Comparative analysis of efficient Pb dopant in R and R–S blocks of $\text{BaFe}_{12}\text{O}_{19}$ structure synthesized by co-precipitation method

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Abstract

Site occupancy plays an important role in the properties of the materials in general, and in the case of ferrites, this makes a significant effect. Barium ferrite has a wide range of applications ranging from everyday applications to sophisticated communication technologies. Two compositions $\text{Ba}_{1-x}\text{Pb}_x\text{Fe}_{12}\text{O}_{19}$ and $\text{BaPb}_x\text{Fe}_{12-x}\text{O}_{19}$ ($x = 0.0-1.0$) were synthesized by co-precipitation method using similar synthesis conditions. The aim was to understand the different behaviors when Pb replaced Ba in R and R* blocks in the first composition, while in the second composition it replaced iron in RSR^*S^* blocks. Microstructural and morphological variations in both synthesized compositions because of Pb dopant were responsible for affecting all properties. Higher ionic radius (1.76 Å), lower melting point (950 °C) of lead and gradually increased concentration were responsible for generating stresses and distortions of different magnitudes in both compositions. Magnetic and DC electrical characterizations were investigated by applying similar conditions. Higher phase purity and better morphology are obtained when Ba is replaced by Pb. Strong variation in coercivity due to decrease in anisotropic energy is useful in high-density storage devices. For the other composition, when Fe is replaced by Pb, higher resistivity is obtained. The obtained range of resistivity is useful against eddy current losses in high-frequency devices.

Keywords $\text{BaFe}_{12}\text{O}_{19}$ · Lead dopant · Coercivity · Resistivity · Smart applications

1 Introduction

Barium hexaferrite and strontium hexaferrite after their discovery from 1950s got the attention of researchers. Their applications vary from common life usage to high-level technology like stealth technology. These ferrites have excellent chemical stability and durable properties which make them reliable for long-life applications. These materials also have applications in microwave devices. Common products of M-type materials are magnetic credit cards, bar codes, door catchers and rotors [1, 2]. Crystal-line structure of this material has space group $\text{P6}_3/\text{mmc}$, No. 194 and lattice parameters almost in the ranges of $a = b = 5.90$ Å and $c = 23.30$ Å. M-type material has large magnetocrystalline anisotropy, high Curie temperature

and high magnetization and coercivity [2, 3]. Its high electrical resistivity and coercivity with sufficiently high residual induction allow the researchers to have its usage as permanent magnets with satisfactory specific magnetic energy. Its high resistivity makes this material to be used as magnet in the presence of high-frequency magnetic fields. Their unit cells contain 38O^{2-} anions, 24Fe^{3+} cations and 2Ba^{2+} , 2Sr^{2+} and 2Pb^{2+} cations. High anisotropy energy constant of such materials like Ba-hexaferrite exceeds almost 100 times that of garnet ferrites. The spin orientation of one site, i.e., $4f_1$ and $4f_2$, is down, while that of $2a$, $2b$ and $12k$ is up, which makes it a unique material for many applications. Currently, its smart applications include magnetic recording media, electric motor and absorption of electromagnetic radiation. Such technology is also known

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as stealth technology [1, 4]. Researchers have also reported that these properties can be modified by substitution of magnetic and nonmagnetic elements. For this, substitution like Al, Sc and Ga particularly oxide dopants like B_2O_3 , Si_2O_3 and CaO not only modify the growth and morphology but also induce fascinating properties [5]. These properties are modified due to microstructural variations in lattice parameters, particle growth and their morphology. Replacement and occupancy of divalent and trivalent ions in different crystallographic positions changed not only the strength of valence, interatomic strength and angle but also exchange interactions. Combination of magnetic and electrical properties of M-type ferrites makes their use as spintronics which is a new area or field of microelectronics [6, 7]. Substitution of oxide dopants like PbO and Al_2O_3 is responsible for modifying magnetic properties.

Based on their structures and chemical compositions, barium-based hexaferrites are classified into six main types [8]. In all of these ferrites, Ba can be replaced by Sr, Pb or other elements [9]. According to Gorter's model of a system of collinear spin structure [10], the net magnetic moment per molecule is given by the sum of the magnetic moments of magnetic ions in the molecule. Moreover, the substitution of Fe^{3+} ions with other trivalent cations such as Al^{3+} , Ga^{3+} , Sc^{3+} and In^{3+} is also possible. In this way, we can obtain an extremely large number of compounds with considerably different magnetic properties. This fact makes the hexagonal ferrites attractive for different technical applications and interesting for basic studies on the magnetic interactions in insulators [11]. In the present work, Pb substitution in place of Ba and Fe is responsible for modifying the properties. Iron occupancy status in R and R-S blocks, i.e., K-series, has different impacts in comparison with A-series where Pb replaced Ba ions. For phase purity development, sintering to high temperatures and long duration is required. To save energy and time, researchers use different methodologies like low-melting point dopants and modified synthesis methodology. In presently studied compositions, Pb is used as dopant which has low melting point. Both compositions $Ba_{1-x}Pb_xFe_{12}O_{19}$ and $BaPb_xFe_{12-x}O_{19}$ ($x = 0.0-1.0$) were synthesized through low-temperature co-precipitation method. Their magnetic and DC electrical properties were investigated and are compared here.

2 Experimental procedure

Analytical graded chemicals 99.99% pure were used to synthesize these compositions. These chemicals were $BaCO_3$, $Fe(NO_3)_3 \cdot 9H_2O$ and PbO in solid form. Calculated and measured quantities were dissolved in known quantities of HNO_3 , $DI-H_2O$ and HCl, respectively. All solutions

were formed and mixed together along with fast magnetic stirring at room temperature. For fertilization, $M = 5$, alkaline NaOH solution was used. All synthesis parameters and related conditions used were optimized during different experiments.

The optimized used parameters were $Fe^{3+}/Ba^{2+} = 12$, $pH = 13$ and $M = 5$ for NaOH solution. Washing was done to minimize the impurities. This improved the purity as well as homogeneity. Paste-like material was dried in an oven at 110 ± 2 °C. Water contents were evaporated, and dry crispy material was obtained and transformed into pellets.

2.1 Pellets formation

Pellets were formed by applying suitable hydraulic pressure of 1000 lbs/in² for 5 min. These pellets were sintered at the same temperature, i.e., 965 ± 5 °C, in a box furnace for 3 h. These pellets were used for different characterizations. For identification, samples of $Ba_{1-x}Pb_xFe_{12}O_{19}$ composition were given names as A_0 , A_1 , A_2 , A_3 , A_4 and A_5 and for $BaPb_xFe_{12-x}O_{19}$ K_0 , K_1 , K_2 , K_3 , K_4 and K_5 for $x = 0.0-1.0$. These pellets were used for different characterizations.

3 Structural analysis

For structural analysis, X-ray diffraction (XRD) and scanning electron microscope (SEM) were used. Both samples were exposed to CuK_α ($\lambda = 1.5406$ Å) in the range of $20^\circ-80^\circ$ as shown in indexed graph in Fig. 1. Lead dopant being diamagnetic nature has low melting point—950 °C, and high mobility was responsible for modifying the growth mechanism. Difference in ionic radii and volatile nature ($Ba^{2+} = 1.37$ Å, $Fe^{3+} = 1.76$ Å and $Fe^{3+} = 0.64$ Å) generated stresses and distortions of different strength values which increased as x [12]. As a result, purity decreased. For A-series, i.e., $Ba_{1-x}Pb_xFe_{12}O_{19}$ almost 70% and for K-series, i.e., $BaPb_xFe_{12-x}O_{19}$ 63% purity levels were obtained. The reasons were dopant intrinsic properties, substitution in place of R and R* and in RSR*S* whole blocks. In spite of all these factors, strict control on synthesis techniques improved the purity level.

Growth of particles was affected by dopant as shown in indexed XRD combined graph; growth was affected at large in K-series than in A-series, where main peaks (107) and (114) in $K_{0.0}$ decreased/weakened and new peaks of the same phase (008) and (110) raised/developed in better magnitude in $K_{0.2}$. These peaks were slightly shifted toward smaller 2θ . It resulted in the modification of the crystallite/grain size (D), i.e., enhancement and restriction in terms of growth have been noted. It is shown in the graph in Fig. 2. Detailed discussion about structural growth and morphology has already been published [13]. It has been reported [13] that oxide dopants enhanced the grain growth up

Fig. 1 Indexed XRD graphs of $\text{Ba}_{1-x}\text{Pb}_x\text{Fe}_{12}\text{O}_{19}$ (A-series) and $\text{BaPb}_x\text{Fe}_{12-x}\text{O}_{19}$ (K-series)

to certain limit; after that, it started to restrict it. It was due to nonuniform movements, and substitution of Pb^{2+} ions on different occupancy sites produced stresses and distortions in different magnitudes. Such trend was also observed and reported by Teh and Jefferson. It caused the volume of unit cell to reduce [5, 13]. Grain size (Fig. 2b) in both compositions lies within 50 nm range, so it is useful for recording media and other storage device applications.

Because synthesization was at room temperature, heat generated during different reaction kinetics not in phase as a result of nonuniform growth of grains and phase was noted. The energy minimization equation responsible for the above discussion is given below [5]:

$$E = E_{\text{exchange}} + E_{\text{magnetostatic}} + E_{\text{magnetocrystalline}} + E_{\text{magnetoelastic}} + E_{\text{domain wall}}$$

Because of different crystallographic occupancy positions of different ions within structure, exchange interactions also varied which affected magnetic properties.

3.1 XRD structural parameters

Lattice parameters, volume of unit cell and crystal growth mechanism also have different behaviors as reported [5]. Both compositions confirmed it. So compact and dense structure formed, which modified the magnet properties. It was due to higher density of lead

Fig. 2 Phase purity (a) and grain size variation (b) in both the series

(11.34 g/cm^3) than that of barium (3.51 g/cm^3) and iron (7.87 g/cm^3). The obtained grain size lies almost in 50 nm range. It has made these compositions a useful addition toward magnetic recording media and storage devices applications [14].

Comparison of both graphs showed nonuniform trends in lattice parameters a and c . It was because of higher mobility and nonuniform diffusion of Pb^{2+} ions in different lattice sites of structure. Figure 2 explains this mechanism. Mobility of lead ions was one big reason for modified morphological trends and dimensional grains growth, which strongly affected the properties.

4 Magnetic properties

DC magnetization automatic measurement and analysis device—Riken Denshi Model BHH-15—were used for this analysis. This machine was used at room temperature. Factors like dopant mobility, occupancy preference, anisotropic energy and higher density of lead (11.34 g/cm^3) than barium (3.51 g/cm^3) and iron (7.87 g/cm^3) were important for affecting these properties. Five crystallographic sites in hexagonal structure are 2a, 2b, 12k, $4f_1$ and $4f_2$ which have contribution in defining magnetic properties [12, 13]. Fe^{3+} ions have higher positive contribution from 2b sites, while there were weak contribution from 12k sites and much weak contribution from $4f_1$, $4f_2$ and 2a sites [15, 16].

For A-series, applied field (H) reduced from 13 kOe to 9 kOe. It was because of lower anisotropy energy of $\text{PbFe}_{12}\text{O}_{19}$ (sample A_5) than $\text{BaFe}_{12}\text{O}_{19}$ (sample A_0) [17]. Here, lead replaced barium up to 70%. In K-series, lead replaced iron up to 63%. In both compositions, coercivity decreased. The first reason was the decrease in anisotropy energy of synthesized material due to occupancy of Pb^{2+} ions on such sites ($4f_1$ and 2b) of Fe^{3+} ions [14]. The second was the increase in grain size ($H_c \propto 1/D$), where D is grain size. There is enhancement in grain size up to certain value of x ; after that, size started to reduce. When it restricted, grain boundaries were modified but lead contents were increased which were responsible for variation in coercivity as seen in K-series. In A-series, substitution of lead in place of barium was responsible for the change of c-axis to c-plane which also caused the magnetocrystalline energy to decrease, so coercivity decreased. Another big reason for decrease in coercivity was the hindrance in domain walls motion [14, 15, 17, 18]. Coercivity is shown in Fig. 3a. Decrease in coercivity was a useful parameter for magnetic recording media applications.

Maximum energy product also increased as shown in Fig. 3b. Remanence increased because of the net alignment of grain magnetization due to strong intergrain interactions under the applied field. It caused the maximum energy product to increase [13]. Decrease in coercivity and increase in $(BH)_{\text{max}}$ were the important parameters for any hard magnetic material to define the merit of this material.

In S and R structures, 12k and 2b sites are very much sensitive particularly when 12k site lies on the boundary of S–R blocks. So 12k–2b interaction played a decisive role in changing the ongoing trend in the all properties particularly in magnetic properties. Because of these reasons, B_r and $(BH)_{\text{max}}$ decreased at $x=0.2$ and 1.0, while its trend increased from 0.4 to 0.8 [19, 20]. It is totally different from A-series as shown in Fig. 3.

Fig. 3 Comparative analysis of coercivity (a), maximum energy product of compositions (b) and representative graph of MH and BH loops of A-series for $x=0.2$ (c)

5 DC properties

DC characterizations of both compositions were analyzed as a function of temperature from room temperature to 733 K and 750 K for $\text{Ba}_{1-x}\text{Pb}_x\text{Fe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12-x}\text{Pb}_x\text{O}_{19}$, respectively. The obtained data were further analyzed in terms of resistivity (ρ), activation energy (ΔE) and mobility (μ_d). Different mathematical expressions used in this analysis are shown in [21].

5.1 Resistivity, activation energy and mobility

Conduction mechanism in these materials is based upon hopping mechanism as explained by Verwey hopping

Fig. 4 Resistivity (a) and activation energy (b) of both samples: a comparative analysis

model [22]. It is well known that the complex 3D metal oxides easily allow the oxygen excess and/or deficit. Exchange near the oxygen vacancies is negative according to Goodenough–Kanamori empirical rules. Oxygen vacancies should lead to the formation of a weak magnetic state like a spin glass one [6, 23]. Variation in charge carrier concentration with the change in temperature generates current. Researchers have established that conduction in ferrites is because of generation and hopping of Fe^{2+} ions from one octahedral site to next octahedral sites of structure. Fe^{2+} is generated because of oxidation of Fe^{3+} ions during sintering. Other factors which affected this mechanism are composition, grains morphology, temperature and activation energy. Dopant physical properties like higher mobility, greater ionic radii and occupancy preference along with varying morphology were important [24]. Small variations or fluctuations within compositions were because of moisture, voids, dislocations, impurities and the change in morphology. Graphs in Fig. 4 explain that these factors were dominant in A-series, while they were not much prominent in K-series. Dopant made difficult the generation and hopping of Fe^{2+} ions. Impurity phases, grains boundaries and morphology provided

hindrance to hopping; as a result, conductivity decreased. Lead dopant having higher ionic radii and nonmagnetic nature, occupies octahedral sites. Conduction in ferrites is due to hopping between octahedral sites so it is reduced or modified. Naturally conduction will decrease. To hop, they need energy in the form of activation energy. Lead substitution was also responsible for changing activation energy. Graphs show that Fe^{2+} ions need extra energy to hop. Graph shows that this energy has increased [24].

Useful achievements obtained from both compositions are acceptable range of grain size within ~ 50 nm, smart range of coercivity and maximum energy product and range of resistivity. So they are useful for magnetic media storage devices like credit cards and smart microwave applications.

6 Conclusions

$\text{Ba}_{1-x}\text{Pb}_x\text{Fe}_{12}\text{O}_{19}$ (A-series) and $\text{BaFe}_{12-x}\text{Pb}_x\text{O}_{19}$ (K-series) (for $x = 0.0$ – 1.0) were synthesized by co-precipitation method at room temperature by applying the same conditions. Both series were sintered at 965 ± 5 °C for 3 h. 70% and 63% purity levels were obtained. Diamagnetic dopant properties affected growth and purity in both compositions. Seventy percentage purity was an improvement from the already reported one. In A-series, lead, a nonmagnetic element, replaced nonmagnetic barium in R blocks only up to 70% which was better than the already reported one. Grain size, coercivity, maximum energy product and range of resistivity are useful achievements obtained from both compositions. Acceptable range of grain size within ~ 50 nm, smart range of coercivity and maximum energy product are useful for magnetic recording media applications, smart storage devices like camcorder and related microwave applications. These magnetic parameters along with modified resistivity can help to design different electronic components against eddy current losses.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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