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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 $Mg_{1-x}Ni_xO$ $(0 \leqslant x \leqslant 1)$ 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.

Keywords: A. Nanostructures; B. Chemical synthesis; C. X-ray diffraction; D. Electron paramagnetic resonance (EPR)

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 face-centered 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 Ni^{2+}, Mg^{2+} 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 Ni^{2+} 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 $= 90^\circ$, while the NNN interactions having antiferromagnetic character with in linear atom chains Ni^{2+}–O^{2-}–Ni^{2+} with angle Ni–O–Ni $= 180^\circ$. 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 cluster-like behavior with enhanced magnetic moment and magnetization is anticipated in the systems with well-defined 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 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 well-known methods are laser ablation, plasma synthesis, chemical vapor deposition, mechanical alloying or high-energy 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 $PbZrO_3$ using citric acid as fuel [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 $Mg_{1-x}Ni_xO$ $(0\leqslant x\leqslant 1)$ 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 (NH_2CONH_2) (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

$$\psi = \frac{n\{(1\times 4_C)+(4\times 1_H)+(2\times 0_N)+(1\times -2_O)\}}{a[(1\times 2_{Mg})+2((1\times 0_N)+(3\times -2_O))]+b[(1\times 2_{Ni})+2((1\times 0_N)+(3\times -2_O))]}, \tag{1}$$

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

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

$$\begin{aligned}&Ni(NO_3)_2\cdot 6H_2O + NH_2CONH_2\\ &\quad\rightarrow NiO(s) + 2H_2O(g) + CO_2(g) + 2N_2(g)\end{aligned} \tag{3}$$

$$\begin{aligned}&Ni(NO_3)_2\cdot 6H_2O + Mg(NO_3)_2\cdot 6H_2O + NH_2CONH_2\\ &\quad\rightarrow MgNiO(s) + H_2O(g) + CO_2(g) + 3N_2(g)\end{aligned} \tag{4}$$