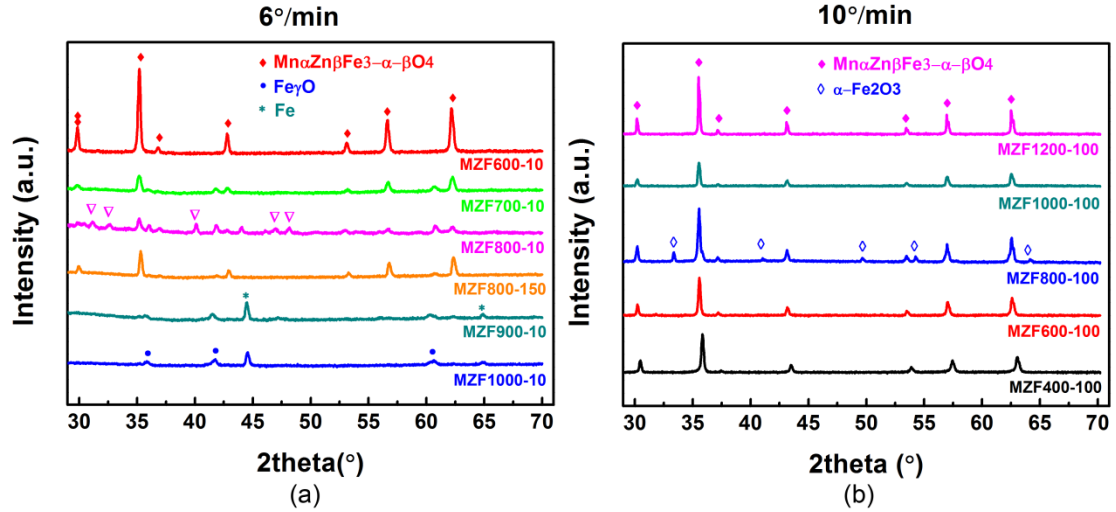


Figure S 1 The XRD patterns of ferrites annealed under different conditions: (a) The heating rate was 6°C/min and the gas flow rate during annealing was 10 sccm; (b) The heating rate was 10°C/min and the gas flow rate during annealing was 100 sccm.

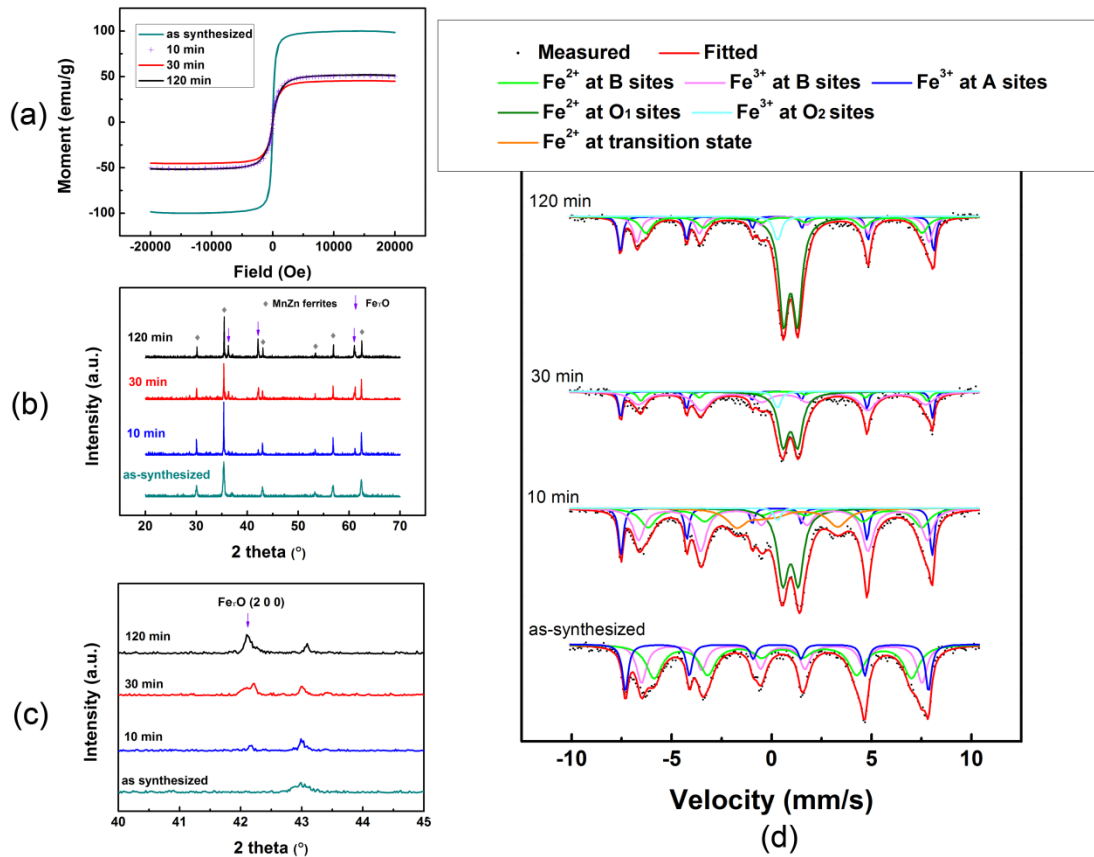


Figure S 2 The characterizations of Mn-Zn ferrites that were annealed at 1000°C for 10, 30, and 120 min with gas flow rate of 150 sccm. (a) M-H loops; (b) XRD patterns; (c) The typical peak of Fe_γO <2 0 0>; and (d) The Mössbauer spectra. The annealing process was performed under the Ar gas flow rate of 150ml/min, and the heating rate was 6 °C/min.

When the ramp rate was 6 °C/min and the gas flow rate was 150 sccm, the saturation magnetization values of annealed ferrites were largely reduced at the annealing temperatures of 1000 °C, as shown by the M–H loops in Figure S2-1a. The composition was identified as a mixture of spinel Mn–Zn ferrite and Fe_γO phase, as shown in Figure S2-1b. The γ is related to the composition of FeO, which is dependent on the ratio of Fe²⁺/Fe³⁺ in the phase. Notably, the occurrence of Fe_γO was less than 10 mins under 1000 °C. The changes in the valence states and cation distributions of Fe ions after annealing were identified by the Mössbauer spectra, as shown in Figure S2-1d. The Mössbauer spectrum of the pristine Mn–Zn ferrite was well fitted by three sextets, which correspond to Fe²⁺/Fe³⁺ at B sites and Fe³⁺ at A sites. The spectrum significantly changed for the annealed samples, where doublet appears and was continually enhanced by increasing the annealing time. The existence of doublet was owing to the formation of Fe_γO,¹ which resulted in the largely reduced saturation magnetization of the pristine Mn–Zn ferrites.

The fitting results of the Mössbauer spectrum are listed in Table S1. The doublet was characteristic for FeO in a paramagnetic state and fitted with two sites, which were ascribed to O₁ and O₂. The O₁ site with the isomer shift of ~0.95 mm/s is typically ascribed to the Fe²⁺ atoms. The O₂ site with IS ~0.30 mm/s represents the Fe³⁺ ions.²⁻³ The ratio of Fe²⁺ and Fe³⁺ (O₁/O₂) can be estimated from the corresponding peak area. It is clear that the Fe²⁺ atoms are increasing with the annealing time, which is also consistent with the XRD measurements in Figure S2-1b. The detailed peak position of Fe_γO <2 0 0> in Figure S2-1c was shifted from 42.17 ° to 42.08 ° from 10 to 120 mins

annealing, indicating a subtle change of m from 0.9536 (PDF#741880) to 0.9646 (PDF#741883). Furthermore, a state transition from Fe^{3+} to Fe^{2+} can be observed in sample annealed with 30 mins where the $\langle 2\ 0\ 0 \rangle$ peak is relatively broader than the other ones.

Table S1 Mössbauer Parameters of Mn–Zn ferrites annealed at 1000°C for 10, 30, and 120 min: Average Magnetic Hyperfine Field (H), Isomer Shift (IS), Quadrupole Splitting (QS), Width and relative area (Area) obtained by fitting Spectra.

Sample	Subspectrum	H(T)	IS(mm/s)	QS(mm/s)	Width(mm/s)	Area(%)	
MnZn ferrites							
Annealed for 10min	Fe ²⁺ at B sites	41.43	0.57380	0.04096	0.94577	40.66	
	Fe ³⁺ at B sites	44.54	0.56428	-0.03846	0.53131	35.81	
	Fe ³⁺ at A sites	48.25	0.26729	0.00318	0.30797	23.53	
	Fe ²⁺ at B sites	44.54	0.58922	0.08185	0.41200	8.32	
	Fe ³⁺ at B sites	44.7	0.59532	-0.12402	0.98200	42.99	
	Fe ³⁺ at A sites	48.5	0.25692	-0.01190	0.22751	13.00	
	Fe ²⁺ at O ₁	-----	0.94289	0.72954	0.58954	32.15	
	Fe ³⁺ at O ₂	-----	0.29500	0.16764	0.33187	3.54	
	Annealed for 30min	Fe ²⁺ at B sites	42.54	0.64656	0.04372	0.92637	18.00
		Fe ³⁺ at B sites	44.90	0.60721	-0.06336	0.68777	31.47
		Fe ³⁺ at A sites	48.4	0.25958	-0.01150	0.27464	13.12
		Fe ²⁺ at O ₁	-----	0.95366	0.77747	0.63418	21.19
		Fe ³⁺ at O ₂	-----	0.29800	0.17182	0.29252	1.97
		Fe ²⁺ at transition sites	15.69	0.33123	0.92837	1.18648	14.25
Annealed for 120min	Fe ²⁺ at B sites	42.94	0.61023	0.02674	0.71197	18.76	
	Fe ³⁺ at B sites	45.45	0.59776	-0.04863	0.44993	18.52	
	Fe ³⁺ at A sites	48.71	0.27930	-0.01390	0.26492	14.99	
	Fe ²⁺ at O ₁	-----	0.95243	0.69309	0.54842	43.6	
	Fe ³⁺ at O ₂	-----	0.30500	0.16700	0.36552	4.13	

Table S1 lists the fitted Mössbauer parameters of Mn–Zn ferrites annealed at 1000°C for 10, 30, and 120 min. Owing to the large gas flow rate of 200ml/min during the annealing process, Mn–Zn ferrites partially changed into the Fe_γO phase. The amount of the Fe_γO phase increased with annealing time. When Mn–Zn ferrites annealed for 30min, there was a transition state from Fe^{3+} to Fe^{2+} , resulting in very broad sextet in

the Mössbauer spectra. Unlike the Fe ions at normal positions, the hyperfine magnetic field of the transition phase was much lower, ca. 15.69 T.

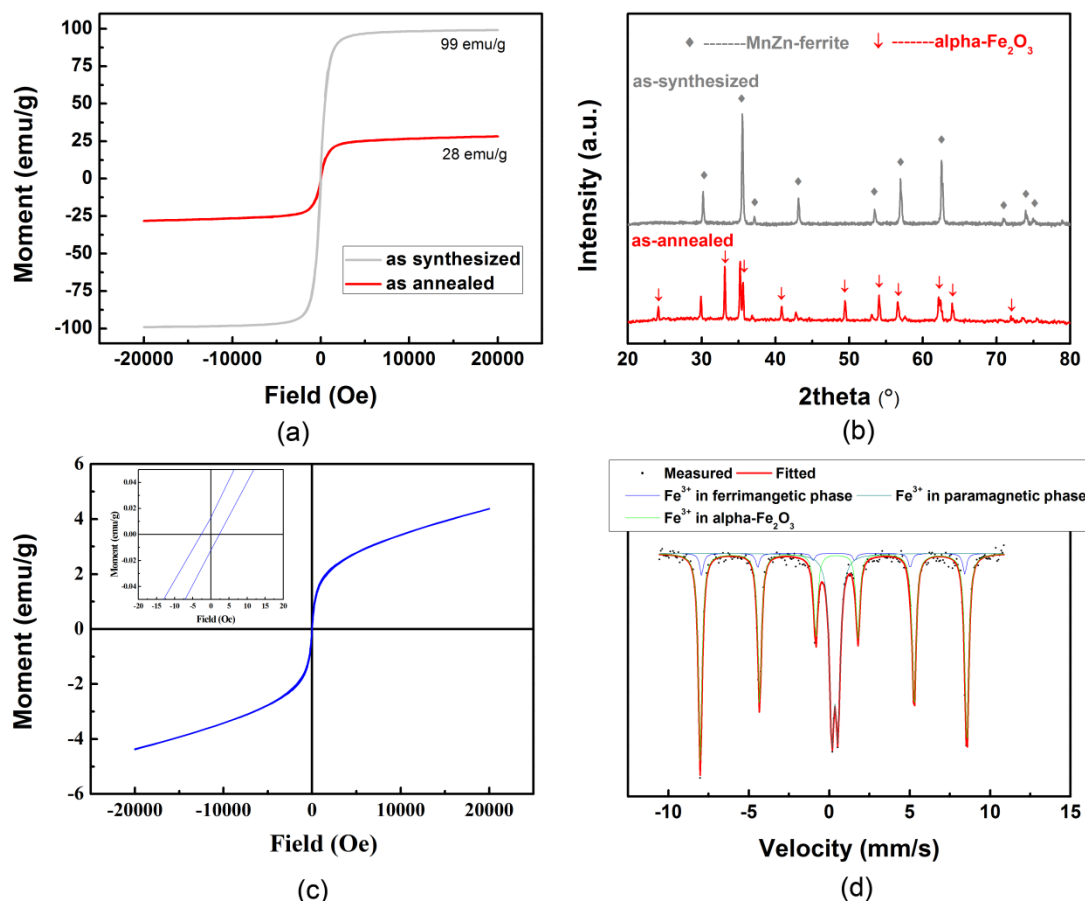


Figure S 3 Characterizations of Mn–Zn ferrites annealing at 1200°C and 1400°C for 2h under the Ar gas flow rate of 20 sccm. (a) M–H loops of Mn–Zn ferrites before and after annealing at 1200°C for 2 h; (b) the corresponding XRD patterns; (c) The M–H loops of Mn–Zn ferrites annealed at 1400°C for 2 h. The inset shows the coercivity and the remanence; and (d) the corresponding Mössbauer spectra.

The phase structures and the magnetic properties of annealed Mn–Zn ferrites at 1200 °C (MZF1200-20) and 1400 °C (MZF1200-20) under the Ar gas flow of 20 sccm were shown in Figure S3. The phase of α -Fe₂O₃ can be obviously observed in these two samples, as shown in Figure S3b. The M–H loops in Figure S3a showed the ferrimagnetism of MZF1200-20 with the saturation magnetization of only 28 emu/g,

while the paramagnetism of MZF1400-20 superimposed on low ferrimagnetism bearing 2.5 Oe coercivity and 0.012 emu/g remanence (the inset of Figure S3c).

When compared with the pristine Mn–Zn ferrites, there are two significant changes in the Mössbauer spectra of MZF1400-20. First, the presence of the middle doublet with zero hyperfine fields indicated the appearance of a paramagnetic phase, which probably corresponded with the ZnFe_2O_4 phase.⁴ Second, the much narrower sextet peaks in Figure S3d indicated the much more homogeneous structures of the annealed nanocrystals. The Mössbauer spectra fitting parameters are given in Table S2 and provide more detail about the valence state of the Fe ions and their distribution. One of two sextets can be attributed to the $\alpha\text{-Fe}_2\text{O}_3$ phase,⁵ which is consistent with the XRD phase analysis. There is another phase of spinel ferrite, as also observed in the XRD patterns. However, both Zn ferrite and $\alpha\text{-Fe}_2\text{O}_3$, which were confirmed by XRD patterns and Mössbauer spectra, are paramagnetic at room temperature. The presence of low ferrimagnetism can only be caused by the formation of Mn ferrites. The stoichiometry in the annealed sample was ca. $\text{Mn}_{0.06}\text{Zn}_{0.31}\text{Fe}_{2.63}\text{O}_4$, as detected by EDS and ICP. The valence state of Mn was determined by analyzing the Mn3s spectra in Figure S4, where Mn^{2+} was confirmed according to the measured ΔE_{3s} (ca. 6 eV). Therefore, MnFe_2O_4 was another type of ferrite that coexisted with ZnFe_2O_4 in the oxidized sample.

Table S2 Fitting Parameters of Mössbauer spectrum of Mn–Zn ferrite annealed at 1400°C with 20 sccm Ar gas flow rate: Average Magnetic Hyperfine Field (H), Isomer Shift (IS), Quadrupole Splitting (QS), Width and relative area (Area) obtained by fitting Spectra.

Subspectrum	H(T)	IS(mm/s)	QS(mm/s)	Width(mm/s)	Area(%)
Fe³⁺ in α-Fe₂O₃	51.52	0.37014	-0.21237	0.27747	64.11
Fe³⁺ at A sites (paramagnetic phase)		0.35030	0.37770	0.34775	29.79
Fe³⁺ at A sites (ferromagnetic phase)	50.83	0.26451	-0.04902	0.27400	6.1

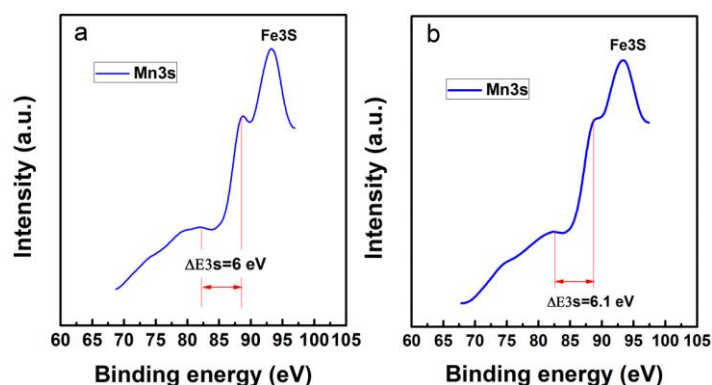


Figure S4 The Mn3s spectra of the annealed Mn–Zn ferrites (a) being oxidized (α -Fe₂O₃ included in the annealed product); and (b) being reduced (Fe₇O included in the annealed product). The Mn3s spectrum is used to estimate the valence state of Mn ions. ΔE_{3s} was measured to be 6 or 6.1 eV, as a result, $V_{Mn} = 9.67 - 1.27\Delta E_{3s}/\text{eV} \approx 2$. Thus the valence state of Mn is Mn²⁺.

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