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XRD, microstructural and EPR susceptibility characterization of combustion synthesized nanoscale $Mg_{1-x}Ni_xO$ solid solutions

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Abstract

The lattice parameter a(x) of the stoichiometric $Mg_{1-x}Ni_xO(0 \le x \le 1)$ solid solutions prepared by urea-based combustion synthesis with fuel to oxidizer ratio ($\psi = 1$) was determined by X-ray diffraction. It was found that the dependence of the lattice parameter a(x) on the composition deviated more from the linear Vegard's model (VM) when compared to Kuzmin–Mironova (KM) model. a(x) in the $Mg_{1-x}Ni_xO$ system differs nontrivially from the predictions of both VM and KM models. For x = 0.4 ($Mg_{0.6}Ni_{0.4}O$), the maximum deviation was about 2 and 1.7 pm, respectively. The increase in the intensity of (1 1 1) peak in XRD with increase of nickel concentration confirms that the substitution induces changes at the unit cell level. Nelson–Riley function (NRF) and Williamson–Hall plots are used to calculate micro strain in the solid solution. This analysis indicates that the micro strain is maximum for the compositions 60–40 ($Mg_{0.6}Ni_{0.4}O$), 50-50 ($Mg_{0.5}Ni_{0.5}O$) and 40-60 ($Mg_{0.4}Ni_{0.6}O$). The crystallite size was estimated using Williamson–Hall plot. We conclude that almost similar sized crystallite is formed in all the compositions studied. Porosity determined using XRD increases with a raise in the nickel concentration. The SEM morphology provides corroborative evidence. EPR susceptibilities of solid solution. $Mg_{1-x}Ni_xO$ are determined at room temperature. Variable temperature of EPR allowed to check the Curie–Weiss law for solid solution. The linearity of $C_M(x)$ and $\Theta(x)$ with concentration of nickel has ruled out chemical clustering in the samples. \mathbb{C} 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Diluted antiferromagnets represent an interesting class of materials whose crystallographic structures are closely related to their magnetic properties [1]. The MgO–NiO solid solution belongs to the class of the diluted facecentered cubic (fcc) antiferromagnets. While NiO is a type-II antiferromagnet and a charge-transfer insulator with Neel temperature $T_N = 523$ K [2,3], MgO is a diamagnetic ionic insulator with fcc structure. The Mg_{1-x}Ni_xO (0 < x < 1) system is ideal for studying the effects of dilution on the magnetic properties. This system forms a continuous series of solid solutions with rock-salt crystal structure due to a small difference, of about 3 pm, in the ionic radii of Ni²⁺, Mg²⁺ ions 0.083 and 0.086 nm, respectively [4]. The lattice constant of the solid solution varies from 0.4209 nm in pure MgO (x = 0) to 0.4177 nm in pure NiO (x = 1), close to the linear dependence [5]. Thus, the variation of lattice parameter is about 0.8% in $Mg_{1-x}Ni_xO$ system. Therefore, the crystal structure does not change upon dilution [6]. Pure NiO in the paramagnetic phase has a rock-salt-type crystal structure with nickel ions located at the center of the NiO octahedra. In the antiferromagnetic phase, the structure of NiO undergoes a weak cubic-to-rhombohedral distortion due to the magnetostriction effect [7]. Substitution of nickel ions by magnesium stabilizes the cubic structure [7]. Magnetic ordering of these compounds depends on the concentration and site distribution of magnetic ions as well as on the signs and relative strengths of J_{NN} and J_{NNN} superexchange interactions between two Ni²⁺ ions via an oxygen ion [8,9].

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The NN interactions, having ferromagnetic and antiferromagnetic characters, occur within the three atom chains $Ni^{2+}-O^{2-}-Ni^{2+}$ with angle Ni–O–Ni = 90°, while the NNN interactions having antiferromagnetic character with in linear atom chains Ni²⁺-O²⁻-Ni²⁺ with angle Ni–O–Ni = 180°. The values of J_{NN} and J_{NNN} for NiO are 34 and 202 K [5,10]. A reduction in the particle size of these solid solutions from micrometer to nanometer dimensions is expected to modify their magnetic behavior by way of increased surface and interface ions and a reduction in the crystalline anisotropy. A change from bulk-like to clusterlike behavior with enhanced magnetic moment and magnetization is anticipated in the systems with welldefined magnetic phase transitions. A change in the transition temperature could arise. In general, the magnetic behavior would show size dependence in addition to dilution dependence. In this work, we described and discussed structural and magnetic characterization of the $Mg_{1-x}Ni_xO$ (0 < x < 1) system samples by chemical combustion method for the first time instead of the commonly employed solid state reaction. Thus, we were able to prepare selected compositions of the $Mg_{1-x}Ni_xO$ system as a more homogeneous product in a short time. Our synthesis results in highly crystalline products without the

[18]. In the present work, nickel nitrate, magnesium nitrate and an organic fuel, typically urea (NH_2CONH_2) have been used. The mechanism of combustion reaction is quite complex. The parameters that influence the reaction include type of fuel, fuel to oxidizer ratio, use of excess oxidizer, ignition temperature and water content of the precursor mixture.

For the preparation of these samples of $Mg_{1-x}Ni_xO$ $(0 \le x \le 1)$ in the present study, the required amounts of two nitrates $Mg(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (MERCK Ltd.) were dissolved in distilled water along with fuel urea (NH₂CONH₂) (QUALIGENS). Stoichiometric compositions of the metal nitrates and fuel are calculated based on the propellant chemistry. Thus, heat of combustion is the maximum for the fuel to oxidizer ratio (ψ) that equals 1 [17]. Based on the concepts used in the propellant chemistry, the elements C, H, Mg, Ni and or any other metals are considered as reducing elements with valences 4+, 1+, 2+, 2+ (or valency of metal ion in that compound), respectively. Oxygen is an oxidizer having the valency of 2⁻. The valency of nitrogen is taken as zero because of its convertibility into molecular nitrogen during the combustion. The fuel to oxidizer ratios (ψ) [17] are calculated using the equation

$$\psi = \frac{n\{(1 \times 4_{\rm C}) + (4 \times 1_{\rm H}) + (2 \times 0_{\rm N}) + (1 \times -2_{\rm O})\}}{a[(1 \times 2_{\rm Mg}) + 2((1 \times 0_{\rm N}) + (3 \times -2_{\rm O}))] + b[(1 \times 2_{\rm Ni}) + 2((1 \times 0_{\rm N}) + (3 \times -2_{\rm O}))]},\tag{1}$$

use of high temperature furnace. Due to evolution of a large amount of gases produced during combustion processes, nanosized, porous and foamy products are obtained [11] which are not easily achieved in other methods. Our results unambiguously show that the composition dependence of the lattice parameter a(x) of Mg_{1-x}Ni_xO system deviates from the linear system assumed within Vegard's and Kuzmin–Mironova models.

2. Samples preparation and experimental techniques

Various techniques are available for the preparation of nanomaterials. They include dividing or breaking down of a bulk solid or building up process. Some of the wellknown methods are laser ablation, plasma synthesis, chemical vapor deposition, mechanical alloying or highenergy milling and sol-gel synthesis [12]. All these techniques involve and require special chemicals and equipments. We prepared $Mg_{1-x}Ni_xO$ solid solutions by employing the low temperature initiated self-propagating, gas producing combustion method [13,14]. Combustion synthesis involves an exothermic reaction between an oxidizer (metal nitrates) and fuel (urea for example). It is an important powder processing technique generally used to produce complex oxide nanomaterials, aluminates [15], ferrites [16], and chromites [17]. We already used this method in the past to make PbZrO₃ using citric acid as fuel

where n is mole of fuel and a, b are mole fractions of Mg and Ni nitrates, respectively.

The aqueous solution is thoroughly stirred with a magnetic stirrer to achieve complete dissolution of all solid reagents and the clear solution is placed on a hot plate to initiate the reaction. As the temperature reached 100 °C, water started to boil and evaporate from the solution, which increased the solution viscosity substantially. Meanwhile, the compound caught fire and finally a black, lightweight powder was obtained. This is the precursor. The precursor and the precursor annealed for 2 h at 250 °C (± 5 °C) are both characterized. The combustion is self-propagating, i.e., once ignited, it automatically goes to completion without supply of additional heat from an external sources. The reaction equations assuming complete combustion of the redox mixture used for synthesis of Mg_{1-x}Ni_xO solid solution may be written as

$$\begin{split} Mg(NO_3)_2 \cdot 6H_2O + NH_2CONH_2 \\ \rightarrow MgO(s) + 2H_2O(g) + CO_2(g) + 2N_2(g) \end{split} \tag{2}$$

$$\begin{split} \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2 \\ \rightarrow \text{NiO}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) + 2\text{N}_2(\text{g}) \end{split} \tag{3}$$

$$\begin{split} \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2 \\ \rightarrow \text{MgNiO}(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g) + 3\text{N}_2(g) \end{split} \tag{4}$$

Structural characterization on these samples was performed using Philips X-ray diffractometer with Cu K α_1 radiation. The principle of operation of this diffractometer can be understood as follows. The sample is spread on a glass plate which is supported on a table rotating about on a particular axis to the plane of drawing. The X-ray tube is normal to the plane of the drawing, therefore parallel to diffractometer axis. X-rays diverge from the source and are diffracted by the specimen to form a convergent beam which comes into focus at a slit and enters into a counter. The intensity of the diffracted beam is measured directly by an electronic counter which converts the incoming X-rays into electric pulses counted by X-ray detector placed on the circumference of a centered circle. The counter is powerdriven at a constant angular velocity about the diffractometer axis. The range of 2θ (30–90°) of interest is covered in this fashion and the curve of intensity versus 2θ is finally plotted on a computer. Microstructure studies were carried out using Philips XL-30 SERIES SEM by spreading asprepared and the ultrasonicated (10 min in toluene) samples over a thoroughly cleaned and dried microscopic slide after applying vacuum grease. EPR spectra were obtained from samples containing 4 mm quartz tube. In the EPR experiment, a highly uniform and reasonably stable static magnetic field H, in the range 0-0.5 T, is applied to the sample placed in a rectangular microwave resonance cavity. The microwave magnetic field component perpendicular to the direction of the static field causes magnetic dipole transitions when the microwave energy quantum hv is equal to the Zeeman splitting $g\beta H$, of the two spin status (M = 1/2 and -1/2) of the paramagnetic, i.e., $v = g\beta H$. The parameter q is the spectroscopic splitting factor representing the nature of unpaired electrons and β is the basic unit of electronic moment called Bohr magnetic moment which is Bohr magnetron. Magnetic dipole transitions in a paramagnetic material are observed in EPR by sweeping the magnetic field intensity rather than sweeping the microwave frequency which is technically impracticable. A typical X-band EPR spectrometer is used here. This contains the Gunn oscillator whose frequency and the intensity of the microwaves produced thereby are controlled and accurately measured by appropriate circuits. The cavity system includes the components, which hold the sample and direct and control the microwave beam to and from the sample. The detection and modulation system-monitor amplifies and records the signal. The EPR spectra of the combustion synthesized solid solution in this work were recorded on a JEOL JES-FA 200X-band EPR spectrometer under optimized conditions of modulation amplitude, receiver gain, time constant and scan time. The instrument is computerized so that data can be retrieved for convenient analysis. JOEL DVT controller was used (323-453 K) for controlling the temperatures while heating and cooling. The spectrometer setting used in recording the spectra were as follows: modulation frequency = $100 \, \text{kHz}$; modulation amplitude = 1 mT; frequency = 9.15966 GHz; power = 0.998 mW.

3. Results and discussion

3.1. Structure and micro strain of $Mg_{1-x}Ni_xO$ solid solution versus crystallite size from X-ray diffraction

The XRD patterns obtained on annealed samples, at 250 °C (\pm 5 °C) for 2h, Mg_{1-x}Ni_xO system are shown in Fig. 1. The patterns were recorded over a range of 2θ angles from 30° to 90° and crystalline phases were identified using the JCPDS data (78-0430, 78-0643). The XRD peaks of MgO are very similar to those of NiO. The peak intensities of (111), (200), (220), (311) and (222) reflections are comparable with JCPDS values. The lattice parameters of the solid solution are in agreement with the earlier work [1]. One can notice a strong variation of the (111) peak intensity for solid solutions in Table 1 occurring due to the difference between the X-ray scattering intensities of the nickel and magnesium sublattices. The intensity of (111) peak in compounds with the NaCl-type crystal structure, which is the structure type of the $Mg_{(1-x)}Ni_xO$ series, depends on the difference between the number of electrons of the anions and cations [15]. This explains the smaller magnitude of the (111) peak for MgO as compared to that of NiO. Table 1 shows the intensity variation of (111) peak when the concentration varies from 0% to 100%. We can see significant variation of the increase in the intensity of the peak. We can further notice

	(111)	(200)		(220)	(311)	(000)
		1	k	,		(222)
	(111)	(200)	j	(220)	(311)	(222)
	(111)	(200)	i	(220)	(311)	(222)
s)	(111)	(200)	h	(220)	(311)	(222)
o.count	(111)	(200)	g	(220)	(311)	(222)
sity (arł	(111)	(200)	f	(220)	(311)	(222)
Inten	(111)	(200)	е	(220)	(311)	(222)
	(111)	(200)	d	(220)	(311)	(222)
	(111)	(200)	с	(220)	(311)	(222)
	(111)	(200)	b	(220)	(311)	(222)
	(111)	(200)	а	(220)	(311)	(222)
3	40	50		60 2°	70	80 90

Fig. 1. X-ray diffractograms of $Mg_{1-x}Ni_xO$ solid solutions at 300 K: (a) MgO (x = 0), (b) Mg_{0.9}Ni_{0.1}O, (c) Mg_{0.8}Ni_{0.2}O, (d) Mg_{0.7}Ni_{0.3}O, (e) Mg_{0.6}Ni_{0.4}O, (f) Mg_{0.5}Ni_{0.5}O, (g) Mg_{0.4}Ni_{0.6}O, (h) Mg_{0.3}Ni_{0.7}O, (i) Mg_{0.2}Ni_{0.8}O, (j) Mg_{0.1}Ni_{0.9}O and (k) NiO (x = 1).

Table 1The intensity and area under the (1 1 1) peak

%Ni	Intensity of (111) peak	Area under (111) peak
0 (MgO)	65 ± 3	44 ± 3
10	56 ± 3	80 ± 5
20	77 ± 4	123 ± 7
30	129 ± 6	126 ± 7
40	198 ± 10	192 ± 11
50	213 ± 11	247 ± 15
60	289 ± 14	251 ± 15
70	335 ± 17	267 ± 15
80	367 ± 18	265 ± 16
90	368 ± 18	267 ± 16
100 (NiO)	360 ± 18	270 ± 16



Fig. 2. Lattice parameter a(x) compared to Vegard's and Kuzmin-Mironova models: (a) $a(x)_{EXP}-a(x)_{VM}$ and (b) $a(x)_{EXP}-a(x)_{KM}$.

the increase in the area of (111) peak results with the increase in the concentration of Ni in Table 1 before and after annealing. We can conclude that the increased concentration of nickel in the $Mg_{1-x}Ni_xO$ solid solution results in a homogeneous dense phase. It was believed for a long time that lattice parameter of $Mg_{1-x}Ni_xO$ system depends linearly on the composition and follows the Vegard's rule $a(x)_{VM} = xa_{NiO} + (1-x)a_{MgO}$ [1,16]. However, the results of the X-ray diffraction strongly suggest deviation from Vegard's model. This is due to a deviation of the local environment around Ni²⁺ ions from the Vegard's model. The lattice parameters measured from XRD are comparable to the previous work [1]. The values obtained for the lattice parameter a(x) and their total uncertainties Δa are reported in Fig. 2 along with those calculated using Vegard's $a(x)_{VM} = xa_{NiO} + (1-x)a_{MgO}$ and Kuzmin-Mironova models. To explain the experimental behavior of a(x), Kuzmin and Mironova suggested a model that assumes that the Ni-Ni inter-atomic distance remains nearly constant at all compositions. Therefore, they supposed that $a_{NN}(x) = a_{NiO} = Constant$. The average Ni-Mg inter-atomic distance varies linearly with concentration and it can be given as a linear function $a_{NM}(x) = f(b_1 + b_2 x)$ and finally they got the expression

$$a(x)_{\rm KM} = x^2 a_{\rm NiO} + 2x(1-x)(b_1 + b_2 x) + (1-x)^2 (xa_{\rm NiO} + (1-x)a_{\rm MgO}).$$
(5)

Taking into account the displacement of nickel atoms upon dilution by magnesium, here b_1 and b_2 are determined by the least-square fit to Eq. (5). x is concentration of Ni varying from 0 to 1 and a_{NiO} , a_{MgO} are lattice parameters of pure NiO and MgO. Using Eq. (5) for the present system, we achieved the values $b_1 = 4207.6 \pm 33 \text{ pm}$ and $b_2 = -13.51 \pm 0.108$ pm. The present results for pure NiO and MgO are in fair agreement with the known values published by others [1,2]. The value of lattice parameter (a) for pure NiO is close to that of Ref. [19]. The ideal cubic cell of NiO, however exists only in the paramagnetic phase that is above the Neel temperature $T_{\rm N} = 532$ K. The NiO structure at room temperature experiences rhombohedral distortion, which however, is small. This distortion is reduced and cubic structure is stabilized due to the Mg^{2+} ion substitution. A careful examination of Fig. 2, the differences $a(x)-a(x)_{VM}$ and $a(x)-a(x)_{KM}$ show that the deviation is less in the case of KM model when compared to VM. This is because in Vegard's model the values of the Ni-O and Mg-O bond lengths in the solid solutions are considered to be constant as in NiO and MgO. Therefore, the lattice parameter a(x) of solid solution becomes equal to the additive sum of the lattice parameter of individual components weighted with concentrations of each other, whereas the KM model takes into account the off-center displacements of nickel ions [1] and is in good agreement with our experimental values.

The variation of the lattice parameter a(x) versus the nickel concentration x is given in Table 2. A least-square fit to the experimental data yields the equation

$$a(x) = (420.77 - 3.10x) \,\mathrm{pm.}$$
 (6)

It was observed that the values of lattice parameter a(x) in the Mg_{1-x}Ni_xO series differ from those predicted by the Vegard's model (VM) and Kuzmin–Mironova model.

Table 2 The variation of lattice parameter a(x) in Mg_(1-x)Ni_xO in solid solution with Ni concentration

%Ni	$a(x)_{\rm vm}$ (nm)	$a(x)_{\rm km}$ (nm)	$a(x)_{\text{EXP}}$ (nm)
0 (MgO)	0.42091	0.42091	0.42091 ± 0.00336
10	0.42060	0.42057	0.42045 ± 0.00336
20	0.42028	0.42025	0.42012 ± 0.00336
30	0.41996	0.41993	0.41981 ± 0.00336
40	0.41964	0.41962	0.41930 ± 0.00335
50	0.41933	0.41931	0.41904 ± 0.00335
60	0.41901	0.41901	0.41887 ± 0.00335
70	0.41869	0.41870	0.41861 ± 0.00335
80	0.41838	0.41839	0.41827 ± 0.00335
90	0.41806	0.41807	0.41802 ± 0.00334
100 (NiO)	0.41774	0.41774	0.41774 + 0.00334

(a) Predicted from Vegard's model $a(x)_{VM}$, (b) predicted from Kuzmin–Mironova model $a(x)_{KM}$, and (c) experimental values $a(x)_{EXP}$.

The maximum deviation is about 2 and 1.7 pm, respectively, for x = 0.4 (Mg_{0.6}Ni_{0.4}O). This can be explained based on the type of local deformation around impurity ions in the MgO and NiO host lattices. To decide on the type of local deformation, one can compare the value of $a_{\rm NM}$ calculated from the coefficient b_i to the host lattice parameter a(x) when x = 0 (MgO) and x = 1 (NiO). At these end compositions, the impurity of Ni(Mg) can be considered to be isolated in the host MgO(NiO) matrix. At x = 0, $a_{\rm NM} = 0.42075$ nm which is smaller than MgO lattice constant (0.42123 nm) but larger than the sum of undistorted Ni–O and Mg–O distances (0.41948 nm). Thus, the local environment in Ni-doped MgO partially relaxes in the direction of impurity ions. In other words, the host lattice MgO shrinks upon Ni-substitution.

3.1.1. Strain analysis

The Nelson–Reily function (NRF) versus $\Delta d/d$ curves [20,21] and least-squares regression line $(2W)^2 \cos^2 \theta$ as a function of $\sin^2 \theta$ [22,23] for Mg_{1-x}Ni_xO system obtained from the XRD data are plotted in Fig. 3. Systematic lattice transformation of all the crystal planes upon Ni substitution is clearly evident (Fig. 3). $\Delta d/d$ values increase up to C = 0.5 and thereafter it starts decreasing all the way up to undoped NiO(x = 1). In the case of Mg-rich and Ni-rich compositions, $\Delta d/d$ values lie on a horizontal line, almost parallel to NRF axis, which indicates the absence of stacking faults in the cubic structure. But, the rather large scatter observed in $\Delta d/d$ values for the intermediate 60–40 (Mg_{0.6}Ni_{0.4}O), 50–50 (Mg_{0.5}Ni_{0.5}O) and 40–60 (Mg_{0.4}Ni_{0.6}O) samples are a measure of the high concentration of stacking faults present in these compositions.



Fig. 3. Strain analysis from NRF of solid solution of $Mg_{1-x}Ni_xO$ obtained from XRD: (a) MgO(x = 0), (b) $Mg_{0.8}Ni_{0.2}$, (c) $Mg_{0.6}Ni_{0.4}$, (d) $Mg_{0.5}Ni_{0.5}$, (e) $Mg_{0.4}Ni_{0.6}$, (f) $Mg_{0.2}Ni_{0.8}O$ and (g) NiO (x = 1).



Fig. 4. Micro strain calculated (a) Williamson–Hall plot, (b) least-squares regression line $(2W)^2 \cos^2 \theta$ as a function of $\sin^2 \theta$.

Ni-rich and Mg-rich samples show less scatter with small slope values whereas intermediate (40%, 50%, 60% Ni doped) compositions give larger slope values. Average micro strain is calculated for all compositions of $Mg_{1-x}Ni_xO$ by measuring slopes of the least-squares regression line. Maximum strain values are observed only in the intermediate 40%, 50% and 60% of Ni doped MgO but not other. Using the Williamson-Hall equation [24], we determined the micro strain. The micro strain calculated using above two methods is as shown in Fig. 4. Obviously, the micro strain is the maximum for intermediate compositions, as is observed in NRF function. This could arise from local distortions which are maximum for compounds with 0.4 < x < 0.6. Both methods of XRD analysis, i.e., NRF and Williamson-Hall plots bring this out and the latter method more prominently.

3.1.2. Crystallite size

All samples produce appreciable diffraction broadening and it is reasonably assumed that this arises from the crystallite size and internal stresses. Diffraction theory predicts that the breadth due to crystallite size varies with angle as sec θ and that due to elastic strain as $\tan \theta$ [22]. The additional broadening in diffraction peaks beyond the inherent peak widths due to instrumental effects can be used to measure crystallite size as low as 1.0 nm. The crystallite size of as-prepared and annealed compositions were calculated from the full width at half maximum (FWHM) of all the peaks (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) using the Debye–Scherrer formula [25]

$$t = \frac{0.9\lambda}{B\cos\theta}.$$
(7)

The Gaussian function gives a better fit to the FWHM of all the peaks than the Lorentzian function. Therefore, the observed XRD peaks are essentially Gaussian, pointing to a uniform crystallite size distribution. We also used another method, the Williamson–Hall equation to calculate strain and particle size of the each composition [24]. The Williamson–Hall equation is expressed as follows:

$$B\cos\theta = \frac{K\lambda}{t} + 2\varepsilon\sin\theta,\tag{8}$$

where *B* is the full-width at half-maximum (FWHM) of the XRD all peaks, K is Scherrer constant, t is the crystalline size, λ the wavelength of the X-ray, ε the lattice strain and θ the Bragg angle. In this method, $B\cos\theta$ is plotted against $2\sin\theta$. Using a linear extrapolation to this plot, the intercept gives the particle size $K\lambda/t$ and slope gives the strain (ϵ). According to Table 3, the crystallite size of pure MgO is 21 + 1 nm and it decreases as the concentration of the Ni increases. At first, the size is decreased to 12 + 1 nm for Mg_{0.8}Ni_{0.2}O concentration and subsequently the size increases very slowly to 29 + 1 nm for Mg_{0.2}Ni_{0.8}O and then decreases to 26 ± 1 nm for pure NiO. As the fuel to oxidizer ratio $\psi = 1$ is used to prepare all the compositions, the heat of combustion is maximum for $\psi = 1$ [17] and hence the size of the particle is minimum. We obtained nearly the same average crystallite size for all the investigated compositions and hence we can conclude that there is no appreciable effect of size on the XRD of $Mg_{(1-x)}Ni_xO$ solid solutions. This is understandable because of the nearly equal lattice parameters of MgO and NiO.

3.2. Porosity measurement

Products of combustion synthesis are highly porous. They possess much less densities compared to theoretical values [26]. The density of prepared and annealed samples was determined by the XRD. The percentage of porosity was calculated from the measured and theoretical density, according to the following equation:

porosity,
$$P = \left(1 - \frac{D}{D_{\rm T}}\right) \times 100,$$
 (9)

where D_T is theoretical density, and D is the density of the samples measured using XRD. Using Eq. (9) the porosity values are calculated. It is clear from Table 4 in

Table 3

Crystallite size calculated from XRD using Debye–Scherrer formal and Williamson–Hall plot

%Ni	Crystalline size from Debye–Scherrer (nm)	Crystalline size from Williamson–Hall plot (nm)
0 (MgO)	20 ± 0.6	21 ± 0.42
10	13 ± 0.39	14 ± 0.28
20	11 ± 0.33	12 ± 0.24
30	13 ± 0.39	13 ± 0.26
40	14 ± 0.42	19 ± 0.38
50	14 ± 0.42	20 ± 0.4
60	16 ± 0.48	21 ± 0.42
70	18 ± 0.54	22 ± 0.44
80	22 ± 0.66	29 ± 0.58
90	23 ± 0.69	24 ± 0.48
100 (NiO)	24 ± 0.72	26 ± 0.52

Table 4 Porosity calculated from the X-ray diffraction before annealing and after annealing

% Ni	Porosity before annealing	Porosity after annealing
0 (MgO)	1.1452 ± 0.0458	0.2486 ± 0.0099
10	1.1031 ± 0.0441	0.4890 ± 0.0196
20	0.9623 ± 0.0385	0.5400 ± 0.0216
30	0.8387 ± 0.0335	0.6804 ± 0.0272
40	$2.0971 \pm .00839$	0.8857 ± 0.0354
50	3.1239 ± 0.1250	1.1115 ± 0.0445
60	2.9297 ± 0.1172	1.3394 ± 0.0536
70	2.4603 ± 0.0984	1.4921 ± 0.597
80	2.7709 ± 0.1108	1.7010 ± 0.0680
90	2.9319 ± 0.1173	1.8210 ± 0.0728
100 (NiO)	2.9274 ± 0.1171	2.0250 ± 0.0810

un-annealed samples the variation of porosity is not uniform, whereas after annealing porosity increases uniformly with Ni doping. This can be explained by taking the density of NiO (6.67 g/cm^3) into account which is more when compared to MgO (3.58 g/cm^3). Mainly, the porosity depends on the density and hence the porosity is more for rich Ni solid solutions. This is directly seen in scanning electron micrographs (SEM).

3.3. Scanning electron microscopy

Secondary electron images show qualitatively the difference in the surface morphology of chemical combustion prepared samples of $Mg_{0.9}Ni_{0.1}O$, $Mg_{0.8}Ni_{0.2}O$, $Mg_{0.7}Ni_{0.3}O$, $Mg_{0.5}Ni_{0.5}O$, $Mg_{0.3}Ni_{0.7}O$ and $Mg_{0.1}Ni_{0.9}O$ as in Fig. 5(a–f). The samples were ultrasonicated in toluene for 10 min to disperse the particles and the SEM micrograph is as shown in Fig. 6(a–c). It is very interesting that in Fig. 5 as the concentration of the Ni is increased the porosity of the samples is increased, same phenomenon was observed in the calculation of porosity from XRD in Section 3.2. Therefore, the same reasoning may be given for the increase of porosity. Fig. 6 shows that all the compositions of uniform and spherical average size are in the range of 100–170 nm.

3.4. Magnetic ions exchange interactions in $Mg_{1-x}Ni_xO$ solid solution

For diluted antiferromagnets [27,28] in the hightemperature limit ($T > T_N$), the leading term for χ yields the Curie–Weiss law

$$\chi(x) = \frac{C(x)}{T + \Theta(x)},\tag{10}$$

where C(x) is the Curie constant and $\Theta(x)$ is the Curie–Weiss temperature. Here, one should understand that χ_g , the susceptibility per gram, and the variations of $C_g(x)$ and molar $C_M(x)$ with x are different. It can



Fig. 5. Scanning electron micrographs of solid solution $Mg_{1-x}Ni_xO$ as-prepared (a) $Mg_{0.9}Ni_{0.1}$, (b) $Mg_{0.8}Ni_{0.2}$, (c) $Mg_{0.7}Ni_{0.3}$, (d) $Mg_{0.5}Ni_{0.5}$, (e) $Mg_{0.3}Ni_{0.7}O$ and (f) $Mg_{0.1}Ni_{0.9}O$.

be shown that

$$C_{\rm M}(x) = C_{\rm M}(1)^* x,$$
 (11)

$$C_{\rm g}(x) = \frac{C_{\rm M}(x)}{W} \tag{12}$$

and

$$\Theta(x) = \Theta(1)^* x, \tag{13}$$

where W is the molecular weight of $Mg_{1-x}Ni_xO$. Thus, although $C_M(x)$ and $\Theta(x)$ vary linearly with x, $C_g(x)$ varies nonlinearly with x. A plot of $1/\chi^*$ against T may be used to determine $C_M(1)$ and $\Theta(x)$. $\Theta(x)$ in a randomly diluted system measures the sum of all magnetic interactions. It should vary linearly with x if there is no chemical clustering (assuming no significant change in lattice constant). Thus, the experimental variations of $\Theta(x)$ with x provide a check on the quality of random dilution of the samples. If $\Theta(x)$ is too large, it would indicate chemical clustering. Since the maximum change in the lattice constant between x = 0 and 1 in Mg_{1-x}Ni_xO is about 0.8%, change in J₁ and J₂ with dilution should be quite negligible [29].

3.5. Susceptibility of the $Mg_{1-x}Ni_xO$ solid solution at room temperature

In their work, Mironova-Ulmane et al. [7] have identified four domains in the $Mg_{1-x}Ni_xO$ solid solution: (1) a homogeneous antiferromagnet ($0.63 \le x \le 1$); (2) a tricritical region or a frustrated antiferromagnet ($0.4 \le x \le 0.63$);



Fig. 6. Scanning electron micrographs of solid solutions: (a) Mg_{0.3}Ni_{0.7}O, (b) Mg_{0.7}Ni_{0.3}O, (c) NiO.

(3) a spin-glass state $(0.25 \le x \le 0.4)$ and (4) a diamagnet $(x \le 0.2)$ [30]. It was found that the regular domain structure is more sensitive to the concentration of magnesium ion than the temperature and appears upon the cooling at temperature well below $T_{\rm N}$. We did EPR at room temperature for all the samples and calculated the number of spins participating in resonance with the help of reference (standard) CuSO₄ · 5H₂O by using the following formula [31,32]:

$$N_x = \frac{A_x (\operatorname{Scan}_x)^2 G_{\mathrm{std}}(B_{\mathrm{m}})_{\mathrm{std}}(g_{\mathrm{std}})^2 \{s(s+1)\}_{\mathrm{std}}(P_{\mathrm{std}})^{1/2}}{A_{\mathrm{std}} (\operatorname{Scan}_{\mathrm{std}})^2 G_x (B_{\mathrm{m}})_x (g_x)^2 \{s(s+1)\}_x (P_x)^{1/2}} N_{\mathrm{std}},$$
(14)

where A_x is the area under the absorption curve which can be obtained by double integrating the first derivate curve of signal after least-square fits to asymmetric Gaussian function. Scan is the magnetic field corresponding to the unit length of the chart; *G* is the gain; B_m is the modulation field width; *g* is the splitting factor; *S* is the spin of the system in its ground state and *P* is the microwave power. The subscripts 'x' and 'std' represent the corresponding quantities for the unknown samples (Mg_{1-x}Ni_xO) and reference, respectively.

The paramagnetic susceptibilities can be calculated from the EPR data by using the formula

$$\chi = \frac{Ng^2\beta^2 J(J+1)}{3K_{\rm B}T},$$
(15)

where N is the number of spins per M^3 , the rest of the symbols have their meaning. N can be calculated using Eq. (14) and q taken from the EPR data. The line width of the solid solution is increased for Mg_{0.9}Ni_{0.1}O $(73.5\pm0.1 \text{ G})$ and goes on increasing to $(365\pm0.1 \text{ G})$ for Mg_{0.1}Ni_{0.9}O with increase in Ni concentration. The number of spins (N) is also increasing with the concentration of the Ni, for Mg_{0.9}Ni_{0.1}O (0.4763) and it increases (100.25) for Mg_{0.3}Ni_{0.7}O. It is decreased for other two compositions 23.4 and 18.6 for Mg_{0.2}Ni_{0.8}O and $Mg_{0,1}Ni_{0,9}O$, respectively. These observations are in accord with the paramagnetic and antiferromagnetic natures of compositions. While paramagnetic nature is exhibited by the compositions x = 40, 50, 60, 70 (%Ni) antiferromagnetic character is displayed by the compositions x = 80, 90(%Ni), respectively. Using the above Eq. (15) susceptibilities were calculated at room temperature. The normalized susceptibility $\chi_g^* = \chi_g/x$, where χ_g is the measured suscept-ibility per gram for each sample of Mg_{1-x}Ni_xO. The calculated susceptibility with concentration is drawn in Fig. 7 and is comparable with the previous results. Fig. 7 shows the variation of the susceptibility of the solid solution with concentration of nickel. The susceptibility is increased as the concentration of Ni is increasing till 60% of Ni ((Mg_{0.4}Ni_{0.6}O) and it decreases. The susceptibility of $(Mg_{0.9}Ni_{0.1}O)$ is $21 \times 10^{-6} M^3/kg$ and it is going to a maximum for $(Mg_{0.4}Ni_{0.6}O)$ and is $576 \times 10^{-6} M^3/kg$. It is decreasing for Ni-rich (Mg_{0.1}Ni_{0.9}O) $113 \times 10^{-6} \text{ M}^3/\text{kg}$. The above results can be understood in the light of the



Fig. 7. Susceptibility of the solid solution $Mg_{1-x}Ni_xO$ obtained form EPR verses Ni concentration.

previous work as follows. The whole compositional region is divided into four parts: (1) the Mg-rich compositions $(Mg_{0.9}Ni_{0.1}O, Mg_{0.8}Ni_{0.2}O)$ exhibit diamagnetic behavior because MgO is diamagnetic martial and Ni content is very small; (2) the compositions $(Mg_{0.7}Ni_{0.3}O, Mg_{0.6}Ni_{0.4}O)$ are said to be in spin-glass state as the Ni concentration is moderate; (3) the compositions $(Mg_{0.5}Ni_{0.5}O, Mg_{0.4}Ni_{0.6}O)$ are having maximum susceptibility and it is named as tricritical region or anti ferromagnetic frustrated region as the concentration of Ni is increased; (4) the Ni-rich compositions are named as homogeneous antiferromagnetic region.

3.5.1. Susceptibility of the $Mg_{1-x}Ni_xO$ solid solution at different temperatures (323–453 K)

Using Eqs. (14) and (15), the susceptibilities of all the solid solutions are calculated at different temperatures ranging from 323 to 453 K as in the above method (the temperature range is limited because of EPR instrument). Here, the number of spins participating in resonance were calculated first using Eq. (14). The spins are increasing with increase in the temperature. This could be due to progressive breakup of antiferromagnetic coupling and a corresponding increase in the number of (uncoupled) paramagnetic spins, also possibly due to diamagnetic dilution and defect creation. The temperature dependence of the normalized susceptibility $\chi_g^* = \chi_g/x$, where χ_g is the measured susceptibility per gram for each sample of Mg_{1-x}Ni_xO. To check the validity of the Curie-Weiss (CW) law in Mg_{1-x}Ni_xO and to determine the $C_g(x)$ and $\Theta(x)$ according to equation (CW) (Eq. (10)) a plot of $1/\chi_g^*$ versus T can be used in the region 323-453 K. The values of $C_{g}(x)$ and $\Theta(x)$ so determined are plotted against composition concentration (x) of Ni in Figs. 8 and 9, respectively. An examination of Figs. 8 and 9 enables us to conclude that $C_g(x)$ and $\Theta(x)$ are linearly varying with concentration of Ni. This linearity of $C_g(x)$ and $\Theta(x)$ is very important because it rules out chemical clustering in these compositions. Thus, the experimental variation of



Fig. 8. Variation of molar Curie constant $C(x)_{M}$ plotted against x concentration of Ni which is determined from slope of Eq. (10) (see text).



Fig. 9. Variation of the Curie–Weiss temperature $\Theta(x)$ plotted against the x which is determined the from the intercept of Eq. (10) (see text). The solid line is least-square fit to present data.

 $\Theta(x)$ and $C_g(x)$ with x provides a check on the quality of random dilution of the samples. Least-square fit to the data yield for $\Theta(x)$ versus x is $\Theta(x) = 3.174x - 7.24$ which is in agreement with previous result [8,29]. Least-square fit to the data yield for $C_g(x)$ versus x is $C_g(x) = 8.28x$ which is agreement with previous results where x is concentration Ni [29]. Here, $\Theta(x)$ is not too large and thus there is apparently no chemical clustering in the prepared solid solutions of Mg_{1-x}Ni_xO [29].

4. Conclusions

XRD, SEM and EPR susceptibility measurements of combustion synthesized MgO–NiO solid solutions have been described and discussed in this work. The lattice parameter a(x) of the stoichiometric Mg_{1-x}Ni_xO ($0 \le x \le 1$) solid solutions prepared by urea-based combustion synthesis with fuel to oxidizer ratio ($\psi = 1$) was determined by X-ray diffraction. It was found that the composition dependence of the lattice parameter a(x) deviates more

from the linear Vegard's model (VM) when compared to Kuzmin-Mironova (KM) model. It was observed that a(x)in the $Mg_{1-x}Ni_xO$ system differs nontrivially from the predictions of both VM and KM models and the maximum deviation is about 2 and 1.7 pm for x = 0.4 (Mg_{0.6}Ni_{0.4}O) in the two models, respectively. The increase in the intensity of (111) peak in XRD with increase of nickel concentration confirms substitution changes at the unit cell. Micro strain is calculated in the solid solutions using Nelson-Rilev function (NRF) and Williamson-Hall plot. It was observed that in both methods the micro strain is maximum for the compositions 60-40 (Mg_{0.6}Ni_{0.4}O), 50-50 $(Mg_{0.5}Ni_{0.5}O)$ and 40–60 $(Mg_{0.4}Ni_{0.6}O)$. The crystallite size was estimated using Williamson-Hall plot and was observed that almost same crystalline size with all the compositions. Porosity, as determined using XRD, increases with an increase of nickel concentration. The SEM morphology provides corroborative evidence. EPR susceptibilities of solid solution $Mg_{1-x}Ni_xO$ are determined at room temperature. Variable temperature EPR is allowed to check the Curie-Weiss law for solid solution and the linearity of $C_{M}(x)$ and $\Theta(x)$ with concentration of nickel has ruled out chemical clustering in the samples.

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