Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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**To cite this article:** Wenfei Xu, Zhi Wang, Jing Yang, Wei Bai, Yuanyuan Zhang & Xiaodong Tang (2014) Magnetic and Dielectric Properties in Multiferroic Y-type Hexaferrite, Molecular Crystals and Liquid Crystals, 603:1, 235-239, DOI: 10.1080/15421406.2014.967614

**To link to this article:** http://dx.doi.org/10.1080/15421406.2014.967614

Published online: 15 Dec 2014.

*Mol. Cryst. Liq. Cryst.*, Vol. 603: pp. 235–239, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.967614



# Magnetic and Dielectric Properties in Multiferroic Y-type Hexaferrite

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*Polycrystalline samples of $Ba_{0.5}Sr_{1.5}Zn_2(Fe_{0.96}Al_{0.04})_{12}O_{22}$ were synthesized by solid-state reaction method, and structural, magnetic and dielectric properties were investigated. The magnetic data indicate four magnetic spin-order structures exist in the samples. The Curie temperature is found to be 712 K. The sample also exhibits obvious dispersion in dielectric permittivity and dielectric loss values as a function of the frequency at room temperature, which may be interpreted as Maxwell-Wagner type dielectric relaxation.*

**Keywords** Synthesis; hexaferrites; conical spin; hysteresis

## I. Introduction

Recently, non-collinear magnetic-ordered hexaferrite has been extensively investigated due to its magnetoelectric effects and complex helical-spin-structure induced ferroelectric polarization which can appear in room temperature and a low magnetic field [1, 2]. Hexaferrites are classified into six types according to their chemical formulas and structures, namely M-, W-, Y-, Z-, X-, and U-type. The structures of various hexaferrites can be described as stacking sequences of three basic blocks: $S$ ($Me^{2+}Fe_4O_8$; spinel block), $R$ $[(Ba,Sr)Fe_6O_{11}]^{2-}$, and $T$ $[(Ba,Sr)_2Fe_8O_{14}]$, where Me denotes divalent metal ion [3].

For device applications, the realization of small-magnetic-field induced the electric polarization or dielectric constant near room temperature is necessary. Y-type hexaferrite is a good candidate for improving the current situation because it is predicted that the compound can exhibit filed-induced ferroelectricity at room temperature under a rather small magnetic filed [4, 5]. Recently, S. Ishiwata et al. reported the low-magnetic-field (∼30 mT) control of the polarization vector in $Ba_2Mg_2Fe_{12}O_{22}$ [2]. Moreover, magnetic field-induced ferroelectricity at a filed value of less than 0.1 T near room temperature in $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$

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(BSZFO) was reported by Y.S. Chai et al. [4]. The crystal structures of Y-type hexaferrites belong to $R\bar{3}m$, and which have fairly long c-axis parameters in the hexagonal setting. The magnetic $Fe^{3+}$ ions are located inside either oxygen tetrahedra or oxygen octahedra, which form series of layers perpendicular to the c axis. Strong superexchange between them is responsible for setting up long-range magnetic order above room temperature [6]. As reported in many papers, the arrangement of the magnetic moments produces conical spin phase at low temperature, with increasing the temperature, followed by a transition into a proper-screw spin phase, further transits into a collinear ferrimagnetic phase, and at high temperature, and finally changes to be the stabilization of the paramagnetic spin phase [2, 7].

In this paper, polycrystalline samples of Y-type hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2(Fe_{0.96}Al_{0.04})_{12}O_{22}$ (BSZFAO) were prepared by solid-state reaction method. Then the structural, magnetic and dielectric properties of BSZFAO were investigated. Here, Al-doped samples rather than Al-free samples were studied, it is because the field-dependent behaviors of this compound turned out to be much simpler than Al-free BSZFO, and could provide a simpler model [6].

## II. Experimental Details

Polycrystalline samples of BSZFAO were sintered by the conventional solid-state reaction method. Stoichiometric mixtures of $BaCO_3$, $SrCO_3$, ZnO, $Fe_2O_3$, and $Al_2O_3$ were ball-milled in ethanol for 12 h. The dried powders were pressed into pellets and then calcinated in air at 940°C for 10 h. The sintered ferrites were crushed, ball-milled again for 12 h, dried, palletized again, and finally were sintered at 1200°C in air for 24 h and cooled down to room temperature at a rate of 5°C/min. The crystalline structure of the ferrites was indicated by x-ray diffraction (XRD, D/Max-2550 V, Rigaku Co.) using a Ni filtered Cu K$\alpha$ radiation source. The cross-sectional microstructure was characterized by a scanning electron microscopy (SEM, JSM7500SF, JEOL, Japan). The magnetic properties were measured by a 9T physical property measurement system (PPMS, Quantum Design, USA) equipped with a vibrating sample magnetometer over a wide temperature range from 1.9 to 1000 K. For dielectric measurement, silver paste was first deposited on polished sample surfaces as the electrodes, dielectric properties as a function of frequency was performed using an Agilent E4980A LCR meter at 300 K.

## III. Results and Discussion

Figure 1 shows XRD patterns of BSZFAO samples at room temperature, and all the diffraction peaks can be indexed. The main diffraction peaks in XRD patterns are consistent with the standard patterns of Y-type hexaferrites, as labeled by rectangles. Two weak reflections (triangles) at 30.5 and 32.5° indicate the presence of a small amount of M-type phase in the sample. Multiple-phase reflections in BSZFAO can be assigned to the explanation by R.C. Pullar et al., formation of the hexaferrites was an extremely complicated process, and the different hexagonal phases all overlap in different temperature regions when heated the reactants [8]. This makes it extremely hard to obtain single phase hexaferrites, and the formation of secondary phase might inevitable. Furthermore, the SEM image of the polycrystalline sample illustrated in the inset of Fig. 1 shows hexagonal shape grains and the average grain size is about a few micrometers.

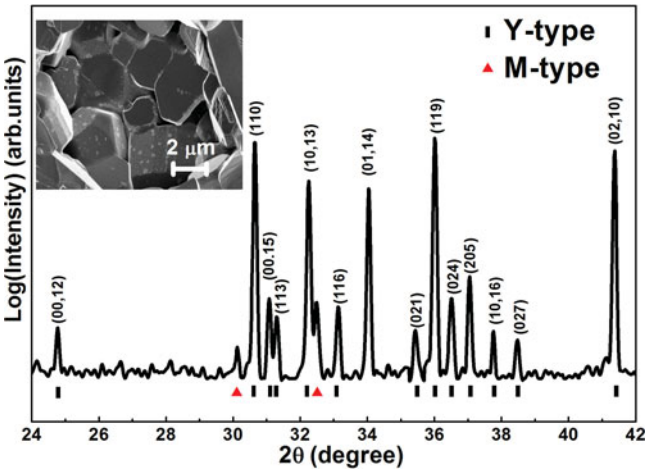


**Figure 1.** X-ray diffraction patterns of BSZFAO ploycrystalline samples at room temperature. Inset shows the SEM image of the samples.

The temperature dependence of magnetization M(T) curves were measured in both zero field-cooled (ZFC) and field-cooled (FC) processes in order to determine the magnetic transition temperature. Figure 2 shows the M(T) curves of BSZFAO measured in an applied magnetic field of 0.01 T from 5 to 800 K. The M(T) curves exhibit three transition temperatures at least (marked as $T_I$, $T_{II}$, $T_C$), implying the existence of four magnetic spin-order structures. At low temperature ($T_I = 25$ K), transition occurs from longitudinal conical spin phase into proper-screw spin phase. With increasing the temperature, transition changes from proper-screw spin phase into ferrimagnetic spin phase with collinear arrangement

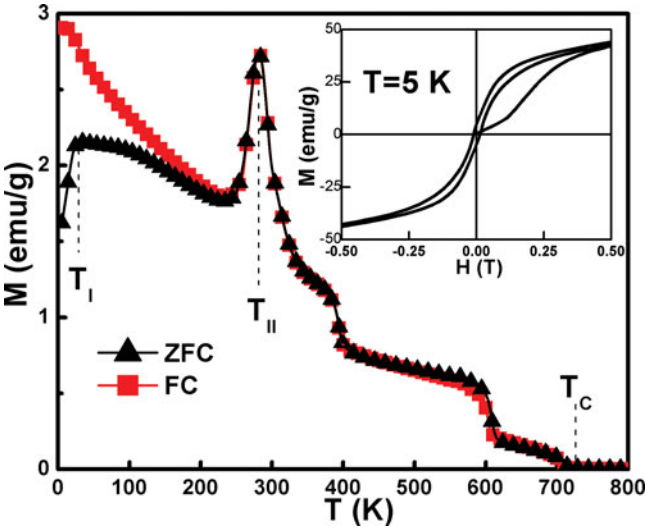


**Figure 2.** Temperature dependence of ZFC and FC magnetization curves for BSZFAO with a temperature range from 5 K to 800 K under a magnetic field of 0.01 T. Inset shows the hysteresis loops near zero field at 5 K.

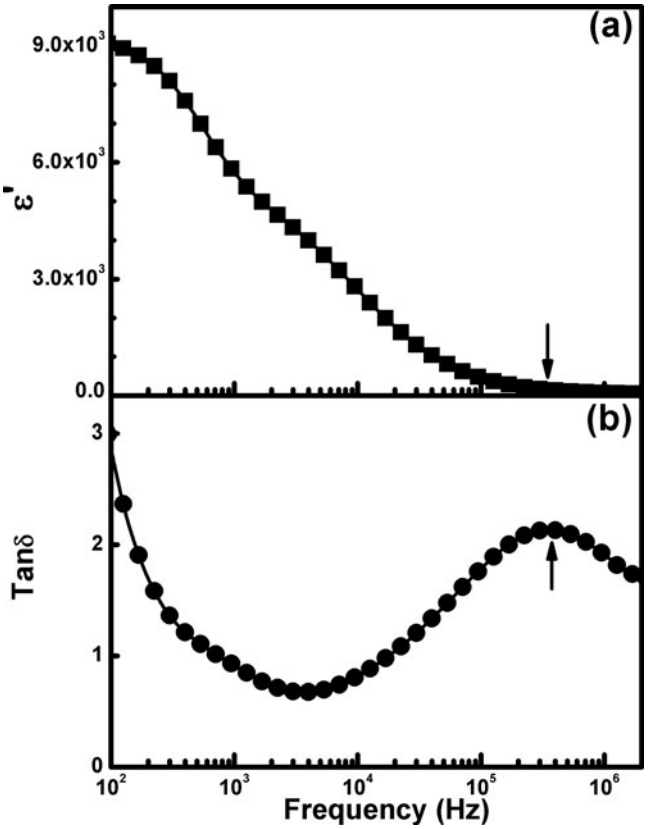


**Figure 3.** The (a) dielectric permittivity and (b) dielectric loss as the function of frequency for BSZFAO at 300 K.

at $T_{II} = 279$ K, and followed by the stabilization of the paramagnetic spin phase above Curie temperature $T_C = 712$ K [7]. Note that two steps are observed at 400 and 600 K, respectively, which can be attributed to the intermediate phase (between proper-screw and ferrimagnetic spin phase). In addition, the inset of Fig. 2 shows the hysteresis loops near zero filed at 5 K, which displays a typical conical spin-order behavior. After increasing H up to 0.5 T, one can observe a triple hysteresis loop in low magnetic field range between 0 and 0.5 T, which is agreed with the report in Y-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$ [9].

Figure 3(a) and 3(b) show frequency dependence of the dielectric permittivity ($\varepsilon'$) and loss (tan$\delta$) for BSZFAO at room temperature. One can see that the $\varepsilon'$ strongly depends on the frequency and implies obvious dielectric dispersion. A step can be observed in the $\varepsilon'$ spectrum, as signed by downward arrow (Fig. 3(a)). Namely, $\varepsilon'$ decreases with increasing frequency, and this decrease in the $\varepsilon'$ values is fast at low frequency region, then becomes slow at high frequency region, and finally $\varepsilon'$ arrives a platform with the value of 60. On the other side, the step-like feature in $\varepsilon'$ is accompanied by relaxation peak marked by upward arrow in tan$\delta$ spectrum (see Fig. 3(b)). Therefore, a series of dielectric relaxations may exist in this case. In general, the dielectric relaxations in polycrystalline samples mainly derive from extrinsic structural inhomogeneity (e.g. grain/grain boundaries, electrode/film interfaces) inducing Maxwell-Wagner interfacial polarization. These interfaces are always constructed by electrical heterogeneity of two different phases or media that are connected

in series. When ac electrical current passes through inhomogeneous interfaces, the free charged carriers would be localized and accumulate at the interfaces between two media with different conductivities. This process could give rise to a Debye-like relaxation, termed Maxwell-Wagner interfacial relaxation. Hence, the relaxations in present case may come from interfacial polarization relaxation in grain/grain boundaries or sample/electrodes. However, in high frequency, space charge in the interfaces can not catch the change of extrinsic electric fields, and the capacitance of space charge layers would be shorted. Consequently, high frequency dielectric constant is correspond to intrinsic value of grains, which is consistent with the reported value in low temperature [5].

## IV. Conclusions

In summary, polycrystalline samples of Y-type hexaferrite BSZFAO were synthesized by the conventional solid-state reaction method in atmosphere. The structural, magnetic and dielectric properties of the samples were investigated. Hexagonal shape grains can be observed. The magnetic measurement suggests four magnetic spin-order structures exist in BSZFAO samples. The variation of the $\varepsilon'$ and the tan$\delta$ as the function of frequency was discussed by Maxwell-Wagner interfacial relaxation involved grain/grain boundaries or sample/electrodes.



## Funding

The work was supported by Natural Science Foundation of China (Grant Nos. 61176011, 61376129, and 51302084), Natural Science Foundation of Shanghai (Nos. 11ZR1410800 and 13ZR1412200), KLIFMD-2011-06, and Fundamental Research Funds for the Central Universities (ECNU).

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