MULTIFERROICS - PREPARATION METHOD AND PHYSICAL PROPERTIES

Svetoslav Kolev[1,2], Tatyana Koutzarova[1], Borislava Georgieva[1],
Todor Cholakov[2], Lan Maria Tran[3], Michal Babij[3]

[1]*Institute of Electronics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, Sofia 1784, Bulgaria, svet_kolev@swu.bg (S.K.); tatyana_koutzarova@yahoo.com (T.K.); b.georgiewa@abv.bg (B.G.).*
[2]*Neofit Rilski South - Western University, 66 Ivan Mihailov St. Blagoevgrad 2700, Bulgaria, svet_kolev@swu.bg (S.K.); ton4eto64@swu.bg (T.C.).*
[3]*Institute of Low Temperature and Structure Research Polish Academy of Sciences, Ul. Okólna 2, 50 - 422 Wroclaw Poland, l.m.tran@intibs.pl (L.M.T.); m.babij@intibs.pl (M.B.).*

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ABSTRACT

Polycrystalline $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_1O_{22}$ powder materials were synthesized by modified citric acid - assisted sol - gel auto - combustion method. To enhance its crystallinity and phase purity, the material was sintered at 1190°C in air for five hours under ambient atmospheric conditions. The structural and magnetic properties of the prepared samples were evaluated by various techniques in view of understanding the correlations between their functional properties and crystal structure. Further, the magnetic measurement performed showed a decrease in the blocking temperature when the strength of the external magnetic field was increased. Such behavior indicates the presence of a spin - frozen or a spin - glass - like state, which we observed for the first time in this type of composite samples.

Keywords: *multiferroics, magnetic properties, preparation method, nanoparticles, low temperature measurement.*

INTRODUCTION

The Y - type hexaferrites have received a great deal of attention after the discovery of the magnetoelectric phenomena and ferroelectricity [1]. $(Ba,Sr)_2Me_2Fe_{12}O_{22}$ is the typical formula for Y - type hexaferrites [2], where Me can be nickel (Ni^{2+}), cobalt (Co^{2+}), iron (Fe^{2+}) and zinc (Zn^{2+}), etc. [3]. The Y - type hexaferrites contain a hexagonal barium M - type ferrite hexagonal phase with a space group of R - 3m [4] and a unit cell comprising three T - blocks and three S - blocks [4], together with the fundamental components of the cubic type of spinel ferrites [5]. Despite this complicated structure, they maintain a hexagonal form parallel to the c - axis [6]. The researchers' interest to studying them has been raised due to their properties allowing potential uses in various fields, including electromagnetism, ferroelectricity, hyperthermia, dye photodegradation, and in magnetoelectric equipment [7]. These ferrites can be produced in many ways, with the specific techniques used significantly impacting the material's characteristics. For example, the classical ceramic technique is a high - temperature solid - phase approach. Additionally, a sol - gel technique can be employed, which is a wet chemical technique that makes it possible to create samples with excellent purity. Also, the Y - type hexaferrites can be prepared by annealing at significantly reduced temperatures (900 - 1100°C) compared to other hexaferrites [4]. In this study, we used a modified citric acid - assisted sol - gel auto - combustion method to synthesize polycrystalline $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_1O_{22}$ powder materials.

EXPERIMENTAL

A modified citric acid - assisted sol - gel auto -

combustion method was employed to synthesize polycrystalline $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_{1}O_{22}$ powder materials. Stoichiometric amounts of high - purity metal nitrates were used as precursors, while an aqueous citric acid solution served as both a chelating agent and combustion fuel, facilitating the formation of stable metal - citrate complexes and ensuring homogeneous cation distribution. Following gelation and dehydration at 120°C, the material underwent a self - propagating combustion reaction. The resulting combusted precursor powder was homogenized and subjected to a multi - stage thermal treatment in a Carbolite tube furnace. Initial calcination at 800°C for 3.5 h promoted the removal of residual organic constituents. Crystallization and phase development were subsequently initiated through annealing at 1170°C [8], leading to the formation of the desired Y - type hexaferrite phase. Finally, to enhance the crystallinity and phase purity, the material was sintered at 1190°C in air for five hours under ambient atmospheric conditions.

The structural and magnetic properties of the synthesized powders were investigated using X - ray diffraction (XRD) and magnetization measurements; XRD analysis was performed to identify crystallographic phases and evaluate structural purity; and magnetic measurements provided insight into the material's magnetic behaviour. Magnetic hysteresis loops were recorded at 4.2 K. Additionally, the magnetization's temperature dependence was studied under an applied magnetic field using zero - field - cooled (ZFC) and field - cooled (FC) protocols in the temperature range of 4.2 K to 300 K.

RESULTS AND DISCUSSION

Due to the thermodynamic complexity and narrow stability range of the Y - type hexaferrite phase, its synthesis is frequently accompanied by the formation of secondary magnetic phases.

The XRD pattern of the $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_{1}O_{22}$ powders, recorded at room temperature and shown in Fig. 1, reveals diffraction peaks consistent with a hexagonal Y - type hexaferrite structure. These peaks correspond to the centrosymmetric R-3m space group, confirming the successful synthesis of the intended phase. However, the presence of low - intensity reflections attributed to a secondary spinel phase, $NiFe_2O_4$, was also detected. Quantitative analysis estimated the content of this secondary phase to be approximately 5 wt.%.

Fig. 2 provides the initial magnetization and hysteresis curves of $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_{1}O_{22}$ powder measured at 4.2 K. The material exhibits soft magnetic behaviour, which is attributed to its planar magnetic anisotropy. At applied magnetic fields above 50 kOe, the magnetization approaches saturation, reaching a value of 34.5 emu g^{-1}.

Temperature - dependent magnetization measurements under ZFC and FC were performed to investigate the magnetic properties of the prepared $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_{1}O_{22}$ hexaferrite powders. Fig. 3 presents the corresponding M-T curves measured at applied magnetic fields of 50 Oe (a), 100 Oe (b) and 500 Oe (c) over the temperature range of 4.2 - 300 K. In the case of the ZFC protocol, the sample was initially cooled to 4.2 K in the absence of an external magnetic field. Subsequently, a magnetic field was applied, and the magnetization was recorded during the warming process up to 300 K. In contrast, the cooling process of the FC measurement was carried out under an applied magnetic field.

As can be seen, all M-T curves present a clear irreversibility, namely, at a particular temperature (the irreversibility temperature, T_{irr}), the ZFC/FC curves split. The irreversibility temperature T_{irr} (where $M_{ZFC} = M_{FC}$) is approximately 120 K at 50 Oe and decreases to around 110 K and 100 K at applied fields of 100 Oe

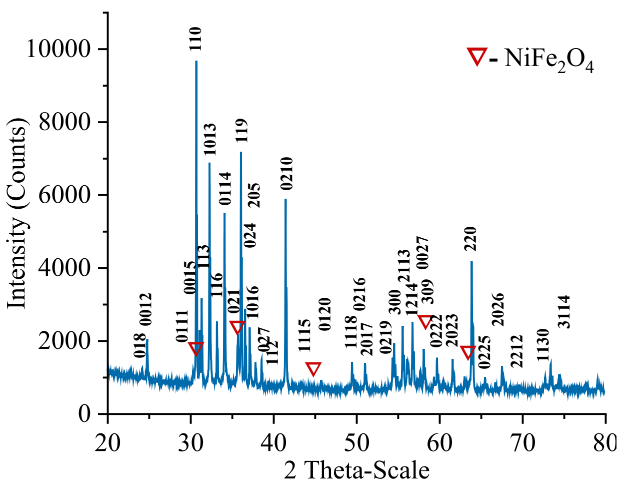

Fig. 1. XRD patterns of $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_{1}O_{22}$ powder.

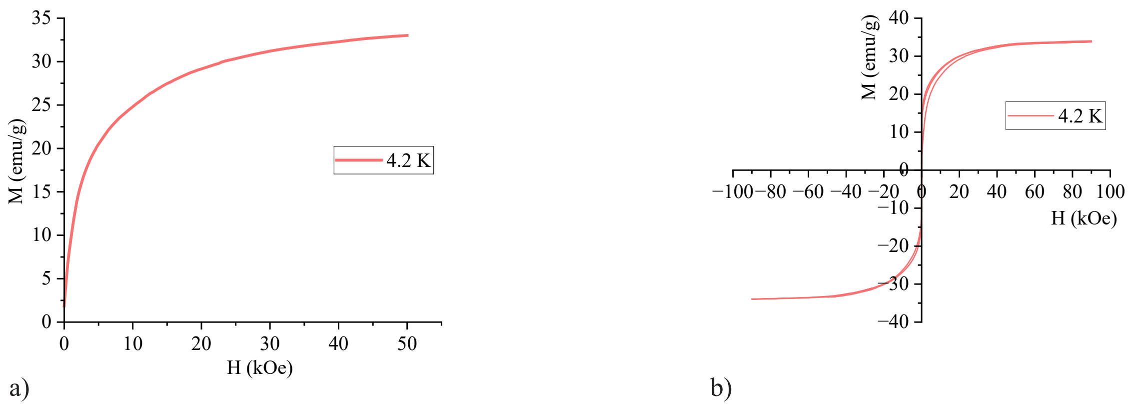

Fig. 2. Initial magnetization (a) and hysteresis curve (b) of $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_1O_{22}$ powder at 4.2 K.

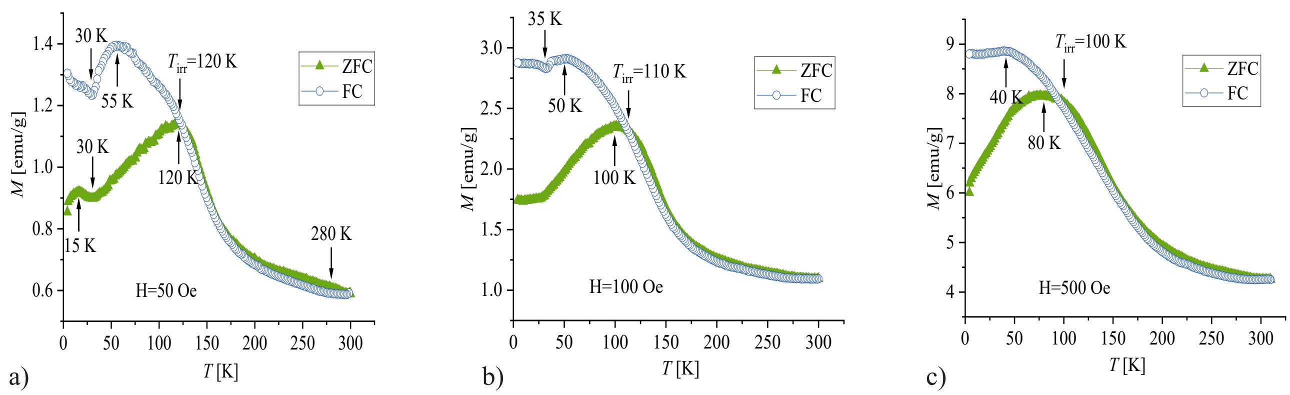

Fig. 3. ZFC - and FC - magnetization *vs* temperature of $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_1O_{22}$ powder under magnetic fields of 50 Oe (a), 100 Oe (b) and 500 Oe (c).

and 500 Oe, respectively. Such behaviour indicates the presence of a spin - frozen or a spin - glass - like state, which becomes progressively suppressed under higher magnetic fields. [9, 10].

CONCLUSIONS

In conclusion, polycrystalline $Ba_{0.5}Sr_{1.5}MgNiFe_{11}Al_1O_{22}$ powder materials were synthesized using a modified citric acid - assisted sol - gel auto - combustion. The structural analysis performed indicated the presence of a minor secondary phase. The magnetic measurements revealed a pronounced irreversibility between the ZFC and FC magnetization curves, as well as two distinct anomalies in the ZFC branch around 40 K and 130 K. The low - temperature transition is attributed to the formation of a spin - glass - like state. These findings contribute to the more comprehensive understanding of the magnetic behavior of Y - type hexaferrite materials.

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Authors' contributions

Conceptualization, S.K. and T.K.; formal analysis, T.K., S.K., B.G., L.M.T., M.B. and A.Z.; funding acquisition, T.K., B.G.; investigation, T.K., S.K., B.G., L.M.T. and M.B.; methodology, T.K. and B.G.; resources, T.K., S.K., B.G., L.M.T., M.B.; supervision, S.K. and T.K.; validation, T.K., S.K., B.G., L.M.T., M.B. and T.Ch.; visualization, S.K. and B.G.; writing – original draft, S.K., B.G. and T.K. All authors have read and agreed to the published version of the manuscript.

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