

Realizing NiO nanocrystals from a simple chemical method

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Abstract. Nanocrystalline NiO has been prepared successfully by a simple chemical route using NiCl₂·6H₂O and NaOH aqueous solution at a temperature of 70°C. The prepared material has been characterized from XRD, SEM, and M–H characteristics. It has been found that NiO nanocrystals have been formed which shows a superparamagnetic/superantiferromagnetic behaviour.

Keywords. Nanostructures; chemical synthesis; X-ray diffraction; SEM.

1. Introduction

Nanomaterials have become the caption of the activity now a days in the area of material science. Magnetism of nanomaterials has become a significant concern in nanoscience due to the expected spectacular properties for its wide applications in diverse fields such as high density recording media, spin valves, magnetic resonance imaging, ferrofluid technology and magnetocaloric refrigeration (Gleiter 2000; McHenry and Laughlin 2000). More recently, magnetic properties were experimentally studied in some antiferromagnetic nanoparticles such as MnO (Kodama *et al* 1997) and α -Fe₂O₃ (Bødker *et al* 2000a, b). Nanoparticles with antiferromagnetic ordering of spins have received much interest due to their interesting properties such as superparamagnetism, enhanced magnetic moments and field reversal due to quantum tunneling (Zhang *et al* 1997; Chen and Zhang 1998). In this context, nanosized nickel oxide (NiO) is an interesting material due to its useful electronic (Biju and Khadar 2001) and magnetic properties (Bødker *et al* 2000a, b).

So far many synthesis routes have been reported for preparing NiO nanocrystals. For example, Qian and co-workers synthesized NiO nanoplatelets by thermal decomposition of the prepared nickel hydroxide precursor (Wang *et al* 2006). Wang and coworkers prepared NiO nanowires by annealing the freshly prepared precursor (Xu *et al* 2003). Deki *et al* (2003) prepared highly concentrated nanosized NiO by means of vacuum evaporation of Ni on NH₂-terminated PEO film. Zheng and Zhang (2007) reported a molten-salt synthesis method using NaCl as a flux at 1000°C to prepare NiO nanoparticles with uniform morphology of hexagon plates. In this paper, we report on the preparation of NiO nanocrystals by a simple chemical method using aqueous solution of nickel chloride and sodium hydroxide at 70°C. The formed material has been characterized from XRD, SEM and M–H behaviour to show the formation of NiO nanocrystals.

2. Experimental

NiO nanoparticles have been prepared by sol–gel chemical method. The chemicals used in the preparation were of analytical grade and were used without further purification. 0.1 M of NiCl₂·6H₂O and 0.3 M of NaOH pellets were dissolved in appropriate amount of distilled water separately. Aqueous solution of NiCl₂·6H₂O was kept on a heated magnetic stirrer (at 70°C) and NaOH solution was added drop-wise till the turbidity occurred, for 10 h. Thus, the green gel was formed which was washed several times with distilled water. Then, the sample was allowed to dry in an oven (furnace) at 300°C for 5 h. Finally, the dried powder was ground in an agate mortar.

To identify the structure and phase purity of the prepared sample, powder X-ray diffraction (XRD) measurement was performed by using a Philips PW-1710 diffractometer with CuK_α radiation ($\lambda=1.540598\text{ \AA}$) at room temperature. The surface morphology of the prepared sample was carried out by scanning electron microscopy (SEM, Philips XL-20). Magnetization measurement (M–H characteristics) of the sample was recorded from a vibrating sample magnetometer (VSM) where magnetic field could be varied up to 1.8 Tesla.

3. Results and discussion

The X-ray diffraction data (table 1) have been recorded for powdered sample as shown in figure 1. This data clearly shows distinct peaks at 2θ of 37.060, 43.095, 62.620, 75.090, and 79.185. The peaks have been identified as peaks of cubic NiO crystallites with various diffracting planes [111], [200], [220], [311] and [222]. The XRD pattern revealed the formation of cubic phase of NiO (JCPDS Card 47-1049) with lattice constant, $a = 4.1771\text{ \AA}$. The other peaks observed at an angle (2θ) of 31.575, 56.310, 66.050 which have been identified as Ni₂O₃ corresponds to [002], [202] and [004] crystal planes, respectively. A peak

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Table 1. XRD data of NiO nanoparticles.

Angle (2 θ)	<i>d</i> -value (Å)	Peak width (2 θ)	Peak intensity (counts)	Relative intensity (counts)	Identification (from XRD std. data)	Crystallite size (nm)
37.060	2.4298	0.200	353	19.7	NiO [111]	41.77
43.095	2.1025	0.250	590	32.8	NiO [200]	34.19
62.620	1.4859	0.350	262	14.6	NiO [220]	26.60
75.090	1.2672	0.150	313	17.4	NiO [311]	67.25
79.185	1.2062	0.400	55	3.0	NiO [222]	25.70

observed at 2 θ of 45.315 have been identified for Ni [111] phase. A peak at 2 θ of 27.230 is frequently observed which corresponds to the cello tape, used for holding the samples.

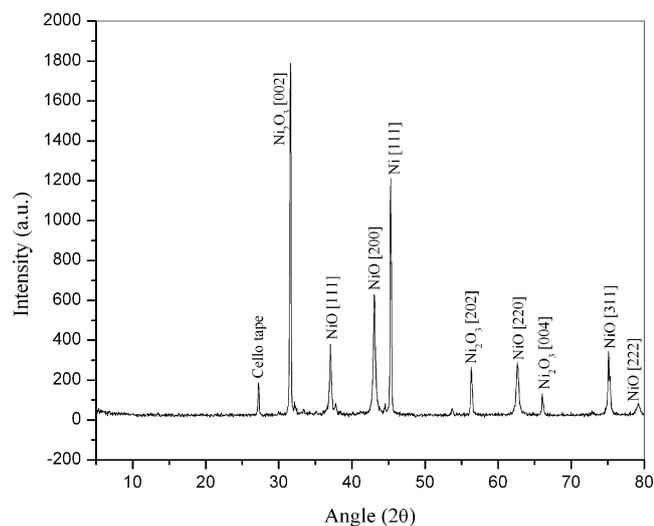
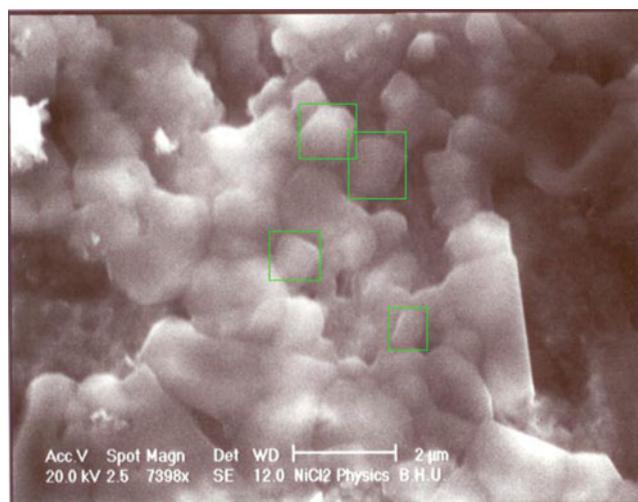
XRD data (table 1) shows the peak width, 2 θ , for various peaks. The broadened peak shows the nanometer-sized crystallites. The crystallite size has been estimated (by using the Scherrer relation (Eberhart 1989)), which has been found to vary between 25 nm and 67 nm for various identified diffraction peaks (table 1).

The SEM micrographs of the prepared NiO crystals are shown in figure 2. The SEM micrograph shows cubic crystallites. Some of the cubic crystallites are marked by the boxes in figure 2. Moreover, the micrograph also shows the agglomeration of the crystallites. The agglomeration may occur due to the crystallites being of nanodimension. The small nanocrystals possess large surface energy, which leads the nanocrystals to aggregate in order to lower their surface energy during crystal growth.

M–H behaviour, for in plane (\parallel) and out of plane (\perp) applied magnetic fields, of the prepared NiO nanoparticles is shown in figure 3. The magnetization has been observed not to saturate up to a maximum applied field of 18 kOe. The M–H characteristics do not show any significant hysteresis,

coercivity, and retentivity and thus it clearly shows the feature of superantiferromagnetic/superparamagnetic behaviour.

The magnetic behaviour of the particle surface differs from that of core. NiO is basically antiferromagnetic below Neel temperature (523 K). The magnetic ordering in NiO nanoparticles results from the super exchange interaction (Anderson 1950). This super exchange interaction is an indirect exchange mechanism whereby electrons are shared between 3*d* orbitals of metal ions, i.e. Ni⁺² ions and 2*p* orbitals of the intervening oxygen ions (O⁻² ions). This interaction strength is proportional to the overlap between these orbitals; hence it depends on the bond length and angle between the metal ion and oxygen ions. When some exchange bonds are broken from the surface, there can be frustration and spin disorder. As the particle size is reduced to nanometer size, then surface to volume ratio ($\propto 1/r$, where *r* is the particle size) increases and hence the role of the surface atoms in the magnetic behaviour becomes significant and energy consideration favours the formation of single domain particles. This could also show unique magnetic properties such as superparamagnetism (Kittel 1974). Neel (1962) suggested a two-sublattice model, one with spin ‘up’ and another with spin ‘down’ at the surface.

**Figure 1.** XRD pattern of NiO nanoparticles.**Figure 2.** SEM micrograph of NiO nanoparticles prepared by heating Ni(OH)₂ precursor.

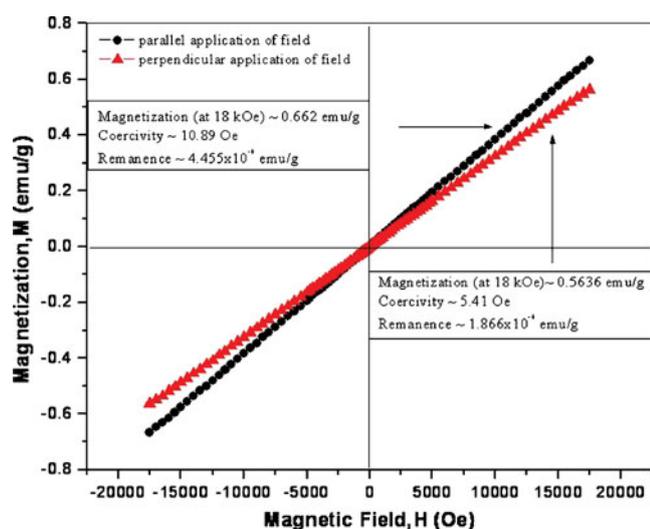


Figure 3. M–H characteristics of NiO nanoparticles.

There is a net magnetic moment in antiferromagnetic nanoparticles due to the non-compensation of surface spins. The paramagnetic susceptibility due to the non-compensation of surface spins can easily dominate over the antiferromagnetic contribution itself. Because of the structural disorder, the surface spin can be more easily deviated from the antiferromagnetic alignment by a magnetic field. Since, a surface spin has smaller number of neighbours than it would have in bulk and hence experiences a reduced mean field. For very small particle size, the surface area is much larger and hence makes a large contribution to the magnetization.

The two main contributions to the magnetization are:

$$M(H, T) = M_0(T) + \chi_{AF}H(T), \quad (1)$$

where the first term, $M_0(T)$ in the magnetization equation is responsible for the rapid increase in the magnetization due to the non-compensation of surface spins whereas the second term $\chi_{AF}H(T)$ is responsible for the non-saturation of the magnetization at high fields due to some antiferromagnetic contribution.

From figure 3, it is clear that the magnetization behaviour of NiO nanoparticles shows more or less linear dependence on the applied field. Schuele and Deetscreek (1962) had also earlier reported the linear dependence of magnetization on the applied field for NiO nanoparticles with an average particle size between 21 Å and ~1000 Å. From figure 3, the susceptibility, χ , has been calculated to be $\sim 39.6 \times 10^{-6}$ emu/g (for in plane magnetization) and $\sim 36 \times 10^{-6}$ emu/g (for out of plane magnetization). These values obtained are approximately five times the antiferromagnetic susceptibility of bulk NiO at room temperature, which is reported as $\sim 8 \times 10^{-6}$ emu/g (Singer 1956).

This observation is in good agreement with the statement made by Neel (1961) in which he has already

discussed two surface effects: (i) weaker mean field of the surface spins implies that they can be more easily deviated from antiferromagnetic alignment by a magnetic field. This will give rise to an enhanced antiferromagnetic susceptibility, which Neel called ‘superantiferromagnetism’ and (ii) Neel recognized that the effect of reduced surface magnetization which was observed in Monte Carlo simulations (Wildpaner 1974) for ferromagnets may be even more important for antiferromagnetic particles for which ‘superparamagnetism’ arises from the uncompensated spins.

Again, it is also in good agreement with the result reported by Khadar *et al* (2003) that at room temperature NiO nanoparticles with average particle size $> \sim 10$ nm may exhibit superantiferromagnetism with the magnetization curve showing a linear dependence on the applied field. Hence, the susceptibility values observed are larger in comparison with the antiferromagnetic susceptibility of bulk NiO.

Thus, the above magnetic properties show typical behaviour of NiO nanoparticles.

4. Conclusions

NiO nanocrystals have been prepared by the thermal decomposition of the as-prepared $\text{Ni}(\text{OH})_2$ precursor which is prepared from the aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH at 70°C. XRD features have revealed the formation of cubic phase of NiO nanocrystals. SEM micrograph also shows the features of cubic crystallite and aggregation of nanocrystallites. M–H characteristics clearly show the feature of superparamagnetism/superantiferromagnetism which is a typical behaviour of NiO nanocrystallites.

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