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To cite this article: B Georgieva *et al* 2021 *J. Phys.: Conf. Ser.* **1762** 012034

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Magnetic phase transitions in $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{11.92}\text{Al}_{0.08}\text{O}_{22}$ hexaferrites

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Abstract. We report studies on the effect of substituting the magnetic Fe^{3+} cations with non-magnetic Al^{3+} cations in Y-type hexaferrite $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{11.92}\text{Al}_{0.08}\text{O}_{22}$ powders on their magnetic properties and especially on the magnetic phase transitions responsible for observing the magnetoelectric effect. In this research, the Y-type hexaferrite powders were synthesized by citric acid sol-gel auto-combustion. After the auto-combustion process, the precursor powders were annealed at 1170 °C in air to obtain the Y-type hexaferrite materials. The effects of Al substitution on the structural, microstructural properties and phase content were investigated in detail using X-ray powder diffraction and scanning electron microscopy. Hysteresis measurements were performed by a physical-property-measurement-system (PPMS) (Quantum Design) at 4.2 K and at room temperature. Dc-magnetic measurements of the temperature dependence of the magnetization at magnetic fields of 50 Oe, 100 Oe and 500 Oe were used to determine the effect of applying a magnetic field on the temperature of magnetic-phase transitions. We demonstrated that the helical spin state can be modified further by varying the magnetic field.

1. Introduction

In recent years, there has been a renewed interest in the properties of Y-type hexaferrites due to the presence of a distinct magneto-electric (ME) effect in some of them at elevated temperatures. The ME coupling is of high technological importance because the electrical properties of a material are affected by a magnetic field or, conversely, its magnetic properties can be changed by an electric field. In particular, the electric field control of magnetism is a hot topic as there are many potential applications in magnetic memory storage, sensors, and spintronics [1–6]. Thus, studying the ME effect has become one of the central topics in modern materials science.

An intriguing example is $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, which is a non-ferroelectric helimagnetic insulator in the zero-field ground state, while a sizeable net electric polarization can be induced at room temperature by applying the relatively weak magnetic field of 0.1 T, as reported for the first time by Kimura et al. [7]. Later on, Chun et al. [8] reported observing as well a significant magnetoelectric



effect in the Al-doped material $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2(\text{Fe}_{1-x}\text{Al}_x)_{12}\text{O}_{22}$, $x > 0.08$, at much lower magnetic fields. It was shown that this Y-type hexaferrite has a considerable ME coupling even at room temperature. Thus, the magnetoelectric effect was proved for both the undoped and Al-doped Y-type hexaferrite material $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ as a single crystal. However, preparing a single-phase monocrystalline material of good quality is a highly challenging task, which is the case of most complex hexaferrites. Consequently, regarding the study of the magnetoelectric effect in these materials and its application in practice, the question arises about the use of polycrystalline samples.

The process of synthesizing Y-type hexaferrites as a rule involves the appearance of various accompanying magnetic oxides; the main cause of this is the fact that the temperature interval for Y-phase synthesis is very narrow. Typically, the Y-type hexaferrite phase synthesis begins at 900°C and ends at 1200°C . Pullar [9] provided a detailed study on the stages of hexaferrites' synthesis. In summary, at the beginning of the process, the production of Y-type hexaferrite is accompanied by the presence of another type of hexaferrite, most commonly of the M-type and Z-type. The type of second phases present depends largely on the type of Me^{2+} cations and on the way of preparation.

The most common way of producing hexaferrite materials is the ceramic technique, which comprises a number of annealing and sintering steps; however, in recent years, and in view of in-depth studies of the Y-type hexaferrites properties, some other pathways known as "wet chemistry" have been explored and implemented successfully.

In this study we present details of the structural and magnetic properties of $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ powders obtained by a sol-gel auto-combustion method. Special attention was paid to revealing in the powders the manifestation of the magnetic phase transitions found in single crystals responsible for the observation of the magnetoelectric effect.

2. Experimental

The $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ polycrystalline material was synthesized by citric acid sol-gel auto-combustion. The corresponding metal nitrates were used as starting materials, and a citric acid solution was slowly added to the mixed nitrates as a chelator to form stable complexes with the metal cations. The solution was slowly evaporated to form a gel, which was dehydrated at 120°C , turned into a fluffy mass and burned in a self-propagating combustion manner. The auto-combusted material was annealed at 1170°C in air. The resulting powder material was characterized by X-ray diffraction (XRD) complemented by scanning electron microscopy (SEM) and magnetic measurements.

The XRD measurements were performed using a Bruker D8 Advanced diffractometer (40 kV, 30 mA) controlled by a DIFFRACT^{plus} software in Bragg-Brentano reflection geometry with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). To determine the morphology of the samples, SEM images were taken using the electron microscope system FEI XL30 FEG-ESEM. The magnetic properties were measured by means of a commercial physical-property-measurement-system (PPMS) from Quantum Design equipped with an ACMS option. The hysteresis measurements were conducted at 4.2 K. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization vs. temperature (4.2 – 300 K) measurements were performed at magnetic fields of 50 Oe, 100 Oe and 500 Oe. In the ZFC protocol, the sample under study was cooled from room temperature down to 4.2 K without any magnetic field; the magnetization was measured with the temperature being raised from 4.2 K to 300 K at a heating rate of 3 K/min in the applied magnetic field. The FC curve was recorded on the same sample upon cooling from 300 K to 4.2 K in the same magnetic field.

3. Results and discussion

$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ was obtained as a well-crystallized polycrystalline powder. The room temperature XRD pattern of the final powder material depicts the formation of a well-defined hexagonal phase (figure 1). The very sharp and narrow peaks indicate a high degree of crystallinity and show the characteristic peaks (standard card ICSD-01-079-1409) corresponding to the Y-type hexaferrite structure as the main phase. The refined lattice parameters were found to be 5.85 \AA and 43.46 \AA in the R-3m space group with hexagonal settings. The few extra peaks marked as a minor

phase were identified as belonging to the spinel ZnFe_2O_4 amounting to 2.7 wt% (standard card ICSD-04-006-1956).

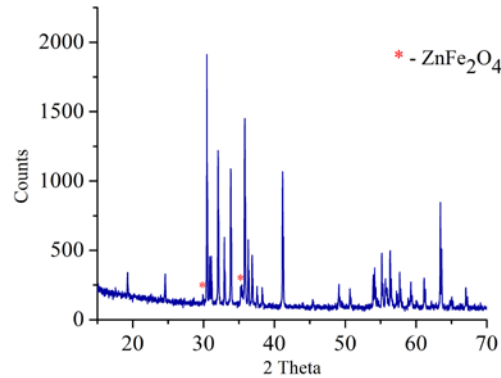


Figure 1. XRD patterns of $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ powder.

The SEM images of the powder material shown in figure 2 demonstrate the well-developed hexagonal shape of the particles of $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$.

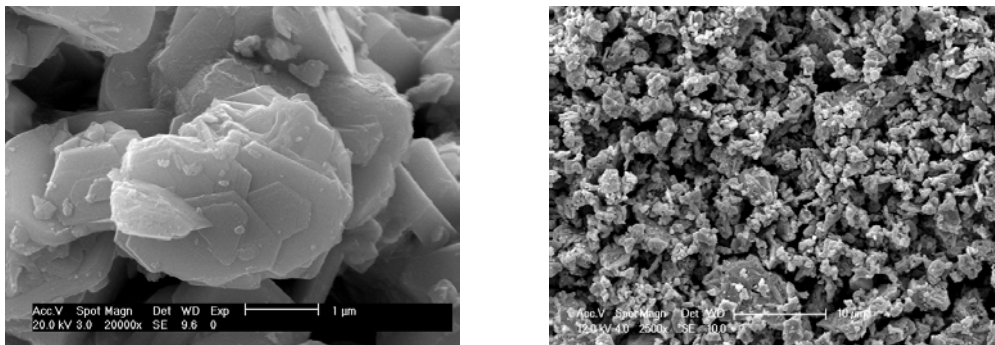


Figure 2. SEM images of $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ powder.

Figure 3 (a), (b) shows the magnetization curves $M(H)$ and figure 3 (c) shows the initial magnetization at 4.2 K and 300 K. The magnetization curve at 4.2 K saturates at a magnetic field H below 50 kOe, while at 300 K no saturation is observed indicating a non-collinear ordering of the magnetic moments. The magnetization values M measured at $H = 50$ kOe were 70 emu/g and 31 emu/g at 4.2 K and 300 K, respectively. A change in the ferromagnetic behavior of the material, as evidenced by the change in the slope of the $M(H)$ curve at 4.2 K, is observed for magnetic field strengths between 5 – 20 kOe. This is due to metamagnetic transitions taking place and to intermediate phases, which can be attributed to conical arrangements of the magnetic moments in the crystal lattice. The magnetization loop exhibits a small hysteresis at 4.2 K typical of a conical spin order phase. The changes in the behavior of the hysteresis loop at 300 K in the low magnetic field range for the $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ sample indicates the presence of two kinds of ferromagnetic states with different magnetic moments order. As it is in the low magnetic field range, it can correspond to the ferrimagnetic spin order and the helical spin order. The values of the coercive field H_c are very low and typical for hexaferrites with planar crystal magnetic anisotropy. It is worth recalling that these structures have an easy plane of magnetization perpendicular to the c -axis, which reduces the applied magnetic field required for ferromagnetic resonance and provides for a perfect material for use at GHz frequencies [8].

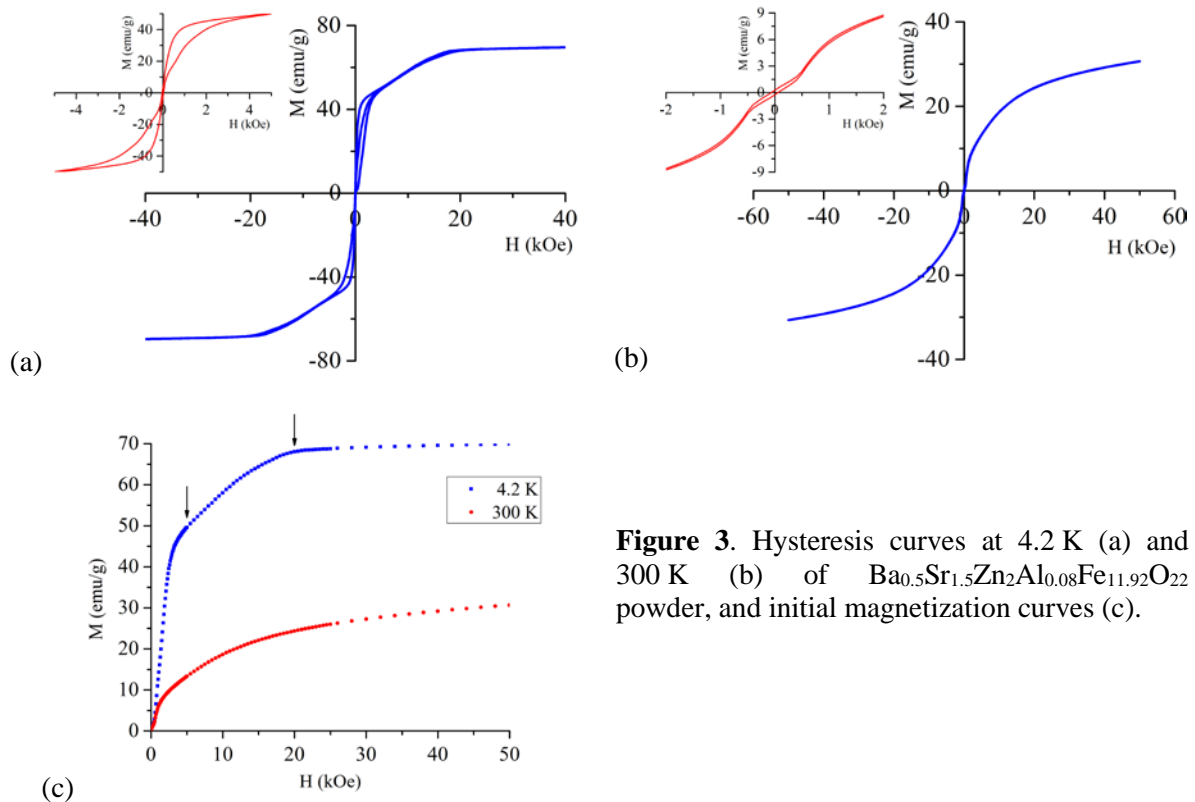


Figure 3. Hysteresis curves at 4.2 K (a) and 300 K (b) of $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ powder, and initial magnetization curves (c).

Figure 4 shows the temperature dependence of the ZFC and FC magnetization curves of the $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ polycrystalline powder material at magnetic fields of 50 Oe, 100 Oe and 500 Oe in the temperature range 4.2 – 300 K. The magnetization curves at 50 Oe and 100 Oe (figure 4 (a), (b)) exhibit a similar behavior in the temperature range 15 – 300 K. The magnetization decreases slowly up to around 285 K and starts to grow as the temperature is raised further above 300 K. A similar behavior was also reported by Khazaradze et al. [10] for a $\text{Ba}_{0.4}\text{Sr}_{1.6}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ single crystal, namely, a sharp peak at 331 K, which the authors associated with a magnetic transition from a collinear ferrimagnetic phase to a proper screw spin phase. The transition temperature to the paramagnetic phase is much higher than room temperature, so this transition could not be observed by us due to equipment limitations. Xu et al. [11] have reported a similar behavior for $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2(\text{Fe}_{0.96}\text{Al}_{0.04})_{12}\text{O}_{22}$ polycrystalline bulk sample obtained by the solid state technique. They showed that the minimum exhibited by the ZFC and FC curves at about 285 K is the onset of the magnetic order changing from a proper-screw spin phase to a collinear ferrimagnetic arrangement as the temperature is raised. Accordingly, a helical spin screw magnetic order can be expected below 285 K in our case. Under a magnetic field of 50 Oe, at low temperatures around 15 K, a magnetic transition occurs from a longitudinal conical spin order to a proper-screw spin order. The behavior of the ZFC and FC magnetization curves under a magnetic field of 500 Oe is quite different from that at low fields (figure 4 (c)). Based on the single-crystal evidence [8], the well-defined maximum at 95 K (ZFC curve) should be considered an indication that a longitudinal conical magnetic spin order sets in below this temperature. Increasing the magnetic field strength from 50 Oe to 500 Oe does not affect the onset temperature of the magnetic order transition from proper-screw to collinear ferrimagnetic one, namely, 285 K

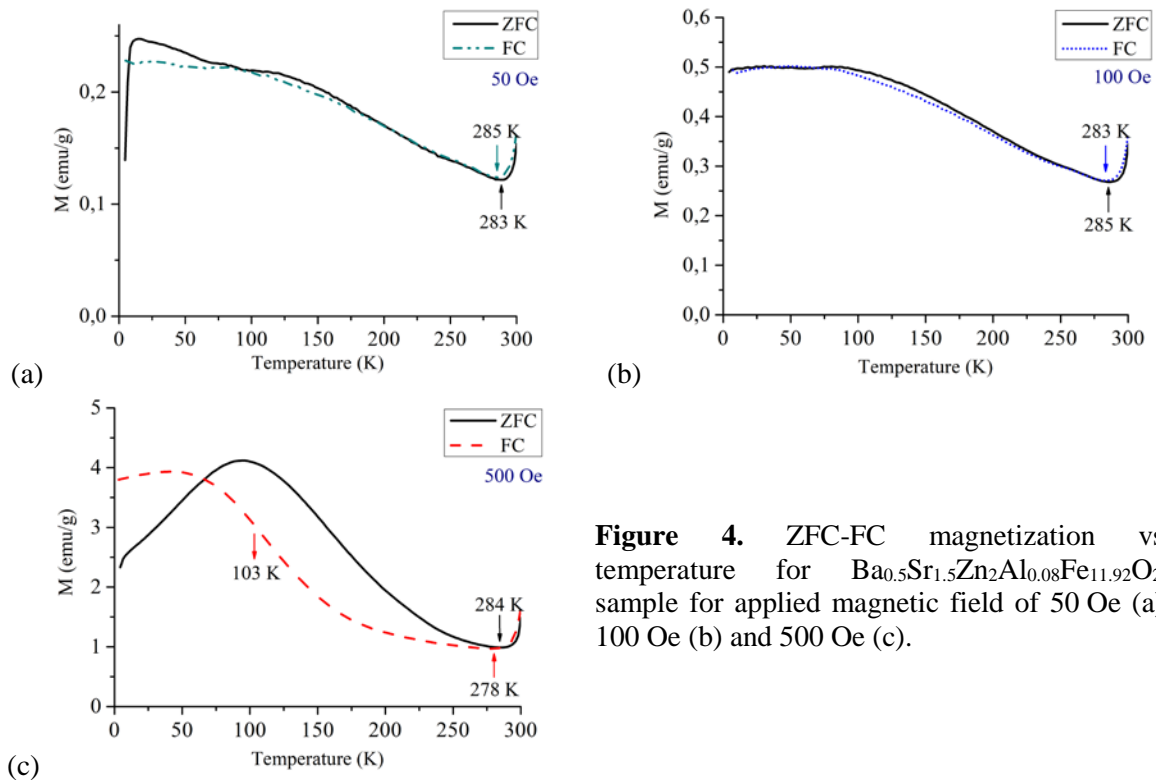


Figure 4. ZFC-FC magnetization vs. temperature for $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ sample for applied magnetic field of 50 Oe (a), 100 Oe (b) and 500 Oe (c).

4. Conclusion

$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Al}_{0.08}\text{Fe}_{11.92}\text{O}_{22}$ powder of high crystallinity was produced by sol-gel auto-combustion followed by thermal annealing. SEM micrographs indicate that the grains tend to have a platelet-like shape. The magnetic measurements show that a magnetic phase transition takes place below 285 K, which is considered as associated with a spin rearrangement to a proper-screw magnetic spin order, as found in the single-crystal hexaferrite with the same composition. Increasing the magnetic field from 50 Oe to 500 Oe does not affect the onset temperature of the magnetic ordering changing from a proper-screw spin order to a collinear ferrimagnetic arrangement. Also, the spin rearrangement below 95 K to a longitudinal conical magnetic spin order becomes observable at the highest magnetic field (500 Oe).

Acknowledgments

B. Georgieva was supported by the Bulgarian Ministry of Education and Science under the National Research Program “Young scientists and postdoctoral students” approved by DCM # 577/17.08.2018. This work was supported in part by a joint research project between the Bulgarian Academy of Sciences and WBI, Belgium, and by a joint research project between the Bulgarian Academy of Sciences and the Institute of Low Temperature and Structure Research, Polish Academy of Sciences.

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