



## Spin dependent electrical abnormal in TbFeO<sub>3</sub>

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### ARTICLE INFO

#### Article history:

Received 27 November 2011

Received in revised form 7 December 2011

Accepted 14 December 2011

Available online 23 December 2011

#### Keywords:

Solid state reaction

Superexchange effect

Spin-reorientation transition

Magnetolectric coupling effect

### ABSTRACT

Perovskite-type polycrystalline TbFeO<sub>3</sub> ceramic was synthesized by a conventional solid state reaction method. Crystal structure, optical properties and electrical properties were investigated. The temperature dependent X-ray diffraction results show that the sample crystallized in an orthorhombic perovskite structure with space group *Pbnm* and the crystal structure had no obvious change with the decrease of temperature down to 200 K. The electrical characterization result show an interesting electrical transition in the temperature range of 200–300 K, such abnormal electrical transition is considered to be related to the spin-reorientation behavior happened in the temperature range mentioned above. The magneto-electric coupling phenomenon in TbFeO<sub>3</sub> is mainly due to superexchange interaction, which can be significantly affected by spin direction.

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### 1. Introduction

The perovskite structure rare-earth orthoferrites with a general formula RFeO<sub>3</sub> (R = rare earths) have attracted many attentions due to their applications in magnetic and electric devices [1–4]. TbFeO<sub>3</sub> is a typical orthoferrites crystallized in an orthorhombically distorted perovskite structure with *Pbnm* space group [5]. The magnetic properties and crystal structure have been studied by using various techniques, e.g. neutron diffraction and Mössbauer spectroscopy [6–9]. The Fe<sup>3+</sup> spin system in TbFeO<sub>3</sub> order antiferromagnetically below Néel temperature  $T_{N1} = 692$  K, and the Tb<sup>3+</sup> spin system order antiferromagnetically below Néel temperature  $T_{N2} = 4.2$  K [10]. The Fe site ordering structure is the G-type AFM with spin canting, resulting in weak ferromagnetism. The ferromagnetic (FM) moment is along the *c*-axis [11]. The Tb ion sublattice is paramagnetic above  $T_{N2}$ , the magnetic spins in Tb site are expected to be disordered well above  $T_{N2}$  and are partially polarized by the molecular field of the net FM moment of the ordered Fe sublattice [12]. Since the Fe and the Tb sublattices contribute to the total magnetization, the induced moments of Tb vary with temperature and are also possibly affected by the spin reorientation (SRT) happened in Fe sublattice. As a result, the magnetization is expected to exhibit rather complicated temperature-dependent behavior [10,12–14].

As is known to all, in rare-earth orthoferrites electron transport by superexchange (SE) mechanism [15,16], such transport is

intensely related to the orientation of the spin motion. But there was no report about electrical transport properties of TbFeO<sub>3</sub> in previous research works. In order to understand the physical mechanism and magnetolectrical coupling effect in TbFeO<sub>3</sub>, it is very necessary to investigate the electrical transport properties. In this paper, TbFeO<sub>3</sub> ceramic sample was synthesized by using solid state reaction method and its electrical transport properties were studied.

### 2. Experimental

Polycrystalline TbFeO<sub>3</sub> was prepared by the conventional solid state reaction method. The chemical reagents used in this work were Tb<sub>4</sub>O<sub>7</sub> and Fe<sub>2</sub>O<sub>3</sub> powders with of high purity. The stoichiometric amounts of Tb<sub>4</sub>O<sub>7</sub> and Fe<sub>2</sub>O<sub>3</sub> powders were mixed and ground for 1 h, then the mixture was put in tube furnace to sinter at 1000 °C for 10 h in air, after that, the sintered powder was ground for 30 min and pelletized, the pellet was sintered in tube furnace at 1400 °C for 15 h in air.

The X-ray powder diffraction (XRD) experiment was performed on a Bruker AXS D8 DISCOVER X-ray diffractometer with Cu K<sub>α</sub> radiation ( $\lambda = 1.5406$  Å). The patterns were taken in the  $2\theta$  range from 10 to 120° with a scanning step of 0.02° and exposure time of 4 s per step. The temperature dependence of resistance was measured on a home-made electrical transport properties measurement system in a four-probe configuration. The FT-IR spectrum was recorded at room temperature on an Image-Pro Nicolet 5700 FT-IR spectrometer with KBr pellets over 400–4000 cm<sup>-1</sup> range.

### 3. Results and discussion

The sample of TbFeO<sub>3</sub> was first characterized by the X-ray diffraction (XRD). The result indicates that the sample is single phase and well crystallized. This result is in good agreement with values in the Joint Committee on Powder Diffraction Standards (JCPDS#47-0068). *Fullprof* software was used to analysis

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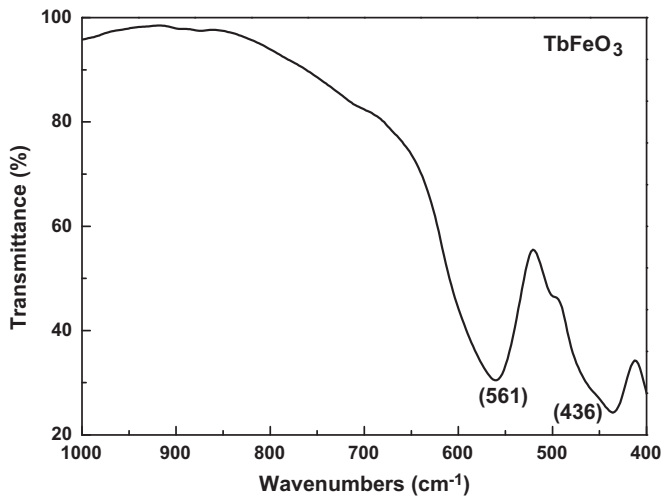


Fig. 1. IR spectrum of the obtained polycrystalline TbFeO<sub>3</sub>.

the XRD Pattern and the lattice constants were calculated to be  $a = 5.329(8) \text{ \AA}$ ,  $b = 5.593(8) \text{ \AA}$ ,  $c = 7.646(4) \text{ \AA}$ .

Further evidence for the formation of TbFeO<sub>3</sub> comes from IR. The IR spectrum of the polycrystalline ferrite in the frequency range from  $1000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  has been shown in Fig. 1. The spectrum shows well-established strong absorption bands around  $\sim 561 \text{ cm}^{-1}$  and  $\sim 436 \text{ cm}^{-1}$ . The existence of a band around  $561 \text{ cm}^{-1}$  strongly suggests the Fe–O<sub>I</sub> stretching vibration ( $\gamma_1$  mode), and the  $436 \text{ cm}^{-1}$  band corresponds to the O<sub>II</sub>–Fe–O<sub>II</sub> deformation vibration ( $\gamma_2$  mode) [17,18].

The temperature dependence of resistance was measured in the temperature range of 5–300 K. The result is shown in Fig. 2. Above 263 K, the resistance decreases with temperature. Below 263 K, the resistance starts to decrease, and after a minimum value around 218 K, it eventually goes up along with the decreasing of temperature. It can be seen clearly that there is an abnormal transition in the temperature range from 200 K to room temperature.

To find if there was phase transition in the polycrystalline TbFeO<sub>3</sub> in the temperature range from 200 K to room temperature, temperature dependent XRD was characterized. Fig. 3 shows the temperature dependent XRD patterns of TbFeO<sub>3</sub>. From the results,

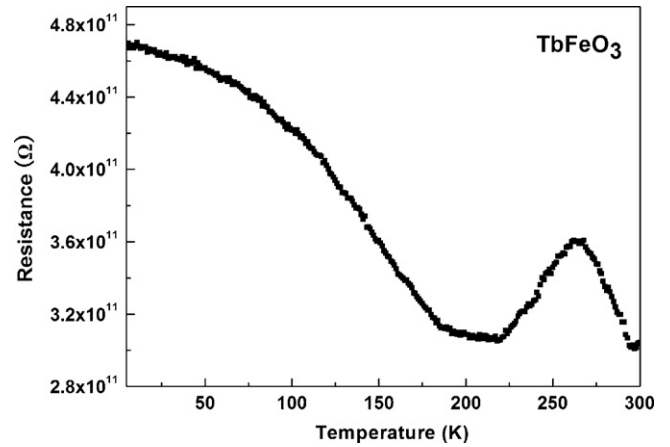


Fig. 2. The temperature dependent electrical resistance of polycrystalline TbFeO<sub>3</sub>.

no phase or crystal structure transition was observed, that means the abnormal resistance behavior in the temperature range from 200 K to room temperature was not caused by any phase or crystal structure transition.

Since superexchange is the mainly electrical transport mechanism in rare-earth orthoferrites, it is necessary to consider the magnetic properties of TbFeO<sub>3</sub> with the aim to well understand the electrical transport properties here. Recently, Kim et al. reported an extraordinary magnetic behavior in polycrystalline TbFeO<sub>3</sub>, and they supposed that such extraordinary magnetic behavior was attributed to SRT [10]. SRT was related to the Fe local spin, Park et al. explained that the Fe local spin axis rotates from the  $a$ -axis ( $x$ -direction) to the  $c$ -axis ( $z$ -direction), the diagram figure of magnetic structure before and after the SRT is shown in Fig. 4 [12]. In Ref. [10], temperature dependence of the magnetic moment of polycrystalline TbFeO<sub>3</sub> was characterized, and it was found that the magnetic moment rapidly decreased with increase in temperature up to 250 K, above 250 K, it began to increasing and had a convex maximum at about 350 K; and then, it eventually reached to zero. It was explained that the inflection points in the  $M$ – $T$  curve can arise from a SRT in the antiferromagnetically ordered state of the perovskite structure [13]. For superexchange, the spin directions of adjacent Fe atoms in the FeO<sub>6</sub> octahedron play an important role

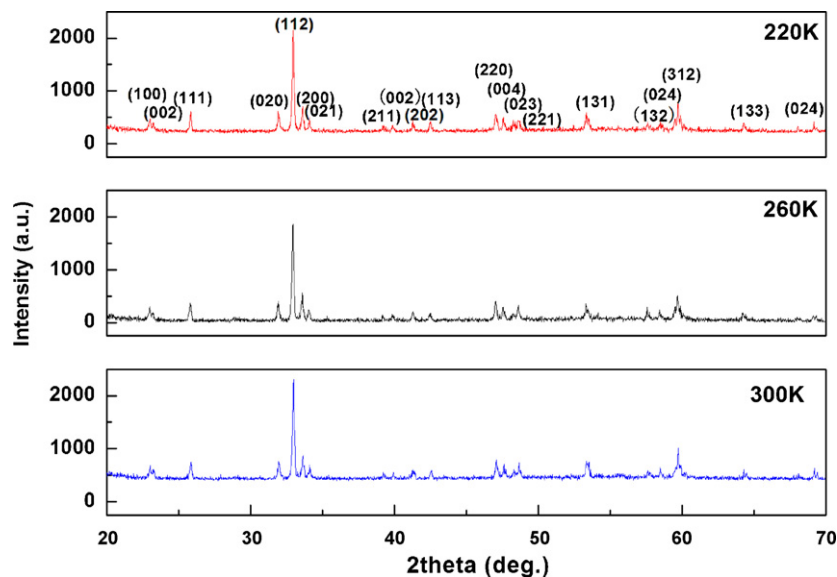
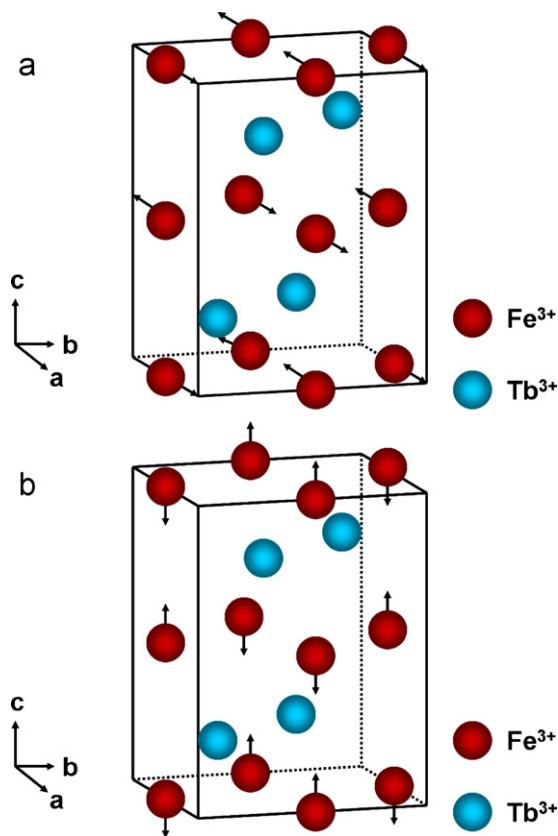


Fig. 3. Low-temperature XRD curves of polycrystalline TbFeO<sub>3</sub> powder.



**Fig. 4.** Diagram figure of magnetic ordering of Fe<sup>3+</sup> ions (red spheres) before (a) and after (b) the spin reorientation transition in the crystal structure of TbFeO<sub>3</sub>. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[15,16,19,20]. From the electrical result, it would be clear that the SRT affected the Fe–O–Fe link for superexchange interaction seriously, so we conclude that the abnormal electrical properties are caused by SRT behavior in TbFeO<sub>3</sub>.

#### 4. Conclusion

Polycrystalline TbFeO<sub>3</sub> was synthesized by using solid state reaction method, the crystal structure and temperature dependent

electrical transport properties were characterized. An abnormal electrical transport behavior was observed in temperature range from 200K to room temperature. Such behavior was not caused by any phase transition or crystal structure change. It was considered to be related to coupling effect between magnetic and electrical properties. In the temperature range, there is an extraordinary magnetic property, which is related to SRT in TbFeO<sub>3</sub>. The SE effect was strengthened in polycrystalline TbFeO<sub>3</sub> due to Fe site magnetic spin rotation with the temperature increase.

#### Acknowledgements

This work was supported by the National Basic Research Program of China (973 Program) (Grant No. 2010CB933501), the National Natural Science Foundation of China (Grant No. 51072182, 51172208 and 60806045), and the Innovative Youth Team of Natural Science Foundation of Zhejiang Province (Grant No. R4090058).

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