Co-Doped NdFeO₃ Nanoparticles: Synthesis, Optical, and Magnetic Properties Study

Tien Anh Nguyen 1,2,*, Thanh Le Pham 3, Irina Yakovlevna Mittova 4, Valentina Olegovna Mittova 5, Truc Linh Thi Nguyen 3, Hung Van Nguyen 6 and Vuong Xuan Bui 7,*

Abstract: In this work, single-phase nanostructured NdFe₁₋ₓCoₓO₃ (x = 0, 0.1, 0.2, and 0.3) perovskite materials were obtained by annealing stoichiometry mixtures of their component hydroxides at 750 °C for 60 min. The partial substitution of Fe by Co in the NdFeO₃ crystal lattice leads to significant changes in the structural characteristics, and as a consequence, also alters both the magnetic and optical properties of the resulting perovskites. The low optical band gap (E_g = 2.06 ± 1.46 eV) and high coercivity (H_c = 136.76 ± 416.06 Oe) give Co-doped NdFeO₃ nanoparticles a huge advantage for application in both photocatalysis and hard magnetic devices.

Keywords: nanocrystals; co-doped NdFeO₃; co-precipitation method; optical properties; magnetic properties

1. Introduction

Perovskite orthoferrite materials have been intensively studied because of their diverse unique properties, variable formulae, variable structures, and wide technological applications. Especially, the substitution of Ln or Fe sites of the LnFeO₃ perovskite-type oxides (where Ln is a rare-earth element such as La, Nd, and Pr) by other elements which can exhibit considerable multi-valence and defect sites in their structures, which lead to the tunable redox and electromagnetic characteristics of the materials [1–3].

In NdFeO₃, the magnetic moments of Fe and Nd are two antiparallel coupled nonequivalent magnetic sublattices. The electrons in the 3d and 4f orbitals of these two sublattices interact with spin-lattice coupling, leading to a very unstable magnetic state and, thus, they result in unusually large magnetic anisotropy, magnetization reversal, and spin switching in low magnetic fields [10]. In order to adjust their optical, electrical, and magnetic properties and to enhance the performance of pristine perovskite, transition metal ions can be doped into their crystal lattices. Co-doped LnFeO₃ materials have attracted extensive study thanks to their exciting dielectric, sensing, optical, and magnetic properties. Owing
to the multiple spins and oxidation states of Co, the process of catalysts may be modified by changing the concentration of Co in solid solutions [3,6,11–14].

Several studies [15–20] described the formation of LnFeO$_3$ orthoferrites nanoparticles (Ln = La, Y), including those doped with metals (for example, Mn, Co, Ni, and Ba) by a simple co-precipitation method via the hydrolysis of cations in boiling water followed by the addition of appropriate precipitants. In our recent work [21], NdFeO$_3$ nanoparticles, of 30 nm in size, were obtained via the simple co-precipitation method mentioned above, their crystal structure and magnetic properties were also studied therein.

In this paper, single-phase Co-doped NdFeO$_3$ nanoparticles were synthesized and the changes in their crystal structure, their magnetic and optical properties were also studied. To the best of our knowledge, similar work has not been reported elsewhere.

2. Materials and Methods

All reagents in this work are analytical grade and were used without any further purification. The procedure for synthesizing Co-doped NdFeO$_3$ nanoparticles is similar to that of NdFeO$_3$ [21], with NaOH 5% as the precipitant instead of a NH$_3$ 5% solution, in order to avoid the generation of soluble complex from the reaction of cobalt (II) hydroxide precipitate (Co(OH)$_2$↓) and ammonium solution according to Equation (1) [22].

$$\text{Co(OH)}_2↓ + 6\text{NH}_3 \rightarrow [\text{Co(NH}_3)_6]\text{OH}_2$$ (1)

The structure and phase composition of the samples were investigated by X-ray powder diffraction (XRD, D8-ADVANCE, Brucker, Bremen, Germany) with Cu $K_α$ radiation ($\lambda = 1.54056$ Å), the step size is chosen to be 0.02 in range of 10° to 80°. The average crystal size was determined according to the Debye–Scherrer equation [23]; lattice constants $a$, $b$, $c$, and the unit cell volume $V$ were determined using the Rietveld method [23] implemented in the X’pert High Score Plus 2.2b software package [18–20].

The energy-dispersive X-ray spectroscopy (EDX) was carried out with a FE-SEM S-4800 spectrometer (Hitachi, Tokyo, Japan). The average value of five different positions in each sample was taken as the final result of the corresponding sample. Particle size and morphology of Co-doped NdFeO$_3$ nanoparticles were determined using transmission electron microscopy (TEM; JEOL-1400, Jeol Ltd., Tokyo, Japan).

The UV-Vis absorption spectra of NdFe$_{1-x}$Co$_x$O$_3$ nanocrystals were studied on a UV-Visible spectrophotometer (UV-Vis, JASCO V-550, Shimadzu, Tokyo, Japan). The optical energy gap ($E_g$, eV) was determined by fitting the absorption data to the direct transition as in previous publication [24].

Magnetic properties of the samples (the saturation magnetization $M_s$ in the maximal field, the coercive force $H_c$ and remanent magnetization $M_r$) were investigated at 300 K via a vibrating sample magnetometer (VSM, MICROSENE EV11, Tokyo, Japan).

3. Result and Discussion

3.1. Structures and Morphologies of Nanostructured NdFe$_{1-x}$Co$_x$O$_3$

The XRD patterns of the NdFe$_{1-x}$Co$_x$O$_3$ products ($x = 0, 0.1, 0.2, 0.3$, and 0.4) compared with those of the Nd$_2$O$_3$, Fe$_2$O$_3$, and Co$_3$O$_4$ component oxides independently prepared under similar conditions (annealed at 750 °C during 60 min) are shown in Figure 1. The annealing condition was determined according to the previous work [21]. Those patterns confirmed that the NdFe$_{1-x}$Co$_x$O$_3$ samples with $x = 0, 0.1, 0.2$, and 0.3 were pure orthoferrite phase perovskite structure (NdFeO$_3$, JCPDS No. 01-074-1473), with no identified peaks of oxide impurities. Interestingly, Co$_3$O$_4$ oxide was obtained instead of CoO since Co(OH)$_2$ hydroxide can be oxidized and decomposed after annealing at high temperature [24].
Co into NdFeO₃ crystal structures only took place when x was less than 0.4. With the increase in Co concentration, the XRD peak shifted toward a higher 2θ (right shift) and gradually broadened while the intensity of peaks decreased. Consequently, there was a decrease in unit cell volume (from V = 238.56 to V = 233.29 Å³) and in crystal size (from DXRD = 28 ± 5 to DXRD = 19 ± 3 nm) Figure 2 and Table 1. Such a decrease is also a confirmation for the Co (III) substitution to Fe (III) in the NdFeO₃ crystal lattice. The substitution of Fe³⁺ ions (rFe³⁺ = 0.65 Å [24]) by smaller Co³⁺ ions (rCo³⁺ = 0.55 Å [24]) led to the reduction of the unit cell parameters and crystal size following Vegard’s law, in which lattice parameters linearly varies with the degree of substitution of atoms or ions by others in ideal solid solution. The similar results were published in the previous research [12,13,18].

Figure 1. X-ray powder diffraction (XRD) patterns of NdFe₁₋ₓCoₓO₃ samples (x = 0, 0.1, 0.2, 0.3, and 0.4) and Nd₂O₃, Fe₂O₃, and Co₃O₄ annealed at 750 °C for 60 min.

In the case of x = 0.4, aside from the peaks corresponding to the NdFeO₃ phase, there were peaks of the Nd₂O₃ phase (JCPDS No. 00-041-1089) at 2θ = 25.71 and 30.74°, and Co₃O₄ phase (JCPDS No. 00-043-1003) at 2θ = 38.87°. Thus, the successful substitution of Co into NdFeO₃ crystal structures only took place when x was less than 0.4. With the increase in Co concentration, the XRD peak shifted toward a higher 2θ (right shift) and gradually broadened while the intensity of peaks decreased. Consequently, there was a decrease in unit cell volume (from V = 238.56 to V = 233.29 Å³) and in crystal size (from DXRD = 28 ± 5 to DXRD = 19 ± 3 nm) Figure 2 and Table 1. Such a decrease is also a confirmation for the Co (III) substitution to Fe (III) in the NdFeO₃ crystal lattice. The substitution of Fe³⁺ ions (rFe³⁺ = 0.65 Å [24]) by smaller Co³⁺ ions (rCo³⁺ = 0.55 Å [24]) led to the reduction of the unit cell parameters and crystal size following Vegard’s law, in which lattice parameters linearly varies with the degree of substitution of atoms or ions by others in ideal solid solution. The similar results were published in the previous research [12,13,18].
An analysis of the results of the size distribution of NdFe$_{1-x}$Co$_x$O$_3$ particles Figure 3 allows us to conclude that the average crystallite size decreases monotonically with an increase in the dopant content in the synthesized samples. The lower values of $D_{\text{avg}}$ calculated based on the XRD data as compared to the TEM results were due to the peculiarities of the used methods. The determination of the average crystallite size by the calculation method according to the Debye–Scherrer formula leads to significant errors that can be caused by the choice of a mathematical model for analyzing the X-ray line profile for the determination of the particle size and the influence of various factors on the broadening effect of diffraction maxima. In addition, the diffraction method is volumetric and therefore determines the size of crystallites averaged over the entire volume, in contrast to electron microscopy, which is a local visual method for estimating the size of particles (not crystallites) [25]. TEM results, to a certain extent, depend on the possibility of investigating only a relatively small number of particles under real conditions and on the quality of preliminary dispersion of nanopowders, which introduces a certain amount of uncertainty into the obtained results. Nevertheless, transmission electron microscopy is a direct and accurate method for determining the size and shape of nanoobject particles.

Table 1. Lattice parameters and crystallite sizes of NdFe$_{1-x}$Co$_x$O$_3$ samples annealed at 750 °C for 60 min.

| NdFe$_{1-x}$Co$_x$O$_3$ | 2θ$^0$ (112) | $D_{\text{avg}}$, nm | Lattice Constants, Å | $V$, Å$^3$ |
|------------------------|--------------|----------------------|---------------------|-----------|
| NdFeO$_3$ [21]         | 32.49        | 28 ± 5               | 4.9900              | 5.9100    | 7.7592    | 238.56    |
| NdFe$_{0.9}$Co$_{0.1}$O$_3$ | 32.54   | 25 ± 3               | 4.5297              | 5.9919    | 7.7638    | 235.55    |
| NdFe$_{0.8}$Co$_{0.2}$O$_3$ | 32.57 | 22 ± 2               | 4.4245              | 5.5292    | 7.7616    | 233.57    |
| NdFe$_{0.7}$Co$_{0.3}$O$_3$ | 32.61 | 19 ± 3               | 5.4113              | 5.5504    | 7.7673    | 233.29    |

Figure 2. Slow-scan XRD patterns of peak (112) of NdFe$_{1-x}$Co$_x$O$_3$ samples annealed at 750 °C for 60 min.
3.3. Optical and Magnetic Properties of Nano-Structured NdFe$_{1-x}$Co$_x$O$_3$ (x = 0, 0.1, 0.2, and 0.3) Materials

The magnetic and optical characterizations of the NdFe$_{1-x}$Co$_x$O$_3$ (x = 0, 0.1, 0.2, and 0.3) nanomaterials (annealed at 750 °C for 60 min) were carried out at room temperature. The results prove that beside the structure, the substitution of Co in the NdFeO$_3$ crystal lattice also impressively change the magnetic and optical properties of the samples Table 3 and Figures 4 and 5.

Table 3. Optical and Magnetic characteristics of NdFe$_{1-x}$Co$_x$O$_3$ nanomaterials annealed at 750 °C for 60 min.

| NdFe$_{1-x}$Co$_x$O$_3$ | $H_c$, Oe | $M_r$, emu/g | $M_s$, emu/g | $E_g$, eV |
|--------------------------|-----------|-------------|-------------|----------|
| NdFeO$_3$ [21]           | 136.76    | 0.68        | 0.80        | 2.06     |
| NdFe$_{0.9}$Co$_{0.1}$O$_3$ | 258.22  | 0.13        | 0.93        | 1.74     |
| NdFe$_{0.8}$Co$_{0.2}$O$_3$ | 395.79  | 0.15        | 0.97        | 1.53     |
| NdFe$_{0.7}$Co$_{0.3}$O$_3$ | 416.06  | 0.18        | 0.98        | 1.46     |
3.3. Optical and Magnetic Properties of Nano-Structured NdFe$_{1-x}$Co$_x$O$_3$ ($x = 0, 0.1, 0.2, \text{and} 0.3$) Materials

The magnetic and optical characterizations of the NdFe$_{1-x}$Co$_x$O$_3$ ($x = 0, 0.1, 0.2, \text{and} 0.3$) nanomaterials (annealed at 750 °C for 60 min) were carried out at room temperature. The results prove that beside the structure, the substitution of Co in the NdFeO$_3$ crystal lattice also impressively change the magnetic and optical properties of the samples Table 3 and Figures 4 and 5.

Table 3. Optical and Magnetic characteristics of NdFe$_{1-x}$Co$_x$O$_3$ nanomaterials annealed at 750 °C for 60 min.

| NdFe$_{1-x}$Co$_x$O$_3$ | $H_c$, Oe | $M_r$, emu/g | $M_s$, emu/g | $E_g$, eV |
|----------------------|----------|-------------|-------------|---------|
| NdFeO$_3$ [21]       | 136.76   | 0.68        | 0.80        | 2.06    |
| NdFe$_{0.9}$Co$_{0.1}$O$_3$ | 258.22 | 0.13        | 0.93        | 1.74    |
| NdFe$_{0.8}$Co$_{0.2}$O$_3$ | 395.79 | 0.15        | 0.97        | 1.53    |
| NdFe$_{0.7}$Co$_{0.3}$O$_3$ | 416.06 | 0.18        | 0.98        | 1.46    |

Indeed, when the concentration of Co ions in NdFeO$_3$ crystal lattice increased, all magnetic parameters, including $H_c$ (258.22–416.04 Oe), $M_s$ (0.93–0.98 emu/g), and $M_r$ (0.13–0.18 emu/g) increased with the rise of Co concentration in the NdFeO$_3$ lattice. In addition, these values were significantly higher than those of the original NdFeO$_3$ material [21] (with the exception of $M_r$). It can be explained by the fact that the substitution of Co ions into the NdFeO$_3$ lattice can intensify the magneto-crystalline anisotropy. Besides, Co substitution also led to a change in Fe–O–Fe angles, as well as the oxidation of a small amount of Fe$^{3+}$ ions to Fe$^{4+}$ ions, to compensate for the charge caused by the appearance of Co$^{2+}$ at the sites of Fe$^{3+}$. The similar phenomenon was also reported for HoFe$_{1-x}$Ni$_x$O$_3$ [26], NdFe$_{1-x}$Ni$_x$O$_3$ [27], GdFe$_{1-x}$Ni$_x$O$_3$ [28], YFe$_{1-x}$Co$_x$O$_3$ [18], and LaFe$_{1-x}$Ni$_x$O$_3$ series [19]. Remarkably, under the same synthesis conditions, the magnetic parameters, especially $H_c$, of the NdFe$_{1-x}$Co$_x$O$_3$ nano-crystalline perovskite oxides are higher than those of other perovskite oxides, such as YFe$_{1-x}$Mn$_x$O$_3$, YFe$_{1-x}$Co$_x$O$_3$, and LaFe$_{1-x}$Ni$_x$O$_3$ [17–19]. From those results, the magnetic properties of perovskite-type nanostructured materials can be easily tuned by varying the element and the degree of doping. This important feature of nanosized perovskites give them a wide variety of application in many different fields of magnetic materials.

Figure 4. (a) Room-temperature optical absorbance spectra and (b) plot of $(Ahv)^2$ as a function of photon energy for NdFe$_{1-x}$Co$_x$O$_3$ materials annealed at 750 °C for 60 min.

Figure 5. Field dependence of the magnetization of NdFe$_{1-x}$Co$_x$O$_3$ nanoparticles annealed at 750 °C for 60 min.
Indeed, when the concentration of Co ions in NdFeO$_3$ crystal lattice increased, all magnetic parameters, including $H_t$ (258.22–416.04 Oe), $M_s$ (0.93–0.98 emu/g), and $M_r$ (0.13–0.18 emu/g) increased with the rise of Co concentration in the NdFeO$_3$ lattice. In addition, these values were significantly higher than those of the original NdFeO$_3$ material [21] (with the exception of $M_t$). It can be explained by the fact that the substitution of Co ions into the NdFeO$_3$ lattice can intensify the magneto-crystalline anisotropy. Besides, Co substitution also led to a change in Fe–O–Fe angles, as well as the oxidation of a small amount of Fe$^{3+}$ ions to Fe$^{4+}$ ions, to compensate for the charge caused by the appearance of Co$^{2+}$ at the sites of Fe$^{3+}$. The similar phenomenon was also reported for HoFe$_{1−x}$Ni$_3$O$_5$ [26], NdFe$_{1−x}$Ni$_3$O$_5$ [27], GdFe$_{1−x}$Ni$_3$O$_5$ [28], YFe$_{1−x}$Co$_x$O$_3$ [18], and LaFe$_{1−x}$Ni$_3$O$_5$ series [19]. Remarkably, under the same synthesis conditions, the magnetic parameters, especially $H_c$, of the NdFe$_{1−x}$Co$_x$O$_3$ nano-crystalline perovskite oxides are higher than those of other perovskite oxides, such as YFe$_{1−x}$Mn$_3$O$_5$, YFe$_{1−x}$Co$_x$O$_3$, and LaFe$_{1−x}$Ni$_3$O$_5$ [17–19]. From those results, the magnetic properties of perovskite-type nanostructured materials can be easily tuned by varying the element and the degree of doping. This important feature of nanosized perovskites give them a wide variety of application in many different fields of magnetic materials.

The UV-Vis absorption spectra of the Co-doped NdFeO$_3$ nanoparticles showed strong absorption in the ultraviolet (~300–400 nm) and visible light regions (~400–600 nm) Figure 4a. As the concentration of Co ions increased, there was a red-shift in the UV-Vis absorption spectra (toward the visible light region). The optical energy gaps ($E_g$, eV) of the NdFe$_{1−x}$Co$_x$O$_3$ nanomaterials (x = 0, 0.1, 0.2, and 0.3) were calculated similarly to other publications [24,26] and are shown in Table 2 and Figure 4b. The estimated direct band gaps of all products are in the range of 2.06–1.46 eV and increase when Co content in NdFeO$_3$ lattice increases. Particularly, the Co-doped NdFeO$_3$ nanoparticles in this work exhibited much narrower band-gap compared to some other related orthoferrites synthesized by other methods. For instance, the direct band-gaps of NdFe$_{1−x}$Co$_x$O$_3$ (x = 0–0.4) and HoFe$_{1−x}$Ni$_3$O$_5$ (x = 0–0.5) nanoparticles were reported to be $3.35 \div 3.04$ and $3.39 \div 3.28$ eV, respectively [26,29], and the values for LaFe$_{1−x}$Ti$_3$O$_7$ (x = 0.2–0.8) nanoparticles prepared by co-precipitation technique were 2.05–2.61 eV [2]. The small band gaps of NdFe$_{1−x}$Co$_x$O$_3$ can give an advantage for the application of this material series in photocatalysis, gas sensor, and electrode materials in solid oxide fuel cells [12,13,29–31].

4. Conclusions

The single-phase nanostructured NdFe$_{1−x}$Co$_x$O$_3$ (x = 0, 0.1, 0.2, and 0.3) perovskites have been synthesized by the simple co-precipitation method. The maximum level of substitution of iron with cobalt, which was $x < 0.4$ (XRD) was established. At $x = 0.4$, the homogeneity region was impaired and a phase mixture, consisting of Nd$_2$O$_3$ and Co$_3$O$_4$ was formed.

Obtained Co-doped NdFeO$_3$ nanoparticles, after annealing at 750 °C for 60 min, have their crystal size ($D_{XRD} = 25 \pm 3 \div 19 \pm 3$ nm, $D_{TEM} = 47 \pm 5 \div 42 \pm 3$ nm), unit cell volume ($V = 238.56 \div 233.29$ Å$^3$).

The study of the effect of the degree of substitution in NdFe$_{1−x}$Co$_x$O$_3$ crystals on their optical and magnetic characteristics showed that optical band-gap values ($E_g = 2.06 \div 1.46$ eV) decreased while the coercive force ($H_c = 136.76 \div 416.06$ Oe) and saturation magnetization ($M_s = 0.80 \div 0.98$ emu/g) increased with the increase of Co content. Co-doped NdFeO$_3$ nanoparticles have low optical energy gaps and high coercivity, which are beneficial not only for application in photocatalysis, but also for hard magnetic devices (permanent magnets or recorders).

Author Contributions: Conceptualization, T.A.N. and T.L.P.; methodology, T.A.N.; validation, I.Y.M., V.O.M. and V.X.B.; formal analysis, T.L.T.N. and H.V.N.; investigation, V.X.B. and H.V.N.; data curation, T.A.N. and T.L.P.; writing—original draft preparation, T.A.N., T.L.T.N. and I.Y.M.; writing—review and editing, V.O.M. and V.X.B. All authors have read and agreed to the published version of the manuscript.
Funding: This research received no external funding.

Data Availability Statement: Not Applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ahmad, I.; Akhtar, M.J.; Siddique, M.; Iqbal, M.; Hasan, M.M. Origin of anomalous octahedral distortions and collapse of magnetic ordering in Nd$_{1-x}$Sr$_x$Fe$_3$O$\delta$ ($0 \leq x \leq 0.5$). *Ceram. Int.* 2013, 39, 8901–8909. [CrossRef]

2. Sasikala, C.; Durairaj, N.; Baskaran, I.; Sathyaseelan, B.; Henini, M. Transition metal titanium (Ti) doped LaFeO$_3$ nanoparticles for enhanced optical structure and magnetic properties. *J. Alloys Compd.* 2017, 712, 870–877. [CrossRef]

3. Haron, W.; Thaweechai, T.; Wattanathana, W.; Laobuthee, A.; Manaspiya, H.; Veranitisagul, C.; Koosang, N. Structure characteristics and dielectric properties of La$_{1-x}$Co$_x$Fe$_2$O$_4$ and LaFe$_{1-x}$Co$_x$O$_3$ synthesized via metal organic complexes. *Energy Procedia* 2013, 34, 791–800. [CrossRef]

4. Xu, J.J.; Xu, D.; Wang, Z.L.; Wang, H.G.; Zhang, L.L.; Zhang, X.B. Synthesis of perovskite-based porous La$_{0.75}$Sr$_{0.25}$MnO$_3$ nanotubes as a highly efficient electrocatalyst for rechargeable lithium–oxygen system. *Angew. Chem. Int. Ed.* 2013, 52, 3887–3890. [CrossRef]

5. Tijare, S.N.; Bakardjieva, S.; Subrt, J.; Joshi, M.V.; Rayalu, S.S.; Hishita, S.; Labhsetwar, N. Synthesis and visible light photocatalytic activity of nanocrystalline PrFeO$_3$ perovskite for hydrogen generation in ethanol-water system. *J. Chem.* 2014, 125, 517–525. [CrossRef]

6. Megarajan, S.K.; Rayalu, S.; Nishibori, M.; Labhsetwar, N. Improved catalytic activity of PrFeO$_3$ (M = Co and Fe) perovskites: Synthesis of thermally stable magnetic nanoparticles by a novel hydrothermal method. *N. J. Chem.* 2015, 39, 2345–2348. [CrossRef]

7. Shin, N.; Isao, A.; Yasuhiko, I.; Takeo, H. Preparation of Y(Mn$_{1-x}$Fe)$_{2}$O$_3$ and electrical properties of the sintered bodies. *Open J. Inorg. Chem.* 2015, 5, 54514589.

8. Fang, F.; Zhao, P.; Feng, N.; Wan, H.; Guan, G. Surface engineering on popous perovskite-type La$_{0.3}$Sr$_{0.7}$Co$_{1-x}$Fe$_x$O$_3$–$\delta$ nanotubes for an enhanced performance in diesel soot elimination. *J. Hazardous Mater.* 2020, 399, 123014. [CrossRef]

9. Mir, F.A.; Sharma, S.K.; Kumar, R. Magnetizations and magneto-transport properties of Ni-doped PrFeO$_3$ thin films. *Chin. Phys. B* 2014, 23, 048101. [CrossRef]

10. Yuan, S.J.; Ren, W.; Hong, F.; Wang, Y.B.; Zhang, J.C.; Bellachie, L.; Cao, S.X.; Cao, G. Spin switching and magnetization reversal in single-crystal NdFeO$_3$. *Phys. Rev. B* 2013, 87, 184405. [CrossRef]

11. Pekinchak, O.; Vasylicheko, L.; Lutsyuk, I.; Vakhula, Y.; Prots, Y.; Cabrera, W.C. Sol-gel prepared nanoparticles of mixed praseodymium cobaltites ferrites. *Nanoscale Res. Lett.* 2016, 11, 75. [CrossRef] [PubMed]

12. Zhang, R.; Hu, J.; Han, Z.; Wu, Z.; Zhang, Y.; Qin, H. Electrical and CO-sensing properties of NdFe$_{1-x}$Co$_x$O$_3$ perovskite system. *J. Rare Earths* 2010, 28, 591–595. [CrossRef]

13. M. Arhun, S.; Li, J.; Zou, B.; Luo, J.; Chen, W.; Dong, W.; Wu, F. Ethanol sensing properties of LaCo$_{1-x}$Fe$_x$O$_3$–$\delta$ nanoparticles: Effects of calcination temperature, Co-doping, and carbon nanotube-treatment. *Sens. Actuators B Chem.* 2011, 155, 232–238. [CrossRef]

14. Zhou, Z.; Guo, L.; Yang, H.; Liu, Q.; Ye, F. Hydrothermal synthesis and magnetic properties of multiferroic rare-earth orthoferrites. *J. Alloys Compd.* 2014, 583, 21–31. [CrossRef]

15. Nguyen, T.A.; Mittova, I.Y.; Almajshaeva, O.V.; Kirillova, S.A.; Gusarov, V.V. Influence of the preparation conditions on the size and morphology of nanocrystalline lanthanum orthoferrite. *Glass Phys. Chem.* 2008, 34, 756–761.

16. Yuan, A.T.; Almjasheva, O.V.; Mittova, I.Y.; Stognei, O.V.; Soldatenko, S.A. Synthesis and magnetic properties of YFeO$_3$ nanocrystals. *Inorg. Mater.* 2009, 45, 1304–1308.

17. Arhun, A.T.; Pham, V.N.; Nguyen, T.T.L.; Mittova, I.Y.; Vo, Q.M.; Berezhnaya, M.V.; Mittova, I.Y.; Do, T.H.; Chau, H.D. Crystal structure and magnetic properties of perovskite YFe$_{1-x}$Mn$_x$O$_3$ nanopowders synthesized by co-precipitation method. *Solid State Sci.* 2019, 96, 105922. [CrossRef]

18. Arhun, A.T.; Chau, D.H.; Nguyen, L.T.T.; Mittova, V.O.; Do, H.T.; Mittova, I.Y. Structural and magnetic properties of YFe$_{1-x}$Co$_x$O$_3$ ($0.1 \leq x \leq 0.5$) perovskite nanomaterials synthesized by co-precipitation method. *Nanosyst. Phys. Chem. Math.* 2018, 9, 424–429. [CrossRef]

19. Arhun, A.T.; Pham, V.N.T.; Le, H.T.; Chau, D.H.; Mittova, I.Y.; Nguyen, L.T.T.; Dinh, D.A.; Hao, T.N.; Mittova, I.Y. Crystal structure and magnetic properties of LaFe$_{1-x}$Ni$_x$O$_3$ nanomaterials prepared via a simple co-precipitation method. *Ceram. Int.* 2019, 45, 21768–21772. [CrossRef]

20. Arhun, A.T.; Pham, V.; Chau, D.H.; Mittova, I.Y.; Kopeychenko, E.L.; Nguyen, L.T.T.; Bui, V.X.; Nguyen, A.T.P. Effect of Ni substitution on phase transition, crystal structure and magnetic properties of nanostructured YFeO$_3$ perovskite. *J. Mol. Struct.* 2020, 1215, 128293. [CrossRef]

21. Arhun, A.T.; Pham, V.; Pham, T.L.; Nguyen, L.T.T.; Mittova, I.Y.; Mittova, V.O.; Vo, L.N.; Nguyen, B.T.T.; Bui, V.X.; Viryutina, E.L. Simple synthesis of NdFeO$_3$ by the co-precipitation method based on a study of thermal behaviors of Fe (III) and Nd (III) hydroxides. *Crystals* 2020, 10, 219. [CrossRef]

22. Housecroft, C.E.; Sharpe, A.G. *Inorganic Chemistry*, 2nd ed.; Pearson, Prentice Hall: Upper Saddle River, NJ, USA, 2005; 950p.
23. Yousefi, M.; Zeid, S.S.; Motlagh, M.K. Synthesis and characterization of nano-structured perovskite type neodymium orthoferrite NdFeO$_3$. *Curr. Chem. Lett.* **2017**, *6*, 23–30. [CrossRef]

24. Ghobadi, N. Band gap determination using absorption spectrum fitting procedure. *Int. Nano Lett.* **2013**, *3*, 2. [CrossRef]

25. Krurova, M.V.; Mittova, I.Y.; Perov, N.S.; Al’myasheva, O.V.; Nguyen, T.A.; Mittova, V.O.; Bessalova, V.V.; Viryutina, E.L. Effect of the degree of doping on the size and magnetic properties of nanocrystals La$_{1-x}$Zn$_x$FeO$_3$ synthesized by the sol-gel method. *Russ. J. Inorg. Chem.* **2017**, *62*, 281–287. [CrossRef]

26. Habib, Z.; Majid, K.; Ikram, M.; Sultan, K. Influence of Ni substitution at B-site for Fe$^{3+}$ ions on morphological, optical, and magnetic properties of HoFeO$_3$ ceramics. *Appl. Phys. A Mater. Sci. Process.* **2016**, *12*, 550. [CrossRef]

27. Mir, S.A.; Ikram, M.; Asokan, K. Effect of Ni doping on optical, electrical and magnetic properties of Nd orthoferrite. *J. Phys. Conf. Ser.* **2014**, *534*, 012017. [CrossRef]

28. Bashir, A.; Ikram, M.; Kumar, R.; Lisboa-Filho, P.N. Structural, electronic structure and magnetic studies of GdFe$_{1-x}$Ni$_x$O$_3$ ($x \leq 0.5$). *J. Alloys Compd.* **2012**, *521*, 183–188. [CrossRef]

29. Somvanshi, A.; Husain, S.; Khan, W. Investigation of structure and physical properties of cobalt doped nano-crystalline neodymium orthoferrite. *J. Alloys Compd.* **2019**, *778*, 439. [CrossRef]

30. Nguyen, T.A.; Nguyen, L.T.T.; Bui, V.X.; Nguyen, D.H.; Lieu, H.D.; Le, L.M.; Pham, V. Optical and magnetic properties of HoFeO$_3$ nanocrystals prepared by a simple co-precipitation method using ethanol. *J. Alloys Compd.* **2020**, *834*, 155098. [CrossRef]

31. Phokha, S.; Pintsoontorn, S.; Maensiri, S.; Rujirawat, S. Structure, optical and magnetic properties of LaFeO$_3$ nanoparticles prepared by polymerized complex method. *J. Sol Gel Sci. Technol.* **2014**, *71*, 333–341. [CrossRef]