A Effect of Ni doping on the structure of $MgFe_2O_4$: X-ray diffraction profile analysis and Raman spectroscopy study

The 6th International Hybrid Conference on X-Ray analysis

D. Naranchimeg[a] , I. Khishigdemberel[b] , D. Sangaa[b]
[a] School of Applied Sciences, Mongolian University of Science and Technology, Mongolia
[b] Institute of Physics and Technology, Mongolian Academy of Sciences, Mongolia

1. Introduction

Magnetic spinels in combination with various types. The elements of binary and ternary systems are extensively studied with respect to potential applications in electronics, magnetics, catalysis, and biomedicine [1,2]. The soft magnetic behavior in ferrites is due to the exchange interaction between cations in polyhedral sites [2,4]. In spinel, a unit cell consists of 8 tetrahedral and 16 octahedral sites [5]. From previous reports on MgFe2O4, nonmagnetic Mg and magnetic Fe ions occupy the tetrahedral and octahedral sites, mediated by oxygen ions [7-9]. It is well known that nickel affects magnetic materials [6-8]. If the soft magnetic properties of MgFe2O4 spinel could be improved by nickel substitution, it would lead to the development of new multiferroic materials. Khishigdemberel et al. carried out a detailed study of the crystal structure of Cu- and Cr-doped MgFe2O4 at different temperatures [10,11]. The structural properties were investigated by X-ray diffraction and Raman spectroscopy. In the present work we have performed a detailed investigation of the crystal structure of Ni doped MgFe2O4 at room temperature.

2. Experimental procedure

Spinel-ferrite samples $Mg_{1-x}Ni_xFe_2O_4$ $(0 \le x \le 1)$ were prepared by the sol-gel method in the Laboratory of Nanomaterials studies of Institute of the Physics and Technology of the Mongolian Academy of Sciences. The samples were characterized by XRD (Shimadzu X-Ray diffractometer, with $CoK\alpha$, $\lambda = 1.7903\dot{A}$ radiation). The XRD patterns were taken for angles 10^0-80^0 with step 0.02^0. The Raman scattering spectra were recorded using Raman spectrometer LabRAM HR (Horiba scientific), Joint Institute for Nuclear Research, Dubna, Russia. The spectra were recorded for all samples in the range from 100 to 1000 cm^{-1}. Raman spectra at ambient temperature were collected using a LabRAM HR spectrometer (Horiba Gr, France) with a wavelength of 633 nm emitted by a He–Ne laser. An air cooled (-68^0C) CCD detector with multiple channels. All spectra were calibrated in wavenumber using a standard neon source.

Conclusions

Polycrystalline Mg1-xNixFe2O4 (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) ferrites samples were synthesized by sol-gel method. XRD analysis revealed that the prepared samples are cubic spinel with a single phase at all concentrations, confirming that the Ni3+ ions replaced the Fe3+ ions without distorting the cubic symmetry of the host magnesium ferrite. The lattice parameters were found to decrease with Ni substitution due to the smaller ionic radii of the Ni3+ ions. The Raman spectra confirms the five active phonon modes MgFe2O4 and solid solution. The Raman active modes are also in good agreement with the reported literature confirming the spinel structure of the synthesized samples.

References

[1] S. Vladimir, F. Armin, H. Paul, K. Frank, M. Dirk, J.L. Fred, B. Ingo, D.B. Klaus, Chem. Mater. 18 (2006) 3067.
[2] S.M. Daliya, S.J. Ruey, Chem. Eng. J. 129 (2007) 65.
[3] A.S. Nicola, F. Manfred, Science 309 (2005) 392.
[4] L.M. Corliss, J.M. Hastings, Phys. Rev. 90 (1953) 1018
[5] H.S.C.O. Neill, H.Annersten, D. irgo Americ, Mineral 77 (1992) 740.
[6] V. Sepelak, D. Baabe, D. Mienert, F.J. Litterst, K.D. Becker, Scr. Mater. 48 (2003) 966
[7] V. Sepelak, M. Menzel, K.D. Becker, F. Krumeich, J. Phys. Chem. B 106 (2002) 6678.
[8] R.J. Harrison, A. Putnis, Phys. Chem. Miner. 26 (1999) 332.
[9] V.K. Mittal, B. Santanu, R. Nithya, M.P. Srinivasan, S. Velmurugan S.V. Narasimhan, J. Nucl. Mater. 335 (2004) 310.
[10] I. Khishigdemberel, E. Uyanga, H. Hirazawa, D. Sangaa, Physica B: Condensed Matter, 544 (2018) 73.
[11] B. Enkhmend, I. Khishigdemberel, N. Jargalan, D. Sangaa, Adv. Phys. Res. 3 (2021), 59.

3. Results and discussions

3.1. XRD analysis

X-ray diffraction patterns of all samples were recorded with the diffractometer using $CoK\alpha$ radiation $(\lambda = 0.1793nm)$. The XRD patterns of $Mg_{1-x}Ni_xFe_2O_4$ nanocomposites with different Ni^{+3} content $(0 \le x \le 1)$ are shown in Fig.1. All XRD patterns were analyzed by the Rietveld refinement technique] using the space group Fd-3m in cubic symmetry. Rietveld analysis of the diffraction pattern of nanocrystalline $Mg_{1-x}Ni_xFe_2O_4$ was performed using FullProf software program. First, the global parameters such as background and scale factors were refined during time refinement. Then the structural parameters, asymmetry, atomic coordinates, preferred orientation, and site occupancies were refined successively. The structural parameters of the model are then adjusted until the best fit to the experimental diffraction data is obtained. The fit of experimental data depends on χ^2 (goodness of fit) and R factors (R_p-profile, R_{wp}- weighted factor, R_{exp}- expected, R_B- Bragg). The crystal structure and the derived parameters are well satisfied when the values of χ^2 and R factors reach a minimum.

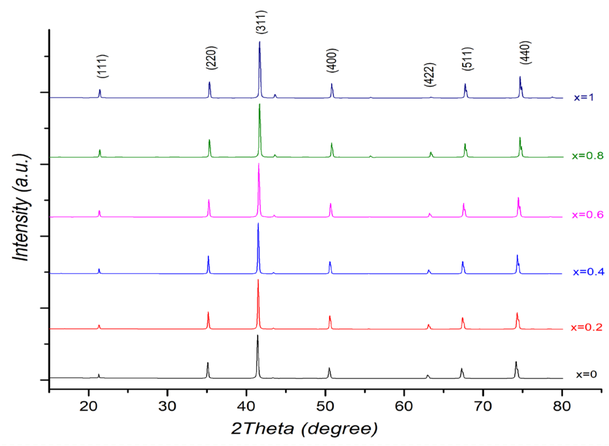


Fig.1. XRD patterns of the $Mg_{1-x}Ni_xFe2O4$ $(0 \le x \le 1)$

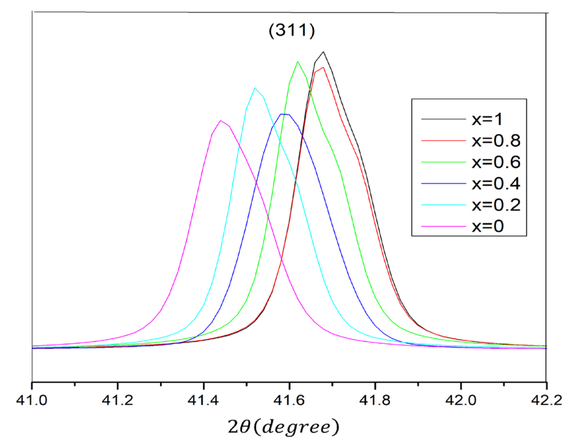


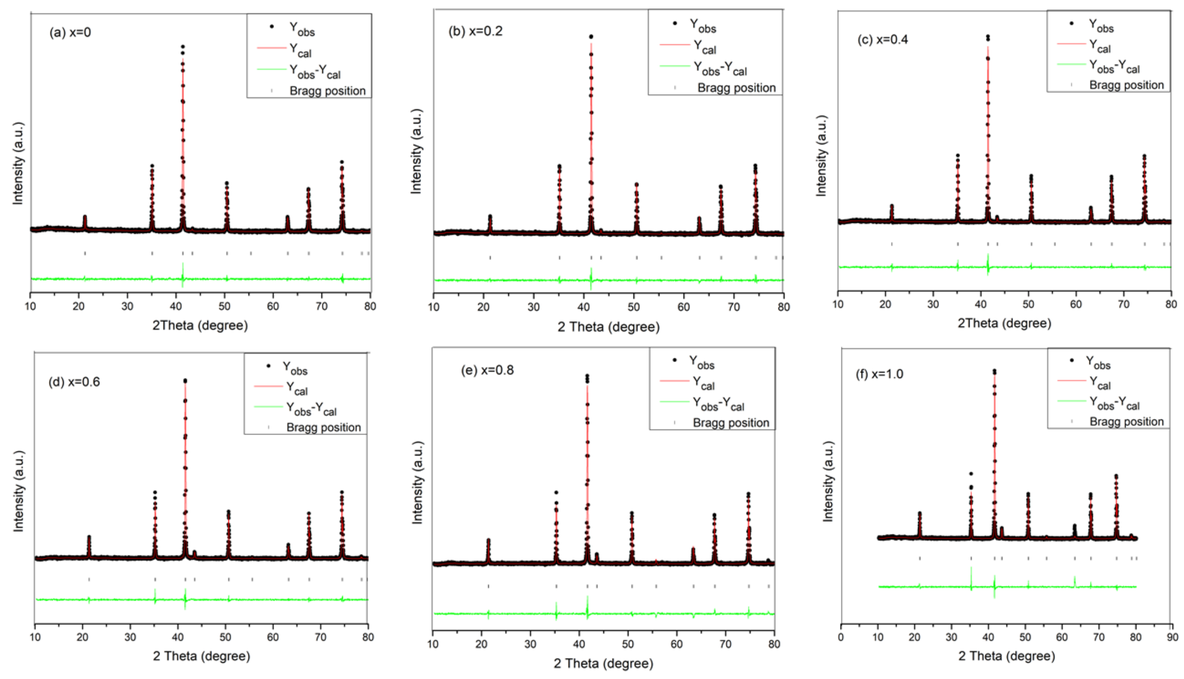
Fig.2. Analysis of the (311) peak

The refinement of the X-ray diffraction patterns of the $Mg_{1-x}Ni_xFe_2O_4$ samples with x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 is shown in Fig.1. Here the peaks are identified with Miller indices. The data show intense, sharp peaks and reveal well crystalline single spinel structures. Fig.2 shows a shift in peak (311) at $x = 0, 0.2, 0.4, 0.6, 0.8 \text{ and } 1.0$, indicating a change in lattice parameters due to nickel content.

Table 1. Structural parameters of $Mg_{1-x}Ni_xFe_2O_4$ $(0 \le x \le 1)$

Ni content (x)	$\mathbf{a(\dot{A})}$	$\mathbf{V(\dot{A})^3}$	D(nm)	$\mathbf{R_p}$	$\mathbf{R_{wp}}$	$\mathbf{R_{exp}}$	$\mathbf{R_B}$	$\boldsymbol{\chi^2}$
0.0	8.3936	591.3607	49.55	5.84	7.45	6.66	1.30	1.25
0.2	8.3802	558.5213	53.28	6.06	7.63	6.69	2.40	1.30
0.4	8.3770	587.8441	54.61	6.02	7.97	6.80	4.17	1.37
0.6	8.3643	585.1843	52.95	6.04	7.61	6.61	1.68	1.32
0.8	8.3441	580.9558	53.02	6.74	8.70	6.61	3.56	1.73
1.0	8.3433	580.7809	53.50	6.58	9.07	6.55	6.13	1.92

The refined parameters such as lattice parameters, unit cell volume, crystal size, R factors and χ^2 for all samples are listed in Table 1. The lattice parameters decrease with increasing doping, and thus, the cell volume decreases with increasing doping.



The Rietveld refinement of the X-ray diffraction patterns is shown in Fig.3a-f for $Mg_{1-x}Ni_xFe_2O_4$ $(0 \le x \le 1)$ ferrites. In the Rietveld refinement data, the experimental data are shown as a solid circle and the calculated intensities are shown as a solid line.

3.2. Raman analysis

Raman spectra for undoped $MgFe_2O_4$ and $Mg_{1-x}Ni_xFe_2O_4$ powders were recorded at room temperature. $MgFe_2O_4$ spinel has a cubic structure belonging to the space group Fd3m. From the theoretical calculations, there are five Raman active modes, namely A1g + Eg + 3F2g are also observed.

Table 2. Assignments for Raman modes in the spinel MgFe2O4

Raman modes (cm^{-1})	Assignment
202	$F_{2g}(1)$
307	E_g
463	$F_{2g}(2)$
557	$F_{2g}(3)$
691	A_{1g}

Five Raman modes for $Mg_{1-x}Ni_xFe_2O_4$ $(0 \le x \le 1)$ ferrites were observed at the 202, 307, 463, 557 and 691 cm^{-1}. In the present study, five observed Raman modes (Table 2).

Acknowledgements
The authors are grateful to all staffs of the Frank Laboratory of Neutron Physics for their help in X-ray diffraction and Raman spectroscopy experiments in Joint Institute for Nuclear Research, Dubna, Russia.