In-situ high-temperature X-ray diffraction studies of non-stoichiometric Ni–Zr substituted barium hexagonal ferrites prepared by citrate precursor route

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Abstract

The mechanism of evolution of hexaferrite has been studied in non-stoichiometric Ni–Zr substituted barium ferrites using the technique of in-situ high-temperature X-ray diffraction. Vacancies in the lattice and a small excess of Ba2+ have been found to aid phase formation at lower temperatures. Furthermore, the mechanism of hexaferrite formation is different in non-stoichiometric compositions as compared to the stoichiometric samples. The thermal expansion data shows lowering of the thermal expansion coefficients due to relaxing of bonds in non-stoichiometric compositions.

Keywords: Barium hexagonal ferrites; Citrate precursor route; X-ray diffraction

1. Introduction

Single-domain nanosized particles of Co–Ti substituted barium hexaferrites possess attractive properties for perpendicular recording media [1,2]. Such a combination of substitutions at iron sites is effective in reducing the magnetocristalline anisotropy and, hence, the coercivity without significant reduction of the saturation magnetization required for high signal strength during readout of stored information. Several chemical routes have been attempted to prepare nanosized single-domain particles [3,4]. In most cases, the attempt to get single-phase material failed when the heat treatment temperature remained below 1300°C. Additionally, such a heat treatment yields large multidomain particles not suitable for recording applications.

The citrate gel route has recently been tried for Co–Zr substituted hexagonal ferrite. However, complete single-phase formation did not occur until an annealing temperature of 1200°C was reached [4,5]. The present authors were recently successful in synthesizing non-stoichiometric Ni–Zr substituted barium ferrite as a single-phase material after heating citrate nitrate gel precursor at only 700°C for 6 h. The presence of vacancies possibly facilitates rapid diffusion of ions, giving a single-phase compound at a much lower temperature. To obtain more insight, we investigated the evolution of the hexaferrite phase as well as the minimum temperature and time for the single-phase formation, and their grain characteristics using in-situ high-temperature X-ray powder diffraction (HT-XRD). The measurements were carried out on the precursors of compositions BaFe_{12-2x}Ni_{0.63+}Zr_{0.50+}O_{19-δ} (x = 0, 0.3, 0.7 and 1.0) synthesized via the citrate gel route. For comparison, we also took the stoichiometric composition BaFe_{12-2x}Ni_{x}Zr_{x}O_{19} with x = 0.3. From the X-ray line analysis of the line breadth of the reflections, the average size of the particles was obtained, which diffracted coherently. The particle size determined from a scanning electron micrograph was misleading as it gave an average of agglomerated particles [6], particularly so when the particle size was in the nanometer range. The HT-XRD method is perhaps the only way to obtain the thermal expansion coefficient (TEC) in nanosized magnetic oxide powder. From high-temperature XRD data we also derived the TEC. The HT-XRD data are discussed in the light of non-stoichiometry and other magnetic properties.
2. Experimental

The samples of compositions $\text{BaFe}_{12-2x}\text{Ni}_{6x}\text{Zr}_{0.50}\text{O}_{19-x}$ ($x = 0, 0.3, 0.7$ and $1.0$) were synthesized by the citrate gel route [5]. The Ni content has been taken to be larger than Zr. The nominal compositions, the vacancy in the Fe site and the sample labels are given in Table 1. The oxygen content has been calculated assuming the following valences: $\text{Ba}^{2+}$, $\text{Ni}^{2+}$, $\text{Fe}^{3+}$ and $\text{Zr}^{4+}$.

X-ray diffractograms of the precursors of $\text{BaM}$, NNZ(0.3), NNZ(0.7) and NNZ(1.0) were acquired at room temperature and in situ in the range 600–1300°C. For comparison, the same measurements were provided for the stoichiometric sample $\text{BaFe}_{11.4}\text{Ni}_{0.3}\text{Zr}_{0.3}\text{O}_{19}$, labeled as NZ(0.3). Data received for temperatures 800, 900, 1000 and 1100°C are denoted by 8, 9, 10 and 11, respectively. The sample label used in evaluation is a combination of the above introduced label (Table 1) and the temperature (e.g. NNZ(0.3)10, NNZ(0.7)13). The reflections of the Pt heating strip were used as internal standard for correction of a displacement error for the sample. Pseudo-Voigt2 profiles were fitted to the reflections.因重叠的Bragg reflections, only the (107), (114), (203) and (205) reflections were chosen for estimating the particle size.

High-temperature X-ray diffraction patterns were recorded from 15° to 75° ($2\theta$) with a step width of 0.02°, using a SIEMENS D5000 diffractometer in Bragg–Brentano geometry. The diffractometer was equipped with a diffracted beam graphite monochromator. Cu Kα radiation was used. The high-temperature attachment was a commercial one (HDK S1, Buehler, Germany). The sample was deposited from a slurry onto a platinum strip, which was d.c. heated in air. The sample temperature was increased from 600 to 1300°C in steps of 100 K and controlled using a Pt–PtRh10 thermocouple, which was welded to the rare side of the Pt strip. The fluctuation of temperature was less than 5 K, but a relative error of about 2% in the absolute temperature of the sample is to be expected. The heating and cooling speed was 1 and 10 K s$^{-1}$, respectively.

The reflections of the Pt heating strip were used as internal standard for correction of a displacement error for the sample. Pseudo-Voigt2 profiles were fitted to the reflections. Unit cell parameters have been calculated by Rietveld refinement. For apparent particle size estimation, the instrumental broadening was determined using Si powder reference material measured under identical conditions and evaluated in the same manner.

The ‘single line method’ was used for estimation of the particles. Due to overlap of the Bragg reflections, only the (107), (114), (203) and (205) reflections were chosen for estimating the particle size.

Scanning electron microscopy (SEM) micrographs were taken on a Stereoscan 90 microscope (Cambridge Instruments). Magnetic measurements were done using a PAR (EG and G) vibrating sample magnetometer (model 4508) at a maximum field of 12 kOe.

3. Results and discussion

3.1. Evolution of hexaferrite phase

The citrate gel precursors are X-ray amorphous. After heating at 400°C for 24 h in air, the precursors of the substituted samples show lines of $\text{BaCO}_3$, $\alpha$-$\text{Fe}_2\text{O}_3$ and $\gamma$-$\text{Fe}_2\text{O}_3$. Thermogravimetry measurements (TGA) of the precursor showed major weight loss (50%) when heated up to 400°C (Fig. 1). Beyond 400°C, the weight loss is essentially negligible. The weight loss has been attributed to decomposition of citrate nitrate gel into oxides, releasing CO, CO$_2$, H$_2$O and NO$_x$. The equation for formation of barium ferrite from the starting material can be written as:

$$\text{BaCO}_3 + 2\alpha\text{Fe}_2\text{O}_3 + \gamma\text{Fe}_2\text{O}_3 \rightarrow \text{BaFe}_{12-2x}\text{Ni}_{6x}\text{Zr}_{0.50}\text{O}_{19-x}$$
Fig. 2. HT-XRD patterns of precursor of BaM heated from RT to 1300°C.

BaNO₃ + 12C₆H₅FeO₇·H₂O + C₆H₈O₇ (Δ 400°C)
→ BaCO₃ + 6Fe₂O₃

BaCO₃ + 6Fe₂O₃ (Δ 1000°C) → BaFe₁₂O₁₉

The theoretical weight loss upon heating the precursor according to the above equation is 68%. According to Anderson and Sale [7], the weight loss in the temperature range 40–180°C is mainly due to loss of H₂O, decomposition of NO₃⁻, and from 180 to 320°C it is due to decomposition of some citrate chains. Above 320°C, catastrophic breakdown of citrate chains takes place.

Figs. 2 and 3 show in-situ measured diffractograms of the precursors of BaM and NNZ(0.3) heated at various temperatures for about 0.75 h. The XRD patterns at 400 and 600°C show essentially an amorphous behavior in the case of NNZ(0.3). The line intensity of the maghemite phase is seen to increase at 600°C as compared to BaM heated at 400°C for 24 h.

The XRD of BaM after heating at 600°C for 1 h (Fig. 4) shows peaks of BaCO₃, α-Fe₂O₃ and γ-Fe₂O₃. This XRD is similar in essence to the XRD pattern of BaM heated at 600°C for 0.75 h (Fig. 2). There is a considerable difference in the x- and y-scales of the two. The peak positions of the XRD lines observed in Fig. 2 are identical to those in Fig. 4, though a large difference is seen in their baseline. Considerable downscaling of the y-axis in Fig. 2 leads to an almost flat baseline and the low-intensity peaks of BaCO₃ and α-Fe₂O₃ are no longer discernible.

In the X-ray diffraction pattern of BaM and NNZ(0.3) heated at 800°C and above, all the major peaks were observed, though their relative line intensities were different from that reported for barium ferrite in the JCPDS index. This is because in in-situ measurements, the hexaferrite formation is an ongoing process and the rate of growth of various lattice planes is different.

The presence of maghemite and hematite in the case of the BaM sample even at 1100°C indicates that: (a) the precursor of BaM is less reactive than that of NNZ(0.3); and/or (b) the mechanism of hexaferrite formation is different in the case of NNZ(0.3) and BaM.

If from BaFe₁₂O₁₉ a Ba²⁺ ion from the Ba layer and one O²⁻ (for charge compensation) are removed, then BaFe₁₂O₁₉ becomes Fe₁₂O₁₈, which is nothing but Fe₃O₄. BaFe₁₂O₁₉ can be considered as a Ba-containing hexagonal block sandwiched between two spinel blocks. In NNZ(0.3), hexaferrite formation takes place directly...
from the precursor, whereas in BaM hexaferrite phase formation also occurs via spinel phase formation, followed by diffusion of Ba\(^{2+}\) ions to yield barium ferrite. The peak positions are much less shifted in NNZ(0.3) with increasing temperature compared to stoichiometric compounds, as seen in Figs. 2 and 3. Ba\(^{2+}\), being a large cation as compared to Fe\(^{3+}\), is responsible for the high-temperature requirement for single-phase formation. Fe\(_2\)O\(_3\) has octahedral (2a) and tetrahedral (4f\(_1\)) sites. The 2b site originates due to the Ba layer. The 4f\(_2\) and 12k sites are formed by slight rearrangement of the Fe\(^{3+}\) and O\(^{2-}\) ions. The vacancies in NNZ(0.3) permit faster diffusion of the cations as compared to the stoichiometric compositions. From Figs. 2 and 3 it is seen that pure hexaferrite phase formation occurs at 800°C in the case of NNZ(0.3), while in BaM, although hexaferrite formation is initiated at 800°C, pure hexaferrite phase is observed only at 1300°C. In NZ(0.3), which is stoichiometric, single-phase formation was found to occur only at 1000°C, showing peaks of hematite up to 900°C. XRD of these samples heated at 700°C for 6 h shows single-phase formation in the case of NNZ\(_x\) (x ≠ 0).

At lower temperatures (600°C), the XRD lines are broad and weak in intensity. As the temperature is increased, the baseline of the HT-XRD pattern becomes increasingly flat, the line intensity increases and the line widths of the hexaferrite phase decrease with temperature in all the compositions, indicating an increase in crystallinity of the hexaferrite. According to Licci et al. [8], prolonged reaction time enhances the reactivity and single-domain particles are still present even after a prolonged reaction time; thus, the magnetic properties can be optimized/enhanced by increasing the reaction time rather than the temperature.

Intermediate phases such as BaFe\(_2\)O\(_4\) or any other phases of barium iron oxide were not observed, as is normally observed in samples synthesized by the ceramic route. This indicates that the solid-state reaction is exclusively heterogeneous, and hexaferrite phase formation proceeds by formation and growth at the expense of the existing phases, namely barium carbonate, hematite and maghemite. This is possible since, in the citrate gel route of synthesis, mixing of cations takes place at the atomic level, thus reducing the paths of diffusion for various cations, as compared to the ceramic route where the diffusion distances are considerable. The small particle size of the precursor powder increases the diffusion area of the particles, thus enhancing the volume diffusion [9].
1.13

Fig. 4. XRD of BaM after heating at 600°C for 1 h.

It may be pointed out that the amount of vacancy at the Fe sites is as high as 7.25% in one of the compositions, and yet the hexaferrite structure does not break down nor do any other phases occur, indicating that the structure is stable.

3.2. Thermal expansion coefficient

From HT-XRD, a continuous increase in the lattice parameters with temperature for all compositions was observed and is shown in Fig. 5. The variation in the lattice parameters is also seen to increase with substitution. The accuracy for the x-axis (temperature axis) is ±10°C, while the accuracy in the lattice parameters, a and c, varies between ±0.002 and ±0.005, as is indicated in Table 2. The lattice parameters usually increase with increasing temperature owing to thermal expansion. Thermal expansion can also cause thermal stresses. Dimensional changes are closely related to the lattice parameter changes, but vacancies add to the dimensional changes with increasing temperature. The variation with substitution is larger in lattice parameter c as compared to a. This is because in a unit cell, 10 oxygen planes are stacked along the c-axis, the Fe, Ni and Zr ions occupy interstitial positions, and the ionic radii of Ni²⁺ and Zr⁴⁺ are larger than that of Fe³⁺, whereas along the a-axis, there are only two oxygen atoms. The lattice parameters and the lattice volumes calculated are given in Table 2.

The lattice constants of NZ(0.3) are smaller than those of NNZ(0.3). Both have the same Fe and Ba content, but there is a 2.2% vacancy in the Fe sites of NNZ(0.3).

The thermal expansion coefficients were determined by measuring the increase in lattice constant with temperature. The average thermal expansion coefficients in the hexagonal system are given by Ref. [10]:

\[ \alpha_a = \frac{(a_2 - a_1)/(T_2 - T_1)}{a_1} \]  
(3)

and

\[ \alpha_c = \frac{(c_2 - c_1)/(T_2 - T_1)}{c_1} \]  
(4)

where \( a_1 \) and \( c_1 \) are the cell parameters at temperature \( T_1 \); and \( a_2 \) and \( c_2 \) are the cell parameters at temperature \( T_2 \). The volume thermal expansion, for random orientation of particles, is given by Ref. [11]:

\[ \alpha = \frac{1}{V} \frac{dV}{dT} \]

where \( V \) is the volume of the particle.
Fig. 5. Variation in lattice parameters with temperature for BaM, NNZ(0.3), NNZ(0.7) and NNZ(1.0) samples.

\[ \alpha_c = \frac{2}{3}\alpha_a + \frac{1}{3}\alpha_c \]  

(5)

The coefficients of axial and volume thermal expansion are given in Table 3. The TEC is greater in the \( c \)-direction as compared to the \( a \)-direction.

In the non-stoichiometric compositions, the coefficient of thermal expansion along the \( c \)-direction and the coefficient of volume expansion are seen to increase with increasing \( x \), or vacancy content. The TEC of NNZ\((x)\) up to \( x = 0.7 \) substitution is smaller than that of BaM. If we compare the TECs of NZ(0.3) and NNZ(0.3), which have the same Ba and Fe content, with the TEC of BaM, it is observed that the TECs of NZ(0.3) are larger than those of NNZ(0.3) and BaM. It appears that in NNZ\((x)\), the TEC decreases up to a certain limit with increasing vacancy content, while in NZ\((x)\), the TEC increases for NNZ(0.3) as compared to BaM (or NZ(0)). Kojima [12] reported a TEC value of \( 11.1 \times 10^{-6} \text{ K}^{-1} \) for BaM, obtained from XRD measurements. This value lies in the same range as ours.

The vacancies present in NNZ\((x)\) presumably accommodate most of the thermal vibrations of the ions. It has been observed in some silicate glasses, where introducing a few percent of Al\(_2\)O\(_3\) or B\(_2\)O\(_3\) (network forming ions) does not alter the TEC [13]. However, when a comparable percentage content of monovalent or divalent ions such as Na\(^+\) or Ca\(^{2+}\) were introduced, remarkable changes in thermal expansion occurred. The network modifying ions enter the vacant spaces in the silicate network, allowing only transverse vibrations of oxygen ions, and thus giving larger TEC [12]. In the present situation also, vacancies in the NNZ samples are possibly responsible for lower TEC than in NZ(0.3) and BaM.

It is well known that polymers, which are mostly organic compounds, have large TECs. The TEC can be regarded as a measure of the covalency of the bonds. The more covalent a bond, the greater would be the thermal expansion. Ionic compounds are known to have low thermal expansion coefficients. In the present case, in BaM, NNZ\((x)\) and NZ(0.3), Ba\(^{2+}\), Fe\(^{3+}\) and O\(^{2-}\) ions are common to all three. The electronegativity of Ni (1.91) is slightly larger than that of Fe (1.83), but the electronegativity of Zr (1.33) is considerably smaller than that of Fe. Hence, in effect the degree of covalency has increased in Ni–Zr substituted systems. This explains why the TEC of NZ(0.3) is larger than that of BaM.
Table 2
Lattice constants of different compositions at RT after heat treatment at 1300°C during the HT-XRD experiment

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameter $a$ (Å)</th>
<th>Lattice parameter $c$ (Å)</th>
<th>Lattice volume $v$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaM</td>
<td>5.886 (+ 0.002)</td>
<td>23.257 (+ 0.005)</td>
<td>697.74 (+ 0.007)</td>
</tr>
<tr>
<td>NNZ(0.3)</td>
<td>5.907 (+ 0.002)</td>
<td>23.314 (+ 0.005)</td>
<td>704.48 (+ 0.007)</td>
</tr>
<tr>
<td>NNZ(0.7)</td>
<td>5.903 (+ 0.002)</td>
<td>23.406 (+ 0.004)</td>
<td>706.30 (+ 0.006)</td>
</tr>
<tr>
<td>NNZ(1.0)</td>
<td>5.916 (+ 0.002)</td>
<td>23.483 (+ 0.004)</td>
<td>711.75 (+ 0.006)</td>
</tr>
<tr>
<td>NZ(0.3)</td>
<td>5.893 (+ 0.002)</td>
<td>23.283 (+ 0.005)</td>
<td>700.21 (+ 0.007)</td>
</tr>
</tbody>
</table>

Shortening of the bond lengths in Ni–O and Fe–O has been reported to be due to the large electronegativity of Fe and Ni atoms [14]. This was not possible in stoichiometric NZ(0.3), since the lattice is already considerably strained [15]. In case of NNZ($x$), the large Ni content as compared to Zr is responsible for increasing the ionic character of the bonds; moreover, the vacancies facilitate shortening of some of the Fe–O and Ni–O bond lengths. Thus, the TEC is reduced to a certain extent.

3.3. Particle size analysis

The particle size has been determined using X-ray line broadening analysis. This method has optimum sensitivity for a particle size less than 0.3 µm [16]. The X-ray diffraction peak breadth was corrected for the breadth due to instrumental broadening. Scanning electron microscopy sometimes fails to give a clear idea of individual grain size due to agglomeration. In XRD analysis, individual grains diffract coherently even when agglomerated. Hence, line broadening analysis gives a correct estimate of the particle size. Fig. 6 shows a SEM micrograph of sample NNZ(0.3)11 which exhibits agglomerated particles, as a result of which the individual crystallite size is not discernible.

The peak breadth was found to decrease with increasing grain size. The grain size was found to increase even during the cooling cycle, possibly due to thermal hysteresis and/or thermal diffuse scattering [17].

The crystallite size calculated is given by [18]:

$$B = 0.94\lambda/\beta \cos \theta$$  \hspace{1cm} (6)

where $B$ is the crystallite size, $\lambda$ is the XRD wavelength, $\beta$ is the line breadth in radians and $\theta$ is the Bragg angle.

In the case of BaM, Cabanas et al. [6] reported negligible lattice strain, attributing the entire XRD line broadening to the crystallite size. The particle size was found to vary in the range 100–400 Å in the samples under investigation. At 900, 1100 and 1300°C, the average particle sizes are approximately in the ranges 100–200, 100–300 and 200–400 Å, respectively. The maximum crystallite size is seen to increase with the heating temperature, indicating grain growth. Fig. 7 shows the variation of the particle size with temperature for BaM, NZ(0.3) and NNZ(0.3) substitutions. Assuming platelet-shaped particles, the critical length for a single-domain particle of BaM has been calculated to be 730 Å [19]. The domain wall thickness is 93 Å, the superparamagnetic limit being 142 Å, i.e. the platelets of diameter below 142 Å are superparamagnetic. Hence, it is envisaged that the multidomain particles are essentially absent from all the present compositions, although the presence of superparamagnetic particles is not ruled out. The presence of single domain particles is also evident from the magnetic hysteresis data. $H_c$ values obtained from this measurement on samples NNZ(0.3), NNZ(0.7) and NNZ(1.0) are 3090, 1450 and 730 Oe, respectively. They transform into multidomain particles, when heated at 1100°C for 6 h. For

Table 3
Coefficients of thermal expansion as obtained from HT-XRD

<table>
<thead>
<tr>
<th>Sample label</th>
<th>$a_x \times 10^{-6}$ (K$^{-1}$)</th>
<th>$a_y \times 10^{-6}$ (K$^{-1}$)</th>
<th>$a_z \times 10^{-6}$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaM</td>
<td>8.7 (+ 0.3)</td>
<td>15.0 (+ 0.8)</td>
<td>10.9 (+ 0.5)</td>
</tr>
<tr>
<td>NNZ(0.3)</td>
<td>8.9 (+ 1.0)</td>
<td>11.5 (+ 0.6)</td>
<td>9.8 (+ 0.9)</td>
</tr>
<tr>
<td>NNZ(0.7)</td>
<td>8.3 (+ 0.5)</td>
<td>13.8 (+ 0.9)</td>
<td>10.1 (+ 0.6)</td>
</tr>
<tr>
<td>NNZ(1.0)</td>
<td>8.3 (+ 0.7)</td>
<td>16.7 (+ 1.0)</td>
<td>11.1 (+ 0.8)</td>
</tr>
<tr>
<td>NZ(0.3)</td>
<td>10.5 (+ 0.8)</td>
<td>16.8 (+ 2.0)</td>
<td>12.5 (+ 1.0)</td>
</tr>
</tbody>
</table>

Fig. 6. SEM micrograph of NNZ(0.3)11 sample.
Fig. 7. Variation in particle size with temperature for BaM, NNZ(0.3) and NZ(0.3) samples.

the above samples, $H_c$ reduces to 980, 1000 and 270 Oe, respectively, due to growth of multidomain grains.

4. Summary

HT-XRD data on non-stoichiometric Ni–Zr substituted barium ferrite has been compared with data on stoichiometric Ni–Zr substituted barium ferrite and pure barium ferrite. From these measurements, the evolution of the hexaferrite phase, thermal expansion and particle size analysis were obtained.

In non-stoichiometric compositions, single-phase formation was observed at 700°C as against 1000°C in stoichiometric compositions. This was attributed to different mechanisms of hexaferrite phase formation in the two cases. The particle sizes are in the range 10–40 nm. The thermal expansion coefficients were found to be lower in non-stoichiometric compositions as compared to stoichiometric samples. Vacancies play a major role in phase formation and thermal expansion behavior. Thus, non-stoichiometric compositions exhibit better microstructural and magnetic properties.

References