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Interchange core/shell assembly of diluted magnetic semiconductor CeO$_2$ and ferromagnetic ferrite Fe$_3$O$_4$ for microwave absorption

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Core/shell-structured CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ nanocapsules are prepared by interchange assembly of diluted magnetic semiconductor CeO$_2$ and ferromagnetic ferrite Fe$_3$O$_4$ as the core and the shell, and vice versa, using a facile two-step polar solvothermal method in order to utilize the room-temperature ferromagnetism and abundant O-vacancies in CeO$_2$, the large natural resonance in Fe$_3$O$_4$, and the O-vacancy-enhanced interfacial polarization between CeO$_2$ and Fe$_3$O$_4$ for new generation microwave absorbers. Comparing to Fe$_3$O$_4$/CeO$_2$ nanocapsules, the CeO$_2$/Fe$_3$O$_4$ nanocapsules show an improved real permittivity of 3–10% and an enhanced dielectric resonance of 1.5 times at 15.3 GHz due to the increased O-vacancy concentration in the CeO$_2$ cores of larger grains as well as the O-vacancy-induced enhancement in interfacial polarization between the CeO$_2$ cores and the Fe$_3$O$_4$ shells, respectively. Both nanocapsules exhibit relatively high permeability in the low-frequency S and C microwave bands as a result of the bi-magnetic core/shell combination of CeO$_2$ and Fe$_3$O$_4$. The CeO$_2$/Fe$_3$O$_4$ nanocapsules effectively enhance permittivity and permeability in the high-frequency Ku band with interfacial polarization and natural resonance at ~15 GHz, thereby improving absorption with a large reflection loss of -28.9 dB at 15.3 GHz. Experimental and theoretical comparisons with CeO$_2$ and Fe$_3$O$_4$ nanoparticles are also made. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4973204]

I. INTRODUCTION

The integration of microwave absorbers in electronic devices and systems has become an essential strategy in minimizing electromagnetic (EM) radiation and improving EM compatibility. Core/shell-structured nanocapsules, typically in the form of a magnetic nanoparticle core coated by a dielectric shell of nanometer size, have attracted great interest in recent years because of their generally strong absorption, small thickness, and low density in the S, C, X, and/or Ku bands of microwaves covering the 2–18 GHz range. Many of the recent reports have focused on preserving strong absorption while extending the frequency and thickness ranges by minimizing the interface reflection caused by the EM mismatch between permittivity and permeability.

Besides the traditional magnetic/dielectric combination for the core/shell structure, several different and interesting combinations involving magnetic cores and piezoelectric, ferroelectric,
multiferroic, semiconducting, insulating/conducting, conducting/insulating, etc. shells have been proposed in the core/shell and even core/double-shell structure. In addition to combining different core and shell material phases, the effect of interchange core and shell on the microwave absorption properties has ignited new research interest and direction in more recent years. From a physical perspective, the distinct dielectric, electrical, and/or magnetic properties of these shells will lead to characteristically different interfacial effects and hence microwave absorption properties.

Diluted magnetic semiconductors and oxides, especially for those without doping of magnetic elements, possess versatile physical properties, and so are scientifically interesting and technologically important for magnetoelectronics. CeO$_2$ is an interesting diluted magnetic semiconducting oxide of such kind. It exhibits ferromagnetism at room temperature and contains abundant O-vacancies. By combining these unique features in CeO$_2$ with the large natural resonance in an appropriate ferromagnetic ferrite (e.g., Fe$_3$O$_4$), it is likely to observe interestingly strong absorption with broad absorption bandwidth and absorber thickness range underpinned by new physics in such a bi-magnetic core/shell structure. Moreover, the space charges at the interface between CeO$_2$ and Fe$_3$O$_4$ are capable of inducing an enhancement in interfacial polarization by the abundant O-vacancies in CeO$_2$.

In this work, we report the use of a facile two-step polar solvothermal method to prepare two different types of core/shell-structured bi-magnetic nanocapsules by interchange assembly of diluted magnetic semiconductor CeO$_2$ and ferromagnetic ferrite Fe$_3$O$_4$ as the core and the shell (i.e., CeO$_2$/Fe$_3$O$_4$ nanocapsules) and vice versa (i.e., Fe$_3$O$_4$/CeO$_2$ nanocapsules). Our aim is to utilize the room-temperature ferromagnetism and abundant O-vacancies in CeO$_2$, the large natural resonance in Fe$_3$O$_4$, and the O-vacancy-enhanced interfacial polarization between CeO$_2$ and Fe$_3$O$_4$ for providing an improved strategy to realize new generation microwave absorbers. The phase, lattice parameters, morphology, and interface nanostructure of the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ nanocapsules are studied, and their microwave absorption properties are evaluated in the full S–Ku microwave bands of 2–18 GHz. The results are also discussed experimentally and theoretically with their CeO$_2$ and Fe$_3$O$_4$ nanoparticle counterparts.

II. EXPERIMENTS

A facile two-step polar solvothermal method with PVP-assisted interface activation was utilized to prepare CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ core/shell-structured nanocapsules. In a typical reaction for CeO$_2$/Fe$_3$O$_4$ nanocapsules, Ce(NO$_3$)$_3$ of 1.5 mmol was dissolved in distilled water of 30 ml, and NaOH of 2 g was rapidly added into the solution under magnetic stirring. The stirring process was maintained until a uniform precursor was formed. The precursor was transferred into a stainless steel autoclave of 50 ml with Teflon line before being heated in an oven at 200 °C for 6 h. The CeO$_2$ product was collected by centrifugation and treated ultrasonically in 5 g/L PVP aqueous solution for 12 h. After further centrifugation, the CeO$_2$ product was dispersed in EG of 30 ml with FeCl$_3$ of 1.5 mmol and PEG of 0.15 g under magnetic stirring. The mixture was sealed in the autoclave and heated in the oven at 200 °C for 4 h. The CeO$_2$/Fe$_3$O$_4$ product was obtained after being washed by distilled water and ethanol and then dried in a vacuum at 60 °C for 6 h.

Fe$_3$O$_4$/CeO$_2$ nanocapsules were prepared using the reverse steps of the above with slightly different solvents and heating conditions. In a typical reaction, Fe$_3$O$_4$ cores were prepared by dissolving FeCl$_3$ of 1.5 mmol and PEG of 0.15 g in EG of 30 ml, and the mixture was solvothermally treated at 200 °C for 8 h. The Fe$_3$O$_4$ product was added into the CeO$_2$ precursor formed by Ce(NO$_3$)$_3$ of 1.5 mmol, ammonia hydroxide of 1.5 ml, and ethanol of 30 ml after it was ultrasonically treated in 5 g/L PVP aqueous solution for 12 h. The mixture was solvothermally treated in the autoclave at 120 °C for 6 h. The Fe$_3$O$_4$/CeO$_2$ product was washed by distilled water and ethanol, collected by centrifugation, and dried in a vacuum at 60 °C for 6 h.

The phase and lattice parameters of the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ products were examined by an X-ray diffractometer (XRD, Bruker D8 Advance) with Cu-Kα radiation (λ = 1.54 Å) at a θ/2θ scan rate of 4 °/min. The morphology and interface nanostructure were investigated in a transmission electron microscope (TEM, JEM 2100F) with an emission voltage of 200 kV. The CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ nanocapsules were mixed with 60 wt.%, microwave-transparent paraffin to form paraffin-bonded CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ nanocapsule composites, respectively. The CeO$_2$ and
Fe$_3$O$_4$ nanoparticles were also fabricated into paraffin-bonded CeO$_2$ and Fe$_3$O$_4$ nanoparticle composites for comparison and further discussion. The complex relative permittivity ($\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$) and permeability ($\mu_r = \mu'_r - j\mu''_r$) of the composites were measured by a transmission/reflection coaxial line method in the 2–18 GHz microwave range using a vector network analyzer (Agilent 5244A). The frequency ($f$) and thickness ($d$) dependence of reflection loss ($RL$) was determined using:

$$RL = 20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right|$$

where $Z_{in} = Z_0 (\mu_r/\varepsilon_r)^{1/2} \tanh \left[j (2\pi f d/c) (\mu_r\varepsilon_r)^{1/2}\right]$ is the input impedance of composite, $Z_0 \sim 377$ Ω is the characteristic impedance of air, $c = 3 \times 10^8$ m/s is the velocity of light, and $d$ is the thickness of composite.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD $\theta - 2\theta$ patterns of typical CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ products. The diffraction peaks in both products can be indexed to two phases: cubic fluorite CeO$_2$ ($Fm\overline{3}m$) phase and inverse spinel Fe$_3$O$_4$ ($Fd\overline{3}m$) phase, according to JCPDS 34-0394 and 65-3107 for CeO$_2$ and Fe$_3$O$_4$, respectively. Since FeCl$_3$ can only produce Fe$_3$O$_4$ phase in a solvothermal reaction with EG, the formation of $\gamma$-Fe$_2$O$_3$ phase can be excluded. No diffraction peaks in relation to other impurities are detected. The intensity and full width at half maximum (FWHM) of CeO$_2$ peaks exhibit great differences in the two products in that they are strong and sharp in the CeO$_2$/Fe$_3$O$_4$ product but weak and broad in the Fe$_3$O$_4$/CeO$_2$ product. This is because the particle size of CeO$_2$ in the CeO$_2$/Fe$_3$O$_4$ product is much larger than that in the Fe$_3$O$_4$/CeO$_2$ product based on the Scherer’s equation. The hydroxyls of ethanol may promote the nucleation and limit the growth of CeO$_2$ grains during the preparation of the Fe$_3$O$_4$/CeO$_2$ product. As O-vacancies may break the electric neutrality of the CeO$_2$ lattice and affect the microwave absorption properties of the resulting product, the O-vacancy concentration of CeO$_2$ in the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ products was calculated to be 1.52 and 0.08%, respectively, using the Zhou’s equation. The 19-times higher in the CeO$_2$/Fe$_3$O$_4$ product than the Fe$_3$O$_4$/CeO$_2$ product suggests that more O-vacancies are available in the CeO$_2$ cores than the CeO$_2$ shells owing to its larger grains. The grain size of Fe$_3$O$_4$, as suggested by FWHM, shows.

![Fig. 1](image-url)

**FIG. 1.** (a) XRD $\theta - 2\theta$ patterns of typical CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ products. (b) TEM image of a typical CeO$_2$/Fe$_3$O$_4$ product. (c) HRTEM image of the interface of CeO$_2$/Fe$_3$O$_4$ product in (b). (d) TEM image of a typical Fe$_3$O$_4$/CeO$_2$ product. (e) HRTEM image of the interface of Fe$_3$O$_4$/CeO$_2$ product in (d). The insets in (c) and (e) are the SAED patterns.
a similar phenomenon but a larger value in the Fe$_3$O$_4$ cores than in the Fe$_3$O$_4$ shells owing to the different heating times. The strong, sharp peaks of Fe$_3$O$_4$ in the Fe$_3$O$_4$/CeO$_2$ product indicate that the grain size may have already exceeded 100 nm and is unable to be estimated by the Scherer’s equation.

Figure 1(b) illustrates the TEM image of a typical CeO$_2$/Fe$_3$O$_4$ product. The CeO$_2$ core is in spherical shape of ~160 nm diameter. The core surface is coated with many smaller sized Fe$_3$O$_4$ nanoparticles to form the Fe$_3$O$_4$ shell. The HRTEM image in Fig. 1(c) displays the interface of the CeO$_2$/Fe$_3$O$_4$ product in Fig. 1(b). Fe$_3$O$_4$ nanoparticles of ~10 nm diameter (with an image of periodic stripes) are closely packed on the surface of the CeO$_2$ core as the Fe$_3$O$_4$ shell. The concentric rings in the SAED pattern (the inset of Fig. 1(c)) suggest that the CeO$_2$ core is also a closely packed cluster of many CeO$_2$ nanoparticles. Figure 1(d) gives the TEM image of a typical Fe$_3$O$_4$/CeO$_2$ product. The Fe$_3$O$_4$ core is in cubic shape of ~300 nm length. The HRTEM image in Fig. 1(e) reveals a close-packing of CeO$_2$ nanoparticles of ~5 nm diameter on the surface of the Fe$_3$O$_4$ core to form the CeO$_2$ shell. The periodical spots and concentric rings in the SAED pattern (the inset of Fig. 1(e)) infer that a Fe$_3$O$_4$/CeO$_2$ nanocapsule consists of a single-crystal Fe$_3$O$_4$ core coated by closely packed CeO$_2$ nanoparticles as the shell.

Figure 2(a) shows the $f$ dependence of $\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$ for the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites, together with the CeO$_2$ and Fe$_3$O$_4$ composites. The CeO$_2$/Fe$_3$O$_4$ composite exhibits relatively stable $\varepsilon'_r$ and $\varepsilon''_r$ responses in the S, C, and X bands of 2–12 GHz even though there are slight fluctuations of 3.5 in $\varepsilon'_r$ and 0.15 in $\varepsilon''_r$. A strong dielectric resonance is detected in both the $\varepsilon'_r$ and $\varepsilon''_r$ spectra in the Ku band of 12–18 GHz and with the resonance peak at 15.3 GHz. This dielectric resonance is a strong Debye interfacial polarization originated from interfacial space charges between the CeO$_2$ cores and the Fe$_3$O$_4$ shells in the composite, as confirmed by the big semicircle in the Cole-Cole ($\varepsilon''_r - \varepsilon'_r$) plot in Fig. 2(b) and described by the Debye theory as follows: \[ (\varepsilon'_r - \varepsilon_\infty)^2 + (\varepsilon''_r)^2 = (\varepsilon_3 - \varepsilon_\infty)^2 \] (2)

where $\varepsilon_\infty$ and $\varepsilon_3$ are the optical and stationary permittivity constants, respectively. By contrast, the Fe$_3$O$_4$/CeO$_2$ composite has a general reduction in $\varepsilon'_r$ of 3–10% because the CeO$_2$ shells are less conductive which, in turn, isolate the Fe$_3$O$_4$ cores from one another as well as suppress electronic polarization in the higher conductive Fe$_3$O$_4$ cores. The dielectric resonance as described by interfacial polarization in the Fe$_3$O$_4$/CeO$_2$ composite has a slight upshift to 15.9 GHz and an obvious reduction of 1.5 times. As O-vacancies can affect the polarity of the CeO$_2$ lattice, the interfacial polarization between CeO$_2$ and Fe$_3$O$_4$ should have a relationship with the concentration of O-vacancies in CeO$_2$ near the interface. Thus, that’s why the interfacial polarization is stronger in the CeO$_2$/Fe$_3$O$_4$ composite compared to the Fe$_3$O$_4$/CeO$_2$ composite. Although it is possible to increase the O-vacancy concentration of the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites by annealing them with inert gas, over-annealing will increase the grain size of both cores and shells, destroy the core/shell structure, and diminish the interfacial polarization. Besides, excess O-vacancies has been reported to suppress the ferromagnetic properties of CeO$_2$. For comparison, the CeO$_2$ and Fe$_3$O$_4$ composites display a low $\varepsilon'_r$ of ~3.1 and a high $\varepsilon'_r$ of ~4.3, respectively, while their $\varepsilon''_r$ is almost coincident with the value of ~0.1. A very small dielectric resonance can be observed in the Fe$_3$O$_4$ composite at 14.8 GHz but not in the CeO$_2$ composite.

Figure 2(c) shows the $f$ dependence of $\mu_r = \mu'_r - j\mu''_r$ for the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites, together with the CeO$_2$ and Fe$_3$O$_4$ composites. $\mu'_r$ and $\mu''_r$ of both CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites demonstrate similar quantitative decreasing trends with increasing $f$ throughout the whole $f$ range of measurement. The $\mu'_r$ and $\mu''_r$ values remain relatively high in the S and C bands of 2–8 GHz owing to the bi-magnetic core/shell combination of CeO$_2$ and Fe$_3$O$_4$. For the Fe$_3$O$_4$/CeO$_2$ composite, the slight reduction in $\mu'_r$ in the X and Ku bands of 8–18 GHz and that in $\mu''_r$ in the latter part of the Ku band agree well with other reports on the use of resistive shells in nanocapsules. The magnetic resonance detected at 15.4 GHz in the CeO$_2$/Fe$_3$O$_4$ composite is the natural resonance of the Fe$_3$O$_4$ shells. As all of the CeO$_2$ and Fe$_3$O$_4$ grains are in nanoscale below the critical size of single domain, the domain-wall displacement and weak hysteresis loss can be neglected.

The eddy-current loss caused by skin effect does not exist since the nanocapsules are embedded in the microwave transparent, insulating paraffin matrix under the threshold of percolation so that the $f$
dependence of $\mu''_r (\mu'_r)^{-2} f^{-1}$ is not a constant value of $2\pi \mu_0 d^2 \sigma$ as shown in Fig. 2(d). Therefore, the enhancement of $\mu'_r$ in the Ku band for the CeO$_2$/Fe$_3$O$_4$ composite is essentially attributed to the natural resonance of the CeO$_2$ cores and the Fe$_3$O$_4$ shells. For comparison, the Fe$_3$O$_4$ composite has higher $\mu'_r$ and $\mu''_r$ in the 2–8 and 2–14 GHz ranges, respectively; while the CeO$_2$ composite varies more steadily in both $\mu'_r$ and $\mu''_r$.

In order to investigate the effect of interchange core/shell assembly on the microwave absorption properties, the complex effective permittivity and permeability of a particulate composite having the spherical CeO$_2$ and Fe$_3$O$_4$ nanoparticles with a molar ratio of 1:1 bonded by the same 60 wt.% of paraffin were calculated using the measured $\varepsilon'_r$ and $\mu'_r$ data of Fe$_3$O$_4$ and CeO$_2$ composites, as shown in Figs. 2(a) and 2(c), respectively, in the Bruggeman’s effective-medium theory described as follows:

$$\sum_{i=1}^{n} p_i \frac{\varepsilon_i - \varepsilon_{eff}}{\varepsilon_i + 2 \varepsilon_{eff}} = 0; \quad \sum_{i=1}^{n} p_i \frac{\mu_i - \mu_{eff}}{\mu_i + 2 \mu_{eff}} = 0 \quad (3)$$

where $\varepsilon_i$ and $\varepsilon_{eff}$ are the complex permittivity of components and complex effective permittivity of the particulate composite, respectively; $\mu_i$ and $\mu_{eff}$ are the corresponding permeabilities; $p_i$ is the volume fraction of component in the composite. The calculated $\varepsilon_{eff}$ and $\mu_{eff}$ are plotted as the dotted lines in Figs. 2(a) and 2(c), respectively. It is seen that the calculated $\varepsilon'_{eff}$ in Fig. 2(a) is $\sim 3.9$, which
is higher than the measured $\varepsilon'$ in both CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites. A small dielectric resonance (interfacial polarization) is observed at 14.8 GHz, which is the same as that of the Fe$_3$O$_4$ composite. The core/shell assembly is capable of reducing $\varepsilon'$ and enhancing interfacial polarization in the Ku band of 12–18 GHz, implying the existence of a better electromagnetic match for microwave absorption. The calculated $\varepsilon''_{\text{eff}}$ in Fig. 2(a) varies at a lower level of ~0.05 and coincides with the measured $\varepsilon''_{\text{r}}$ in the CeO$_2$ and Fe$_3$O$_4$ composites. This suggests the dielectric attenuation contributed by the interfacial polarization. The calculated $\mu'_{\text{eff}}$ and $\mu''_{\text{eff}}$ in Fig. 2(c) show similar trends and levels with the measured $\mu'_{\text{r}}$ and $\mu''_{\text{r}}$. $\mu'_{\text{r}}$ shows a reduction in the S and C band of 2–8 GHz and an enhancement in the X and Ku band of 8–18 GHz, while $\mu''_{\text{r}}$ displays a slight reduction in the S, C, and X bands and an enhancement in the Ku band. The magnetic attenuation of nanocapsules in the Ku band is elevated by the bi-magnetic core/shell assembly, making $\mu'_{\text{r}}$ and $\mu''_{\text{r}}$ more steadily in the whole $f$ range.

Figure 3 shows the 3D-mapping plots of $RL$–$f$–$d$ for (a) CeO$_2$/Fe$_3$O$_4$ and (b) Fe$_3$O$_4$/CeO$_2$ composites.

is higher than the measured $\varepsilon'$ in both CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites. A small dielectric resonance (interfacial polarization) is observed at 14.8 GHz, which is the same as that of the Fe$_3$O$_4$ composite. The core/shell assembly is capable of reducing $\varepsilon'$ and enhancing interfacial polarization in the Ku band of 12–18 GHz, implying the existence of a better electromagnetic match for microwave absorption. The calculated $\varepsilon''_{\text{eff}}$ in Fig. 2(a) varies at a lower level of ~0.05 and coincides with the measured $\varepsilon''_{\text{r}}$ in the CeO$_2$ and Fe$_3$O$_4$ composites. This suggests the dielectric attenuation contributed by the interfacial polarization. The calculated $\mu'_{\text{eff}}$ and $\mu''_{\text{eff}}$ in Fig. 2(c) show similar trends and levels with the measured $\mu'_{\text{r}}$ and $\mu''_{\text{r}}$. $\mu'_{\text{r}}$ shows a reduction in the S and C band of 2–8 GHz and an enhancement in the X and Ku band of 8–18 GHz, while $\mu''_{\text{r}}$ displays a slight reduction in the S, C, and X bands and an enhancement in the Ku band. The magnetic attenuation of nanocapsules in the Ku band is elevated by the bi-magnetic core/shell assembly, making $\mu'_{\text{r}}$ and $\mu''_{\text{r}}$ more steadily in the whole $f$ range.

Figure 3 shows the 3D-mapping plots of $RL$–$f$–$d$ for the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites. The $RL$ values are determined in accordance with Eq. (1). It is clear that the main absorption band of both CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites are in the Ku band of 12–18 GHz. The strongest absorption with $RL=-28.9$ dB is detected at $f=15.3$ GHz and $d=7.8$ mm in the CeO$_2$/Fe$_3$O$_4$ composite because of the enhancement in both interfacial polarization between the CeO$_2$ cores and the Fe$_3$O$_4$ shells as well as in their natural resonances. Moreover, broad absorption $f$ range of 14.2–18 GHz and $d$ range of 6–10 mm are obtained for $RL<-5$ dB. By comparison, similar enhancement at high $f$ is not obvious in the Fe$_3$O$_4$/CeO$_2$ composite. First, the weak dielectric resonance induced by interfacial polarization at ~15 GHz is a result of the existence of smaller amount of O-vacancies in the CeO$_2$ shells. Second, the reduction of $\mu''_{\text{r}}$ in the Ku band is an effect of the use of less conductive CeO$_2$ shells.

Figure 3 shows the 3D-mapping plots of $RL$–$f$–$d$ for the CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites. The $RL$ values are determined in accordance with Eq. (1). It is clear that the main absorption band of both CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ composites are in the Ku band of 12–18 GHz. The strongest absorption with $RL=-28.9$ dB is detected at $f=15.3$ GHz and $d=7.8$ mm in the CeO$_2$/Fe$_3$O$_4$ composite because of the enhancement in both interfacial polarization between the CeO$_2$ cores and the Fe$_3$O$_4$ shells as well as in their natural resonances. Moreover, broad absorption $f$ range of 14.2–18 GHz and $d$ range of 6–10 mm are obtained for $RL<-5$ dB. By comparison, similar enhancement at high $f$ is not obvious in the Fe$_3$O$_4$/CeO$_2$ composite. First, the weak dielectric resonance induced by interfacial polarization at ~15 GHz is a result of the existence of smaller amount of O-vacancies in the CeO$_2$ shells. Second, the reduction of $\mu''_{\text{r}}$ in the Ku band is an effect of the use of less conductive CeO$_2$ shells.

IV. CONCLUSION

We have prepared CeO$_2$/Fe$_3$O$_4$ and Fe$_3$O$_4$/CeO$_2$ nanocapsules in order to impart the room-temperature ferromagnetism and abundant O-vacancies of CeO$_2$, the large natural resonance of Fe$_3$O$_4$, and the O-vacancy-enhanced interfacial polarization between CeO$_2$ and Fe$_3$O$_4$ in the nanocapsules as well as to study the effect of interchange assembly of CeO$_2$ and Fe$_3$O$_4$ on their phase, lattice parameters, morphology, interface nanostructure, and microwave absorption properties. We have also performed experimental and theoretical comparisons with their CeO$_2$ and Fe$_3$O$_4$ nanoparticle counterparts. We have found that the use of CeO$_2$ as the core and Fe$_3$O$_4$ as the shell (CeO$_2$/Fe$_3$O$_4$ nanocapsules) can increase both permittivity and permeability at the high-frequency microwave Ku band of 12–18 GHz due to the increased O-vacancy concentration in the CeO$_2$ cores of larger grains, the O-vacancy-induced enhancement in interfacial polarization between the CeO$_2$ cores and the Fe$_3$O$_4$ shells at ~15 GHz, and the natural resonance at ~15 GHz. As a result, a strong absorption with $RL=-28.9$ dB at $f=15.3$ GHz and $d=7.8$ mm, together with broad absorption $f$ range of
14.2–18 GHz and $d$ range of 6–10 mm for $RL<-5$ dB, have been achieved in the CeO$_2$/Fe$_3$O$_4$ composite. Both nanocapsules exhibit relatively high permeability in the low-frequency S and C microwave bands as a result of the bi-magnetic core/shell combination of CeO$_2$ and Fe$_3$O$_4$.

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