Study Of Negative Permittivity Behavior $Sr_7Mn_4O_{15}$.SrO Nanocomposite

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Abstract

Negative permittivity has been researched extensively in a wide range of metamaterials and composites. Using a solid-state ceramic route, a composite of $Sr_7Mn_4O_{15}$ - SrO has been produced. Above a specified temperature (Tc), a change in permittivity sign from positive to negative is observed at all measured frequencies (10 Hz-2MHz). Experimental data of real part of permittivity was fitted to Drude-Lorentz oscillator model. Plasma oscillations of thermally excited free carriers have been identified as the cause of negative permittivity. High temperature plasma plasmonic activity of synthesized composite make it promising metamaterial for electromagnetic devices working in the radio frequency (10 Hz -2MHz) range.

Keywords: $Sr_7Mn_4O_{15}$; Composite; Negative permittivity; Drude-Lorentz model.

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Introduction

Recently, materials exhibiting negative permittivity have received attention due to their potential for application in a wide range of electromagnetic applications [1-3]. Metals have a negative permittivity (NP) below their plasma frequency caused by the plasmonic oscillation of free electrons [4]. The negative dielectric properties of metals prompted research and development of metamaterials, in which the metal building blocks and their geometrical dimensions and arrangements determine negative permittivity [5]. A model for the negative permittivity behaviour of metals was put proposed by Drude in 1900 [6-9]. According to the Drude's model, oscillation frequency of plasma can be reduced by decreasing charge carrier concentration/density. It has been attempted to lower the frequency of plasmonic oscillations from the ultraviolet to the radio frequency range by dilution of carrier concentration. Towards this approach composites having functional metal fillers randomly spread in an insulator matrix have been synthesized and their dielectric properties were measured [10,11]. Additionally, identifying a system showing NP is difficult task, and only few systems have been explored. The $Sr_7Mn_4O_{15}$ is a semiconductor whose band gap decreases from 1.14 eV to 0.34 eV with increasing temperature [12]. In this work an attempt has been made to synthesized composite of semiconductor $Sr_7Mn_4O_{15}$ and insulator SrO in equal mole ratio and study its dielectric properties in wide temperature (30 -600oC) and frequency range (20 Hz- 2MHz) with expectation of getting negative permittivity at least at high temperature.

Experimental

The typical solid-state reaction approach was used to make the $Sr_7Mn_4O_{15}$-SrO composite. The raw materials MnO_2 (purity 99.9%, Sigma-Aldrich) and $SrCO_3$ (purity 99.9%, Sigma-Aldrich) were stoichiometrically measured and mixed in a ball mill for 8 hours. In a furnace, the ball-milled mixture was calcined at 1200 °C for a period of 12 hours. For electrical tests, Pellets of thickness of 2–3 mm and a diameter of 7-8 mm were manufactured utilizing a hydraulic press with a 5 kN pressure. Density of the green pellets were increased by sintering them at 1500 °C for 12 hours in the same furnace. The surfaces of the sintered pellets were polished using emery paper, which afterward had a thin film coating of silver paste at a high temperature. As a function of temperature (between 30°C and 600°C) and frequency (20Hz to 2MHz), the complex impedance (Z*) was measured using an inductance-capacitance-resistance (LCR) meter (Agilent E-4980, USA).

Results and Discussion

1. Phase analysis and microstructural characterization

The x-ray diffraction (XRD) patterns of the sample at room temperature found within the following range: 20° ≤ 2θ ≤ 80°. The range 24° ≤ 2θ ≤ 40° contains the principal peaks of the reactant, product, and impurity phases. For clarity, the sample's XRD patterns are shown in Fig. 1(a) in the 24° ≤ 2θ ≤ 40° range. The Crystallography Open Database (COD) was used to match and index the XRD peaks for the $Sr_7Mn_4O_{15}$ (1526876) and $SrCO_3$ (5000093) phases. Different colors bars represent relative intensities and peak positions of different CODs. The sample's XRD patterns are quite similar to the XRD patterns of phase $Sr_7Mn_4O_{15}$. A broad but low-intensity intensity peak at 25.3° corresponds to $SrCO_3$ may be seen in the XRD patterns. The SrO could react with CO_2 and form $SrCO_3$.

Scanning electron microphotographs (SEM) were used to examine surface morphology of sintered pellet, shown in Fig. 1(b). Micrograph of the sample shows grains of two different shapes and sizes. The XRD peaks of materials with tiny crystallites are usually broad. A sizable and broad peak of $SrCO_3$ was seen in the sample's XRD pattern. Thereby, we can infer that the agglomerated small crystallites are $SrCO_3$ and well-developed grains are of $Sr_7Mn_4O_{15}$.

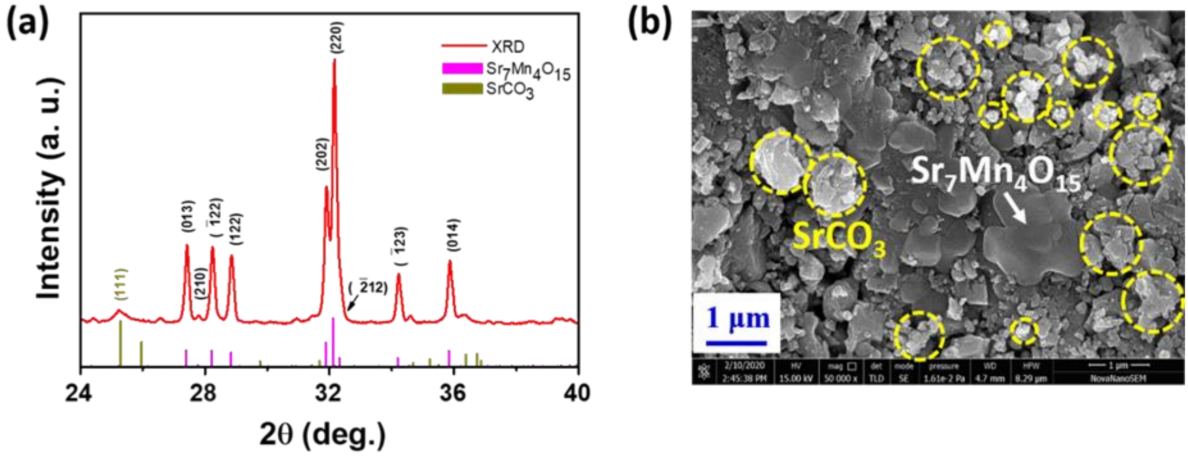

FIGURE 1. (a) Room temperature XRD and (b) SEM image

2. Negative dielectric permittivity

The permittivity, $\varepsilon_r^*(=\varepsilon_r'+i\varepsilon_r'')$was computed using the following equation from measured impedance, $Z^*(=Z'+iZ'')$ data:

$$\varepsilon_r^*=\frac{1}{i\omega C_0 Z^*} \qquad \ldots\ldots..(1)$$

Where, ω = applied signal angular frequency, $C_0=\varepsilon_0 A/d$, ε_0 = free space permittivity, d = separation between electrodes' surface and A = electrode surface area.

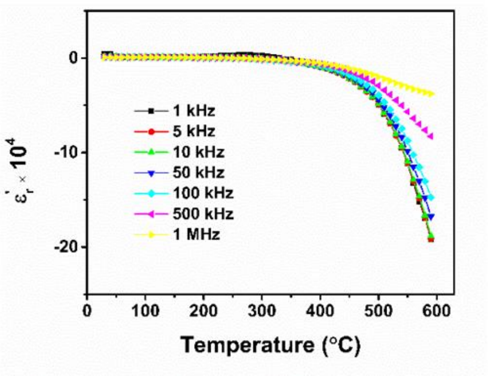

FIGURE 2. Temperature-dependent dispersion of the relative permittivity (real component).

Fig. 2 shows the relative permittivity variation with temperature at a few frequencies. After a specific critical transition temperature, 'T_c', the real relative permittivity changes sign from positive to negative. Negative permittivity is especially common in metals or metal-like substances (metamaterials), i.e., materials with high free carrier concentrations.

According to the Drude model, free charge carriers of the matrix are the source of negative permittivity in metals or metamaterials [8,13]. The free carriers contained in the metal matrix oscillate with the applied electric field resulting in negative permittivity [9,13]. In metals only free electrons are accessible to respond to an applied electric field. On the other hand, in ceramics both localised and delocalized charge carriers react to the applied electric field. Free charge carriers oscillate periodically parallel to the applied electric field direction and localised charges orientate or polarise. The Lorentz oscillator model describes how localized charge carriers respond to an applied electric field. Consequently, the Drude-Lorentz (DL) oscillator model—a hybrid of the Drude and Lorentz oscillator models—was used to investigate reported negative permittivity characteristics above the critical transition temperature (Tc). The real complex permittivity (ε') is as follows according to DL model [14]:

$$\varepsilon'=\varepsilon_\infty-\frac{\omega_{pd}^2}{\omega^2+\tau^{-2}}+\frac{\omega_{pl}^2(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+\omega^2\gamma^2} \qquad \ldots\ldots\ldots.(2)$$

where, ε_∞= permittivity at high frequency, ω_0= resonance frequency, ω_{pl}= Lorentz angular plasma frequency, ω_{pd}= Drude angular plasma frequency, which is governed by carrier concentration (n_{eff}), charge of an electron (e = 1.6×10^{-19} C) and effective mass (m^*).

$$\omega_{pd} = \sqrt{\frac{n_{eff}.e^2}{m^*.\varepsilon_0}} \qquad \ldots\ldots\ldots(3)$$

Fig. 3 shows the relative permittivity's frequency dependence. In Fig. 3(a), the fitting curves generated in accordance with Eqn. (2) are shown as solid lines. The relative permittivity fits well with Eqn. (2) above T_c; nevertheless, it didn't fit well, below T_c (Fig. 3 (b)). Below plasma frequency, the realised negative permittivity is similar to metal plasmonic oscillation behaviour. The free charge carrier plasmonic oscillations above Tc, may have suppressed resonant response of localised charges in the applied electric field [14,15]. Above T_c, plasma like oscillations of free charge carriers is dominating and hence negative permittivity is observed.

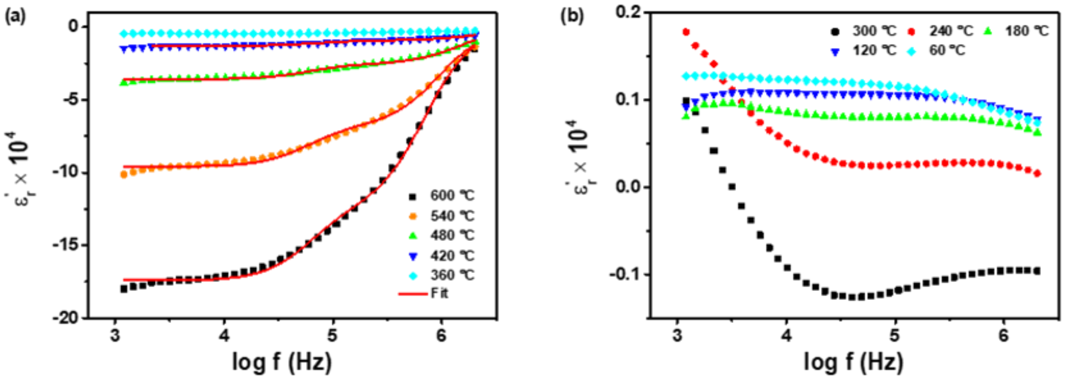

FIGURE 3. Variation of relative permittivity (real part) with frequency (a) above T_c and (b) below T_c at different temperature.

As already mentioned, dc conductivity (σ_{dc}) is related to the variation of relative permittivity with temperature. The band gap of $Sr_7Mn_4O_{15}$ drops considerably with temperature, as noted in the introduction section. Thus, thermal excitation induced localized electrons in the valence band to delocalize to the conduction band's edge, will act as free charge carriers, and a substantial increase in free charge carriers, n_{eff}, can be expected as temperature rises. The synthesized composite's DC conductivity, σ_{dc}, increases linearly with temperature, as shown in Fig. 4. The DC conductivity, σ_{dc}(= $n_{eff}e^2\tau/m^*$), is proportional to charge carrier density. As a result, an increase in σ_{dc} with increasing temperature is equivalent to increase in n_{eff} with temperature it results in the crossover of permittivity at and above the critical transition temperature, Tc, from positive to negative.

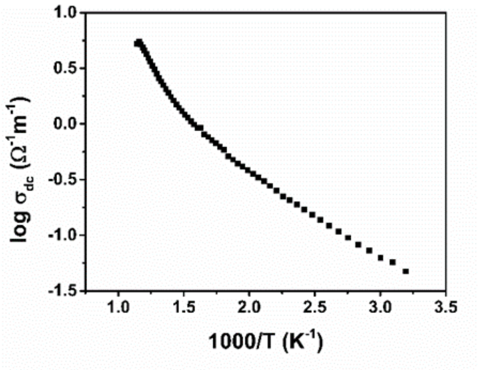

FIGURE 4. Variation of DC conductivity with inverse of temperature.

Conclusion

Using standard solid-state method composite of $Sr_7Mn_4O_{15}$ - SrO was successfully synthesized. XRD pattern of the composite confirmed the presence of both the components, although SrO is present in the form of $SrCO_3$. SEM image has also exhibited presence of two phases of different morphology. The negative permittivity behaviour of the composite was observed above 300 °C, which is explained by the thermally excited free carriers' plasmonic oscillation. Increase in the DC conductivity with increasing temperature is ascribed to increase in charge carrier concentration. Negative permittivity behaviour of the composite is its inherent property which is linked to the effective carrier concentration at and above a particular temperature. This composite has potential for those applications where meta-materials are used.

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