Electronic Supplementary Information

The effect of Sr doping on electronic structure and electromagnetic properties of $LaCo_{0.9}Fe_{0.1}O_3$ perovskites

Fan Wang [1, a], Yue Wu [1, a], Yue Zhao [1], Ming Zhou [1], Shaolong Tang [2], and Guangbin Ji [1, *]

[1] *College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 211100, China.*

[2] *National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P. R. China.*

[a] Fan Wang and Yue Wu contributed equally to this work.

* Corresponding author. Prof. Dr. Guangbin Ji., Tel: +86-25-52112902

E-mail address: gbji@nuaa.edu.cn

Reagents

Ferric nitrate nine hydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99.99%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%), citric acid (99.5%), lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, 99.99%) and strontium nitrate ($Sr(NO_3)_2$, 99.3%), ammonia ($NH_3 \cdot H_2O$, 25~28%) were purchased from Aladdin Industrial Corporation.

Characterization

The phase analysis and crystal structure for series of LSCFO perovskites were characterized by X-ray diffractometer (XRD, Bruker-D8). The morphology observation was analyzed by field emission scanning electron microscope (SEM, Hitachi S4800). The static magnetic property was determined by the vibrating sample magnetometer (VSM) at room temperature. To investigate the valence state of Sr-doping LSCFO perovskites, the X-ray photoelectron spectroscopy (XPS) was measured by the Al-Ka source gun Kratos axis hyperspectrometer.

EM parameters measurement

The EM parameters (ε', ε'', μ', μ'') for LSCFO perovskites were measured by Agilent PNA N5244A vector network analyzer (VNA) according to the coaxial line method. The samples were uniformly mixed with the paraffin in a 1:1 mass ratio to obtain a ring (Φ_{in}: 3.04 mm and Φ_{out}: 7.00 mm). The microwave absorbing performance could be assessed by the RL value that was calculated by the following equations:[1-3]

$$RL(\mathrm{dB}) = 20\lg\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right| \quad \text{(S1)}$$

$$Z_{in} = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\left(\frac{2\pi fd}{c}\right)\sqrt{\mu_r\varepsilon_r}\right] \quad \text{(S2)}$$

Where Z_{in} and Z_0 were the input impedance and free space impedance, c, f and d were the light speed, frequency and matching thickness, respectively.

The impedance matching performance was described as follows:[4-6]

$$K = \frac{4\pi\sqrt{\mu'\varepsilon'}}{\mathrm{c}} \frac{\sin\left[\frac{(\delta_e + \delta_m}{2}\right]}{\cos\delta_e \cos\delta_m} \tag{S3}$$

$$M = \left[4\mu'\cos\delta_e\varepsilon'\cos\delta_m\right]\cdot\left[\left(\mu'\cos\delta_e - \varepsilon'\cos\delta_m\right)^2 + \left(\tan\frac{\delta_m + \delta_e}{2}\right)^2\left(\mu'\cos\delta_e + \varepsilon'\cos\delta_m\right)^2\right]^{-1} \tag{S4}$$

$$\Delta = \left|\sin h^2\left(Kfd\right) - M\right| \tag{S5}$$

Where $\tan\delta_E = \varepsilon''/\varepsilon'$ and $\tan\delta_M = \mu''/\mu'$ were the dielectric loss tangent and magnetic loss tangent, respectively. Δ value was the impedance matching factor (the ideal impedance matching can be obtained when Δ value is 0).

Computational details

The calculation was completed by the CASTEP module in the material studio 8.0 software package, which takes the periodic boundary for the limited condition. The generalized gradient approximation Perdew-wang91 exchange correlation function was conducted to computed exchange correlation energy, and the ultra-soft pseudopotential way is employed to computed the interaction between electrons. Regarding the selection of parameters for K-grid point and plane wave truncation energy, the convergence test was employed to maintain the energy values to a minimum. Furthermore, given the orbital spin, the electron exchange correlation energy was coped with the orbital generalization LDA+U. The cutoff energy and k-mesh were 400 eV and 3*3*3 for geometry optimizations, respectively. The convergence criterion for self-

consistence total-energy calculation was 2.0*10^-6. In the geometrical optimization, all forces on atoms were converged to less than 0.05 eV/Å, the maximum ionic displacement was within 0.002 Å and the total stress tensor was reduced to the order of 0.1 GPa.[7] Besides, the U values of Fe, Co, and La elements during DFT+U calculation were 2.5 eV, 2.5 eV and 6.0 eV, respectively, which could be seen in Table S1. The $LaCoO_3$ unit cell was established, and the supercell of 5a*b*c was selected for calculation, 3 of the 29 cobalt atoms were selected for Fe atom replacement, 1 of the 10 La atoms was selected respectively. 2 and 3 are substituted by Sr atoms, and the number of substituted atoms was shown in Table S2. After the unit cell model was constructed, the crystal structures of the LCFO and LSCFO systems were optimized, the total energy of the combined models of different substitution positions was compared, and the model with the lowest energy was selected as the crystal structure. Regarding the parameter selection of k grid points and plane wave truncation energy, the convergence test was used to take the minimum total energy value as the standard.

Table S1 The U values during DFT+U calculation.

Elements	U value (eV)	Orbit
Fe	2.5	d
Co	2.5	d
La	6.0	f

Table S2 Substitution structures of LCFO, LSCFO-1, LSCFO-2, and LSCFO-3.

Samples	LCFO	LSCFO-1	LSCFO-2	LSCFO-3
Super-cellular composition	5a*b*c	5a*b*c	5a*b*c	5a*b*c
A-site ion ratio (Sr^{2+}/Co^{3+})	0	1:9	2:8	3:7
A-site ion ratio after substitution (Sr^{2+}/Co^{3+})	0	1:9	2:8	3:7
B-site ion ratio after (Co^{3+}/Fe^{3+})	1:9	1:9	1:9	1:9
B-site ion ratio after substitution (Co^{3+}/Fe^{3+})	3:26	3:26	3:26	3:26

Reference

1 B. Quan, W. H. Gu, J. Q. Sheng, X. F. Lv, Y. Y. Mao, L. Liu, X. G. Huang, Z. J. Tian, G. B. Ji, From Intrinsic Dielectric Loss to Geometry Patterns: Dual-Principles Strategy for Ultrabroad Band Microwave Absorption, *Nano Res.*, 2021, **14**, 1495-1501.

2 J. Li, D. Zhou, P. J. Wang, C. Du, W. F. Liu, C. Du, W. F. Liu, J. Z. Su, L. X. Pang, M. S. Cao, L. B. Kong, Recent Progress in Two-Dimensional Materials for Microwave Absorption Applications, *Chem. Eng. J.*, 2021, **425**, 131558.

3 J. T. Feng, Y. C. Wang, Y. H. Hou, L. C. Li, Tunable Design of Yolk-Shell $ZnFe_2O_4$@RGO@TiO_2 Microspheres for Enhanced High-Frequency Microwave Absorption, *Inorg. Chem. Front.*, 2017, **4**, 935-945.

4 Z. Y. Zhang, Y. X. Li, Y. J. Liao, H. W. Rong, W. T. Zhang, M. Zhang, G. W. Qin, X. F. Zhang, Synthesizing CN_x Heterostructures on Ferromagnetic Nanoparticles for Improving Microwave Absorption Property, *Appl. Surf. Sci.*, 2021, **564**, 150480.

5 Y. L. Zhou, N. Wang, J. Muhammad, D. X. Wang, Y. P. Duan, X. F. Zhang, Graphene Nanoflakes with Optimized Nitrogen Doping Fabricated by Arc Discharge Method as Highly Efficient Absorbers Toward Microwave Absorption, *Carbon*, 2019, **148**, 204-213.

6 L. Quan, F. X. Qin, D. Estevez, H. Wang, H. X. Peng, Magnetic Graphene for Microwave Absorbing Application: Towards the Lightest Graphene-based Absorber, *Carbon*, 2017, **125**, 630-639.

7 H. Peng, C. L. Wang, J. C. Li, Enhanced thermoelectric properties of $AgGaTe_2$ utilizing carrier concentration adjusting, *Phys. B*, 2014, **441**, 68-71.