Study of quasi-monophase Y-type hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powders

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Y-type hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder was synthesized by ultrasonic co-precipitation. The XRD spectrum showed the presence of small amount of a second spinel phase of $ZnFe_2O_4$. The powder exhibited a triple hysteresis loop at room temperature corresponding to the presence of an intermediate magnetic phase between ferromagnetic and proper-screw spin. Magnetic phase transitions in the temperature range of 4.2 K - 300 K were also observed connected to the different spin structure.

Keywords: Y-type hexaferrites, ultrasonic co-precipitation, magnetic phase

INTRODUCTION

Multiferroics are a class of multifunctional materials in which at least two of the ferroic order parameters, including ferroelectricity, ferromagnetism, and ferroelasticity, exist simultaneously. In some multiferroics, where ferroelectricity and ferromagnetism co-exist, one can control the magnetic phase by applying an external electric field, as well as to influence the electric phase by applying an external magnetic field (magneto-electric effect). From the viewpoint of applying multiferroics to multifunctional devices, it is important to be able to control the electric polarization, or the dielectric constant, by means of weak magnetic fields at temperatures close to room temperature. In recent years, there has been increasing interest in M-, Y- and Z-type hexaferrites, because some of them are multiferroic materials at room temperature and have large magneto-electric effect, which is associated with the presence of spinoidal and spiral magnetic structures [1, 2]. The magneto-electric effect in the Y-type hexagonal ferrite $Ba_{1.5}Sr_{0.5}Zn_2Fe_{12}O_{22}$ at room temperature in a low magnetic field of 0.1 T was reported for the first time by Kimura et al. [3]. Chun et al. [4] reported a large magnetoelectric effect in $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$, which occurred at a much lower magnetic field.

The prospects of applications as a multiferroic material prompted extensive studies of the structural, magnetic and ferroelectric properties of single crystals of Y-type hexaferrites [5-8]. However, the properties of powder Y-type hexaferrites have not been sufficiently explored. One of the reasons is that preparing a single-phase sample is very difficult, as is the case with most complex hexaferrites. The process of synthesizing Y-type hexaferrites always involves the presence of various accompanying magnetic oxides, the main cause of this is being the fact that the temperature interval for Y-phase synthesis is very narrow. Typically, the Y-type hexaferrite phase synthesis begins at 900 ^{o}C and ends at 1200 ^{o}C. R. Pullar [9] provided a detailed study on the processes of hexaferrites synthesis. In brief, at the beginning, the preparation of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ is accompanied by the presence of another type of hexaferrite, namely, M-type barium hexaferrite and of small amounts of second phases of barium ferrite, strontium ferrite and zinc ferrite. A Z-type hexaferrite appears at temperatures above 1200 ^{o}C. The type of the second phases present depends to a large extent on the type of the Me^{2+} cations and the preparation technique. On the other hand, the most common method for fabrication of these materials is the ceramic method, which requires multiple annealing and sintering steps.

Here we present a single-step annealing process for the synthesis of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$

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powders by ultrasonic co-precipitation. A study on the powders' structural and magnetic properties is also presented.

EXPERIMENTAL

The $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder was prepared by ultrasonic co-precipitation. Stoichiometric amounts of the corresponding metal nitrates were dissolved in deionized water and, after homogenization, the co-precipitation process was initiated by adding NaOH at pH = 12. High-power ultrasound stirring was applied to assist this process, which, as it is known, enhances the reaction rate, the mass transport and the thermal effects. Ultrasound with amplitude 40% was applied for 15 min, pulse on: 2 s, pulse off: 2 s, by an ultrasonic processor (Sonics, 750 W). The precipitate was separated in a centrifuge, dried and milled. The precursor was calcined at 1170°C for 7 h to obtain the $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder.

The $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder was characterized using X-ray diffraction analysis with Cu-K_α radiation and scanning electron microscopy (Philips ESEM XL30 FEG). The magnetic measurements were carried out at room temperature using a PPMS (Quantum Design) at a maximum magnetic field of 50 kOe. The *ac* magnetization was performed on an Oxford Design susceptometer in an *ac* magnetic field with amplitude 10 Oe and frequency 1 kHz. The sample was first cooled down to 4 K without magnetic field and the *ac* magnetization was measured at increasing temperature up to 300 K.

RESULTS AND DISCUSSIONS

The XRD spectra of the powder showed the characteristic peaks corresponding to the Y-type hexaferrite structure ($Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$) as a main phase and to some $ZnFe_2O_4$ as a second phase (Fig. 1). Unlike preparation of $BaFe_{12}O_{19}$, the $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ cannot be directly obtained due to the complexity of its structure, which imposes progressive transformation through intermediate ferrites before achieving the final structure required. This is the main reason why the second phase of $ZnFe_2O_4$ with a spinel structure is present.

A SEM image of the $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ sample is presented in Fig. 2. The powder consists almost entirely of large hexaferrite-phase particles with a size of about 1 nm and an almost perfect hexagonal shape. We assume that the small particles with a size of less than 200 nm and an irregular shape are of $ZnFe_2O_4$.

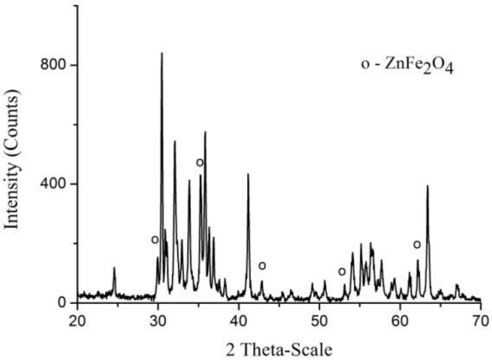

Fig. 1 XRD spectrum of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder.

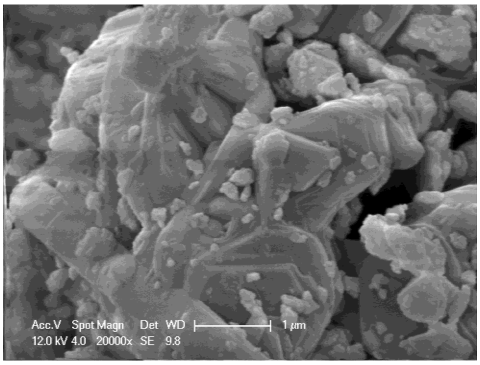

Fig. 2. SEM image of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder.

The hysteresis loops of the powder at room temperature and at 4.2 K are shown in Fig. 3. The $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ sample shows a triple loop at room temperature, which is different from typical ferromagnetic materials. This observation of a triple hysteresis loop in low magnetic fields ranging from 1 to −1 kOe indicates that there are two kinds of ferrimagnetic phases (states) with different magnetization values with H between 50 and −50 kOe. The magnetization loop exhibits a small hysteresis at 4.2 K typical for a conical spin phase. The absence of a triple loop at 4.2 K means that the hysteresis observed at 300 K is due to the presence of two kinds of ferrimagnetic states in the $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ phase. Khanduri et al. [10] had also observed a similar hysteresis loop in $Ba_{2-x}Sr_xMg_2Fe_{12}O_{22}$ when x was greater than 1. In our case, the triple hysteresis loop is due to an intermediate phase between the proper screw spin phase and the collinear ferrimagnetic one at room temperature.

All Y-type hexaferrites have planar anisotropy at room temperature, i.e. they have an easy axis of magnetization lying in a plane normal to the *c*-axis direction. This is the main reason for the low coercivity field of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$.

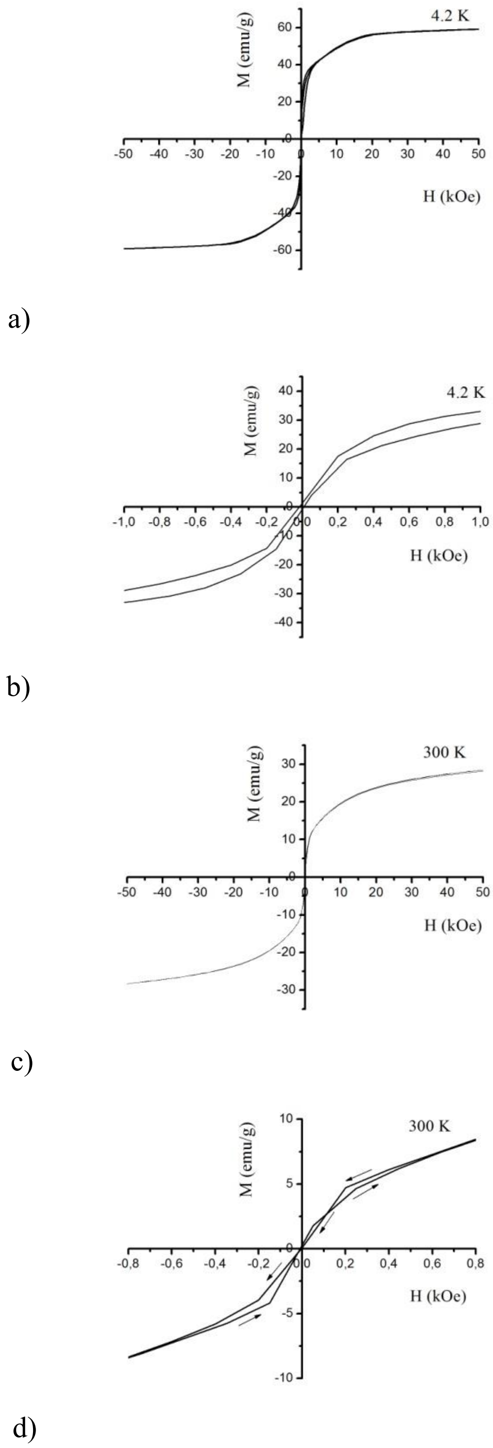

Fig. 3. Magnetization measurements of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder at 4.2 K (a) and 300 K (c); (b) and (d) - expanded view of the hysteresis loops in the low magnetic field range at 4.2 K and 300 K, respectively.

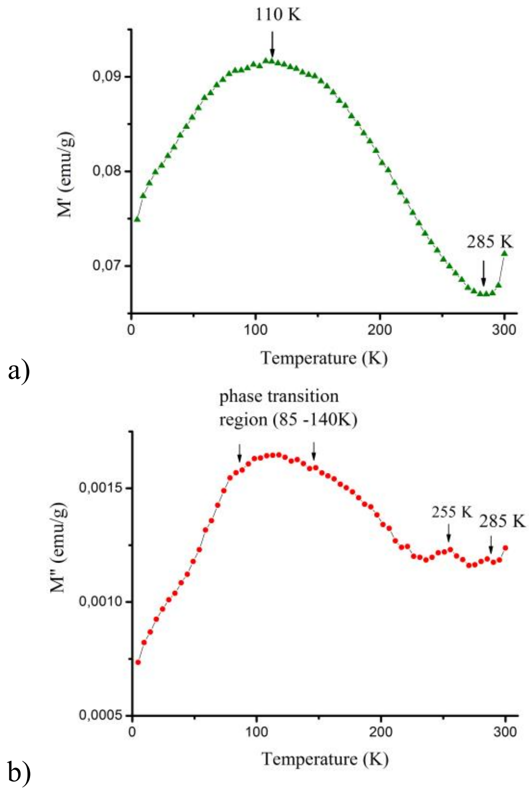

Fig. 4. Temperature dependence of the *ac* differential magnetization of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ in an *ac* magnetic field with amplitude 10 Oe and frequency 1 kHz: a) $M'(T)$ – the real part of the differential magnetization; b) $M''(T)$ – the imaginary part of the differential magnetization.

The magnetic phase transitions were investigated in an *ac* magnetic field. The phase transition temperatures were determined by following the variation of the powder's *ac* differential magnetization as the temperature was raised in an *ac* magnetic field with frequency 1 kHz and amplitude 10 Oe (Fig. 4). The minimum in M' at 285 K and maximum in M'' at the same temperature corresponds to the collinear ferromagnetic to a proper-screw spin phase transition. This phase transition being near 300 K confirms our suggestion that the triple hysteresis loop in Fig. 3 (c, d) is due to the presence of an intermediate magnetic phase between the ferromagnetic and the proper-screw spin. This transition determines the multiferroic properties of $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$. The small maximum in M'' at 255 K is associated with the magnetic order changes from a screw spin to a longitudinal conical spin phase, while the large maximum between 85 K and 140 K is associated with the alternating longitudinal conical phase.

CONCLUSIONS

$Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ powder was synthesized by ultrasonic co-precipitation followed by a single-step sintering at 1170°C. We observed several magnetic phase transitions in the temperature range from 4.2 K to 300 K. The magnetic phase transition from collinear ferromagnetic ordering to proper-screw spin one allows us to assume that $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ is a multiferroic below 285 K. Future studies of the electrical polarization is necessary to confirm the magneto-electric effect in $Ba_{0.5}Sr_{1.5}Zn_2Al_{0.08}Fe_{11.92}O_{22}$ near room temperature.

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