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Facile Synthesis of Epsilon Iron Oxides via Spray Drying for Millimeter-wave Absorption

Gi Ryeon Jo[a,b], Min Byeol Yun[a,b], Yeong Hun Son[a,b], Byeongjin Park[c], Jung-Goo Lee[a],
Young-Kuk Kim[a], Young-Guk Son[b,*] and Youn-Kyoung Baek[a,*]

[a] *Powder Materials Division, Korea Institute of Materials Science, Changwon, 51508, South Korea*

[b] *School of Materials Science & Engineering, Pusan National University, Busan, 46241, South Korea*

[c] *Composites Research Division, Korea Institute of Materials Science, Changwon, 51508, South Korea*

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*corresponding author. Tel: +82-55-3605

E-mail address: ykbaek@kims.re.kr

Chemicals

The following chemical reagents were used: iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, ≥ 98% Sigma-Aldrich, USA), tetraethoxysilane (TEOS, 99.999% Sigma-Aldrich, USA), ethyl alcohol (99.5% Samchun Chemical Co., Korea), and sodium hydroxide (NaOH, 98.0% Samchun Chemical Co., Korea). All the chemicals were of analytical grade and were used without further purification. A thermoplastic polyurethane (TPU) solution containing 30 wt% TPU dissolved in N, N-dimethylformamide (DMF) was supplied by Songwon Industrial Co., Ltd.

Aerosol-assisted synthesis of ε-Fe_2O_3

To prepare the precursor solution for spray drying, $Fe(NO_3)_3 \cdot 9H_2O$ (14.6 mmol) was dissolved in a mixture of deionized water (1.2 mol) and ethanol (0.6 mol). Subsequently, tetraethyl orthosilicate (TEOS) was added dropwise to the mixture under mild stirring to provide an Fe/Si molar ratio in the range of 0.15–0.80. The obtained solution was spray dried using a Buchi mini spray drier B-290 with an inlet temperature of 220 °C, evaporation rate of approximately 1.0 kg/h, aspiration rate of 100%, rotameter setting of 60 mm, and pump rate of 3.0 mL/min. The as-sprayed precursor powders were then annealed in air at different temperatures (930–1270 °C) for 4 h at a temperature ramp rate of 4 °C/min. The silica matrix was etched with aqueous NaOH solution (5M) for 24 h at 70 °C to remove the silica matrix. The final product was obtained after subsequent washing of the etched solution. The Ga-substituted ε-Fe_2O_3 powders (ε-$Ga_xFe_{2-x}O_3$, x= 0.24, 0.32, 0.42, 0.48) were prepared using $Ga(NO_3)_3 \cdot 9H_2O$ in the precursor solution with a (Fe+Ga)/Si molar ratio of approximately 0.4 via the same process. As-spray-dried particles were annealed at 1180 °C for 4 h and subsequently washed using the same etching method.

Fabrication of millimeter-wave absorbing film

The TPU solution and ε-Fe_2O_3 powders were mixed for 5 min at 2000 rpm using a planetary mixer (ARE-310, Thinky), and the ratio of the magnetic powder to TPU was 8:2, corresponding to a ε-Fe_2O_3 content of 80 wt%. The mixed solution was cast by setting a doctor blade (Test-one, TO-500) at a speed of 10 mm/s and a blade gap of 1000 μm to obtain a composite film with the desired thickness (200 μm). It was dried at 110 °C to evaporate the solvent in the film.

Material characterization and magnetic measurement

The synthesized magnetic powders were characterized using an X-ray diffractometer (XRD, Rigaku, D/MAX-2500) with Cu Kα radiation, operating at 40 kV and 250 mA. The relative weight fractions of the crystalline phases were calculated based on the XRD patterns by Rietveld refinement in JADE 9.0 (Materials Data, Inc.). The XRD patterns of each sample were obtained at a scan rate of 4°/min from 10° to 90°. The formulas were determined to be $Ga_xFe_{2-x}O_3$ with x = 0.24, 0.32, 0.42, and 0.48, as per the results of inductively coupled plasma mass spectroscopy (ICP-MS, NexION 350D, Perkin-Elmer, USA). The morphology of the obtained particles was observed using a field-emission transmission electron microscope (JEM 2100, Jeol). Mössbauer spectra were recorded at room temperature using a 50 mCi ^{57}Co γ-ray source in the Rh matrix with the spectrometer moving at a constant acceleration. The magnetic properties were analyzed using a Magnetic Property Measurement System (Quantum Design Inc., MPMS3-Evercool) at 298 K with an applied external field of 50 kOe.

Millimeter-wave absorption measurement

The electromagnetic wave absorption characteristics, permittivity, and permeability of the composite samples were measured using a vector network analyzer (VNA, Keysight N5291A) and a free space antenna measurement system (FSM, EMlabs FS-110) in the range of 33–110 GHz. Note that a different waveguide was used to integrate VNA and FSM for each frequency band, WR-22 for the Q-Band (33–50 GHz), WR-15 for the V-Band (50–75 GHz), and WR-10 for the W-Band (75–110 GHz), respectively. A 7-cm-square sample with a thickness of 200 μm was loaded into the FSM for measurement. The complex permittivity and permeability of each sample were computed from the VNA-measured S-parameters using the Nicolson–Ross–Weir (NRW) theory [1].

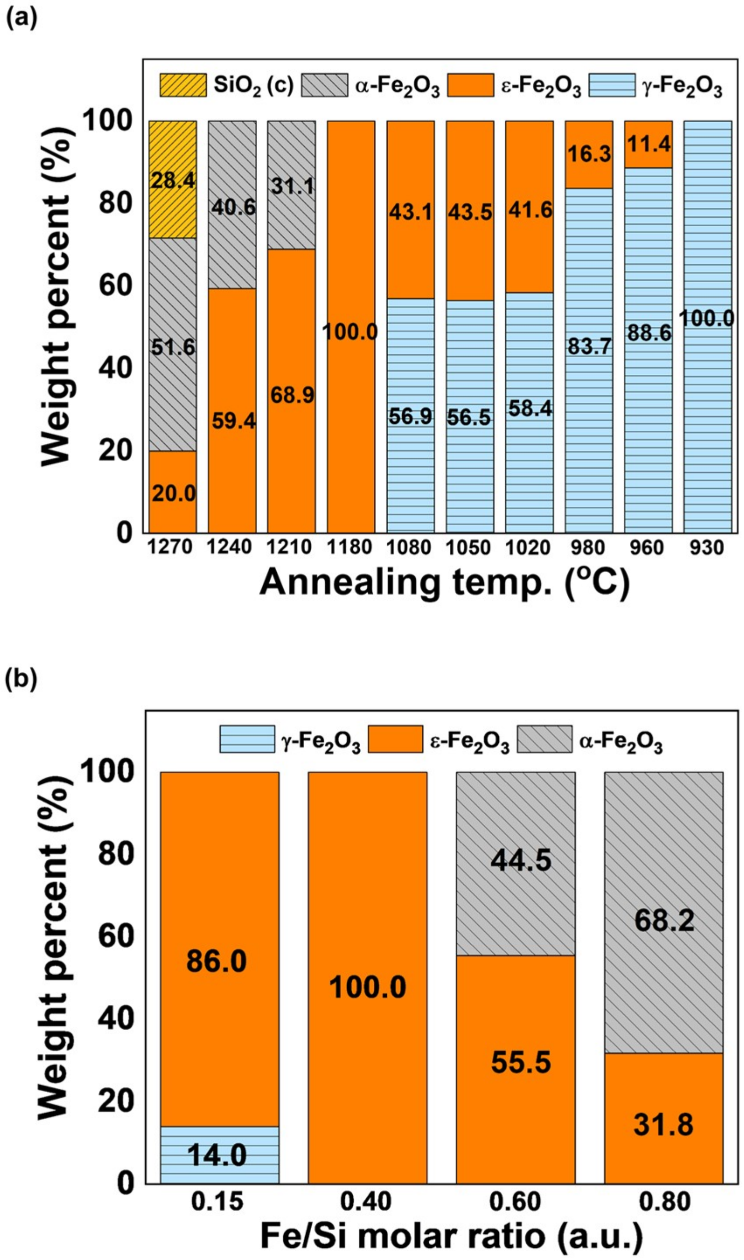


Fig. S1. Phase fraction (wt%) of Fe_2O_3 @SiO_2 particles obtained by varying the (a) annealing temperature and (b) molar ratio of the precursors (Fe/Si), corresponding to the XRD patterns in Fig. 2.

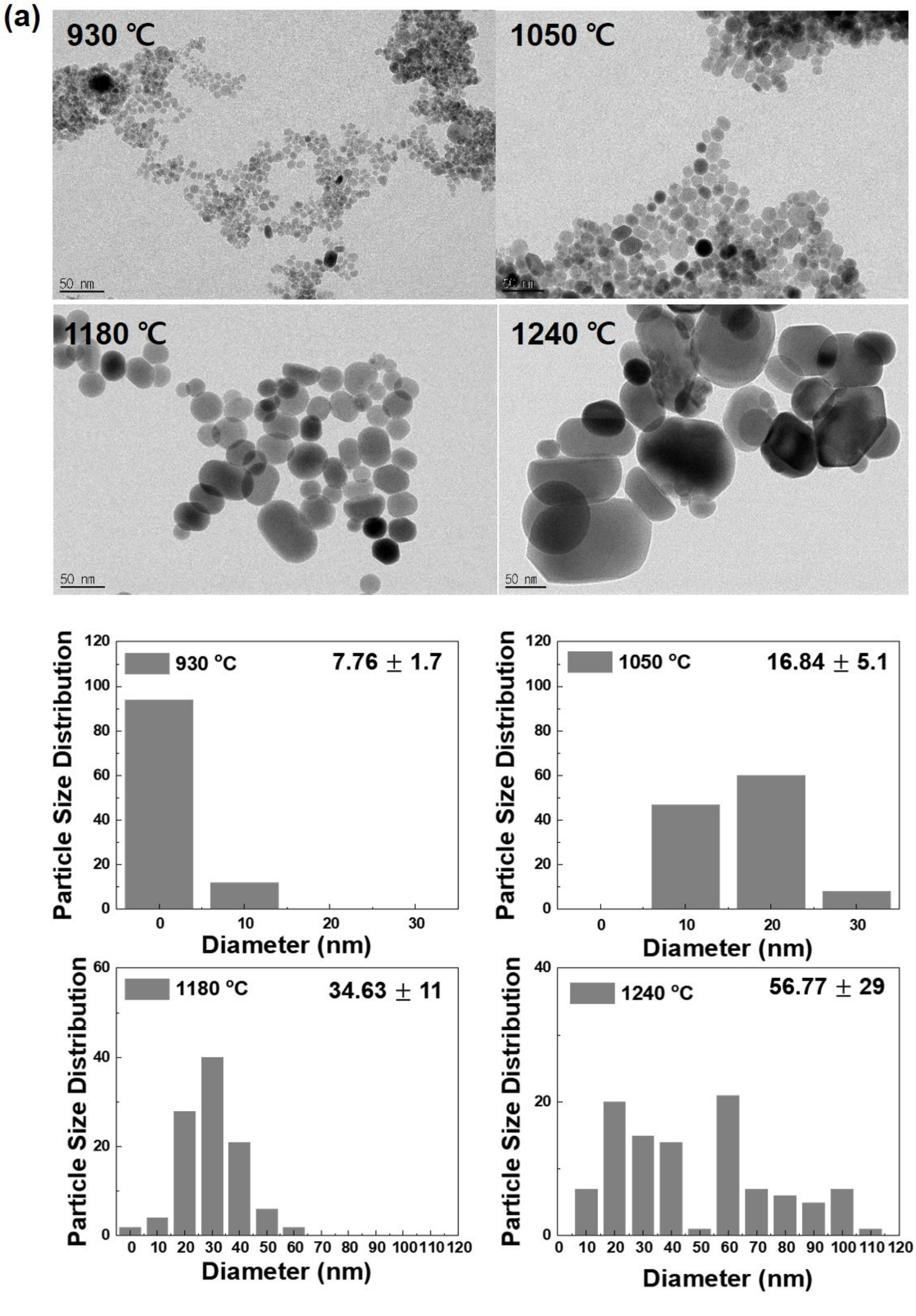
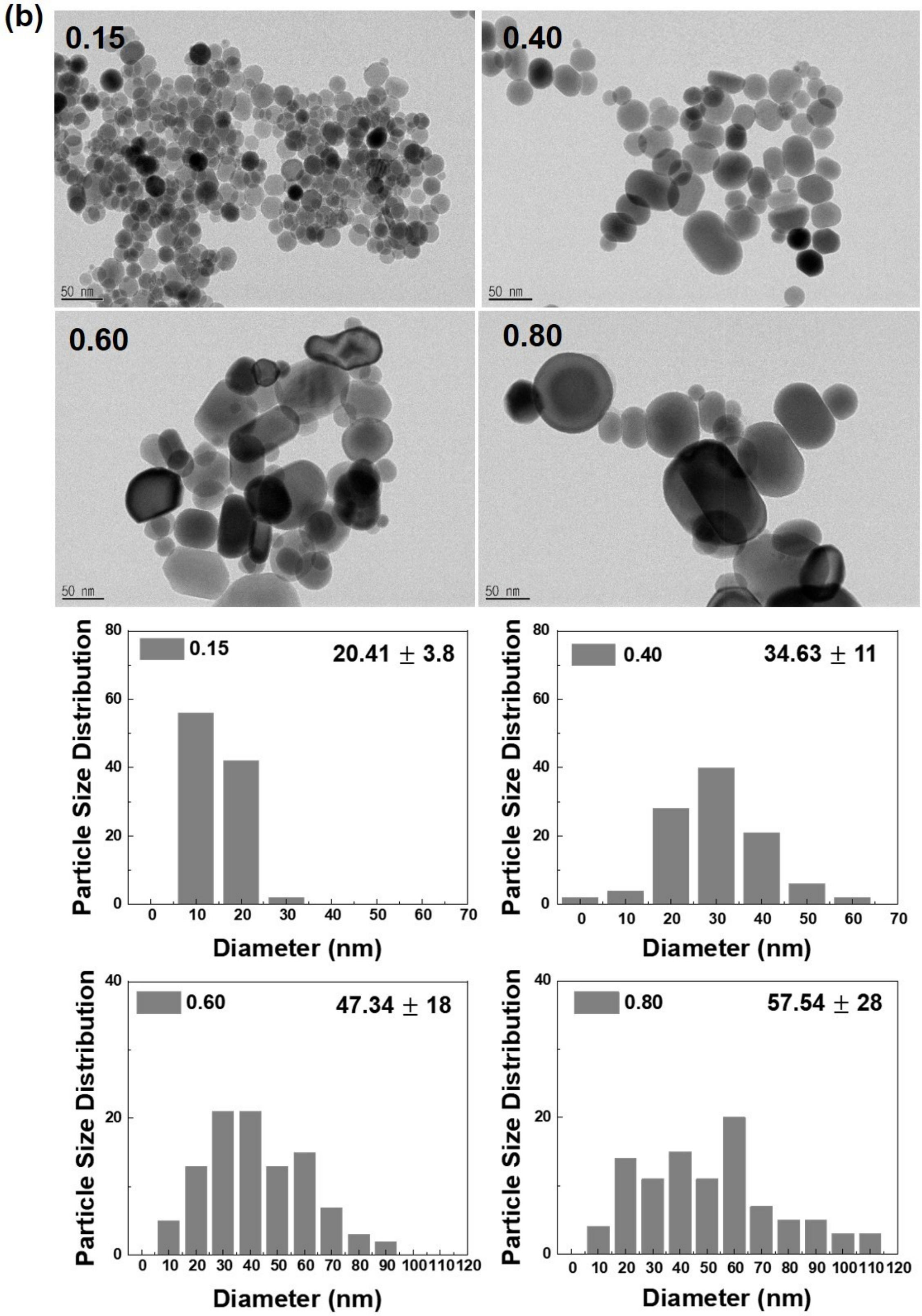


Fig. S2. Representative transmission electron microscopy images, corresponding particle size distributions, and average diameters and standard deviations determined from ~100 nanoparticles obtained from Fe_2O_3 nanoparticles synthetized under (a) different annealing temperatures and (b) various Fe/Si molar ratios.



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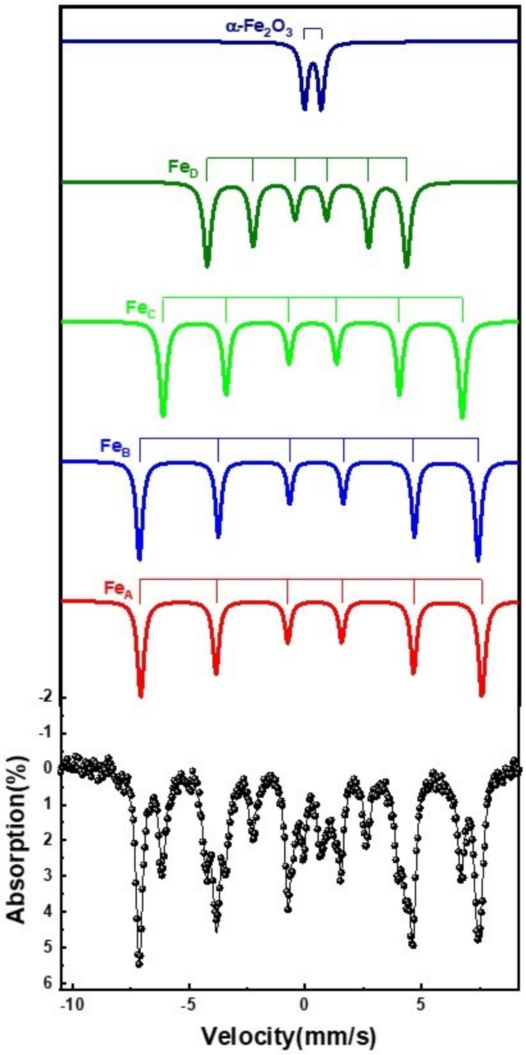

Fig. S3. Mössbauer spectrum of the ε-Fe$_2$O$_3$ synthesized under the optimized conditions (Fe/Si molar ratio = 0.4 and annealing temperature = 1180 ℃), recorded at room temperature and without an external magnetic field.

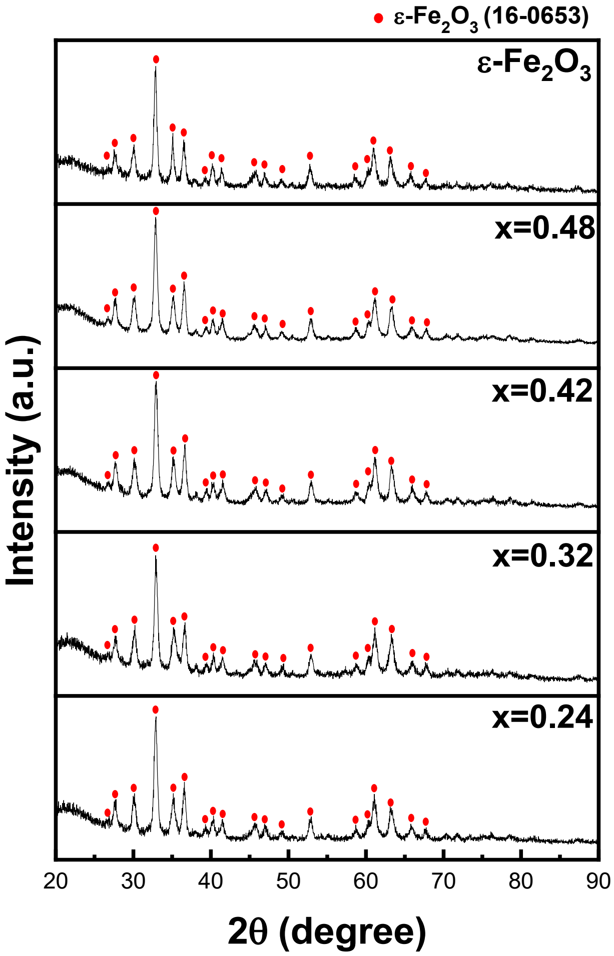

Fig. S4. XRD spectra of Ga-substituted ε-Fe_2O_3 nanoparticles synthesized by spray drying.

Fig. S5. Millimeter-wave absorbing film composed of ε-$Ga_xFe_{2-x}O_3$ and thermoplastic polyurethane.

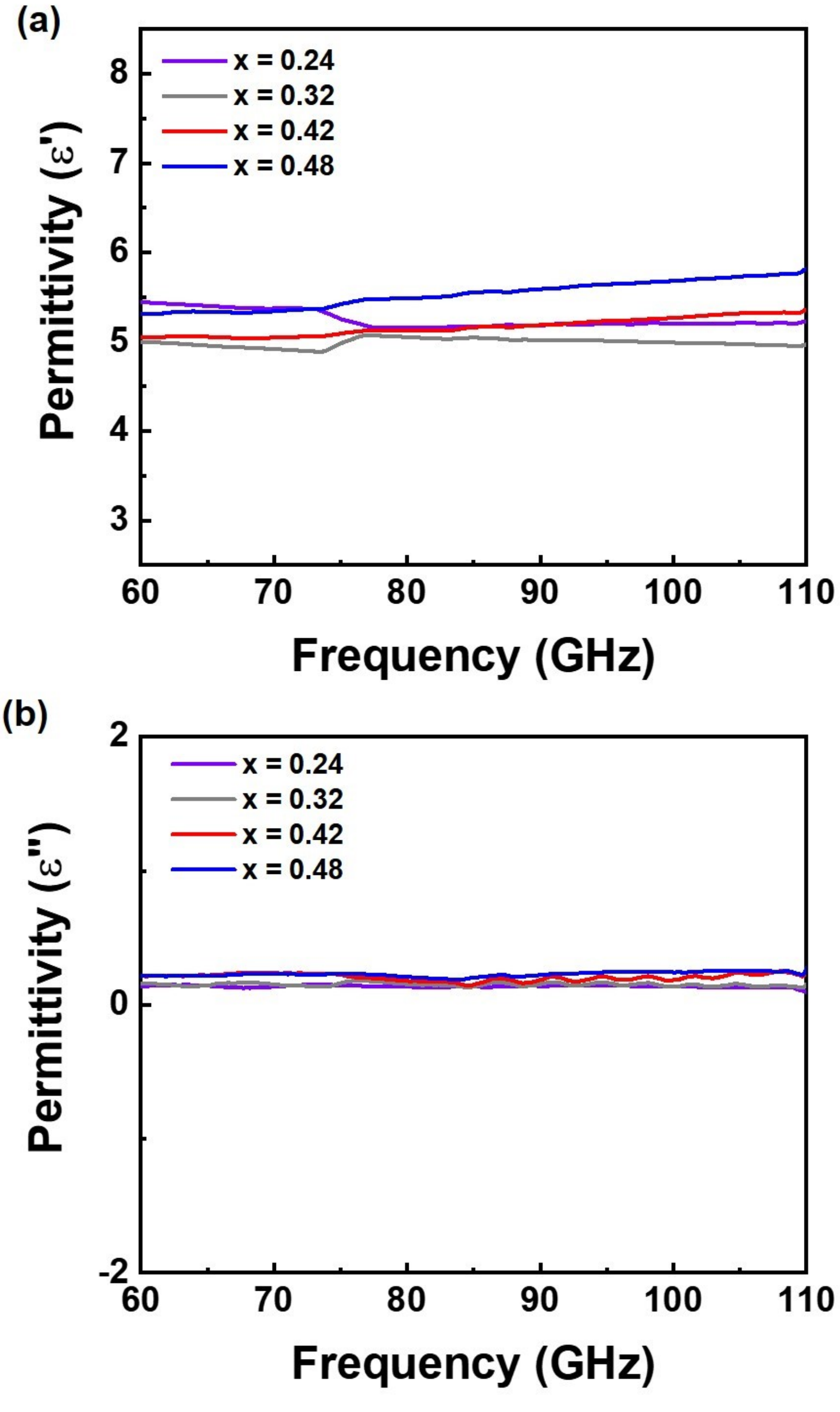

Fig. S6. (a) Real (ε’) and (b) imaginary (ε”) parts of the magnetic permittivity obtained from ε-Ga$_x$Fe $_{2-x}$ O$_3$-based TPU composite films.

Table S1. Typical Mössbauer hyperfine parameters of ε-Fe_2O_3.

	Component			
	Isomer shift, δ (mm/s)	Quadrupole splitting, ΔE_Q (mm/s)	Hyperfine magnetic field, B_{hf} (kOe)	Relative spectral area of individual spectral components, RA (%)
ε-Fe_2O_3 Fe_A	0.29	–0.07	455.06	23.49
ε-Fe_2O_3 Fe_B	0.27	–0.16	452.72	22.57
ε-Fe_2O_3 Fe_C	0.28	–0.00	399.03	23.65
ε-Fe_2O_3 Fe_D	0.11	–0.08	266.86	22.99
α-Fe_2O_3	0.28	0.72	-	7.30

Table S2. Room-temperature magnetic parameters of the obtained magnetic particles as functions of the annealing temperature and Fe/Si molar ratio.

		Magnetic properties		
		$M_{5.0T}$ (emu/g)	M_r (emu/g)	H_c (kOe)
Annealing Temperature (Fe/Si = 0.40)	930 °C	19.3	0.6	0.2
	1050 °C	18.2	8.3	14.5
	1180 °C	14.3	7.7	22.4
	1240 °C	7.4	3.7	23.0
Fe/Si molar ratio (1180 °C, 4 h)	0.15	17.9	9.0	19.8
	0.40	14.3	7.7	22.4
	0.60	7.0	3.8	22.3
	0.80	6.6	3.6	22.6

Table S3. Magnetic properties resonant frequencies (f_r) of ε-$Ga_xFe_{2-x}O_3$ ($0.22 \leq x \leq 0.47$) obtained in a previous study [2].

	Magnetic properties			
	M_s (emu/g)	M_r (emu/g)	H_c (kOe)	f_r (GHz)
x = 0.00.	15.0	-	20.0	190
x = 0.22	24.7	-	11.6	115
x = 0.35	28.7	-	9.3	88
x = 0.40	30.1	-	8.8	84
x = 0.47	28.5	-	6.8	73

Table S4. Magnetic properties and resonant frequencies (f_r) of ε-$Ga_xFe_{2-x}O_3$ ($0.24 \leq x \leq 0.48$) measured at room temperature.

	Magnetic properties			
	M_s (emu/g)	**M_r (emu/g)**	**H_c (kOe)**	**f_r (GHz)**
x = 0.00	**14.2**	**7.7**	**22.3**	**-**
x = 0.24	**26.7**	**13.5**	**10.9**	**105**
x = 0.32	**26.8**	**12.8**	**8.6**	**93**
x = 0.42	**26.3**	**12.7**	**7.1**	**82**
x = 0.48	**23.5**	**10.8**	**5.4**	**71**

References

1. P.J. Bora, G. Lakhani, P.C. Ramamurthy and G. Madras, *RSC Adv*. 2016, **6**, 79058.
2. S. Ohkoshi, S. Kuroki, S. Sakurai, K. Matsumoto, K. Sato and S. Sasaki, *Angew. Chem. Int. Ed*. 2007, **46**, 8392-8395.