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To cite this article: B Georgieva *et al* 2022 *J. Phys.: Conf. Ser.* **2240** 012023

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## Effect of cation substitutions in Y-type $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ hexaferrites on the magnetic phase transitions

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**Abstract.** We investigated the magnetic properties and magnetic phase transition in Y-type  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  hexaferrite powder prepared by citrate sol-gel spontaneous combustion. The saturation magnetisation value of 32 emu/g at 4.2 K was lowered to 24 emu/g at 300 K. The magnetisation curves did not saturate even at a magnetic field of 50 kOe for both temperatures – 4.2 K and 300 K. A step-like behaviour appeared in the initial magnetisation curve at 4.2 K. A magnetic phase transformation from a spiral magnetic ordering to a conical spin one was observed at 40 K.

### 1. Introduction

The studies of the magnetic properties and, in particular, of the magnetic phase transitions in Y-type hexaferrites during the last decade were provoked by the observation of a distinct magnetoelectric effect close to room temperature. This gave rise to opportunities of broadening the field of Y-type hexaferrites applications: multi-ferroic gyrators, electrical-field-controlled spintronic devices, ac/dc magnetic and electric field sensors in, e.g., biomedicine, power generators, electrical-field-controlled microwave components, e.g., filters and switches for wireless technologies, among many others [1-3]. The magnetoelectric effect in hexaferrites was first observed by T. Kimura et al. [4] in a  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  single crystal in a magnetic field of about 1 T near room temperature, with the effect being significant at  $T < 130$  K [5].  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  is a Y-type hexaferrite ( $\text{A}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ ), with A = Ba or Sr and Me, a divalent cation. It is a dielectric ferromagnetic material with a spiral spin order stabilised beneath its Neel temperature ( $T_N \approx 326$  K); it goes through several thermally-induced magnetic phase transitions [4, 6]. In general, the hexaferrites  $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$  assume a  $R\bar{3}m$  space group structure. The  $\text{Me}^{2+}$  and

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$\text{Fe}^{3+}$  ions are distributed over six distinct crystallographic sites, both tetrahedral and octahedral. The type of these divalent cations and the sites they occupy within the lattice cell can give rise to significant changes in these materials' structural and magnetic properties. Their unit cell comprises three formula units and is constructed by a sequential arrangement of the S and the T-blocks, namely, TST'ST''S'', the primes denoting a  $120^\circ$  rotation around the  $c$ -axis; the easy magnetisation axis is in a plane perpendicular to the  $c$  axis [7]. The magnetic configuration can be presented by L and S blocks lumped alternately in parallel with the [001] axis with oppositely directed large and small magnetisation  $M$ , respectively, thus forming the magnetic sublattice.

The studies on the magnetic properties and magnetoelectric effect have been mainly focused on the  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  hexaferrite and on the effect of substituting Zn with other cations. The results of our previous works [8, 9] on replacing the non-magnetic  $\text{Zn}^{2+}$  with the magnetic  $\text{Ni}^{2+}$  cations in  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2-x}\text{Ni}_x\text{Fe}_{12}\text{O}_{22}$  demonstrated that a half substitution of  $\text{Zn}^{2+}$  with  $\text{Ni}^{2+}$  displaces the helical spin magnetic order to higher temperatures. Also, the electrical polarisation caused by a weak magnetic field in  $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$  has to do with the  $\text{Mg}^{2+}$  cations reducing the magnetic anisotropy [10]. Zhang et al. [11] found an increase of the temperature of transformation from a proper screw spin ordering to a collinear ferrimagnetic spin ordering in  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{22}$  due to the Mg doping. Bearing this in mind, in this paper we present a study on the effect of combining the magnetic  $\text{Ni}^{2+}$  and the non-magnetic  $\text{Mg}^{2+}$  on the magnetic parameters and magnetic-phase transitions in the hexaferrite  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  powder.

## 2. Experimental

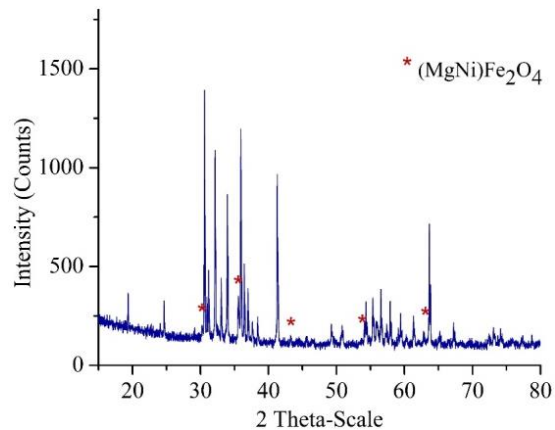
The  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  powder was prepared by citrate sol-gel spontaneous combustion. The procedure started with mixing the respective metal nitrates; solution of citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) was carefully introduced to the mixture as a chelating agent, thus forming a homogenous solution with the metal cations. At  $120^\circ\text{C}$  by slow dehydration, it was converted to a dark brown bulk, which self-ignited afterward and burned. The spontaneously combusted powders were annealed at  $600^\circ\text{C}$ . The precursor powders thus produced were homogenized and retained in an oven at  $1170^\circ\text{C}$  for five hours in air to obtain the material of desired composition  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$ .

The structure and phase content of the sintered powder material were explored by X-ray diffraction (XRD) on a Bruker D8 instrument (40 kV, 30 mA, Cu- $K_\alpha$  radiation,  $1.5418\text{ \AA}$ ) operated by DIFFRACTPLUS software in Bragg-Brentano geometry. The magnetic characteristics were determined by a PPMS magnetometer (Quantum Design). The hysteresis measurements were conducted at 4.2 K and at room temperature. The measurements of the magnetisation-*vs*-temperature dependence (4.2 – 300 K) were carried out by first cooling the sample from 300 K down to 4.2 K with no magnetic field applied (zero-field cooling, ZFC); the magnetisation was then measured as the temperature was raised from 4.2 K to 300 K at a rate of 3 K/min in a 50-Oe magnetic field. The field cooling (FC) plot was registered by cooling the sample from 300 K to 4.2 K in the same magnetic field.

## 3. Result and discussion

The XRD pattern (figure 1) at room temperature of the synthesized  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  powder was indexed successfully in the centrosymmetric  $R\bar{3}m$  space group; it exhibits peaks characteristic of the Y-type hexaferrite structure studied as the major phase. The additional peaks indicate a minor phase amounting to 2.4 wt% and identified as belonging to the spinel  $(\text{MgNi})\text{Fe}_2\text{O}_4$ .

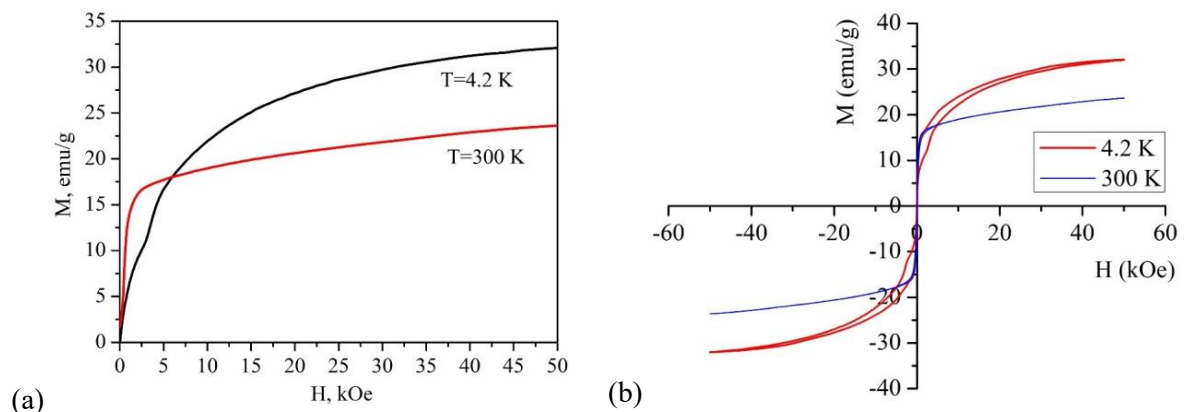
As is known, Y-type hexaferrites are complex oxides, so that a number of obstacles are encountered in attempting to produce single-phase samples. The synthesis of Y-type hexaferrites is commonly accompanied by the formation of different oxides, usually spinels, mainly because the temperature range for synthesising the Y-phase is rather narrow. However, in what concerns the magnetic phase transitions, our previous studies [9, 12, 13] on other Y-hexaferrite compositions have shown that the trace amount of spinel ferrites in the material studied does not affect the magnetic-phase transition temperatures.



**Figure 1.** XRD pattern of  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  powder.

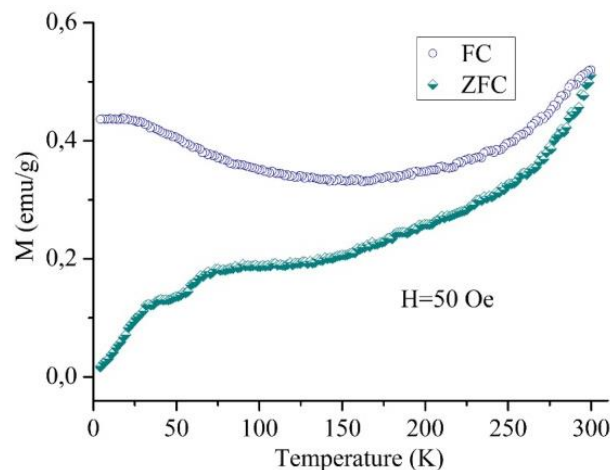
In figure 2, we display the initial magnetisation and the hysteresis curves of the  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  powder at 300 K and 4.2 K. As seen, the magnetisation curves for both temperatures do not reach saturation at the highest magnetic field used of 50 kOe, the highest magnetisation values being 32 emu/g and 24 emu/g respectively at 4.2 K and 300 K. The magnetisation values determined are typical for Y-type hexaferrites. At 300 K, the magnetisation grows sharply up to  $H \approx 1$  kOe, then adheres to the behaviour typical for ferrimagnetic compounds. A stepwise behaviour is seen in the initial magnetisation plot at 4.2 K. Analogous behaviour has been described for a  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Ni}_2\text{Fe}_{12}\text{O}_{22}$  single crystal at 20 K, as well as for other Y-type hexagonal ferrites with distinct magnetoelectric coupling, e.g.,  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Co}_2\text{Fe}_{12}\text{O}_{22}$  [14]; it points to transformations taking place between various magnetic orders effected by the magnetic field [14, 15]. Such a behaviour is usually associated with a spiral magnetic order and the presence of metamagnetic or intermediate phases [16]. In our case, three different magnetic phases are present depending of the applied magnetic field. The first one appears up to a magnetic field of 2.6 kOe; the second magnetic phase exists in the range 2.6 – 3.5 kOe. The magnetisation curves have a typical ferromagnetic behaviour for magnetic field values higher than 3.5 kOe.

The hysteresis curve at 300 K is very narrow with a coercive field  $H_c$  of 35 Oe. This value is representative for hexaferrites with a planar magneto-crystalline anisotropy. The  $H_c$  value is 44 Oe at 4.2 K. The remanent magnetisation is very low. The hysteresis curve behaviour at 4.2 K is similar to that of  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{22}$  [11] pointing to the existence of two orderings both of ferrimagnetic type with differing magnetisation values.



**Figure 2.** Magnetic field dependence of the initial magnetisation (a) and hysteresis curves (b) at 4.2 K and 300 K.

Figure 3 presents the ZFC and FC magnetisation plots of the  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  powder in a 50-Oe magnetic field as depending on the temperature in the 4.2 – 300 K range. The data presented in the figure bear some comment: In both bulk and nanostructured ferrites of the system  $\text{Mg}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ , the reduction of the saturation magnetisation and magnetisation with the increasing magnesium content has been convincingly evidenced. According to literature data [17] and our previous studies [18], no magnetic phase transitions take place at low temperatures (e.g. below 100 K for  $x = 0$ ) in these spinel ferrites. Moreover, in the ZFC and FC magnetisation graphs presented here, no behaviour is seen characteristic of a blocking temperature, as is commonly the case in spinel ferrites. Consequently, no contribution of the spinel phase (about 2.4 wt%) could be clearly distinguished in the material's magnetic response. The FC magnetisation curve begins decreasing gradually at a temperature of about 38 K, but around 150 K the trend changes to a smooth increase. Conversely, the ZFC magnetisation clearly increases as the temperature is raised. The maximum observed at 70 K is related to the intermediate magnetic phase transition. Another maximum at 40 K is also seen – it arises from the magnetic phase transformation from a spiral magnetic order to a conical spin order at low temperatures. Such a maximum was not observed in our earlier study on the  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{ZnNiFe}_{12}\text{O}_{22}$  powder [9]; this indicates that replacing the  $\text{Zn}^{2+}$  ionic species with the smaller  $\text{Mg}^{2+}$  cations [19] leads to important changes in the paths of magnetic interactions leading to a conical spin structure arising at low temperatures. The ZFC and FC curves showing a stable magnetisation growth at temperatures approaching 300 K means that the temperature of transformation to a paramagnetic state exceeds this temperature, so that this transition could not be registered in the experiments reported here. In accordance with Hiraoka's works [14, 15] for  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Ni}_2\text{Fe}_{12}\text{O}_{22}$ , one might expect that the transition from a screw-type magnetic ordering to a ferrimagnetic state above room temperature should take place via consecutive magnetic field-caused (metamagnetic) transformations related to the development of magnetic structures having to do with the magnetoelectric effect.



**Figure 3.** ZFC- and FC-magnetisation vs temperature of  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{MgNiFe}_{12}\text{O}_{22}$  powder in a 50-Oe magnetic field.

#### 4. Conclusions

$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{NiMgFe}_{12}\text{O}_{22}$  polycrystalline powder was prepared by citrate sol-gel spontaneous combustion. The magnetisation loop taken at 4.2 K showed a behaviour pointing to the existence of two types of ferromagnetic orderings with differing magnetisation values. The transition to conical spin order at 40 K in a magnetic field of 50 Oe is known to bring about the appearance of strong magnetoelectric correlation. The combination of the magnetic  $\text{Ni}^{2+}$  and the non-magnetic  $\text{Mg}^{2+}$  instead of  $\text{Zn}^{2+}$  in  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  shifts the transition temperature from a screw magnetic state to a ferrimagnetic arrangement at temperatures exceeding 300 K.

### Acknowledgements

This study is financed by the BNSF, contract KP-06-N48/5 "Multifunctional composite structures based on ferrites (including magnetoelectrics) and carbon materials". B. Georgieva would like to acknowledge the assistance of the Bulgarian Ministry of Education and Science under the National Research Program "Young scientists and postdoctoral students" approved by DCM # 577/17.08.2018. The research is carried out in the framework of a joint project between the Bulgarian Academy of Sciences and WBI, Belgium, and a joint project between the Bulgarian Academy of Sciences and W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences.

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