Materials Letters 166 (2016) 235–238

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Terahertz magnetic response and high dielectric constant in Ti:$SmFeO_3$ composite ceramics

Xiaojian Fu [a], Xinxi Zeng [b,c], Hao Chi Zhang [a], Tie Jun Cui [a,*]

[a] State Key Laboratory of Millimeter Waves, School of Information Science and Engineering, Southeast University, Nanjing 210096, China
[b] Division of Energy & Environment, Tsinghua University Graduate School at Shenzhen, Guangdong 518055, China
[c] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 7 October 2015
Received in revised form
2 December 2015
Accepted 22 December 2015
Available online 22 December 2015

Keywords:
Ceramics
Magnetic materials
Terahertz spectroscopy
Enhanced magnetization
Terahertz magnetic resonance
High dielectric constant

ABSTRACT

In this letter, the macroscopic magnetic properties as well as terahertz magnetic and electric responses of Ti doped $SmFeO_3$ ceramic are thoroughly investigated. It is observed that the magnetization is enhanced for the composite ceramic, indicating that the ferromagnetic moment becomes easier to reorient with the applied field after adding Ti. The antiferromagnetic mode has a blue-shift for the doped sample below 273 K due to the increased anisotropy constant. It is also shown that the terahertz dielectric constants increase about 11% although the Ti concentration is only 1 at%. The composite ceramic with the electromagnetic properties of enhanced magnetism, high dielectric constant, as well as sensitivity of temperature and external field will have potentials for application in magnetic devices, miniaturized and tunable devices.

1. Introduction

Magnetic materials and spin devices have been the research hotspots of material science for centuries [1]. Recently, ferrites have attracted lots of attentions due to magnetic resonances at microwave and terahertz frequencies as well as the application in magnetic devices and magnetically tunable metamaterials [2–6]. Actually, the magnetism disappears above terahertz frequencies for most magnetic materials. Thus, metamaterials with various periodic structures have been designed to realize the artificial magnetism [7,8]. However, the exception is the orthoferrite family who extends the intrinsic magnetic resonant frequency to the terahertz regime. As a typical member, $SmFeO_3$ has an antiferromagnetic mode frequency of 0.95 THz at 3 K [9]. Besides, the orthoferrite usually exhibits weak macroscopic magnetization due to the canting spins [10]. However, the magnetic properties are hard to be tuned by external field because of the Fe–Fe interaction and the resulting strong internal magnetic field.

Rare earth titanates (La–Sm) with distorted perovskite structure possess similar magnetic properties with orthoferrites [11,12]. For instance, $SmTiO_3$ undergoes two antiferromagnetic phase transitions at 70 K and 45 K, respectively. The ion radius of Ti^{3+} is close to that of Fe^{3+}, and hence $SmFeO_3$ and $SmTiO_3$ can form continuous solid solutions with a small lattice distortion. Moreover, the titanates usually have temperature sensitive electromagnetic performances and high dielectric constant, and thus optimized magnetic properties and tunable magnetic responses can be expected in the Fe–Ti composite ceramics.

In this letter, Ti doped and undoped $SmFeO_3$ ceramics are prepared. The phase structure is investigated using an X-ray diffraction and Raman scattering spectroscopy, while the magnetic properties are studied through the magnetization measurement and terahertz spectroscopy characterization.

2. Experimental

The $SmFeO_3$ and $SmFe_{0.99}Ti_{0.01}O_3$ ceramics are prepared by using the solid-phase pressureless sintering method. The phase structure of the ceramic samples is measured on an X-ray diffractometer (Rigaku D/max2500, Japan) with CuKα radiation. The Raman spectra between 113 K and 693 K are detected (LabRAM HR800, HORIBA Jobin-Yvon Ltd.) with exciting wavelength of 632.8 nm. The macroscopic magnetic properties are characterized by magnetic measuring system (SQUID-VSM, Quantum Design). Lastly, the terahertz magnetic resonances and dielectric responses are investigated using the terahertz transmission spectra.

3. Results and discussions

Fig. 1 presents the XRD patterns of the orthoferrite ceramics. It

* Corresponding author.
E-mail address: tjcui@seu.edu.cn (T.J. Cui).

http://dx.doi.org/10.1016/j.matlet.2015.12.091
0167-577X/

is found that the samarium orthoferrite belongs to the orthorhombic lattice system, and a small amount of Ti doping does not give rise to the phase transition and peak shift. Actually, the cell parameters for $SmFeO_3$ and $SmTiO_3$ are very close: the former's are a=5.6001(3), b=7.7060 (7), and c=5.3995(6) Å; while the latter's are a=5.669(1), b=7.742(1), and c=5.467(1) Å [11,13].

The Raman spectra of ceramics are presented in Fig. 2. For $SmFeO_3$, the Raman bands during 100–200 cm^{-1} can be attributed to the stretching modes of Sm–O bond, and the peaks between 200 and 400 cm^{-1} are the bending and stretching modes of FeO_6 octahedral, while the two close bands around 465 cm^{-1} (113 K) are related to the bending mode of O–Fe–O bond [14,15]. All these peaks exhibit obvious redshifts during heating. However, the strongest Raman peak at 621.6 cm^{-1} attributing to the stretching mode of Fe–O bond does not exhibit significant high-temperature softening phenomenon. It is noted that the spin reorientation transition around 450–480 K and the antiferromagnetic–paramagnetic transition at about 670 K do not change the vibrational modes. The effect of adding Ti is more complicated. Because the content of Ti is very small, the Raman modes and peak positions are almost unchanged. However, the relative peak intensities of different modes vary. For instance, the strongest peak of $SmFeO_3$ ceramic is the Fe–O stretching mode locating at 600–650 cm^{-1}; for Ti doped sample, the strongest peak is the Sm–O stretching mode during 150–200 cm^{-1}, whereas the Fe–O vibrational band gets very weak and broad. It is possible that Ti addition leads to lattice mismatch, which further causes the decrease of ordering degree and wider distribution of Fe–O bond length, and thus, the Raman peaks will weaken and broaden.

Below the spin reorientation transition temperature, Fe^{3+} spins in $SmFeO_3$ orient along the c axis with a weak macroscopic magnetization along the a axis [16]. Fig. 3(a) shows the magnetization curves of ceramics. Compared to the $SmFeO_3$ ceramic, the doped sample has a larger moment, and the maximum for them are 0.698 emu/g and 0.783 emu/g, respectively. It is possibly because the addition of Ti induces the lattice distortion and changes the canting angle, and the ferromagnetic component increases. With the decrease of temperature, the moment reduces due to the activation of the antiparallel Sm^{3+} ferromagnetic component. The transition temperatures are similar for the two compositions. Above the maximum point, the moment decreases during heating. As can be seen, the magnetization is declined more quickly after the Ti addition, which implies the long-range magnetic order is influenced by Fe–Ti interaction and becomes more temperature

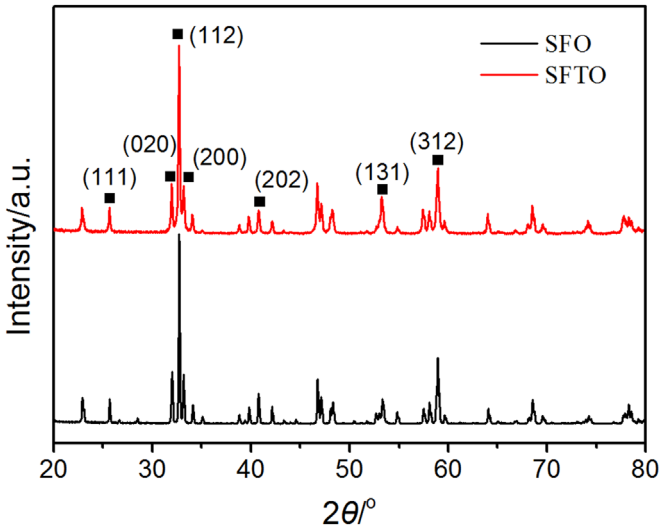

Fig. 1. The XRD patterns of $SmFeO_3$ (SFO) and $SmFe_{0.99}Ti_{0.01}O_3$ (SFTO) ceramics.

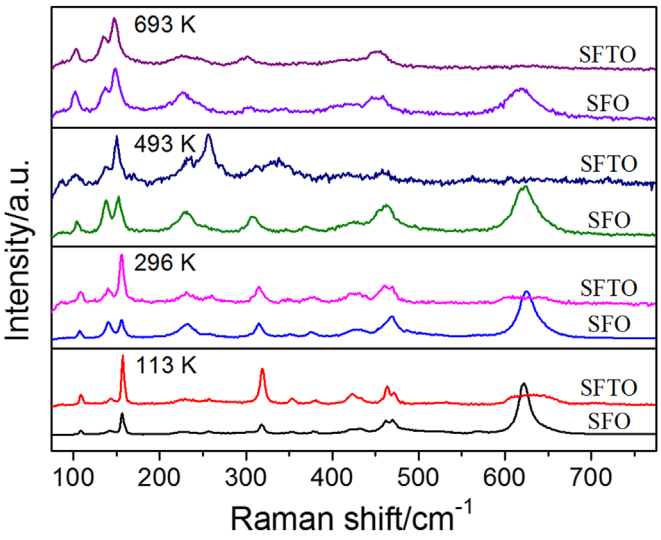

Fig. 2. The Raman spectra of SFO and SFTO ceramics at various temperatures.

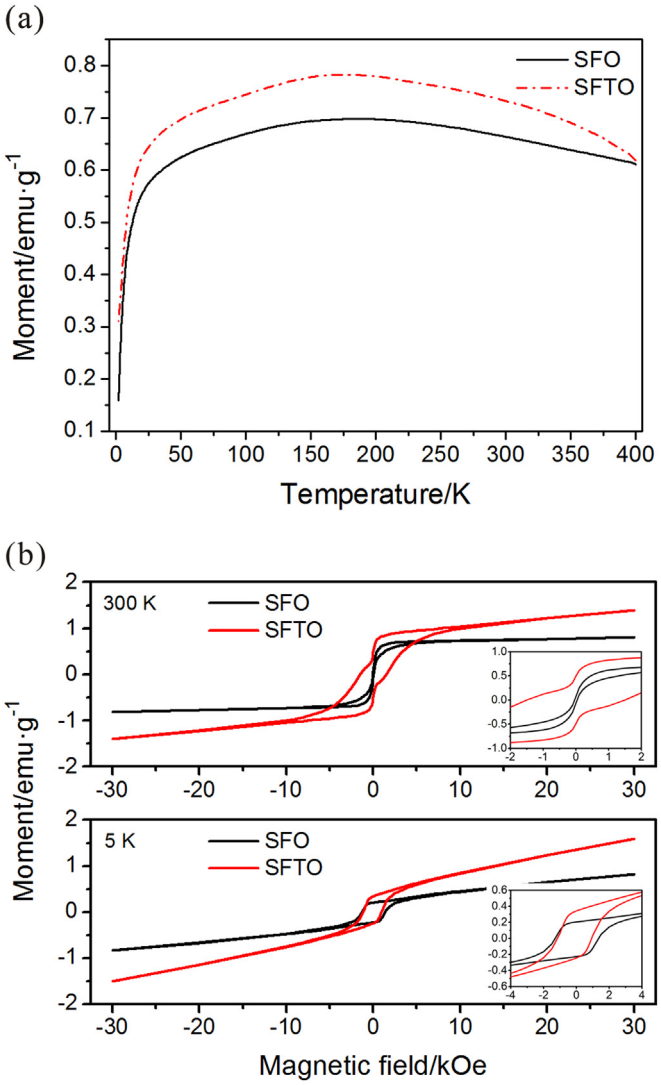

Fig. 3. The magnetization–temperature (M–T) curves (a) and magnetic hysteresis loops (M–H) (b) of SFO and SFTO ceramics. The insets show the enlarged scale for the low field part.