CHIN. PHYS. LETT. Vol. 34, No. 9 (2017) 097701

Origin of Negative Imaginary Part of Effective Permittivity of Passive Materials *

Kai-Lun Zhang(张凯伦)[1], Zhi-Ling Hou(侯志灵)[1**], Ling-Bao Kong(孔令宝)[2], Hui-Min Fang(房慧敏)[1], Ke-Tao Zhan(战可涛)[1]

[1]*School of Science & Beijing Key Laboratory of Environmentally Harmful Chemicals Assessment, Beijing University of Chemical Technology, Beijing 100029*

[2]*School of Science, Beijing Technology and Business University, Beijing 100048*

(Received 10 April 2017)

The anti-resonant phenomenon of effective electromagnetic parameters of metamaterials has aroused controversy due to negative imaginary permittivity or permeability. It is experimentally found that the negative imaginary permittivity can occur for the natural passive materials near the Fabry–Perot resonances. We reveal the nature of negative imaginary permittivity, which is correlated with the magnetoelectric coupling. The anti-resonance of permittivity is a non-inherent feature for passive materials, while it can be inherent for devices or metamaterials. Our finding validates that the negative imaginary part of effective permittivity does not contradict the second law of thermodynamics for metamaterials owing to the magnetoelectric coupling.

PACS: 77.22.Ch, 77.22.−d, 78.67.Pt, 71.45.Gm DOI: 10.1088/0256-307X/34/9/097701

Plasmonic metamaterials have attracted intense interest in the past few years due to the exotic optical properties and wide variety of potential applications such as invisibility cloaks,[1−3] high-resolution imaging,[4,5] quantum levitation,[6] polarization conversion,[7,8] small antennas,[9] ultrasmall cavity[10] and energy harvester.[11] Based on the assumption which treats the periodical collections of resonant inclusions as homogenized bulk materials, several homogenization models were proposed to macroscopically describe the unusual electromagnetic response of metamaterials using the effective permittivity and permeability.[12−16] One of the most common models, the S-parameter retrieval or Nicolson–Ross–Weir (NRW)[17,18] method describing the wave propagation in the natural material, is used to determine the constitutive parameters of metamaterials, when the size of unit cell is much smaller than the wavelength.[12−14] For natural materials, the NRW method provides straightforward analysis and characterization from the transmission and reflection parameters of a finite-thickness slab. However, it is still a challenging work to provide physical insight into the nature of the electromagnetic response of metamaterials. The left-handed or other anomalous behavior is usually accompanied by the presence of anti-resonances of permeability or permittivity. Although it is gradually acceptable in dozens of works, the retrieved effective constitutive parameter has still aroused serious doubts near the metamaterial resonances where most interesting behavior takes place. The focus of the argument is whether the imaginary part of both permittivity and permeability must be positive simultaneously for passive materials.[19−24] Recently, the antiresonance of permeability of metamaterials becomes acceptable,[25−28] since Markel[23] demonstrated that the imaginary part of permeability can be negative in naturally occurring diamagnetics or in artificial materials, which does not contradict the second law of thermodynamics or energy conservation. Nevertheless, the negative imaginary part of permittivity of metamaterials is usually regarded as an artifact that is obtained from the numerical errors or noise of S parameters. Indeed, some small errors or noise near the slab resonances may cause the artifact, when the reflection coefficient tends to zero.[29] For high-loss material with large reflection coefficient, while the origin of negative imaginary permittivity is still unclear, here in our experiment, we report an unexpected antiresonance of permittivity of passive natural materials near the Fabry–Perot resonances (FPR) frequency with normal reflection coefficient. In the following we put forward the origin of the negative imaginary part of permittivity from the magnetoelectric coupling of multiferroic materials. This is a strong indication that the retrieval procedure is not bothered by the opposite sign of permittivity in metamaterials.

The Er-substituted polycrystalline $BiFeO_3$ (BEFO) was synthesized by the sol-gel method. The starting materials are $Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and a solution of Er_2O_3 in HNO_3, with the stoichiometic proportion of 0.95:1:0.05. The ethylene glycol was used as a dispersing agent. The annealing temperature was 600℃. The detailed procedures can be found in Ref. [30]. The as-prepared samples were compacted into a rectangular sheet (22.82 mm×10.12 mm) to fit the geometrical dimensions of the waveguide sample holder. The thicknesses of samples 1 and 2 are 3.34 mm and 0.814 mm, respectively. The S parameters were measured by a vector network analyzer (Anritsu37269D). All numerical simulations were carried out using the commercial available numerical package CST Microwave Studio 2014. The relative complex permittivity and magnetic

*Supported by the National Natural Science Foundation of China under Grant No 51102007, and the Fund for Discipline Construction of Beijing University of Chemical Technology under Grant No XK1702.

**Corresponding author. Email: zhilinghou@gmail.com

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permeability were determined from S parameters by the NRW method[31] in the X band.

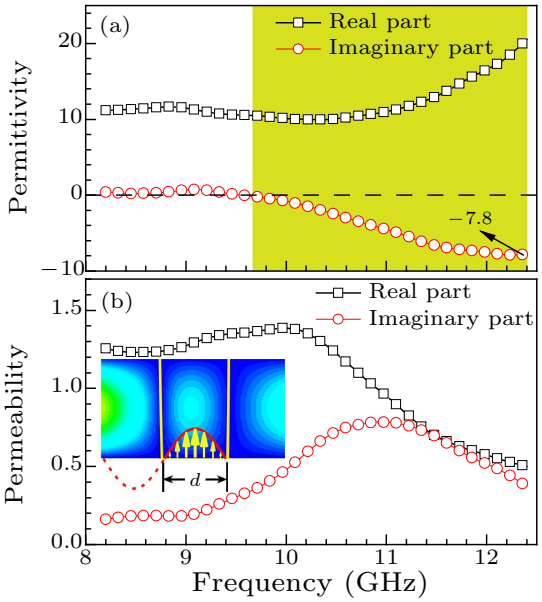

Fig. 1. The effective permittivity (a) and permeability (b) of BEFO near the Fabry–Perot resonances.

Figure 1 shows the experimental complex permittivity and magnetic permeability of the BEFO sample in thicknesses 3.34 mm. It is noteworthy that the negative imaginary part of effective permittivity (ε'') is observed from 9.5 to 12.4 GHz with a minimum value of −7.63 (see Fig. 1(a)). With the increasing frequency, ε'' decreases when the frequency is higher than 9.5 GHz, while the real part of effective permittivity (ε') increases rapidly when the frequency is higher than 10.5 GHz. The corresponding magnetic permeability shows the resonance phenomenon in this frequency region (see Fig. 1(b)). In fact, the negative ε'' in Fig. 1 is not an intrinsic dielectric behavior for the BEFO material because the thickness of sample 1 is half the FPR wavelength shown in the inset of Fig. 1(b) (the FPR frequency is 12.358 GHz). The intrinsic dielectric properties are shown in Fig. 2. The value of ε'' is ∼1.7, and none of these parameters are less than 0 at all frequencies investigated. As is known, when the sample thickness is $\lambda_g/2$, the concomitant FPR can manipulate the reflection of electromagnetic field.[31–33] Then, the retrieved values of permittivity and permeability could be effected near the FPR frequency. For low-loss materials or metamaterials, small errors or noise near the slab resonances may cause the artifact when the reflection coefficient is close to zero.[29] However, both $|S_{11}|$ and the Fresnel reflection coefficient are far from zero for the BEFO material (see Figs. 3(a) and 3(b)). Thus the negative ε'' is not produced by the small errors or noise. The absolute value of ε'' is so large that it should be a special response of BEFO rather than an artifact. To analyze the reasons behind the negative ε'', we investigate whether the thickness affects the dielectric properties of samples by simulating S parameters for homogenous slabs of various thicknesses near the FPR.

The variations of complex permeability and complex permittivity calculated from the S parameters by the NRW method at various slab thicknesses are shown in Fig. 4. The negative ε'' is not observed for any thickness though the FPR occurs at the X band for these thickness. The value of ε'' near the FPR produces some deviation from the norm, and the deviation at the FPR frequency is less than 8% for each thickness. Moreover, both complex permittivity and permeability from simulations show the inverse resonance characteristic as compared with the measured results. In detail, all the ε'' values in the X band are positive, and show an upward peak for each thickness. The value of ε' decreases with increasing frequency at all thickness. Nevertheless, μ'' presents a downward peak for each thickness, which contrasts with the experimental results. Therefore, the inverse resonance between simulation and experiment suggests that the negative ε'' is a special response of BEFO rather than an artifact.

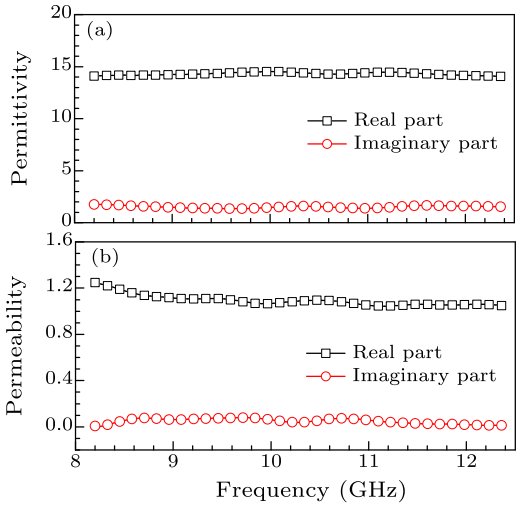

Fig. 2. The intrinsic permittivity (a) and permeability (b) of BEFO.

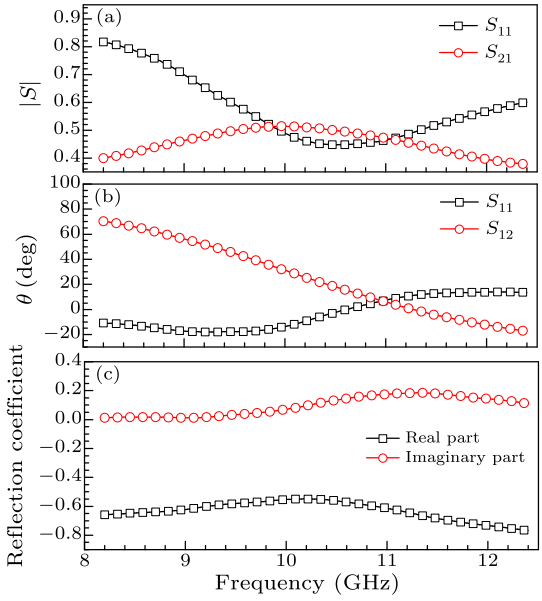

Fig. 3. Magnitude (a) and phase (b) of S parameters and Fresnel reflection coefficient (c) of BEFO.

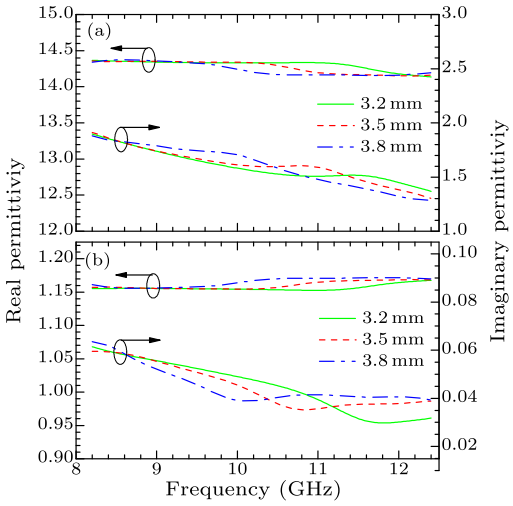

Fig. 4. Thickness effects of complex permittivity (a) and complex permeability (b) retrieved by simulating S parameters for homogenous slabs of various thicknesses near the FPR.

Not only ε'' but also μ'' can be negative in passive natural materials near the Fabry–Perot resonance (for example, Fe_3O_4/SnO_2nanorods,[34] MWCNT/wax,[35] and hollow cobalt nanochain composites[36] show negative μ''). We find that the negative ε'' is related to the magnetoelectric coupling. For magnetoelectric coupling material, $\boldsymbol{B}_{\rm eff}$ and $\boldsymbol{D}_{\rm eff}$ can be written as[37,38]

$$\boldsymbol{D}_{\rm eff} = \varepsilon\varepsilon_0\boldsymbol{E} + \xi\boldsymbol{H}, \tag{1a}$$
$$\boldsymbol{B}_{\rm eff} = \mu\mu_0\boldsymbol{H} - \varsigma\boldsymbol{E}, \tag{1b}$$

where ξ and ς are magnetoelectric parameters, ε and μ are complex permittivity and complex permeability, respectively. For an electromagnetic wave with a time dependent factor $e^{j\omega t}$, the source-free Maxwell equations with magnetoelectric coupling effect can be expressed as follows:

$$\nabla\times\boldsymbol{E} = -j\omega\mu\mu_0\boldsymbol{H} - \boldsymbol{J}_{\rm EM}, \tag{2a}$$
$$\nabla\times\boldsymbol{H} = j\omega\varepsilon\varepsilon_0\boldsymbol{E} + \boldsymbol{J}_{\rm ME}, \tag{2b}$$

where $\boldsymbol{J}_{\rm ME}$ and $\boldsymbol{J}_{\rm EM}$ are the electric current density and magnetic current density resulting from the magnetoelectric coupling, respectively. They can be expressed as follows:

$$\boldsymbol{J}_{\rm ME} = \varepsilon\varepsilon_0\frac{\partial\boldsymbol{E}_{\rm ME}}{\partial t} = \varepsilon\varepsilon_0\frac{\partial(-\varsigma\boldsymbol{E})}{\partial t} = -j\omega\varepsilon\varepsilon_0\varsigma\boldsymbol{E}, \tag{3a}$$
$$\boldsymbol{J}_{\rm EM} = \mu\mu_0\frac{\partial\boldsymbol{H}_{\rm EM}}{\partial t} = j\omega\mu\mu_0\xi\boldsymbol{H}. \tag{3b}$$

Thus the Maxwell Eqs. (2a) and (2b) can be rewritten as

$$\nabla\times\boldsymbol{E} = -j\omega\mu\mu_0(1+\xi)\boldsymbol{H} = -j\omega\mu_{\rm eff}\mu_0\boldsymbol{H}, \tag{4a}$$
$$\nabla\times\boldsymbol{H} = j\omega\varepsilon\varepsilon_0(1-\varsigma)\boldsymbol{E} = j\omega\varepsilon_{\rm eff}\varepsilon_0\boldsymbol{E}. \tag{4b}$$

From Eqs. (4a) and (4b), we have

$$\varepsilon_{\rm eff} = \varepsilon(1-\varsigma), \tag{5a}$$
$$\mu_{\rm eff} = \mu(1+\xi), \tag{5b}$$

where ε, μ, ξ and ς satisfy the constitutive relations: $\varepsilon = \varepsilon' - j\varepsilon''$, $\mu = \mu' - j\mu''$, $\xi = \xi' - j\xi''$, and $\varsigma = \varsigma' - j\varsigma''$. According to Eqs. (5a) and (5b), we obtain

$$\varepsilon_{\rm eff} = \varepsilon'(1-\varsigma') + \varepsilon''\varsigma'' - j[\varepsilon''(1-\varsigma') - \varepsilon'\varsigma''], \tag{6a}$$
$$\mu_{\rm eff} = \mu'(1+\xi') - \mu''\xi'' - j[\mu''(1+\xi') + \mu'\xi'']. \tag{6b}$$

According to Eqs. (6a) and (6b), ξ and ς are calculated as shown in Fig. 5. The values of ξ and ς are strongly dependent on the resonant frequency, which present a large value in the vicinity of the resonance frequency and become very small away from the resonance frequency. The result suggests that the conversion between magnetic energy and electric energy becomes easy in the vicinity of resonance frequency.

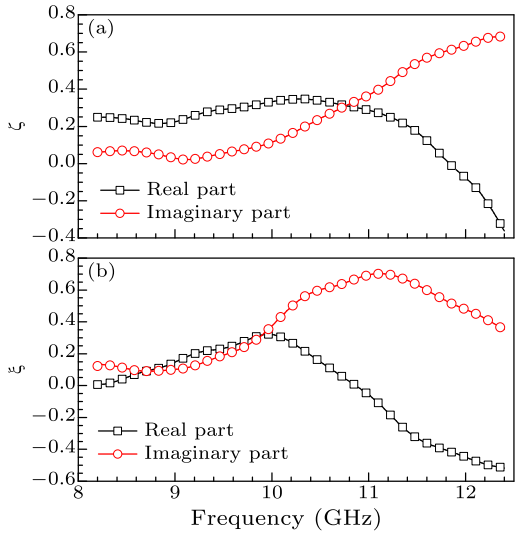

Fig. 5. Magnetoelectric coupling parameters ς (a) and electromagnetic coupling parameter ξ (b) of BEFO near the Fabry–Perot resonances.

When $\xi = 0$ and $\varsigma = 0$, ε'' and μ'' should be positive to meet the requirements of the second law of thermodynamics. When $\xi \neq 0$ and $\varsigma \neq 0$, while according to Eq. (6a), $\varepsilon''_{\rm eff}$ can be negative if $\varepsilon''(1-\varsigma') < \varepsilon'\varsigma''$. Considering the magnetoelectric coupling effect, the magnetic energy is transformed into the electric energy, and the total energy loss is still positive. Thus $\varepsilon''_{\rm eff}$ is negative, which does not contradict the second law of thermodynamics because of the electric loss. In particular, when the FPR or Mie resonance occurs, the transform between magnetic energy and electric energy is easy to conduct. Of course, the negative ε'' is not an intrinsic dielectric attribute for this material because it depends on the slab thickness. However, it may be classified as an intrinsic character when the sample is treated as a device. Owing to the fact that the magnetoelectric coupling can occur in metamaterials,[39,40] thus the retrieval procedure is not bothered by the opposite sign of permittivity in metamaterials. Moreover, the resonance of metamaterials associated with unit cell is not dependent on

the slab thickness. Therefore, negative ε'' can be an intrinsic character of metamaterial.

In summary, we have investigated the effective constitutive parameters retrieved from the scattering properties of the natural passive material BEFO, and found that $\varepsilon''_{\rm eff}$ is negative near the FPR. The negative $\varepsilon''_{\rm eff}$ is not the artifact caused by small unavoidable errors in numerical or experimental reflection and transmission data, due to the fact that the reflection coefficient does not tend to zero. We have shown that the negative $\varepsilon''_{\rm eff}$ may originate from the magnetoelectric coupling effect where a transform between magnetic energy and electric energy is produced. Although the negative ε'' is not an intrinsic dielectric behavior for this material due to the FPR, it is an intrinsic physical character for devices. For metamaterial, if the magnetoelectric coupling occurs, the negative ε'' can be classified as an intrinsic character rather than nonphysical one, as the resonance leading to negative ε'' will not be affected by variations in the slab thickness.

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