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Effect of Ni and Al substitution on the magnetic properties of Y-type hexaferrite Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$ powders

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Abstract. The effect is reported of substituting the non-magnetic Zn$^{2+}$ cations with magnetic Ni$^{2+}$ cations, and of the magnetic Fe$^{3+}$ cations with non-magnetic Al$^{3+}$ cations in Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$ on the resulting magnetic properties. The Y-type hexaferrite powders were synthesized by citric acid sol-gel auto-combustion, followed by appropriate thermal annealing. The saturation magnetization values ($M_s$) in a magnetic field of 50 kOe were 36 emu/g and 30 emu/g at 4.2 K and 300 K, respectively. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization vs. temperature (4.2 – 300 K) were measured in dc magnetic fields of 50 Oe, 100 Oe and 500 Oe. The changes resulting from the dissimilar cationic substitutions were identified and discussed.

1. Introduction
The multiferroic materials, which exhibit a simultaneous existence of long-range magnetic and ferroelectric orders, have recently driven significant research interest in the fields of both basic and applied sciences in search of promising materials for development of novel devices and technologies. In particular, the Y-type hexaferrites – A$_2$Me$_2$Fe$_{12}$O$_{22}$, where A = Ba, Sr and Me is a divalent cation, have been the subject of intensive characterization related to studying the magnetoelectric (ME) effect. Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$ is among the most promising Y-type hexaferrites exhibiting ME effect at room temperature. The crystal structure of Y hexaferrites belongs to the rhombohedral space group R(-3m). The unit cell contains three formula units (Z=3). The structure can be considered as consisting of two types of crystal S- and T-blocks consecutively stacked along the hexagonal c axis in the sequence (TST”ST”S”), with the primes indicating rotation about the c-axis by 120 degrees [1]. The hexagonal unit cell is thus made up of three T blocks and three S blocks, containing 18 oxygen layers. There are repeatedly four cubic close packed oxygen layers followed by two barium-containing hexagonal close-
packed layers, forming a close packing sequence. The S-block (Me₂Fe₆O₁₄; spinel block) can be thought of as a double spinel layer. There are six sites for metals, four of them octahedral and two tetrahedral. The T-block (Ba₃Fe₁₄O₃₃) is made up of four oxygen layers, with a barium atom substituting an oxygen atom in the inner two layers, which are opposite one another in the neighboring layers, resulting in two tetrahedral and six octahedral sites [1]. All cations (Me=² and Fe=³) are positioned in six specific crystallographic sites: two tetrahedral sites (6bIV and 6cVI) and four octahedral sites (3aVI, 3bVI, 6eVI, and 18hVI). The Zn²⁺ cations prefer to occupy tetrahedral sites, together with the Fe³⁺ cations [2, 3]. The easy magnetization axis lies in a plane perpendicular to the c-axis direction, while the non-compensated magnetic moment lying in the ab plane arises from dominating majority spins in tetrahedral 3a, 3b, and 18h sites, and minority spins in tetrahedral 6cT and 6cS and octahedral 6c sites [4]. These majority and minority spins determine two magnetic sublattices that are different from the crystal structural blocks, namely, Lₗ (spins in octahedral 3a, 3b, and 18h sites) and Sₗ (spins in tetrahedral 6cT and 6cS and octahedral 6c sites) blocks alternating along [001], which bear, correspondingly, opposite large and small magnetization [5]. Taking into consideration these two sublattices, Lₗ and Sₗ, helps one understand the magnetic structures of Y-type hexaferrites because the strongest magnetic interaction occurs inside the T block. The super exchange interaction across the boundary of the sublattices, Fe(4)-O(2)-Fe(5), can be affected by a proper substitution, e.g. replacing large Ba²⁺ with smaller Sr²⁺ and the Y-type hexaferrite Ba₁₀.₅Sr₁.₅Zn₂Fe₁₂O₃₂ was the first hexaferrite, where ferroelectric polarization was found in a magnetic field-induced metamagnetic phase. Therefore, the T block, which contains the Fe(4)-O(2)-Fe(5) bonds, is essential to bring into being the non-collinear screw structure in the Y-type hexaferrite. It was shown that a small amount of Fe³⁺ substitutions by Al³⁺ lead to observation of ME room temperature effect at a low magnetic field [6]. As the ME effect is connected with the magnetic spin ordering, it is very important to study the influence of cation substitution on the magnetic phase transition temperatures. In our earlier works [7, 8] we showed that the partial substitution of Zn²⁺ by magnetic Ni²⁺ cations can increase the magnetic phase transition temperature.

Here we report studies on the effect of substituting the non-magnetic Zn²⁺ cations with magnetic cations Ni²⁺, and of the magnetic Fe³⁺ cations with non-magnetic Al³⁺ cations in Y-type hexaferrite Ba₁₀.₅Sr₁.₅Zn₂Fe₁₂O₃₂ powders on their magnetic properties and magnetic-phase transitions.

2. Experimental

The Ba₁₀.₅Sr₁.₅Zn₀.₅Ni₁.₅Fe₁₁.ₙ₂Al₀.ₐ₈O₃₂ 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 XRD measurements were carried out using a Brucker D8 Advanced diffractometer (40 kV, 30 mA) controlled by a DIFFRACTplus software in Bragg-Brentano reflection geometry with Cu-Kα radiation (λ = 1.5418 Å). 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 and 300 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.
Results and discussion

The Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$ was obtained as a well-crystallized polycrystalline powder. The room temperature XRD pattern of the final powder material reveals the formation of a well-defined hexagonal phase (figure 1).

![Figure 1. XRD patterns of Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$ powder.](image)

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.

Figure 2 presents the initial magnetization and the hysteresis loops of the powder material at 4.2 K and 300 K. At high magnetic fields, the magnetization almost reaches saturation. The values of $M_s$ in a magnetic field $H$ of 50 kOe were 36 emu/g and 30 emu/g at 4.2 K and 300 K, respectively. These values are lower than those of the polycrystalline Ba$_{0.5}$Sr$_{1.5}$Zn$_{2}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$ material. This should be related to the known preference of the non-magnetic Zn$^{2+}$ cations to occupy tetrahedral positions, whereas the magnetic Ni$^{2+}$ cations prefer to enter octahedral positions [8]. This entails the migration of iron cations between crystallographic sites with octahedral and tetrahedral oxygen configuration and is accompanied by a corresponding change in the magnetic structure. The magnetization loop exhibits a small hysteresis at 4.2 K typical of a conical spin order phase; the coercive field $H_c$ is 30 Oe. In the range −50 Oe to +50 Oe at 300 K the hysteresis curves behave like superparamagnetic ones—the remanence magnetization and coercive field values are zero. However, at a sufficiently higher magnetic field, the hysteresis effect becomes clear in the course of the magnetization. Similar behavior was observed for the first time in the hexaferrite Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$. [9].

![Figure 2. Hysteresis curves at 4.2 K (a) and 300 K (b) of Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$ powder.](image)
Figure 3 shows the temperature course of the ZFC and FC magnetization curves of \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{0.5}\text{Ni}_{1.5}\text{Fe}_{11.92}\text{Al}_{0.08}\text{O}_{22} \) polycrystalline material at magnetic fields of 50 Oe, 100 Oe, and 500 Oe in the temperature range 4.2 K – 300 K. Evidently, the external magnetic field provokes substantial spin rearrangements leading to a changed magnetic response and a corresponding shift of associated temperature points.

Figure 4 shows the temperature dependence of the ZFC and FC magnetization of \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2}\text{Fe}_{12}\text{O}_{22} \) with a single cationic substitution of either Zn or Fe, i.e., \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{0.5}\text{Ni}_{1.5}\text{Fe}_{12}\text{O}_{22} \) and \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2}\text{Fe}_{11.92}\text{Al}_{0.08}\text{O}_{22} \).

As can be seen, the effect of Ni\(^{2+}\) substitution for Zn\(^{2+}\) on the behavior of magnetization is much more pronounced than that of the Fe\(^{3+}\) substitution with Al\(^{3+}\). The magnetization increases gradually to about 250 K, and then as the temperature rises to 300 K, its increase becomes very steep. A similar behavior was observed for \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_{2}\text{Fe}_{12}\text{O}_{22} \) [7]. By analogy with \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}\text{NiFe}_{12}\text{O}_{22} \) and \( \text{Ba}_{0.5}\text{Sr}_{1.5}\text{Ni}_{2}\text{Fe}_{12}\text{O}_{22} \), it might be inferred that a helical spin arrangement has set below 260 K for
Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$. This temperature is higher than that of Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$O$_{22}$ without partial diamagnetic substitution of iron. Compared with Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$, no transition from a conical spin order to a spiral spin arrangement was observed in Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$.

The behavior of ZFC-FC curves in the temperature range 260 – 300 K indicates that the magnetic order adopts the so-called intermediate phase. The transition temperature to the paramagnetic phase is much higher than room temperature, so this magnetic transition could not be observed. It can be expected that the transformation from the proper screw magnetic ordered state to the ferrimagnetic arrangement above room temperature becomes through successive metamagnetic transitions, with the evolution of the magnetic structures associated with the magnetoelectric effect according to the findings of Hiraoka et al. [11, 12] for single crystal Ba$_{0.5}$Sr$_{1.5}$Ni$_3$Fe$_{15}$O$_{22}$.

3. Conclusion

Single-phase Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{11.92}$Al$_{0.08}$O$_{22}$ polycrystalline material was obtained by citric acid sol-gel auto-combustion. The partial replacement of iron with Al$^{3+}$ leads to dilute magnetic exchange interactions and contributes to intricate changes in the magnetic response both to the temperature and an external magnetic field in comparison with the referent Ba$_{0.5}$Sr$_{1.5}$Zn$_{0.5}$Ni$_{1.5}$Fe$_{12}$O$_{22}$ hexaferrite. The Al$^{3+}$ substitution raises above 260 K the temperature of the frustrated arrangement of the complex spin system toward the intermediate phase and might also increase the transition temperature of the helical spin order to the ferrimagnetic spin alignment to a higher than room temperature.

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