Characterization of crystalline structure of ball-milled nano-Ni–Zn-ferrite by Rietveld method

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Abstract

Nanocrystalline Ni–Zn-ferrite is synthesized at room temperature by high-energy ball milling with the target composition 0.5 ZnO, 0.5 NiO and 1.0 Fe₂O₃ mixture (0.5 + 0.5:1 mole fraction). The formation of non-stoichiometric ferrite phase is noticed after 1 h of ball milling and its content increases with increasing milling time. The structural and microstructural evolution of nickel–zinc-ferrite caused by milling is investigated by X-ray powder diffraction. The relative phase abundances of different phases, particle size, r.m.s. (root mean square) strain, lattice parameter change, etc. have been estimated from Rietveld’s powder structure refinement analysis of XRD data. It is revealed from the XRD pattern that ZnO reflections are completely disappeared within 1 h of milling but a significant amount (∼7 wt.%) of nanocrystalline NiO and α-Fe₂O₃ (∼12 wt.%) remain excess even after 11 h of milling. It indicates that during ball milling a non-stoichiometric mixture of NiO, ZnO and α-Fe₂O₃ may lead to the formation of non-stoichiometric Ni–Zn-ferrite. A considerable amount of ferrite is formed within 11 h of ball milling with lattice parameter higher than that of stoichiometric Ni–Zn-ferrite prepared by conventional ceramic route keeping the same residual parts of NiO and α-Fe₂O₃ in forming the target composition. The post-annealing treatment reveals that within 1 h of post-annealing, stoichiometric Ni–Zn–ferrite is formed and nanocrystalline ferrite particles become almost strain-free within 15 h of post-annealing time.

Keywords: Nanocrystalline Ni–Zn–ferrite; Ball milling; Rietveld’s method

1. Introduction

The synthesis of nanocrystalline spinel Ni–Zn-ferrites has been investigated intensively in recent years due to their potential applications in non-resonant devices, radio frequency circuits, high-quality filters, rod antennas, transformer cores, read/write heads for high-speed digital tapes and operating devices [1–3]. Nowadays, these materials are largely synthesized in nanometric scale for new and unusual properties [9–12]. Reports on synthesis of nanocrystalline Ni–Zn-ferrites by high-energy ball milling of stoichiometric NiO, ZnO and α-Fe₂O₃ mixture are not found in the literature. To the best of our knowledge, so far the microstructure characterization and phase transformation kinetics of ball mill prepared Ni–Zn-ferrites have not been studied yet in detail by X-ray powder structure refinement method. The crystalline Ni–Zn-ferrite (cubic, a = 0.8399 nm, space group Fd3m, Z = 8; ICDD PDF #08-0234) is a normal spinel at room temperature. Spinel structure is known by the general formula AₙB₂O₄, consisting of an almost perfect interstices cubic closed-packed oxygen arrangement, in which the cations reside on tetrahedral (A) and octahedral (B) sites. The structural formula of a ferrite is usually written as (X₁,δ)ₐ(Y₁,δ)ₐ(X₂,δ)ₐ(Y₂,δ)ₐ[Z₂(1-δ)O₄]₂₋δ, where round and square brackets denote sites of tetrahedral (A) and octahedral [B] coordination, respectively, and δ represents the degree of inversion (defined by the fraction of the A sites occupied by Y⁺⁺ cations). The completely random distribution of A and B cations over the three cation sites corresponds to mixed spinel configuration which is asymptotically approached at very high temperatures [13]. Same type of cation distribution is also observed in ball-milled samples [9,14]. The change in temperature or the change in milling parameter may result in change in the degree of inversion. The Ni–Zn-ferrite is a soft magnetic ceramic that has spinel configuration of the type (Zn₁−xFeₓ)[NiₓFe₂−x]O₄. In this
formula the metallic cations Fe$^{3+}$/Zn$^{2+}$ occupy the tetrahe- 
dral A sites and the metallic cations Fe$^{3+}$/Ni$^{2+}$ occupy the 
octahedral B sites [15].

High-energy ball milling has now become one of the con-
nventional methods for production of nano-/non-crystalline 
materials. During the ball milling, materials in powder 
form suffer severe high-energy impacts in the process of 
ball-to-ball and ball-to-wall collisions of the grinding 
media. Formation of nanocrystalline materials in the process 
of ball milling usually caused by the continuous fragmenta-
tion and re-welding mechanism of grains. The process 
sometimes leads to several poly morphic phase transforma-
tions that are reasoned by the formation of huge amount of 
structural and microstructural defects. It is therefore nec-
essary to characterize these defect states of the ball-milled 
material in order to find the reason for phase transforma-
tion. Physical properties of a material depend upon the 
microstructures and therefore by controlling the microstruc-
ture, materials can be designed according to desirable prop-
erties. The powder patterns of almost all the ball-milled 
materials, milled at different milling time are composed of 
a large number of overlapping reflections of α-Fe$_2$O$_3$, 
NiO, ZnO and Ni-Zn-ferrite phases [10–12,14]. Rietveld’s 
analysis based on structure and microstructure refinement 
[16,17] has been adopted in the present analysis for precise 
determination of several microstructural parameters as well 
as relative phase abundance of such multiphase material 
containing a large number of overlapping reflections. The 
purposes of our present work are: (i) to prepare nanocrys-
talline Ni-Zn-ferrite phase by high-energy ball milling the 
stoichiometric mixture (1:1 mol%) of powdered reactants 
containing all the ZnO, NiO, α-Fe$_2$O$_3$, Ni-Zn-ferrite phases 
[10–12,14] was used. The resolving of (1 1 1) reflection of Si at even 2θ ∼ 28.4° 
was used. The step-scan data (of step size 2θ = 0.02° and count-
ing time 5 s) for the entire angular range (2θ = 15–80°) 
of the experimental samples were recorded and stored in a 
PC, coupled with the diffractometer. Post-annealing of the 
11 h ball-milled sample was conducted at 773 K for 1, 4, 7, 
10 and 15 h in a programmable furnace (M/S Thermolyne, 
USA).

3. Method of analysis

In the present study, we have adopted the Rietveld’s 
powder structure refinement analysis [16,18–21] of X-ray 
powder diffraction data to obtain the refined structural pa-
rameters, such as atomic coordinates, occupancies, lattice 
parameters, thermal parameters, etc. and microstructural 
parameters, such as particle size and r.m.s. lattice strain, 
etc. For instrumental broadening correction a specially pro-
cessed Si standard[22] was used. The resolving of (1 1 1) 
reflection of Si at even 2θ ∼ 28.4° into Kα1 and Kα2 compo-
ponents indicates that the instrumental broadening is very 
small. However, U, V, W coefficients from (FWHM)$^2$ versus 
tanθ variations (varies non-linearly with increasing scatter-
ing angle) were estimated and incorporated in the Rietveld’s 
software as instrumental broadening. The Rietveld’s soft-
ware MAUD 1.85 [17] is specially designed to refine simul-
taneously both the structural and microstructural parameters 
through a least-squares method. The peak shape was as-
sumed to be a pseudo-Voigt (pV) function with asymmetry. 
The background of each pattern was fitted by a polynomial 
function of degree 4. In the present study, refinements were 
conducted without refining the isotropic atomic thermal 
parameters.

To simulate the theoretical X-ray powder diffraction pat-
tern containing all the ZnO, NiO, α-Fe$_2$O$_3$, Ni-Zn-ferrite 
(normal spinel) phases in a single pattern the following con-
siderations were made:

(i) For ZnO (hexagonal), the space group was taken as 
P6$_3$mc with all atoms in general Wyckoff position 2(b).
(ii) For NiO (cubic), the space group was taken as Fm$3$m, 
with Ni and O atoms in special Wyckoff positions 4(a) 
and 4(b), respectively.
where the Cauchyian component, $C(x)$, of X-ray profile, $\eta(x)$, is defined as the Gaussian component, $G(x)$, with the expected error, size and strain broadening of the experimental profiles.

Because it takes individual care for both the particle size and strain broadening of the experimental profiles. For both the $K_{01}$ and $K_{02}$ profiles, the line broadening function $B(2\theta)$ and the symmetric part of instrumental function $S(2\theta)$ may be represented by the pV function [20]:

$$\eta(x) = \sum_{\alpha(x)} L_{\alpha} \left[ \exp \left( -\frac{1}{2} \left( \frac{x - \theta_{\alpha}}{\theta_{\alpha}^{\text{FWHM}}} \right)^2 \right) + (1 - \eta) G(x) \right]$$

where the Cauchyian component, $C(x) = \left( 1 + x^2 \right)^{-1}$ and the Gaussian component, $G(x) = \exp\left( -(\ln 2)x^2 \right)$ with $x = (2\theta - 2\theta_{0})$ (FWHM is the half width at half maximum of the X-ray peaks) and $HWHM = (1/2)(U \tan \theta + V \tan \theta + W)^{1/2}$, where $U$, $V$ and $W$ are coefficients of the quadratic polynomial, $\eta$ is the Gaussianity of X-ray profile, $\theta_{0}$ the Bragg angle of $K_{01}$ peak and $L_{\alpha}$ is the scale factor.

The powder diffraction patterns were simulated providing all necessary structural information and some starting values of microstructural parameters of the individual phases with the help of the Rietveld’s software, the MAUD 1.85 [17]. Initially, the positions of the peaks were corrected by successive refinements of zero-shift error. Considering the integrated intensity of the peaks as a function of structural parameters, the Rietveld’s method was successfully applied for determination of the quantitative phase abundances of the composite materials [23–26]. There is a simple relationship between the individual scale factor determined, considering all refined structural parameters of individual phases of a multiphase sample, and the phase concentration (volume/weight fraction) in the mixture. The weight fraction ($W_{i}$) for each phase was obtained from the refinement relation:

$$W_{i} = \frac{S_{i}(ZMV)_{i}}{\sum_{j} S_{j}(ZMV)_{j}}$$

where $i$ is the value of $j$ for a particular phase among the $N$ phases present, $S_{j}$ the refined scale factor, $Z$ the number of formula units per cell, $M$ the atomic weight of the formula unit and $V$ the volume of the unit cell [16,17]. The structure refinement along with size-strain broadening analysis was carried out simultaneously by adopting the standard procedure [16,17].

3.2 Size-strain analysis

The basic consideration of this method is the modeling of the diffraction profiles by an analytical function, which is a combination of Cauchyian, Gaussian, and asymmetry functions as well. It has been well established that the observed peak-broadenings of the sample profiles are mainly due to the presence of small particle size and r.m.s. strain inside the particles. The particle size and strain broadening can be approximated better with Cauchy and Gaussian type functions, respectively [27,28]. Being a linear combination of a Cauchyian and Gaussian functions, the pV function is the most reliable peak-shape function and is being widely used in the Rietveld’s structure refinement software.

The process of successive profile refinements modulated different structural and microstructural parameters of the simulated pattern to fit the experimental diffraction pattern. Profile refinement continues until convergence is reached in each case, with the value of the quality factor (GoF) approaches very close to 1.

4. Results and discussion

The XRD powder patterns recorded from unmilled and ball-milled (BPMR = 40:1) homogeneous powder mixtures

(iii) For $\alpha$-Fe$_2$O$_3$ (rhombohedral), the space group was taken as $R3c$, with Fe and O atoms in special Wyckoff positions 12(c) and 18(c), respectively.

(iv) For Ni–Zn-ferrite (cubic, normal spinel) the space group was taken as Fd$\bar{3}$m with Ni and Zn atom in the special Wyckoff positions 8(f) and Fe and O in the 16(c) and 32(b), respectively.

3.1 Crystalline structure characterization by X-ray powder diffraction

For microstructure characterization the experimental profiles were fitted with the most suitable pV analytical function [20] because it takes individual care for both the particle size and strain broadening of the experimental profiles. For both the $K_{01}$ and $K_{02}$ profiles, the line broadening function $B(2\theta)$ and the symmetric part of instrumental function $S(2\theta)$ may be represented by the pV function [20]:

$$pV(x) = \sum_{\alpha(x)} L_{\alpha}[\eta C(x) + (1 - \eta) G(x)]$$

where the Cauchyian component, $C(x) = (1 + x^2)^{-1}$ and the Gaussian component, $G(x) = \exp\left( -(\ln 2)x^2 \right)$ with $x = (2\theta - 2\theta_{0})$ (FWHM is the half width at half maximum of the X-ray peaks) and $HWHM = (1/2)(U \tan \theta + V \tan \theta + W)^{1/2}$, where $U$, $V$ and $W$ are coefficients of the quadratic polynomial, $\eta$ is the Gaussianity of X-ray profile, $\theta_{0}$ the Bragg angle of $K_{01}$ peak and $L_{\alpha}$ is the scale factor.

The powder diffraction patterns were simulated providing all necessary structural information and some starting values of microstructural parameters of the individual phases with the help of the Rietveld’s software, the MAUD 1.85 [17]. Initially, the positions of the peaks were corrected by successive refinements of zero-shift error. Considering the integrated intensity of the peaks as a function of structural parameters only, the Marquardt least-squares procedures were adopted for minimization the difference between the observed and simulated powder diffraction patterns and the minimization was carried out by using the reliability index parameter, $R_{exp}$ (weighted residual error), and $R_{B}$ (Bragg factor) defined as

$$R_{exp} = \left[ \frac{\sum_{i} w_i (I_i - I_{cal})^2}{\sum_{i} w_i I_{i}} \right]^{1/2}$$

and

$$R_{B} = \frac{100}{\sum_{i} I_{i}} \left[ \frac{\sum_{j} \left| I_{j} - I_{cal} \right|}{\sum_{j} I_{j}} \right]$$

The goodness of fit (GoF) is established by comparing $R_{exp}$ with the expected error, $R_{exp}^{\text{预期}}$

$$R_{exp}^{\text{expected}} = \left[ \frac{N - P}{\sum_{i} w_i I_{i}} \right]^{1/2}$$

where $I_{exp}$ and $I_{cal}$ are the experimental and calculated intensities, respectively, $w_{i}$ (=1/$I_{i}$) and $N$ are the weight and number of experimental observations, and $P$ the number of fitting parameters. This leads to the value of GoF [16,17,21]:

$$\text{GoF} = \frac{R_{exp}}{R_{exp}^{\text{expected}}}$$

Refinement continues till convergence is reached with the value of the quality factor, GoF very close to 1 (varies between 1.07 and 1.25), which confirms the goodness of refinement.

The Rietveld’s method was successfully applied for determination of the quantitative phase abundances of the composite materials [23–26]. There is a simple relationship between the individual scale factor determined, considering all refined structural parameters of individual phases of a multiphase sample, and the phase concentration (volume/weight fraction) in the mixture. The weight fraction ($W_{i}$) for each phase was obtained from the refinement relation:

$$W_{i} = \frac{S_{i}(ZMV)_{i}}{\sum_{j} S_{j}(ZMV)_{j}}$$

where $i$ is the value of $j$ for a particular phase among the $N$ phases present, $S_{j}$ the refined scale factor, $Z$ the number of formula units per cell, $M$ the atomic weight of the formula unit and $V$ the volume of the unit cell [16,17]. The structure refinement along with size-strain broadening analysis was carried out simultaneously by adopting the standard procedure [16,17].

3.2 Size-strain analysis

The basic consideration of this method is the modeling of the diffraction profiles by an analytical function, which is a combination of Cauchyian, Gaussian, and asymmetry functions as well. It has been well established that the observed peak-broadenings of the sample profiles are mainly due to the presence of small particle size and r.m.s. strain inside the particles. The particle size and strain broadening can be approximated better with Cauchy and Gaussian type functions, respectively [27,28]. Being a linear combination of a Cauchyian and Gaussian functions, the pV function is the most reliable peak-shape function and is being widely used in the Rietveld’s structure refinement software.

The process of successive profile refinements modulated different structural and microstructural parameters of the simulated pattern to fit the experimental diffraction pattern. Profile refinement continues until convergence is reached in each case, with the value of the quality factor (GoF) approaches very close to 1.
Fig. 1. X-ray powder diffraction patterns of unmilled and ball-milled NiO + ZnO mixture (1:1 mol%) at RPMR 40:1. Only Ni–Zn-ferrite reflections have been indexed.

are shown in Fig. 1. The powder pattern of unmilled mixture contains only the individual reflections of NiO (ICDD PDF #04-0835), ZnO (ICDD PDF #36-1451), and α-Fe₂O₃ (ICDD PDF #33-0664) phases only. It is evident from the figure that in the course of ball milling the NiO, ZnO and α-Fe₂O₃ mixture, the Ni–Zn-ferrite phase has been formed and its amount increases gradually with increasing milling time. After just 1 h of milling, the formation of Ni–Zn-ferrite phase has been noticed clearly due to the appearance of at least (2 2 0) (isolated, 2θ = 30.13°) and most strongest (3 1 1) (overlapped, 2θ = 35.43°) reflections in the respective XRD pattern. It is also evident from the figure that the content of ZnO phase has been reduced to a large extent in comparison to NiO and α-Fe₂O₃ phase and vanishes within 1 h of ball-milling. It indicates that the ZnO phase is much prone to deformation fault as all the reflections are sufficiently broadened in comparison to other two phases and rate of solid-state diffusion of ZnO into the α-Fe₂O₃ lattice is higher than NiO phase. It seems that initially Zn-ferrite phase is formed from the ZnO-α-Fe₂O₃ solid solution. A small amount of Ni–Zn-ferrite is formed when the NiO phase diffuses slowly into the ZnFe₂O₄ lattice in the course of milling. It has been reported earlier by ourselves [24] the formation of ZnFe₂O₄ within 30 min of ball milling the homogeneous stoichiometric (1:1 mol%) powder mixture of ZnO and α-Fe₂O₃ phases using the same experimental setup. In the course of milling, all the reflections of ferrite phase appear distinctly with sufficient peak-broadening in the XRD pattern of 3 h ball-milled sample. At the same time, intensities of starting materials have been reduced further and except the strongest (1 0 4) (2θ = 33.18°) reflection of α-Fe₂O₃ phase all other reflections are apparently disappeared. It indicates that: (i) contents of the staring phases have been reduced considerably within this time of milling, (ii) peak-broadening increases significantly because the nanocrystalline particles contains a huge amount of lattice strain arising from high-energy milling. As some of the reflections are overlapped with very broadened α-Fe₂O₃ reflections, particle size and lattice strain of individual phases considering all the reflections cannot be estimated with sufficient accuracy without employing any Rietveld’s software based on both structural and microstructure refinements. The rate of mechanosynthesis of Ni-Zn-ferrite is then increased rapidly in course of milling. After 7 h of milling, it seems that all the reflections of starting materials have been disappeared completely and the Ni-Zn-ferrite phase has been grown up completely, because the intensity distribution agrees somewhat well with the standard value (ICDD PDF #08-0234). However, a closer look of XRD pattern of 11 h ball-milled sample reveals the presence of strong reflections of NiO and α-Fe₂O₃ phases. It indicates that stoichiometric Ni-Zn-ferrite phase is not formed completely even after 11 h of ball milling the stoichiometric powder mixture.

For complete formation of stoichiometric Ni-Zn-ferrite phase, a part of 11 h milled sample is post-annealed at 773 K for different durations. The XRD patterns of post-annealed powders along with 11 h ball-milled powder are shown in Fig. 2 for progressive development of Ni-Zn-ferrite phase in the course of post-annealing durations. It is evident from the figure that all the reflections of NiO and α-Fe₂O₃ phases completely disappear in the XRD pattern of 1 h post-annealed sample and the intensity distributions agree well with the standard value. It also evident that the peak-broadening does not reduce considerably with increasing post-annealing durations up to 15 h, which signifies that nanocrystalline Ni-Zn-ferrite
Fig. 2. X-ray powder diffraction patterns of 11 h ball-milled and post-annealed samples. Particles do not grow in size considerably in the course of post-annealing treatment. In the course of milling, peak-broadening as well as the degree of overlapping of neighboring reflections increase with increasing milling time. To estimate the relative phase abundances, structural changes and microstructure parameters of individual phases, all the unmilled, ball-milled and post-annealed XRD patterns are analyzed employing Rietveld’s powder structure and microstructure refinement analysis [16–20]. It is evident from Figs. 1 and 2 that almost all the reflections of these four phases are partially or completely overlapped. Therefore, microstructure parameters and phase content of different phases considering all the symmetry permitted reflections cannot be obtained with sufficient accuracy without adopting the Rietveld’s software having both the microstructure and structure refinement facilities. Some of the fitted XRD patterns are shown in Fig. 3 as typical Rietveld’s analysis output. The experimental data ($I_0$, small dots) are fitted well with the refined simulated patterns ($I_c$, continuous line) because the residue of fitting ($I_0 - I_c$) is negligible and the GoF values for all the fittings lie between 1.07 and 1.25.

Fig. 4 shows the dependence of relative phase abundances of different phases with increasing milling time, milled at a fixed BPMR = 40:1. The content (wt.%) of ZnO phase decreases very rapidly and becomes nil after 1 h of milling. The wt.% of $\alpha$-Fe$_2$O$_3$ decreases continuously but that of NiO phase very slowly with increasing milling time (Table 1). Significant amounts of NiO (~7 wt.%) and $\alpha$-Fe$_2$O$_3$ (~12 wt.%) phases remain excess even after 11 h of milling. It reveals that within 1 h of milling basically a Zn-ferrite phase has been formed from the ZnO-$\alpha$-Fe$_2$O$_3$.
solid solution and a very small amount (∼2 wt.%) of NiO phase diffuses into the Zn-ferrite lattice because at the initial stage of 1 h milling time, the rate of diffusion was very low due to larger crystallite (less reactive) sizes of NiO phase. The amount of ferrite phase increases further due to solid-state diffusion of nanocrystalline NiO and significant amount of α-Fe₂O₃ particles into Zn-ferrite lattice in the course of ball-material-ball/vial collisions. The diffusion rate of NiO is slow. It has been reported earlier [29] that Ni²⁺ ions prefer to occupy the octahedral positions in the spinel lattice. The octahedral positions in Zn-ferrite lattice are already occupied by Fe³⁺ ions and as a result diffusion of Ni²⁺ ions is very slow. However, the formation of NiO-α-Fe₂O₃ solid solution cannot be ruled out. The excess amount of α-Fe₂O₃ and NiO phases may be utilized in formation of stoichiometric Ni-Zn-ferrite phase after a prolonged time of milling. The stoichiometric Ni-Zn-ferrite can also be prepared by post-annealing the ball-milled powder at a moderately low temperature for a short duration of time. The nature of variation of lattice parameters of α-Fe₂O₃, NiO, and Ni-Zn-ferrite phases with increasing milling time is shown in Fig. 5. It is evident from the plots that lattice parameters of α-Fe₂O₃ phase vary nonlinearly as well as anisotropically with increasing milling time. The a and c values of rhombohedral α-Fe₂O₃ phase increases and decreases, respectively, slowly at the early stage and rapidly up to 5 h of milling and then remain constant till the end of milling (11 h). The increase in a value even under compressive stress of ball-material-ball/vial collision may be attributed to the substitution of Fe³⁺ ions (Oct. radius = 0.65 Å) by smaller Zn²⁺ ions (Oct. radius = 0.60 Å) preferably along c-axis (Fig. 5a). Though it was observed earlier [30–32] that high-energy ball milling of α-Fe₂O₃ phase led to formation of different polymorphic iron oxide phases within a very short duration, but surprisingly, in the present study, we did not notice any structural phase transition of α-Fe₂O₃. It indicates that the presence of ZnO and NiO phases prevent the phase transition of α-Fe₂O₃ phase. The variation of lattice parameters with increasing milling time may be further attributed to the accumulation of lattice imperfections in the process of continuous fracture and re-welding of grains under high-energy impact. The lattice parameter of cubic NiO phase increases (Fig. 5b) rapidly up to 5 h of milling and then remains constant till the end of ball milling. The lattice parameter of cubic Ni-Zn-ferrite decreases rapidly up to 5 h of milling and like NiO phase, remains constant till the end of ball milling. As the lattice parameter variations of all the phases do not obey the Vegards law of solid solution (considering lattice deformation by solute addition as deformation induced by increasing milling time), the possibilities of formation of ZnO-α-Fe₂O₃, NiO-α-Fe₂O₃, and ZnO-NiO-α-Fe₂O₃ solid solutions may be ruled out. However, the nanocrystalline Ni-Zn-ferrite is presumed to be formed by different mechanism. Due to high-energy impact, particle sizes of both the NiO and α-Fe₂O₃ phases come down to nanometric order within a very short duration of milling (Table 1). In the course of milling when the nano-sized particles of individual phases come in contact to each other at the time of ball-to-ball and/or ball-to-vial wall collision, nucleation of nanocrystalline Ni-Zn-ferrite particle then takes place by solid-state diffusion between them as both the particle size and collision temperature
Table 1
Microstructure parameters of ball-milled \((\text{NiO} + \text{ZnO})-\alpha-\text{Fe}_2\text{O}_3 (1:1 \text{ mol%})\) powder revealed from Rietveld's X-ray powder structure refinement method

<table>
<thead>
<tr>
<th>Milling time (h)</th>
<th>NiO</th>
<th>(\alpha-\text{Fe}_2\text{O}_3)</th>
<th>((\text{Ni-Zn})\text{Fe}_2\text{O}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lattice parameter (nm)</td>
<td>Particle size (nm)</td>
<td>r.m.s. strain (\times 10^3), (\langle \varepsilon^2 \rangle^{1/2})</td>
</tr>
<tr>
<td>0</td>
<td>0.4174</td>
<td>24.7</td>
<td>0.1523</td>
</tr>
<tr>
<td>1</td>
<td>0.4179</td>
<td>17.7</td>
<td>6.297</td>
</tr>
<tr>
<td>2</td>
<td>0.4181</td>
<td>10.2</td>
<td>6.854</td>
</tr>
<tr>
<td>3</td>
<td>0.4187</td>
<td>9.5</td>
<td>7.528</td>
</tr>
<tr>
<td>4</td>
<td>0.4192</td>
<td>7.5</td>
<td>7.989</td>
</tr>
<tr>
<td>5</td>
<td>0.4197</td>
<td>5.2</td>
<td>8.165</td>
</tr>
<tr>
<td>7</td>
<td>0.4198</td>
<td>5.0</td>
<td>9.524</td>
</tr>
<tr>
<td>9</td>
<td>0.4199</td>
<td>4.9</td>
<td>9.701</td>
</tr>
<tr>
<td>11</td>
<td>0.4199</td>
<td>4.9</td>
<td>9.82</td>
</tr>
</tbody>
</table>
favors the formation mechanism. The lattice parameter of mechano-synthesized nanocrystalline Ni-Zn-ferrite spinel phases is significantly less (Table 1) in comparison to ICDD (International Centre for Diffraction Data) PDF (Powder Diffraction File) reported (prepared by solid-state reaction at 1523 K of pellets of 0.5 NiO and 0.5 ZnO + α-Fe₂O₃) value. This mismatch in lattice parameter indicates that the distribution of cations between A and B sites depends on the method of preparation of Ni-Zn-ferrites. This type of lattice mismatch may also arise due to accumulation of significant amount of lattice strain in the ferrite lattice on the progress of milling. Therefore, the increase in lattice parameter of both the phases may be attributed to the influences of both the lattice imperfections as well as continuous redistribution of cations between tetrahedral and octahedral positions.

The nature of variation of particle size (D) and r.m.s. lattice strain ($\langle \varepsilon^2 \rangle^{1/2}$) of NiO, α-Fe₂O₃ and Ni-Zn-ferrite is shown in Fig. 6. Both the particle size and lattice strain of all the phases are found to be isotropic (Table 1). The particle size of NiO decreases from ~25 to ~17 nm within 1 h ball milling and then decreases slowly with increasing milling time (Fig. 6a). After 7 h of milling, the particle size no longer decreases and remains almost constant till the end of milling. The r.m.s. lattice strain ($\langle \varepsilon^2 \rangle^{1/2}$), increases rapidly within 1 h of milling and then slowly in a usual manner with increasing milling time (Fig. 6b). After 7 h of milling, like particle size variation, lattice strain no longer increases and remains almost constant till the end of milling. It signifies that high-energy impact produces enormous amount of lattice imperfections inside the NiO lattice by constant fracturing the grains and the fracturing mechanism of ball milling is obviously more effective when the grains are relatively large. Particle size of the ball-milled α-Fe₂O₃ phase reduces from ~91 to ~11 nm (Table 1) within 1 h ball milling and then decreases slowly up to 5 h milling and then attains a saturation value of ~4 nm (Fig. 6a). As the particle sizes of both the phases reach almost equal in size (Table 1), it seems that arriving at this critical size particles become
Fig. 6. Variation of: (a) particle size and (b) r.m.s. strain $\langle \varepsilon^2 \rangle^{1/2}$ of NiO, $\alpha$-Fe$_2$O$_3$ and Ni–Zn-ferrite phases with increasing milling time.

(highly vibrant and take part in the formation of Ni–Zn-ferrite nano-particles by individual particle re-welding mechanism. It is also evident from the plot that by increasing the milling time, particle size of $\alpha$-Fe$_2$O$_3$ cannot be reduced further. It is evident from the plot (Fig. 6b) that the $\langle \varepsilon^2 \rangle^{1/2}$ value increases rapidly within 2 h of milling and then remains almost constant till the end of milling. The variation of particle size of normal Ni–Zn-ferrite spinel phase with increasing milling time is shown in Fig. 6a. From the plot it is clearly evident that normal Ni–Zn-ferrite phase has been formed just after 1 h milling and surprisingly, the particle size ($\sim$4 nm) does not vary significantly with increasing milling time (Table 1). It signifies that partial combination of individual particles of these phases under high-energy impact initiates the growth of normal spinel particle. The $\langle \varepsilon^2 \rangle^{1/2}$ value of normal spinel lattice increases rapidly up to 2 h of milling and then like particle size, remains almost unchanged till the end of milling (Table 1). The variation indicates towards the following facts: (i) initially normal spinel was formed with a non-stoichiometric composition because starting stoichiometric ratio was not correctly regulated by milling process since significant amounts of $\alpha$-Fe$_2$O$_3$ and NiO phases were not utilized till the end of 11 h milling. As a result of wrong occupancy of cations in A and B sites, normal spinel lattice became highly strained; (ii) in the course of milling when the particle size attains a critical value ($\sim$4 nm), the grain fracture mechanism of ball milling becomes inoperative and as a result, particle size
as well as lattice strain values of individual phases attain saturation value after a certain period of milling.

The 11 h ball-milled sample was post-annealed at 773 K for 1, 4, 7, 10 and 15 h and XRD pattern of each sample was analyzed by Rietveld’s powder structure refinement method (Fig. 2). It is observed that after just 1 h of post-annealing, the residual part of both NiO and α-Fe₂O₃ phases diffuse completely into the non-stoichiometric Ni–Zn-ferrite lattice and a completely stoichiometric Ni–Zn-ferrite phase has been formed. The lattice parameter of stoichiometric Ni–Zn-ferrite decreases rapidly after just 1 h of post-annealing and then remains almost unchanged with increasing post-annealing durations. This implies that excess amount of both NiO and α-Fe₂O₃ phases diffuse almost completely into the non-stoichiometric ferrite lattice and the redistribution of cations in the tetrahedral and octahedral sites results in contraction of ferrite lattice to get a more complete structure (Fig. 7a). The particle size of the stoichiometric Ni–Zn-ferrite does not increase considerably (Table 2) as the annealing temperature is only 773 K and the variation of the particle size is shown in Fig. 7a. The lattice strain releases continuously with increasing durations of post-annealing (Fig. 7b) and the nanocrystalline stoichiometric Ni–Zn-ferrite particles become almost strain-free after 15 h of post-annealing at 773 K.

Table 2  

<table>
<thead>
<tr>
<th>Duration of annealing (h)</th>
<th>Lattice parameter (nm)</th>
<th>Particle size (nm)</th>
<th>r.m.s. strain × 10⁻³, ⟨ε²⟩₁/₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.8395</td>
<td>4.3</td>
<td>4.412</td>
</tr>
<tr>
<td>1</td>
<td>0.8382</td>
<td>6.9</td>
<td>3.990</td>
</tr>
<tr>
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<td>0.8379</td>
<td>7.2</td>
<td>2.397</td>
</tr>
<tr>
<td>7</td>
<td>0.8378</td>
<td>7.4</td>
<td>1.980</td>
</tr>
<tr>
<td>10</td>
<td>0.8377</td>
<td>7.9</td>
<td>1.785</td>
</tr>
<tr>
<td>15</td>
<td>0.8.76</td>
<td>8.2</td>
<td>1.423</td>
</tr>
</tbody>
</table>
5. Conclusions

Nanostructured Ni-Zn-ferrite powders have been prepared by high-energy ball milling of stoichiometric mixture of NiO, ZnO and α-Fe$_2$O$_3$ powder within a very short time period. Structural changes of ball-milled NiO, α-Fe$_2$O$_3$, and Ni-Zn-ferrite phases have been investigated by Rietveld’s analysis of X-ray powder diffraction data for the first time, to the best of our knowledge. No phase transformation of either NiO or α-Fe$_2$O$_3$ is found throughout the experiment. The quantitative analysis of the XRD data evaluated on the basis of Rietveld’s powder structure refinement method yields detailed information about the structure and microstructure of mechanosynthesized nanoscale Ni–Zn-ferrite phase (normal spinel). The accumulation of stored energy during ball milling through repeated fragmentation and re-welding of small grains leads to creation of lattice distortion of Ni–Zn-ferrite phase which is manifested in contraction/expansion of lattice parameter of this phase. The following important observations may be summarized as follows:

(i) Zn-ferrite phase has been formed within 1 h of ball milling.
(ii) Significant excess amounts of both NiO and α-Fe$_2$O$_3$ phases in 11 h ball-milled indicates that the ball-milled prepared sample is a non-stoichiometric ferrite phase.
(iii) Non-stoichiometric ferrite phase has been formed by the combination of nanoparticles of individual phases.
(iv) Post-annealing at 773 K for 15 h leads to the formation of nanocrystalline strain-free Ni–Zn-ferrite particles.

References