Microwave Memristive-like Nonlinearity in a Dielectric Metamaterial

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Memristor exhibit interesting and valuable circuit properties and have thus become the subject of increasing scientific interest. Scientists wonder if they can conceive a microwave memristor that behaves as a memristor operating with electromagnetic fields. Here, we report a microwave memristive-like nonlinear phenomenon at room temperature in dielectric metamaterials consisting of CaTiO₃-ZrO₂ ceramic dielectric cubes. Hysteretic transmission-incident field power loops (similar to the hysteretic I-V loop of memristor which is the fingerprint of memristor) with various characteristics were systematically observed in the metamaterials, which exhibited designable microwave memristive-like behavior. The effect is attributed to the decreasing permittivity of the dielectric cubes with the increasing temperature generated by the interaction between the electromagnetic waves and the dielectric cubes. This work demonstrates the feasibility of fabrication transient photonic memristor at microwave frequencies with metamaterials.

Memristive behavior has recently attracted significant attention as it offers a potential solution to problems in information technology. Postulated in 1971 as the “missing”, fourth, passive circuit element, memristors are characterized by resistance changes in relation to the charge that passes through the device and the fingerprint of memristor is the hysteresis I-V loop. Furthermore, these elements possess a memory of the last charge that passed through them even when the charge has been removed, a feature that could revolutionize nonvolatile memory, signal processing, control, and learning technology. A number of electric memristive systems have recently been demonstrated, such as TiO₂ films, ZnO nanocrystals, and organic films.

Photonic circuitry is overviewed in which a tapestry of sub-wavelength artificial structures that provide a mechanism for tailoring, patterning, and manipulating local electromagnetic fields and displacement vectors in a sub-wavelength domain, leading to the possibility of information (carried by electromagnetic wave) processing on the sub-wavelength scale. Engheta et al. introduced the pioneering notion of circuit lumped elements at optical frequencies for nanocapacitors, nanoinductors, and nanoresistors, which are based on the interaction of the nanostructures with an optical field. Under such conditions, it is wondered if it is possible to conceive a photonic memristor that behaves as a memristor operating with electromagnetic fields. Emboras et al. reported a nanoscale plasmonic memristor with optical readout functionalities, in which, the optical bistable behavior is attributed to the variation of the absorption and scattering loss of the fundamental plasmonic mode as a result of the voltage induced annihilation/formation of the nanoscale metal filament. Thus, the memory device is characterized by electrical write and optical read. And, the optical transmission switching is not caused by the power of the input light.

Third order optical nonlinearities lead to the possibility of memristive response if the new state can be kept for a certain period of time. Nonlinear transmission phenomena were well studied in many material systems, such as quantum wells, four-level atomic systems, semiconductor resonators and amplifiers, liquid crystals, etc. However, few of these works show photonic memristive behavior based on the optical nonlinearity in the systems.

The development of homogenous media with entirely artificial electromagnetic properties, so-called “metamaterials”, has produced phenomena and devices once considered fantastical, including electromagnetic cloaks; materials with negative permittivities, permeabilities, and index of refraction; perfect lensing; and sub-diffraction imaging. Metamaterials can also present nonlinearity when interacting with electromagnetic (EM) waves. For example, Rose et al. included varactor diodes in the capacitive gaps of split ring resonators (SRRs) and obtained a nonlinear microwave effect in the metamaterials. Lapine et al. reported nonlinearity in metamaterials using a combination of coupled SRRs and elastic substrates, which resulted from attraction between the coupled SRRs. However, these metamaterials do not exhibit memory behavior but instead recover their initial state immediately after the stimulus has been removed, and achieving photonic memristive-like behavior in these...
materials is a significant challenge. Here, we present a mechanism for obtaining microwave memristive-like nonlinearity in dielectric metamaterials based on the Mie resonance-induced thermodielectric effect in dielectric meta-atoms. A switching mechanism driven by competing field-driven heat generation and spontaneous heat dissipation is also proposed.

Results

A unit cell of dielectric metamaterials with dimensions of $5 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$ is shown in Fig. 1a, and the size of the dielectric cube in the cell, which is a CaTiO$_3$-1wt% ZrO$_2$ ceramic, is $2 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$. The structure and material parameters of the metamaterials in the simulation were chosen to coincide with the experimental values. Simulation results for EM wave transmission ($S_{21}$ parameter) of the unit cell for varying permittivity values of the dielectric cube are shown in Fig. 1b. The remarkable resonance peak in the range of 8–12 GHz is associated with the first-order Mie resonance of the dielectric cubes, and the frequency decreases as the permittivity of the cubes increases. Quasistatic scattering theory for a cube of this size predicts many higher order modes excited with appreciable magnitudes. The resonance frequencies of the higher-order modes are higher, and the intensity of the higher-order modes is weaker. So the first-order mode was chosen as an example here.

The EM wave propagation properties of metamaterials with six unit cells (shown as the inset of Fig. 2a) in the waveguide are shown in Fig. 2a. The resonant peak at 11.68 GHz is the first-order Mie resonance of the dielectric cubes, and the simulated results are in good agreement with the experimental results. Figure 2b shows a $T$-$P$ plot of the resonance peak as the output power of the vector network analyzer increased from $-10 \text{ dBm}$ to a maximum ($P_{\text{max}}$) of $0 \text{ dBm}$ at a scan rate of $1 \text{ dBm/s}$. The power was subsequently decreased from $P_{\text{max}}$ to $-10 \text{ dBm}$ at the same rate. The transmission increases nonlinearly with increasing power during the power-up step (step 1) and subsequently decreases during the power-down step (step 2). However, the $T$ value in step 2 is higher than that in step 1, and a hysteretic loop is generated. These results indicate that the transmission of the sample varies with the history of the power loading, which is one of the main characteristics of microwave memristors and microwave memristive systems.

When the power scan rate is increased, the $T$-$P$ loop area decreases, as shown in Fig. 3, which is also a feature of microwave memristive devices. Thus this behavior was a microwave memristive-like nonlinearity.

Figure 4 shows the experimental results of the time-dependent microwave properties, where the output power of the vector network analyzer is $0 \text{ dBm}$. Figure 4(a) shows that the 9.32-GHz resonance exhibits a red shift over time, and a fixed resonance peak is found at 20 s. The transmission increases with time and eventually becomes constant as shown in Fig. 4(b).

When the detection frequency is set to 11.79 GHz, which is the resonance frequency of the system at equilibrium, the transmission decreases with increasing power in step 1, as shown in Fig. 5a. In step 2, the resonance frequency slowly recovers to the initial frequency, leading to persistent transmission. Meanwhile, the transmission decreases with time, as shown in Fig. 5b.

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**Figure 1** | Unit cell characterization. (a) Schematic diagram of the unit cell of one dielectric cube. The propagation of the incident electromagnetic wave is along the y axis, and the electric field and magnetic field are along z and x directions, respectively. (b) Simulated results of the microwave properties of the dielectric metamaterials for various permittivity values of the dielectric cube.

**Figure 2** | Metamaterials characterization. (a) Measured and simulated results of the metamaterials for the same structure and material parameters. The inset of (a) shows an optical image of the metamaterial. (b) $T$-$P$ plot of the metamaterials for a scan rate of 1 dBm/s at 11.68 GHz.
A different condition. A photonic memristive behavior was detected, which can be used under detection frequency is changed, and designable microwave memristive-like materials exhibit different microwave memristive-like behaviors as shown in Fig. 5e and Fig. 5f. Figures 2 and 5 show that the metamaterials finally equivalent to that in the initial measurement in step 1, as shown in Fig. 5c. Meanwhile, the transmission decreases with time before increasing, as shown in Fig. 5d. The transmission results are shown in dB to clearly indicate the switching behavior.

The EM wave propagation properties measured at initial intersect with those measured at equilibrium, as shown in Fig. 4a. When the detection frequency is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same photonic memristive behavior is detected, but the transmission is set to the intersection frequency, the same.

**Discussion**

To elucidate the origin of the switching characteristics, the frequency-dependent Mie responses as a function of temperature were measured using a low-field (~30 dBm) output of the vector network analyzer; these results are shown in Fig. 6a. From 303 K to 317 K, there is a slight but perceptible blue shift of the Mie resonance frequency. It is well known that the Mie resonance exhibits a blue shift with decreasing permittivity, as shown by Eq. (1):

\[
f_1 = \frac{\theta_1 c}{2\pi r \sqrt{\varepsilon_2 \mu_2}},
\]

where \(f_1\) is the first-order Mie resonance frequency, \(\theta_1\) is a constant that is approximately equal to \(\pi\), \(c\) is the speed of light in vacuum, \(r\) is the radius of the dielectric, \(\varepsilon_2\) is the permittivity of the dielectric, and \(\mu_2\) is 1 for the dielectric. Thus, \(f_1\) is determined by \(\varepsilon_2\) and \(r\). In this study, \(r\) is a constant leading to an increase in \(f_1\) with decreasing \(\varepsilon_2\).

As an incipient ferroelectrics, the permittivity of CaTiO\(_3\) decreases with increasing temperature in accordance with the Curie-Weiss law, which is caused by the octahedral structure tilting\(^{43-45}\) as shown in the inset of Fig. 6b. The simulations, performed with the assumption that the permittivity of the dielectric cube varies from 120.61 to 119.21 according to the measured permittivity from 303 K to 317 K (Fig. 6b), are in good agreement with the experiments. These results indicate that the transmission at the Mie resonance frequency at 303 K (11.68 GHz) increases with increasing temperature (decreasing permittivity), due to the blue shift of the Mie resonance frequency.

Heat generation and dissipation occur when the metamaterials react with the incident electromagnetic field and thus affect the temperature of the sample. The rate of heat generation inside the element is shown by Eq. (2). Mie theory for cubes shows that the fields are concentrated the most near the corners, giving rise to largest heating at the corners. So heat generation rate of the cubes is not uniform, and Q, P, q in Eq. (2) are variable varies jointly with x, y, and z.

\[
\dot{Q} = P(x,y,z)\eta x = \int \dot{q}(x,y,z) dV
\]

where \(P\) is the microwave power inside the sample; \(\eta\) is the absorption coefficient; \(\eta\) is the efficiency with which the optical energy absorbed is converted to heat via nonradiative processes. The radiation energy is negligible as the temperature in this experiment is low. The thermal environment around the dielectric cubes is not uniform, so the heat conduction equation in the sample can be written as Eq. (3).

\[
\frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y} (k \frac{\partial T}{\partial y}) + \frac{\partial}{\partial z} (k \frac{\partial T}{\partial z}) + \dot{q}(x,y,z) = \rho c \frac{\partial T}{\partial t}
\]

where \(\rho\) and \(c\) are the density and heat capacity of the sample. \(k\) is the thermal conductivity which could be the thermal conductivity inside the cubes, between the cubes and the air or between the cubes and the Teflon substrate. Thus \(k\) is a variable varies jointly with x, y, and z. Under the condition where \(k\) is not a variable in which case the
medium is homogeneous, Eq. (3) can be written as Eq. (4) as shown below.

\[
\nabla^2 T + \frac{\dot{q}}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t}
\]

(4)

Here, \( \alpha \) is thermal diffusivity which can be written as Eq. (5).

\[
\alpha = \frac{k}{\rho c}
\]

(5)

The first three term on the left-hand side of Eq. (3) describes the heat conduction, the forth term give the rate of heat generation in the sample, and the term on the left-hand side describes the relation between the heat and the temperature variation. This is a particularly complex heat conduction process, and these equations are only used to describe how heat interacts with sample.

A high incident power produces a large absorbance, and thus, more heat will be generated than dissipated. Therefore, heat accumulation will take place, leading to an increase in temperature. A reduction in the permittivity of the sample occurs with increasing temperature, which leads to a blue shift of the Mie resonance, and thus, the transmission at the initial resonance frequency increases. In the power-down step, the accumulated heat slowly dissipates, and the resonance gradually returns to its initial value, resulting in a higher transmission persistence, which leads to the \( T-P \) loop. A smaller amount of heat is generated at high power scan rates, resulting in a smaller temperature rise and a smaller transmission change, and

Figure 5 | Measured microwave properties demonstrating the designability. The measured transmission behavior of (a) \( T-P \) plot and (b) Time-dependent transmission behavior for an incident wave at 11.9 GHz, (c) \( T-P \) plot and (d) Time-dependent transmission behavior for an incident wave at 10.7 GHz, (e) \( T-P \) plot and (f) Time-dependent transmission behavior for an incident wave at 11.72 GHz. The output power of the vector network analyzer is 0 dBm.
thus, the area of the T-P hysteretic loop decreases. When the power was turned on, heat accumulated with time leading to a blue shift of the Mie resonance, thus, the transmission at the resonance frequency increase with time. When thermal equilibrium is reached in the system, the transmission would not change with time as shown in Fig. 4b.

As illustrated by Eq. (2), the generated heat is determined by the output power of the vector network analyzer. Additional heat is generated as $P_{\text{max}}$ increases, leading to an increased equilibrium temperature and a decreased permittivity of the dielectric cube. This trend leads to an enhanced blue shift of the Mie resonance frequency, as shown in Fig. 7. Equation (3) shows that the heat dissipation is related to thermal conductivity. When the metamaterials are encapsulated with materials with a lower thermal conductivity or by a vacuum to remove the heat dissipation, an ideal microwave one-port memristor is obtained.

The measured hysteretic transmission-incident field power loop is similar to the I-V loop of memristor which is the fingerprint of memristor. As this behavior is transient, and the loop area variation with the frequency of input field is different from that in permanent memristor, this behavior is memristive-like effect. And the results in Figs. 2, 3, 6, and 7 clearly indicate a microwave memristive-like nonlinear mechanism in the dielectric metamaterials.

The permittivity of CaTiO$_3$ decreases with increasing temperature, leading to the blue shift of the resonance frequency and the microwave memristive-like nonlinearity of the metamaterials. The permittivity of SrTiO$_3$ decreases with temperature when used at room temperature. When SrTiO$_3$ is used as the dielectric cube material, the same microwave memristive-like nonlinearity behavior can be detected. However, when BaTiO$_3$ is used as the dielectric cube material, which has a Curie temperature above room temperature, the opposite microwave memristive-like nonlinearity can be detected. This result arises because the permittivity increases with temperature in the experiment. Because the Curie temperature of (Ba, Sr)TiO$_3$ varies with the ratio of Ba to Sr content, it would be simple to fabricate different dielectric metamaterials with different microwave memristive-like nonlinear effect. The specific heat capacity and the variation in permittivity differ for these materials, and as a result, different microwave memristive-like nonlinearity can be designed using different materials at different frequencies. Of course, only materials that meet the requirements of the Mie metamaterial should be used as dielectric cubes. The permittivity should vary with temperature, and the temperature of the dielectric cubes will vary when the EM waves interact with the metamaterials.

In summary, a hysteretic transmission-incident field power curve was observed in dielectric metamaterials. Designable microwave memristive-like nonlinear effect was detected at various frequencies. These results suggest that a combination of EM field-driven Joule heating and heat dissipation controls the temperature of the samples, which is reflected in changes in the permittivity of the dielectric cube. The microwave memristive-like nonlinear effect is attributed to the decreasing permittivity of the dielectric cube with increasing temperature generated by EM waves. As the working frequency of dielectric metamaterial based on Mie resonance can be extended to optical wave length, this thermal-dielectric mechanism might open up new opportunities for realizing transient photonic memristor from microwave to optical frequencies.

**Methods**

**Ceramic preparation.** Samples of ceramic CaTiO$_3$-1wt% ZrO$_2$ were prepared using a solid-state reaction. The raw materials used in preparing the sample were commercially available powders of CaCO$_3$, TiO$_2$, and ZrO$_2$. Stoichiometric quantities of these powders were mixed and ball-milled in deionized water for 24 h using a polyamide bottle and zirconia balls. Next, the milled slurry was dried in an oven at 120°C to evaporate the water and was calcined at 1150°C for 2 h in an Al$_2$O$_3$ crucible. The obtained powder was ball-milled again and subsequently pressed into disks with a diameter of 50 mm and a thickness of 15 mm under a pressure of 200 MPa. The powder compacts were sintered at 1350°C for 2 h using a Nabertherm furnace (LTH 08/17, Nabertherm, Germany). The permittivity of the obtained ceramic was 120.8 ± 0.0068i at room temperature.

**Dielectric metamaterials preparation.** The obtained ceramic was cut into dimensions of 2 mm × 2 mm × 2 mm to form the dielectric cubes. The dielectric metamaterials were obtained by assembling the unit cells into an array, and the dimensions of the unit cells were 5 mm × 5 mm × 5 mm. A Teflon substrate was used, and the dielectric cubes were adhered to the substrate.
Microwave memristive-like nonlinearity measurement. The dielectric metamaterials were placed in a WR90 X-band rectangular waveguide (22.86 mm × 10.16 mm × 100 mm). The microwave memristive behavior was measured using a vector network analyzer (N5230C, Agilent Technologies, USA), and a TH1466C amplifier with a gain of 30 dB was connected to the output port of the vector network analyzer to amplify the power. A linear frequency sweep, a power sweep, and a time sweep were used in the experiment. The microwave properties were simulated using the CST Microwave Studio software package. The structural and material parameters for the simulation coincided with the experimental values.

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