BiFeO₃: A Review on Synthesis, Doping and Crystal Structure

Abstract

BiFeO₃, the paradigm of single-phase multiferroic materials, has potential applications in information storage, sensors and actuators. This perovskite has a rhombohedral R3c crystallographic structure and shows a spin-modulated cycloidal magnetic structure with a modulation period of ~62 nm. It reveals magnetoelectric coupling at room temperature. However, its low remanent magnetization and relatively important leakage current are the main limitations for possible applications. In this review we summarize recent studies on doped BiFeO₃. Special attention is put on obtaining and sintering bulk BiFeO₃ ceramics and the effect of doping on the electric and magnetic properties.

Keywords: BiFeO₃; magnetoelectric; multiferroic; synthesis.

Introduction

BiFeO₃ receives noticeable attention due to its potential applications (spintronics, data storage microelectronics, etc.) as well as due to the fascinating physics behind its properties. BiFeO₃ has a rhombohedral distorted perovskite structure with space group R3c. Its ferroelectric order (T_C ~ 830°C) originates from the sterochemical activity of the Bi³⁺ lone electron pair [1]. The magnetic structure of BiFeO₃ is of G-type antiferromagnetism below T_N = 370°C, with a modulated cycloidal spin structure having a long periodicity of 62 nm [2]. Ferroelectricity, with a giant remanent polarization of 2P_r ~ 136 μC · cm⁻² has been observed in BiFeO₃ thin films grown by pulsed laser
deposition [3] and as large as $2P_r \sim 197.1 \, \mu\text{C} \cdot \text{cm}^{-2}$ in films grown by off-axis radio-frequency magnetron sputtering [4].

As for BiFeO$_3$ bulk ceramics, single-phase perovskite is difficult to synthesize. The kinetics of phase formation most frequently leads to impurity phases, such as Bi$_2$Fe$_4$O$_9$, Bi$_2$O$_3$, and Bi$_{25}$FeO$_{39}$ [5, 6]. Nitric acid leaching is applied to eliminate the impurity phases after the calcination of mixed bismuth and iron oxides. In bulk samples, leakage problems make the observation of intrinsic saturated ferroelectric hysteresis loops difficult. Leakage in BiFeO$_3$ ceramics is likely induced by the existence of Fe$^{2+}$ and oxygen vacancies, and both are also detrimental for the intrinsic magnetic properties.

![Figure 1. A diagram showing the preparation techniques used for BiFeO$_3$, each of which is discussed in this review.](image)

Perovskite-type oxides are traditionally prepared through the solid-state reaction of single oxides at high temperature or by mechanical activation at lower temperatures [7].

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Recently, wet chemical methods [8] have received abundant attention. Typical techniques in this family are: a) sol gel, which includes metal complex [9], glycol reaction [10], Pechini method [11] and polymeric precursor [12]; b) hydrothermal [13]; c) sonochemical [14]; d) co-precipitation [8] and e) combustion synthesis [15]. Figure 1 gives a bird’s eye view of the mentioned preparation techniques.

In the literature, we can find useful reviews about BiFeO$_3$ [16, 17]. The focus is often placed on the structure, phase transitions, and the electric, optic and magnetic properties. Bulk ceramic and thin films are considered. In this review, we pay special attention to obtaining and sintering bulk BiFeO$_3$ ceramics and the effect of doping on the electric and magnetic properties.

**Oxide Precursors: Solid State Reaction, Liquid Sintering, and Mechanical Activation**

**Conventional Solid State Reaction:**

The traditional solid-state reaction route for the synthesis of BiFeO$_3$ consists of mixing by milling the appropriate metal oxides or carbonates and then calcinating at high temperature to allow interdiffusion of the cations. The chemical reaction occurs by solid-state diffusion of the ions, which is characterized by a slow kinetic rate. The degrees of mixing and powder particle sizes are of particular importance. The reaction starts at the points of contact between the components Bi$_2$O$_3$ and Fe$_2$O$_3$ and continues successively by ionic interdiffusion through the product phase BiFeO$_3$. The initial reaction is rapid because of short diffusion paths, but further reaction proceeds slower. In many cases, a number of unwanted phases such as Bi$_2$Fe$_4$O$_9$, Bi$_{25}$FeO$_{40}$, Bi$_2$O$_3$, appear.
Once the BiFeO$_3$ phase is obtained, samples are grinded, pressed, and sintered to produce a compact ceramic. This traditional method is widely used. It is relatively inexpensive, simple, and it leads to acceptable results. Some drawbacks that may be identified are poor sintering behavior, non-uniformity of particle size and shape, lack of reproducibility, multiphase character, and loss of stoichiometry (due to volatilization of a Bi$_2$O$_3$ at high temperatures). Regarding doped BiFeO$_3$, a wide spectrum of elements has been added to improve electric and magnetic properties. A low concentration of selected dopants is also considered beneficial from the point of view of avoiding the appearance of secondary phases. Crystal symmetry changes may occur. A survey of pure and doped BiFeO$_3$ variants prepared by solid state method is given in Table 1.

From the dopants reported in Table 1, those which showed the most remarkable increase in magnetic properties are Dy and Ba. Dy, at a concentration of 10%, led to $M_r = 0.12$ emu · g$^{-1}$ in an applied field of 70 kOe [30] and $M_r = 0.15$ emu · g$^{-1}$ in $H = 40$ kOe [31]. Ba, with concentration of 25%, produced $M_r = 0.3$ emu · g$^{-1}$ in a $H = 15$ kOe. Regarding the ferroelectric properties, Eu at 10% is interesting, with $2P_r = 21.96$ μC · cm$^{-2}$.

Rapid Liquid Sintering:

In rapid liquid sintering, the calcination stage is skipped. Initial steps of the process are the same as in the solid state route: high purity Bi$_2$O$_3$ and Fe$_2$O$_3$ powders are weighed in stoichiometric proportions (~1:1 mole ratio), thoroughly mixed in an agate mortar, dried and pressed. The samples are sintered at 880°C for 450 seconds, which is considered a high heating rate and a short sintering period. As the melting point of Bi$_2$O$_3$ is 817°C, the appearance of the liquid phase seems to play an important
role during the synthesizing reaction. The liquid phase accelerates the synthesis, facilitates the sintering, and probably prevents the formation of a second phase. The density of the so-obtained ceramics is high. Table 2 provides a summary of BiFeO$_3$ variants that have been reported in the literature as being obtained by rapid liquid sintering.

Pure BiFeO$_3$ obtained by rapid sintering shows $2P_r = 23.5 \mu$C · cm$^{-2}$. If doped with 20% La, $2P_r$ becomes 19.6 $\mu$C · cm$^{-2}$ [48]. Doping with 12.5% Sm gives $2P_r = 30.18 \mu$C. cm$^{-2}$ [50]. Regarding the magnetic properties, 20% La leads to $M_r = 0.246$ emu · g$^{-1}$ (H = 60 kOe).

Mechanical Activation:

The reactivity of the starting materials can be significantly improved by mechanical activation. This way, calcination can be completed at relatively low temperatures. Maurya et al. reported pure and Sm-doped BiFeO$_3$ [53, 54] obtained by the mechanical activation method. The oxides Bi$_2$O$_3$, Fe$_2$O$_3$, and Sm$_2$O$_3$ were mixed and subsequently milled up to 100 hours in a high energy planetary ball mill. Milling leads to atomic scale mixing of the ingredients, thus forming a homogenous amorphous mixture. In a conventional solid state reaction, BiFeO$_3$ is formed at temperatures above 825°C. With this method, calcination at 700°C produces the BiFeO$_3$ phase. Small amounts of secondary phases are detected. Samples do not show ferroelectric saturated hysteresis loops, probably due to leakage effects. Sm-doped Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ shows higher remnant magnetization and coercive field than un-doped BiFeO$_3$. Freitas and coworkers [55] produced Bi$_{0.95}$Eu$_{0.05}$FeO$_3$ powders. Oxides were mixed for 24 hours and the powders
were annealed at different times at 700°C. In the measured XRD patterns, Eu solid solution in BiFeO₃ and some residual Bi₂O₃ were detected.

Sol-gel:

Metal complex. In the metal complex method, a homogeneous solution is sought as well as a reduction in the motion of metals (Bi, Fe, and dopants). This is achieved by metal-chelating. The most commonly used chelating agents are citric, tartaric, oxalic and malic acids. Once the solvents evaporate, the resulting powder has an amorphous phase. The calcination step allows the release of organics and formation of the desired phase. Table 3 shows the most commonly used solvents and chelating agents in the metal complex method.

Modified Pechini Method. The fundamental idea behind the modified Pechini method is to reduce the mobility of different metal ions, which can be achieved by encircling stable metal-chelate complexes steadily by a growing polymer net. Immobilization of metal-chelate complexes in such a rigid organic polymer net can reduce segregations of particular metals during the decomposition process of the
polymer at high temperatures. The basic chemistry of this process is the dehydration reaction of a carboxylic acid and an alcohol; i.e. esterification. The resulting product of the ester contains one alcoholic hydroxyl group in its left end and one carboxylic acid group in its right end, so that the former can react with another di-carboxylic acid and the latter with another di-alcohol to form a tetramer. This type of reaction occurs in sequence, leading to a polymer molecule. In fact, the original patent for the Pechini process describes the formation of a polymeric resin produced through polyesterification between metal chelate complexes using hydroxycarboxylic acids (citric acid and malic acid) and a polyhydroxy alcohol such as ethylene glycol. Citric acid and ethylene glycol are most widely employed in the Pechini process. Table 4 shows BiFeO$_3$ obtained by Pechini method.

Polymer complex solution (PCS). Unlike the Pechini method, this method does not involve complex polymeric polyesterification reactions. Polyvinyl alcohol (PVA) is one of the most water-soluble polymers used in this method, and it acts as a coordinating organic polymer to cations. This action strongly modifies the rheological characteristics of the initial aqueous precursor solution. Metal ions are capable of playing a role as cross-linking agents between polymers. Random cross-linking across polymer chains entrap the water, allowing the growth of three-dimensional networks, so the system can turn into a gel.
<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Salting agent</th>
<th>( x_{\text{inv}} )</th>
<th>( x_{\text{SPR}} )</th>
<th>Ref</th>
<th>Metal complex powders</th>
<th>( T_{\text{cat}} )</th>
<th>( T_{\text{calc}} )</th>
<th>( T_{\text{start}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiFeO(_3)</td>
<td>( \text{HNO}_{3} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>57</td>
<td>BiFeO(_3)</td>
<td>600</td>
<td>500</td>
<td>580</td>
</tr>
<tr>
<td>BiFeO(_3)</td>
<td>( \text{HNO}<em>{3} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.2</td>
<td>0.2</td>
<td>59</td>
<td>BiFeO(_3)</td>
<td>850</td>
<td>850</td>
<td>850</td>
</tr>
<tr>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>( \text{HNO}<em>{3} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>60</td>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>( \text{H}<em>{2} \text{O} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>61</td>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>150</td>
<td>150</td>
<td>150</td>
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<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>( \text{H}<em>{2} \text{O} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>62</td>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>( \text{H}<em>{2} \text{O} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>63</td>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
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<td>( \text{H}<em>{2} \text{O} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>64</td>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>150</td>
<td>150</td>
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<tr>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>( \text{H}<em>{2} \text{O} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>65</td>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>150</td>
<td>150</td>
<td>150</td>
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<tr>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>( \text{H}<em>{2} \text{O} ), Oxalic acid and ( \text{H}</em>{2} \text{O} ), Oxalic acid</td>
<td>0.1</td>
<td>0.1</td>
<td>66</td>
<td>Bi(_{1-x})La(_x)FeO(_3)</td>
<td>150</td>
<td>150</td>
<td>150</td>
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<tr>
<td>Ceramic</td>
<td>Solvent Cheating Agent</td>
<td>Polymeriser Agt.</td>
<td>$x_{\text{inv}}$</td>
<td>$T_{\text{in}}$</td>
<td>$T_{\text{col}}$</td>
<td>$T_{\text{fin}}$</td>
<td>Secondary phases</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------</td>
<td>------------------</td>
<td>-----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>--------------------</td>
<td></td>
</tr>
<tr>
<td>BiFeO$_3$</td>
<td>H$_2$O, Citric acid, Ethylene glycol</td>
<td>H$_2$O, Ethylene glycol</td>
<td>0.3</td>
<td>120</td>
<td>600</td>
<td>750</td>
<td>Bi$_{2}$Fe$_2$O$_7$ Bi$_2$Fe$<em>3$O$</em>{12}$</td>
<td></td>
</tr>
<tr>
<td>BiFeO$_3$</td>
<td>H$_2$O, Citric acid, Ethylene glycol</td>
<td>H$_2$O, Ethylene glycol</td>
<td>0.25</td>
<td>90</td>
<td>850</td>
<td>1000</td>
<td>Bi$<em>2$(Bi$</em>{1-x}$Fe$_x$)$_2$O$_7$</td>
<td></td>
</tr>
<tr>
<td>BiFeO$_3$</td>
<td>H$_2$O, Citric acid, Ethylene glycol</td>
<td>H$_2$O, Ethylene glycol</td>
<td>0.25</td>
<td>90</td>
<td>850</td>
<td>1000</td>
<td>Bi$<em>2$(Bi$</em>{1-x}$Fe$_x$)$_2$O$_7$</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4**

Modified Pechini method
A promising preparation route has been reported by Liu and coworkers [79]. Pure BiFeO$_3$ powders were synthesized by PCS solution. Bi$_2$O$_3$ was dissolved in HNO$_3$, mixed in 5% PVA (MW = 79000) solution and stirred at the temperature of 70°C. Fe(NO)$_3$$\cdot$9H$_2$O was added to the solution. The xerogel was heated in an oven at 250°C for 2 hours and the precursor was calcined at 400–700°C for 2 hours. The key factor is the molar ratio of metals to hydroxyl groups of PVA (M$^{n+}$/OH). Pure phase BiFEO$_3$ was formed from M$^{n+}$/OH = 2:1 at temperatures from 400°C.

As reported by Jayakumar et al. [80], Bi$_{0.9}$Ba$_{0.1}$FeO$_3$ has been prepared by pyrolysis method from xerogel precursors. Bismuth nitrate pentahydrate, ferric nitrate nonhydrate, and barium nitrate were dissolved along with PVA in distilled water. Acetic acid was added to this solution. The product was dried at 150°C and further heated at 825°C for 2 hours. XRD and selected area electron diffraction show that the so-obtained Bi$_{0.9}$Ba$_{0.1}$FeO$_3$ has a tetragonal structure, and a non-satured ferroelectric hysteresis loop was obtained.

Glycol- gel reaction. Park et al. [67] employed a sol gel methodology in the synthesis of single–crystalline BiFeO$_3$. Bi and Fe nitrates were dissolved in ethylene glycol. The presence of two hydroxyl groups in the molecule makes it easy to keep heterometallic units during the hydrolisis reaction. No second phases were detected. Table 5 shows a survey of results by glycol gel reaction.

Chen et al. [73] used 2-methoxyethanol and acetic acid. The powders were calcined at 450°C and sintered at 800°C by rapid sintering, and then cooled rapidly. Chen et al. report a $2Pr \sim 56 \mu$C/cm$^2$, which is the highest value reported in BiFeO$_3$ ceramics.
Co-precipitation Method:

The co-precipitation process involves the separation of a solid containing various ionic species from a solution phase. An ideal situation is that a quantitative and simultaneous precipitation of all the cations occurs (without segregation of constituents in the precipitates) to form a completely mixed-metal precursor. However, this is a very rare situation in most of the solutions containing more than one metal ion. Homogeneous co-precipitation with respect to metal ions at an atomic level is almost impossible in solution precursor oxides with two or three metal ions. This problem can be reduced by introducing precipitating agents that render the cations insoluble. Chen et al. [81] obtained pure single phase BiFeO₃. Bismuth nitrate and iron nitrate were dissolved in 2N HNO₃, and the solution was slowly dripped into NH₄OH with a PH = 9.5 to co-precipitate the powders. The wash powders were calcined at 450°C for 2 hours, ball milled for 24 hours, and sintered at 800°C.

Hydrothermal Synthesis:

Hydrothermal chemistry has been extensively developed for the synthesis of advanced inorganic materials which are difficult to obtain by high temperature solid state reactions. In particular, hydrated materials are mainly prepared through processes involving such chemistry, since the reactivity increases under high pressure conditions and at moderate temperatures. In using a solvent well-above its boiling point, the solvent is heated in a sealed vessel (autoclave, bomb, etc.), so that the autogenous pressure far exceeds the ambient pressure. This automatically raises the effective boiling point of the solvent. In the special case of the solvent being water, the technique
is often called hydrothermal. See Table 6 for details about fabrication of BiFeO$_3$ by hydrothermal synthesis.

Table 5

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>$x_{inv}$</th>
<th>$T_{Dri}$ °C</th>
<th>$T_{Cal}$ °C</th>
<th>$T_{Sim.}$ °C</th>
<th>$x_{m}$ SPR</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiFe$<em>{0.99}$Co$</em>{0.01}$O$_3$</td>
<td>0.05</td>
<td>80</td>
<td>450</td>
<td>800–900</td>
<td>0.05</td>
<td>68</td>
</tr>
<tr>
<td>BiFe$<em>{0.99}$Zn$</em>{0.01}$O$_3$</td>
<td>0.05</td>
<td>80</td>
<td>450</td>
<td>800–900</td>
<td>0.05</td>
<td>69</td>
</tr>
<tr>
<td>Bi$_{1–x}$D$_x$Fe$_2$O$_5$</td>
<td>0.2</td>
<td>160</td>
<td>400–600</td>
<td>650</td>
<td>&lt; 0.1</td>
<td>70</td>
</tr>
<tr>
<td>Bi$<em>{1–1/3}$Ba$</em>{1/3}$Fe$_2$O$_5$</td>
<td>0.3</td>
<td>160</td>
<td>400–600</td>
<td>650</td>
<td>0.15</td>
<td>71</td>
</tr>
<tr>
<td>Bi$<em>{1–1/3}$Sr$</em>{1/3}$Fe$_2$O$_5$</td>
<td>0.07</td>
<td>80</td>
<td>400–550</td>
<td>650</td>
<td>0.07</td>
<td>72</td>
</tr>
</tbody>
</table>
Microwave Hydrothermal Synthesis:

Single-phase BiFeO₃, without high purity reactants, was obtained by Prado-Gonjal et al. [86]. KOH solution, iron nitrate, and bismuth nitrate were placed in an autoclave. A commercial Milestone ETHOS 1, operating at 2450 MHz, was used at 200°C.

Sonochemical:

Sonochemical rates for homogeneous reactions depend on a variety of experimental parameters such as vapor pressure of precursors, solvent vapor pressure, and ambient gas used. To achieve high sonochemical yields, the precursors should be relatively volatile, because the primary sonochemical reaction site is the vapor inside the cavitating bubbles. In addition, the solvent vapor pressure should be low at the sonication temperature, because significant solvent vapor inside the bubble reduces the bubble collapse efficiency.

An example of this is the preparation of BiFeO₃ [87] particles in the 4–50 nm size range. Powders are prepared in solution under ultrasonic vibration. A mixed aqueous solution of Bi(NO₃)₃ and Fe(NO₃)₂ is sonicated with a power of 1500 W at 20 kHz until the precipitation is complete. A small amount of decalin is used for proper power
transfer and sodium dodecyl sulphate surfactant is also used for preventing agglomeration. The precipitated powder is collected, washed in alcohol, and dried in a vacuum oven at 40°C.

Combustion Method:

The term combustion covers smouldering reactions (heterogeneous), flaming reactions (involving a homogeneous gas phase), and explosive reactions. The rate of combustion determines the nature of reaction, i.e. decomposition, deflagration, or detonation. Synthesis of ceramic oxides is achieved by smouldering and flaming reactions. Table 7 presents results on doped and pure BiFeO$_3$ by combustion methods.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>$x_m$ Inv</th>
<th>Solvent, fuel</th>
<th>$T_{\text{auto combustion}}$</th>
<th>$x_m$ SPR</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiFeO$_3$</td>
<td></td>
<td>H$_2$O, Glycine</td>
<td>202</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>BiFe$_{1-x}$Cr$_x$O$_3$</td>
<td>0.3</td>
<td>H$_2$O, Glycine</td>
<td>$\leq$0.2</td>
<td></td>
<td>89</td>
</tr>
</tbody>
</table>

Conclusions

BiFeO$_3$ synthesis methods were reviewed. Conventional solid state reaction presents more impurities and leaky ferroelectric hysteresis loops. Rapid liquid sintering provides the best ferroelectric hysteresis loops, and this process is limited by the synthesis temperature gap. Wet chemical methods allow for the formation of single-phase samples. Secondary phases may appear in the metal complex method and in the modified Pechini method, depending on the chelating agent used. Agglomeration and conventional sintering result in poor ferroelectric properties, and nano-sintering methods need to be investigated.
Rapid synthesis followed by quenching, even in the sol gel method, has provided the best result in order to obtain a high density and highly electrically resistant ceramic. A small amount of metal doping (either divalent or trivalent) helps in stabilizing the BiFeO₃ phase, as well as in forming a material with improved physical properties. Divalent partial substitution of Bi (by Ca, Sr, Pb, and Ba) in BiFeO₃ resulted in single-phase formation which showed the existence of weak ferromagnetism. Trivalent rare-earth element ions (La, Sm, Pr, Eu, Dy, and Gd) resulted in enhancement of magnetization. Ba has been consistently reported to enhance the remnant magnetism. Other possible candidates that are worth investigating to enhance the remnant magnetization are Dy, La, Eu and Co.

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References


