Synthesis and study of structural, thermal, optical and magnetic properties of stabilized $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system ($0.01 < x < 0.30$)

P P BAKARE, C E DESHPANDE, V G GUNJIKAR, P SINGH,
A B MANDALE and S K DATE*

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

Abstract. A novel chemical passivation route is established to obtain microcrystalline solid solutions of binary oxide system $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($0.01 < x < 0.30$). During the passivation process, controlled thermal decomposition of manganous oxalate is carried out to obtain pure MnO and its subsequent reaction with NiO in oxygen-free nitrogen resulted in microcrystalline powder of these solid solutions. The powder is thoroughly characterized by various physicochemical techniques such as XRD, DTA/TG/DTG, diffused reflectance spectra, magnetic susceptibility, TEM, XPS etc. The observed processing–structure–property correlations confirmed the improved thermal stability of these powders (relative to pure MnO) in air. The important role of dopant paramagnetic Ni^{2+} ions in enhancing the passivation of the bulk Mn^{2+} species is explained on the basis of the formation of mixed oxide complex species on the surface of these microcrystalline powders.

Keywords. Stabilized MnO; chemical synthesis; surface passivation.

1. Introduction

It is well known that freshly prepared pure manganous oxide (MnO) is olive green in colour and highly unstable. Even at ambient conditions, it immediately oxidizes to its higher oxides like $\text{Mn}_2\text{O}_3/\text{MnO}_2$ (black in colour) on its exposure to air (Sidgewick 1950). This poses a difficult problem in carrying out a solid state reaction involving MnO to prepare high performance nickel manganese spinel ferrite. To overcome these difficulties it is essential to protect stoichiometric manganous oxide from its auto-oxidation. We have developed a novel processing route to prepare *in situ* solid solutions of MnO–NiO. In the present paper we report (i) synthesis of different stoichiometric compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($0.01 < x < 0.30$) and (ii) its physicochemical characterization. The structural, thermal, optical, magnetic and surface-electronic properties have been investigated using various techniques such as XRD, DTA/TG/DTG, diffused reflectance spectra, magnetic susceptibility, TEM, XPS, etc and the experimental results and their analysis are presented.

2. Experimental

Figure 1 shows the flow diagram of the chemical passivation process developed in our laboratory. Four different compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ solid solutions are essentially obtained by the controlled pyrolysis of manganous oxalate at 573 K and

*For correspondence.

Figure 1. Preparation of 'stabilized MnO.Ni' system.

its subsequent reaction with NiO in oxygen-free nitrogen at 1123 K. The experimental details for $x = 0.01$ are given in detail below and the other remaining compositions are prepared in identical fashion.

For the preparation of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ with $x = 0.01$, thermal decomposition of the required quantity of manganese oxalate is carried out at 573 K in a slow continuous current of oxygen-free pure nitrogen using the silica unit (Murthy *et al* 1978). It is evacuated till it attains static vacuum and tested for 2–3 h. It is then cooled to room temperature and pure oxygen-free nitrogen is passed into the unit to release vacuum. The required quantity of nickel oxide, prepared earlier by thermal decomposition of nickel nitrate $[\text{Ni}(\text{NO}_3)_2]$ at 773 K in air and degassed separately is added to the freshly prepared MnO in the closed system and mixed homogeneously by careful shaking. It is calcined at 1123 K for 12 h in oxygen-free pure nitrogen. The unit is cooled to room temperature. The polycrystalline material thus obtained, is green in colour (hereafter referred to as 'stabilized MnO.Ni') and quite stable in air which can be easily handled without any fear of its oxidation on its exposure to air. There is no indication of oxygen chemisorption changing its colour from olive green to black. Weighed quantities of 'stabilized MnO.Ni' and NiO in the required proportions are mixed homogeneously and processed further to prepare various compositions with increasing x of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system.

2.1 Physicochemical characterization

The polycrystalline solid solutions of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($0.01 \leq x \leq 0.30$) are characterized

using a variety of analytical techniques. Standard gravimetric methods of chemical analysis (Vogel 1964) are followed to determine the concentration of manganese and nickel in $Mn_{1-x}Ni_xO$ system. Powder X-ray diffractograms for all solid solutions are recorded using Phillips 1730 X-ray diffractometer. The cubic-lattice parameter a is determined from the observed d values and the corresponding intensities. DTA/TG/DTG studies are carried out using Netzsch (STA 409) thermal analyser in the temperature range 295 K to 1273 K in air. Diffused reflectance spectra have been recorded at room temperature on Pye-Unicam SP8-300 UV-VIS spectrometer. Magnetic susceptibility measurements are carried out using Cahn-1000 electrobalance with liquid nitrogen cryostat assembly in the temperature range 80 K to 300 K, calibrated with $HgCo(SCN)_4$. To determine the homogeneity of the composition and to study morphology, samples are examined with JEOL 1200 EX electron microscope with highest acceleration voltage of 120 kV and largest magnification of $\times 10^7$ in the bright field mode. For this study, following sample preparation technique is followed (Carr 1985). A small portion of the powdered sample is dispersed in isopropyl alcohol using ultrasonic bath. A microscope-grid is dipped in the suspension and after drying it becomes ready for viewing. X-ray photoelectron spectra are recorded on the calibrated VG Scientific ESCA-3 MK-II spectrometer with $AlK\alpha$ radiation.

3. Results and discussions

Following well-established analytical method (Vogel 1964), accurate wet-gravimetric analyses have been carried out to establish purity and homogeneity of solid solutions. After establishing their identities, these polycrystalline materials have been characterized for their properties using different techniques.

3.1 XRD

Powder X-ray diffractograms of all solid solutions of $Mn_{1-x}Ni_xO$ ($0.01 \leq x \leq 0.30$) show a characteristic pattern of single phase rock-salt type crystal structure (Rao and Subba Rao 1974). Cubic lattice parameters of these solid solutions are computed from the careful intensity analysis of X-ray diffractograms and are presented in table 1. The lattice parameter decreases linearly with increasing x obeying Vegard's law (Kaelble 1967) and is attributed to the substitutional occupancy of Mn^{2+} ions (ionic radius = 0.080 nm) by Ni^{2+} ions (ionic radius = 0.069 nm) in the lattice. Our experimental results agree with the earlier reported results that MnO and NiO form solid solutions in different proportions (Hahn and Muan 1961; Barret and Evans 1964; Cheetham and Hope 1983).

3.2 TG/DTG/DTA studies

To study the thermal behaviour of the solid solutions and its dependence on concentration of nickel, x , in the system $Mn_{1-x}Ni_xO$ ($0.01 < x < 0.30$), TG/DTG/DTA curves are simultaneously recorded with the heating rate of 10 K/min in the temperature range 298–1273 K in air. Figure 2 shows a typical thermogram for the

Table 1. Cubic lattice parameter a and thermal stability of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system: DTA-TGA-DTG studies.

Concentration of nickel (x) in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$	Cubic lattice parameter a (nm)	Maximum oxygen uptake (%) $\text{MnO} \rightarrow \text{Mn}_2\text{O}_3$ and $\text{NiO} \rightarrow \text{Ni}_2\text{O}_3$		% of Mn^{2+} species	
		Theoretical	Experimental from TG	Oxidized	Unoxidized
0.01	0.4440	11.27	10.26	91.04	8.96
0.10	0.4419	11.22	10.22	91.09	8.91
0.20	0.4399	11.16	9.88	88.53	11.47
0.30	0.4377	11.10	9.67	87.12	12.88

solid solution with lowest conc. $x = 0.01$. It is observed that the sample is gaining weight continuously as indicated by the slow and steady rise in the TG/DTG curves in the temperature range 298–1173 K. The DTA curve also shows a very broad exothermic peak up to 1173 K. This is in contrast with the very fast oxidation of pure MnO i.e. spontaneous reaction taking place in air (Sidgewick 1950) even at room temperature. This gain is understood in terms of the very slow and controlled rate of oxidation as envisaged by the following equation:

The observed gain from the TG/DTG curve is 10.26% which can be compared with complete thermal oxidation of the proportionate physical mixture of MnO plus NiO in air occurring as follows:

This mixture (with same proportion of MnO:NiO as in (1)) has 11.27% uptake of oxygen on its complete oxidation. The observed difference in the % of uptake of oxygen (% of uptake of oxygen in (1) < (2)) shows that 91.04% of Mn^{2+} species present in the solid solution are converted to its higher oxide. It is quite clear now that the remaining 8.96% Mn^{2+} species are not converted to its higher oxide. The % of unconverted species have been attributed to the controlled oxidation of the $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system as a whole. On further heating up to 1223 K a loss in weight of the sample is observed from the TG and the sharp peak of DTG curve. It is an endothermic reaction as also indicated by a sharp DTA peak. The observed % loss in weight is attributed to the reduction of Mn_2O_3 present in the $(\text{Mn}_{1-x}\text{Ni}_x)_2\text{O}_3$ to Mn_3O_4 represented as in (3) (Sidgewick 1950):

No further change in weight of the sample or occurrence of any reaction is observed

Figure 2. Thermogram of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.01$) system.

on further heating the sample in air up to 1273 K. Similar plots have been observed for the remaining compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system and the results are presented in table 1. It shows that the thermal stability (slow rate of oxidation and the % of Mn^{2+} species remaining unoxidized) increases with increasing x . The results will be further substantiated using optical properties, magnetic susceptibility, TEM and XPS studies and will be discussed in the later sections.

3.3 Diffused reflectance spectra

The diffused reflectance spectra of the solid solutions, with $x = 0.01$, 0.2 and 0.3 in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system are recorded at room temperature in the range 380–760 nm (figure 3). All the spectra exhibit characteristic absorption peaks which can be easily assigned on the basis of Tanabe–Sugano diagrams (Tanabe and Sugano 1954) for d^5 and d^8 ions (figure 4). For example, there are three distinct absorption peaks at 16393 cm^{-1} (610 nm), 20833 cm^{-1} (480 nm), 23809 cm^{-1} (420 nm), observed for the sample with $x = 0.01$ in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system (figure 3a). The absorption peak at 20833 cm^{-1} (480 nm) is clearly observed for the sample with lowest concentration, $x = 0.01$ only. Its clear resolution is not observed for the remaining samples with higher concentrations. These observed peaks for the sample with $x = 0.01$ are assigned to

Figure 3. Reflectance spectra of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system (a. $x = 0.01$, b. $x = 0.2$ and c. $x = 0.3$).

Figure 4. Energy level diagram for d^5 (Mn^{2+}) and d^8 (Ni^{2+}) ions in octahedral field.

$${}^6A_1 \rightarrow {}^4T_1, {}^6A_1 \rightarrow {}^4T_2, {}^6A_1 \rightarrow {}^4E,$$

transitions of the ${}^6S_{5/2}$ ground state of Mn^{2+} ions in nearly undistorted octahedral field. These transitions agree very well with the earlier reported optical studies (Pratt and Coelho 1959; Deshpande *et al* 1985; Bakare *et al* 1991) on similar systems. Additional resolvable peaks can be assigned to the Ni^{2+} ions (figures 3a–c). These transitions are ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (23795 cm^{-1}), ${}^3A_{2g} \rightarrow {}^1T_{2g}$ (D) (22180

cm^{-1}), ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (15730 cm^{-1}), ${}^3A_{2g} \rightarrow {}^1E_g$ (D) (14115 cm^{-1}) and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) (9115 cm^{-1}). Experimental data are presented in table 2 for the three samples with different values of x in the $Mn_{1-x}Ni_xO$ system. It is noticed that there is hardly any shift in the transitions of Mn^{2+} ions. This indicates that the local order and electronic structure of Mn^{2+} ions in the surrounding oxygen octahedra remain nearly intact. In other words, the distance between manganese and oxygen, r_{Mn-O} is constant maintaining the ligand parameter, Dq , unchanged. Since Dq is proportional to r^{-5} and r_{Mn-O} is half of its lattice parameter, it is to be expected that the lattice parameter, a , will remain constant with increasing x . However, a small variation in a from 0.4440 nm to 0.4377 nm for $x = 0.01$ to 0.3 is observed which can be attributed to the smaller ionic radii of Ni^{2+} ions (0.069 nm) than Mn^{2+} (0.080 nm) ions. Moreover, it is such a small order that there is hardly any change in Dq so as to cause a shift of the Mn^{2+} peaks in the absorption spectra. In contrast,

$${}^6A_{1g} \rightarrow {}^4T_{2g} \text{ and } {}^6A_{1g} \rightarrow {}^4A_{1g},$$

peaks exhibit considerable shift with increasing x . This results from the direct intermixing and coupling of the $Mn-{}^4T_{2g}$ (G) and $Ni-{}^1T_{2g}$ (D) and $Mn-{}^4A_{1g}$ (G) and $Ni-{}^3T_{1g}$ states (Lever 1984) respectively. Similarly, a small shift is also observed in the peak position of the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (Mn^{2+} transition) due to intermixing and coupling of $Mn-{}^4T_{1g}$ (G) and $Ni-{}^3T_{1g}$ (F) states. These results from the diffused reflectance spectra thus clearly show that (i) Mn^{2+} ions are occupying the nearly perfect local lattice environment of oxygen octahedra, and (ii) the formation of well defined $Mn_{1-x}Ni_xO$ solid solutions.

3.4 Magnetic susceptibility measurements

Magnetic susceptibility measurements of $Mn_{1-x}Ni_xO$ solid solutions with $x = 0.01$, 0.1 , 0.2 and 0.3 have been carried out in the temperature range 77 to 300 K . Representative plots of $1/\chi_g$ vs T for the $Mn_{1-x}Ni_xO$ system with $x = 0.01$ and 0.3 are given in figure 5. All the samples showed a minimum value of $1/\chi_g$ at a temperature which is associated with the antiferromagnetic ordering temperature,

Table 2. Absorption spectra of $Mn_{1-x}Ni_xO$.

Transitions from ground state		Conc. of nickel (<i>x</i>) in Mn _{1-x} Ni _x O				Transitions from ground state
⁶ A _{1g} of MnO	0.00	0.01	0.20	0.30	1.00	³ A _{2g} of NiO
		13660	13735	13775	9115	→ ³ T _{2g} (F)
		15245	15175	15175	14115	→ ¹ E _g (D)
⁴ T _{1g} (G) ← 16393	16555	16510	16500	15730	→ ³ T _{1g} (F)	
⁴ T _{2g} (G) ← 20833	20160	20325	20325	22180	→ ¹ T _{2g} (D)	
⁴ A _{1g} E _g (G)← 23810	23810	23255	23255	23795	→ ³ T _{1g} (P)	

(Frequency in cm^{-1}).

Figure 5. $1/\chi_g$ vs T plots of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$.

T_N . The Weiss temperature, θ , is obtained by extrapolating the paramagnetic linear region of the $1/\chi_g$ vs T plot to give an intercept on the temperature axis. The values of T_N , θ , θ/T_N and μ_{eff} computed from the slopes of the plots of $1/\chi_g$ vs T above 200 K are presented in table 3. It is observed from the plots that the minimum for $x = 0.01$ in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system is sharp and broadens with increasing x and T_N is also same as/very close to that of cubic MnO indicating that host lattice is in tact and T_N shifts to higher temperature with increasing x , obeying Curie-Weiss law. The broad minimum observed in the inverse susceptibility curve, similar to that observed in $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ and $\text{Mn}_{1-x}\text{Mg}_x\text{O}$ systems (Deshpande *et al* 1982), can be explained as due to exchange interactions occurring in the rock-salt crystal structure. In the case of pure MnO , the 90° Mn–O–Mn(NN) and direct Mn–Mn interactions are possible in an antiferromagnetic ordering since d orbitals of Mn^{2+} are half-filled. On the other hand, such direct Ni–Ni exchange is not possible in NiO as the t_{2g} orbitals are full and only 90° cation–anion–cation (NN) interaction is possible (Goodenough 1963). Moreover, an antiferromagnetic (NNN) interaction involving only e_g orbitals is possible in both MnO and NiO . The present system of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ involves both t_{2g} and e_g orbitals of Mn^{2+} ($t_{2g}^3 e_g^2$) and Ni^{2+} ($t_{2g}^6 e_g^2$) exhibiting complex magnetic interaction which may have to be thoroughly studied in the low temperature-high field experiments. It results in (i) a broad minima seen in the plots of $1/\chi_g$ vs T in $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system and (ii) an increasing trend in θ/T_N with increasing x . This behaviour is similar to the trend reported earlier by Aviazov and Gurov (1974) involving the increase in ferromagnetic coupling (Cheetham and Hope 1983) between Mn^{2+} and Ni^{2+} ions indicating the absence of noncollinear oblique antiferromagnetic (OAF) phase (Katsumata *et al* 1979) occurring in the system.

Table 3. Effect of conc. of Ni(x) on the magnetic properties of $Mn_{1-x}Ni_xO$ system.

Conc. of Ni(x) in $Mn_{1-x}Ni_xO$	μ_{eff} (BM) at 300 K	θ (K)	T_N (K)	θ/T_N
0.01	4.76	110	120	0.917
0.10	3.68	112	120	0.933
0.20	3.63	154	123	1.252
0.30	3.76	164	127	1.291

3.5 Electron microscopy and EDS analysis

The morphology of the sample with $x = 0.3$ in $Mn_{1-x}Ni_xO$ system is shown in figure 6a. The shape of the particles is almost spherical and they are well-separated. It indicates that there is no ferromagnetic interaction between these particles. The particles size distribution is obtained from an electron micrograph at 200 K magnification. The average particle size, observed for all the samples, is ≈ 15 – 18 nm. The selected area electron diffraction pattern (SAD) of the sample with $x = 0.3$ in $Mn_{1-x}Ni_xO$ system is shown in figure 6b with zone axis $[100]$, figure 6c with zone axis $[310]$ and figure 6d key to figure 6c. It is comparable with cubic unit cell (FCC) having cubic lattice parameter, $a = 0.438$ nm. This matches well with the cubic lattice parameter a computed from the powder X-ray diffraction pattern. A typical EDS (KeveX) analysis of the representative sample with $x = 0.3$ is presented in figure 7. The ratio of intensity of Ni : Mn counts indicates the desired stoichiometric ratio. However, in addition to these two elements, small quantities of copper and chromium are also detected by EDS. The impurities are from the specimen holder rather than the sample.

3.6 X-ray photoelectron spectroscopy

To differentiate between the bulk and surface oxidation of the solid solution during its exposure to air at room temperature a highly surface sensitive technique such as X-ray photoelectron spectroscopy (XPS) was used. X-ray photoelectron spectra of representative samples were recorded using an $AlK\alpha$ radiation source (1486.6 eV). Initially, full general scans (1000 eV) were recorded to check all appropriate peaks corresponding to the expected chemical composition on the surface. High resolution XPS scans were recorded over a narrower energy scale (30 eV) for the samples with $x = 0.10$ before (figures 8a and 9a) and after heating above 330 K for 2 h (figures 8b and 9b) for nickel ($2p$), manganese ($2p$) and oxygen ($1s$) levels. Table 4 presents XPS data (before and after heating the samples in air) of characteristic peaks usually employed in assigning the oxidation states in transition metal oxides. From characteristic BE values ($2p_{3/2}$) and ΔE_{3s} of Mn^{3+} in Mn_2O_3 (Fadley and Shirley 1970; Carver *et al* 1972; Oku *et al* 1975; Wertheim *et al* 1975; Rao *et al* 1979; De Boer *et al* 1982; Foord *et al* 1984; Zhao and Young 1984) and Ni^{2+} in NiO (Kim and Ninoguard 1974), the observed peaks are assigned to Mn^{3+} and Ni^{2+} species present on the surface (30–40 Å) with high concentrations.

Figure 6. TEM of $Mn_{1-x}Ni_xO$ ($x = 0.3$) system. **a.** Bright field micrograph, **b.** SAD with zone axis $[100]$, **c.** SAD with zone axis $[310]$ and **d.** key to (6c).

The presence of Mn^{3+} and Ni^{2+} species on the surface indicates a possible formation of a mixed $NiO-Mn_2O_3$ phase. On heating the samples in air around 330 K, characteristic shifts in Mn ($3s$), Mn ($2p_{3/2}$) and Ni ($2p_{3/2}$) levels are clearly observed. By comparing with reported data (Fadley and Shirley 1970; Carver *et al* 1972; Oku *et al* 1975; Wertheim *et al* 1975; Rao *et al* 1979; De Boer *et al* 1982; Foord *et al* 1984; Zhao and Young 1984; Deshpande *et al* 1985), of shifts in Mn–O system and Ni–O system (Kim and Ninoguard 1974), these peaks are assigned to Mn^{4+} species and Ni^{3+} species (table 4) present on the surface. It is clear from these observations that the Mn_2O_3-NiO type mixed phase, present on the surface is oxidized to MnO_2 and Ni_2O_3 (table 4). A structural vacancy associated model (Deshpande *et al* 1985; Bakare *et al* 1991) has been earlier proposed by our laboratory to explain the chemical passivation process for $Mn_{1-x}M_xO$ systems ($M = Zn, Mg$). However, this phenomenon of oxidation in the case of $Mn_{1-x}Ni_xO$ is different from that occurring in the case of samples from the $Mn_{1-x}Zn_xO$ and $Mn_{1-x}Mg_xO$ systems (Deshpande *et al* 1985; Bakare *et al* 1991). In the case of $Mn_{1-x}Zn_xO$ system (Deshpande *et al* 1985), the Mn_2O_3-ZnO mixed phase is oxidized on heating at $T >$ stabilization temperature and shows the presence of MnO_2 on the surface, whereas Zn^{2+} ions diffuse into the bulk MnO . Similarly in the case of $Mn_{1-x}Mg_xO$ system (Bakare *et al* 1991), Mg^{2+} ions present on the surface as $MgO-Mn_2O_3$ mixed phase diffuse into the bulk MnO . The present system of $Mn_{1-x}Ni_xO$ is different from the above referred two systems, obviously due to the fact that Ni^{2+} gets oxidized to Ni^{3+} , instead of diffusing inside the bulk MnO like Zn^{2+} , Mg^{2+} ions. This results into slow oxidation of the whole sample. In short, highly active sites (surface) are preferentially occupied by Ni^{2+} ions, which together with Mn^{3+} ions form a mixed phase $NiO-Mn_2O_3$ on the surface. This surface phase prevents the subsequent oxidation of bulk MnO .

Figure 7. EDS analysis of the $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.3$) system.

Figure 8. XPS of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0.10$) before (A) and after heating at 330 K in air (B) for Mn-levels.

4. Conclusion

In summary, we have shown that *in situ* solid solutions $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ ($0.01 < x < 0.30$) system can be successfully prepared. X-ray diffraction studies reveal the formation of single cubic phase and linear decrease of the lattice parameter with increasing

Figure 9. XPS of $Mn_{1-x}Ni_xO$ ($x = 0.10$) before (A) and after heating at 330 K in air (B) for Ni-levels.

Table 4. XPS data on $Mn_{1-x}Ni_xO$ before and after heating { } at 330 K for 2 h in air.

Sample with conc (x) in $Mn_{1-x}Ni_xO$	Binding energy (BE) eV ± 0.2 eV						
	Mn					Ni	O^{2-}
	3s	ΔE 3s	$2p_{3/2}$	$2p_{1/2}$	ΔE 2p	$2p_{3/2}$	1s
0 (MnO)	84.6	6.2	640.9	652.7	11.8	—	529.9
1 (NiO)	—	—	—	—	—	854.6	529.6
0.01	83.9 {84.6}	5.6 {4.8}	641.6 {642.6}	653.4 {653.2}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}
0.10	83.4 {84.3}	5.4 {4.8}	641.6 {642.6}	653.4 {653.2}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}
0.20	83.4 {84.3}	5.4 {4.8}	641.6 {642.6}	653.4 {653.2}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}
0.30	83.6 {84.0}	5.2 {4.6}	641.6 {642.6}	653.4 {653.4}	11.8 {11.6}	854.8 {855.6}	529.6 {529.6}

x (nickel concentration). DTA–TG–DTG studies show their relative thermal stability in air and process of very fast oxidation of pure MnO is considerably controlled to a great extent. The diffused reflectance spectra indicates the presence of a doublet band due to an extensive mixing of Ni^1E_g (D) and Ni^3_{2g} (F) transitions

and exhibit characteristic absorption peaks of both MnO and NiO with a shift in their positions due to intermixing of some of the transitions of Mn^{2+} and Ni^{2+} ions in cubic field. Analysis of the magnetic susceptibility data of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system indicated involvement of both t_{2g} and e_g orbitals of Mn^{2+} ($t_{2g}^3 e_g^2$) and Ni^{2+} ($t_{2g}^6 e_g^2$) exhibiting complex magnetic interaction. It also suggests absence of a non-linear oblique antiferromagnetic phase in the system. T_N indicates that host lattice of cubic MnO remains intact. TEM study shows that the samples have well-separated spherical particles (size $\approx 15\text{--}18\text{ nm}$). It has been qualitatively established by using EDS analysis that weighed in/initial stoichiometry of the compositions is well preserved. Cubic lattice parameters computed using electron diffraction patterns agree well with those observed by XRD. The presence of $\text{Mn}_2\text{O}_3\text{--NiO}$ (mixed phase) on the surface of $\text{Mn}_{1-x}\text{Ni}_x\text{O}$ system prevents the subsequent oxidation of bulk MnO. XPS studies show the formation of mixed $\text{Mn}_2\text{O}_3\text{--NiO}$ phase present on the surface. This phase acts like a passivation layer preventing the fast oxidation (rate of uptake of oxygen) of the solid solutions.

Acknowledgements

Thanks are due to Mrs J J Shrotri, Dr (Mrs) A Mitra for their generous help, Mr M V Kuber for the help given during measurements of magnetic susceptibility and Dr S R Padalkar for recording reflectance spectra.

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