



Dielectric responses in polycrystalline rare-earth iron garnets



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ARTICLE INFO

Article history:

Received 7 June 2016

Received in revised form

8 August 2016

Accepted 30 August 2016

Available online 31 August 2016

Keywords:

Rare-earth iron garnet

Dielectric

Debye relaxation

Maxwell-Wagner effect

ABSTRACT

Rare-earth iron garnets (RIG, R = Y, Tb and Lu) were sintered at 1350 °C. Their crystal structures were refined by the Rietveld method, which showed that the oxygen coordination polyhedra were highly distorted. X-ray photoelectron spectroscopy revealed a similar Fe²⁺/Fe³⁺ ratio (~27/73) in different RIGs. The origins of dielectric responses were identified by cross examination of the permittivity, modulus and impedance presentations. Fitting experimental data with the Debye-type and Maxwell-Wagner models revealed that the dielectric relaxation at room temperature was dominated by the Debye-type process but as temperature increased, the Maxwell-Wagner effect gradually took over. The static permittivity was 750, 785 and 2653 for YIG, TbIG and LuIG, respectively. The particularly large permittivity of LuIG arose from a large difference between the distortions of FeO₆ and FeO₄ in the structure and therefore, a large dipole moment was created when electron hopping between the octahedral and tetrahedral sites took place.

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1. Introduction

Magnetic ceramics, which show an insulating or a semi-conducting electrical character, have a variety of applications in both electrical power equipment (i.e. low frequency applications) and microelectronic devices (i.e. high frequency applications) [1,2]. Rare-earth iron garnets (RIG) with the general formula R₃Fe₅O₁₂ are a family of such magnetic ceramics, among which Y₃Fe₅O₁₂ (YIG) has been studied extensively for the magneto-optical and passive microwave device applications [1–4]. More recently, the RIG family have found their applications in the dielectric resonator antennas [2,5], as well as in some novel devices exploiting the magneto-dielectric property [6–9]. For these later applications, a better understanding of the dielectric response is needed. For example, a large dielectric permittivity may arise from the structural distortion related electrical polarizability or hopping charge carriers, apparently, each of which will interact in a different way with the applied magnetic field, leading to a different mechanism for the magneto-dielectric effect. It was proposed that in the former case the magneto-dielectric effect might be achieved via the magnetostriction effect [7], whereas in the latter case it was achieved by the

redistribution of the spin coupled dipole moments at the hopping sites, upon the application of a magnetic field [8]. However, compared to their magnetic and magneto-optical properties, the dielectric property of the RIG family was far less studied. In many of previous studies of the RIG dielectric properties, the dielectric response was attributed to the electron hopping between the Fe³⁺ and Fe²⁺ ions [8–15]. However, the electron hopping alone seems unable to account for all the experiment results observed in various RIG samples. Therefore, in this work we carried out a detailed study on the dielectric properties of three RIG compounds, i.e. YIG, Tb₃Fe₅O₁₂ (TbIG) and Lu₃Fe₅O₁₂ (LuIG). Attempts were made to reveal the true origin of the measured large dielectric permittivity in the sintered polycrystalline RIG samples.

2. Material and methods

Polycrystalline samples of RIG were synthesized by the solid state reaction method from the oxide powders of Y₂O₃ (99.9% Showa), Tb₄O₇, Lu₂O₃ (99.9%, Alpha Aesar), and Fe₂O₃ (99.9%, Strem). The samples were weighed according to the molar ratio, R/Fe = 3/5, and well mixed by grinding in an agate mortar with the addition of ethanol. The powder mixtures were pressed into pellets of the size about 10 mm in diameter by 2 mm thick under the pressure of 700 psi, which were then pre-sintered at 850 °C in air for 12 h in order to avoid preferential evaporation loss of any component. The pre-sintering process was repeated twice with the

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intermediate grindings to ensure a good homogeneity of the composition. The final sintering was carried out at 1350 °C for 24 h.

The phase purity of the prepared samples was examined by the powder X-ray diffraction (XRD, Rigaku MultiFlex-2kW). The crystal structure was then refined by the Rietveld method based on the recorded d-spacings and reflection intensities. The software for the Rietveld analysis was the General Structure Analysis System (GSAS) [16]. The local structural distortion was examined by the Raman spectroscopy (Jobin-Yvon T64000). The surface morphology and microstructure were observed by the scanning electron microscopy (SEM, Hitachi SU8000) and transmission electron microscopy (TEM, Jeol JEM-2100F). The samples for SEM were polished by the Buehler Micropolish II Deagglomerated Alumina Suspension (0.05 μm). The dielectric characterization was carried out via the measurement of the AC impedance (Waney Kerr 6510B) from room temperature (RT) to about 180 °C, which was taken place in a homemade resistive-heating chamber. For the impedance measurement, the samples were ground to reduce the thickness to about 1.0 mm (i.e. a thin disk shape with size $\Phi 10 \times 1.0 \text{ mm}^3$). Both surfaces of each sample were polished and coated with the silver paint as the electrodes, which was dried at RT for 12 h and then heated at a hotplate (100–150 °C) for 20 min. The oxidation states of the elements in RIG were checked by the X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). In the XPS analysis, the measured binding energies were calibrated against the C 1s peak (284.6 eV) of the residual carbon absorbed on the surface from the ambient atmosphere. The amount of each element with various oxidation states was calculated from the area under its characteristic peak, whose intensity had been corrected by the sensitivity factor of the instrument.

3. Results

3.1. Structural and compositional characterizations

Fig. 1 shows the XRD θ - 2θ scans of the polycrystalline RIG samples. All the reflection lines can be indexed according to the known garnet structures in the powder diffraction database, i.e. PDF 43–0507 (YIG), 71–0697 (TbIG) and 23–0374 (LuIG),

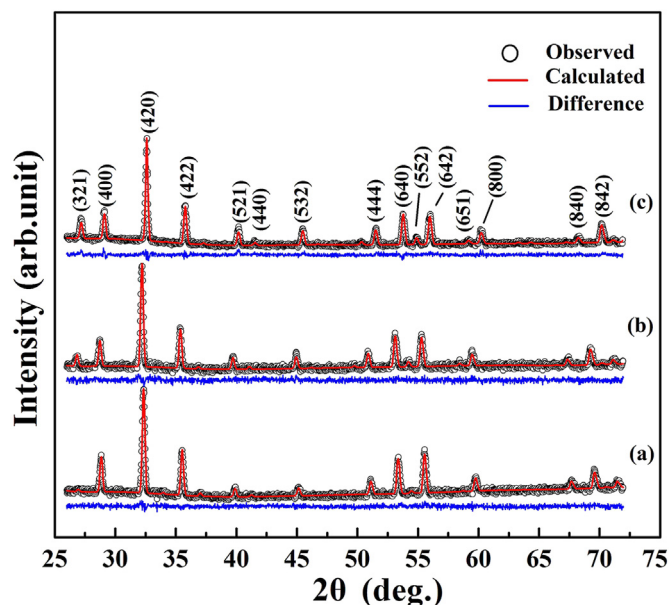


Fig. 1. XRD patterns and Rietveld refinements: (a) YIG, (b) TbIG, and (c) LuIG.

indicating that the samples had a pure phase. Fig. 1 also illustrates the Rietveld fittings of the XRD patterns, all of which have a good match with a small error (R_p) of 1.63%, 1.61% and 2.36% for YIG, TbIG and LuIG, respectively. The refined atomic positions are given in Table 1, which allow us to calculate the bond lengths and angles for the FeO_4 , FeO_6 , and RO_8 polyhedra. The results are presented in Table 2 for all the three RIG samples, while the coordination polyhedra are drawn in Fig. 2 for only one representative RIG (i.e. LuIG) to save the space. It is apparent from Table 2 and Fig. 2 that the polyhedra are highly distorted. The degree of the distortions may be assessed according to the parameters defined below [17,18]:

$$\Delta = \frac{1}{n} \sum_{i=1}^n \left[\frac{(l_i - \bar{l})}{\bar{l}} \right]^2 \quad (1)$$

$$\sigma^2 = \frac{1}{m-1} \sum_{i=1}^m [(\theta_i - \theta_0)]^2 \quad (2)$$

where n is the coordination numbers, l_i is the individual Fe/R-O bond length, \bar{l} is the average of the bond lengths, m is the total numbers of the bond angles, θ_i is the individual O-Fe/R-O bond angle, and θ_0 is the corresponding θ angle in the undistorted polyhedron, which is 109.47° for a regular tetrahedron, 90° for a regular octahedron, and 70.53° (angles facing edges) or 109.47° (angles facing face-diagonals) for a cube. The calculated distortion parameters for the coordination polyhedra are presented in Table 3, which indicates that although the distortions of bond lengths (Δ) are trivial, the angle distortions (σ) are significant for all the FeO_4 , FeO_6 , and RO_8 polyhedra, so that the O^{2-} coordination polyhedra are highly asymmetric against their centers at which the cations are located.

To verify the different distortions of the coordination polyhedra, Raman spectroscopy was performed. It was reported in the previous Raman studies that the peaks below 300 cm^{-1} came from the various motions of both RO_8 and FeO_6 as well as the librational modes of FeO_4 , while the peaks at 300 – 900 cm^{-1} were mainly resulted from the stretching and bending modes of FeO_4 [19–21], which can therefore be compared explicitly for different RIGs. Fig. 3(a) shows the recorded Raman spectra in this wavenumber region, where the observed peaks agree well with those reported previously [19,20]. As shown in Fig. 3(a), the peak at 342 cm^{-1} varies little with different R, confirming that it is indeed only relevant to the Fe-O bonds. Except for this peak, however, all other peaks shift to the higher wavenumber side in the order

Table 1
Atomic positions refined by Rietveld method.

$\text{R}_3\text{Fe}_5\text{O}_{12}$	$Ia\bar{3}d$	R = Y	R = Tb	R = Lu
a (Å)		12.3741	12.4304	12.2773
V (Å ³)		1894.70	1920.68	1850.67
Atomic positions				
R (24c)	x	0.125	0.125	0.125
	y	0	0	0
	z	0.25	0.25	0.25
Fe_1 (16a)	x	0	0	0
	y	0	0	0
	z	0	0	0
Fe_2 (24d)	x	0.375	0.375	0.375
	y	0	0	0
	z	0.25	0.25	0.25
O (96h)	x	−0.0249	−0.02747	−0.0282
	y	0.0578	0.05950	0.0587
	z	0.1518	0.15157	0.1585
χ^2		1.183	1.104	1.550
R_{wp} (%)		2.03	2.04	3.01
R_p (%)		1.63	1.61	2.36

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