

Synthesis and thermogravimetric analysis of non-stoichiometric nickel oxide compounds

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Abstract. Non-stoichiometric nickel oxide was synthesized by the thermal decomposition method at different sintering temperatures upto 1100 °C. The samples were analyzed by thermogravimetric analysis (TGA). Wherein, the stoichiometry of the sample was analyzed by calculating the excess oxygen. It was found that as the sintering temperature of the precursor increases the excess oxygen present in the sample decreases, and at temperature above 700 °C, the sample becomes stoichiometric. These results were interpreted as the decomposition temperature increases, which heals the defects present in the non-stoichiometric nickel oxide. Thus, highly defective nickel oxide at lower decomposition temperature approaches stoichiometric nickel oxide as the temperature is increases above 700 °C.

1. Introduction

Nickel oxide (NiO) is the most comprehensively investigated transition metal oxide over the decades [1]. It is a anti-ferromagnetic oxide semiconductor which crystallizes in NaCl-type crystal structure [2]. NiO has been considered as a promising functional material for varieties of applications, such as, smart windows [3], spin valves giant magneto resistance (GMR) sensor [4], solar cells [5], gas sensors [6], high permittivity dielectric material and electrochromic material for displays [7], photoelectrolysis [8], etc. In fact, bulk material of NiO has a rhombohedral crystal structure and it shows antiferromagnetic behavior below 250 °C and above the Neel temperature of 250 °C, the structure is transformed into a cubic one with paramagnetic behavior [9]. Pure stoichiometric NiO crystals are perfect insulators [10], several efforts have been made to explain the insulating behavior of NiO, were in, appreciable conductivity can be achieved in NiO by creating Ni vacancies or substitution at nickel side, thereby creating Ni vacancies and the composition ratio of Ni and O changes and NiO becomes non-stoichiometric. Hence, in a non-stoichiometric NiO, various property changes, this can be attributed to presence of excess oxygen. Nickel oxide can be prepared by various techniques that involve: thermal decomposition [11], anodic oxidation [12], chemical deposition [13], and sol-gel [14]. In fact, Gray [11] and Iida [15] reported that the properties of nickel oxide also changes with the preparation method. All these characteristics in nickel oxide provide an ideal opportunity and in present case non-stoichiometric nickel oxide was prepared by the thermal decomposition method at different sintering temperature.



2. Experimental

Following [11, 15] nickel nitrate hexa-hydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ sintered at different temperature, which was decomposed to produced nickel oxide samples of various stoichiometries. Nickel nitrate hexa-hydrate was heated in presence of air for 3 hr. at temperatures range from 400 °C to 1100 °C. By sintering at four different temperature samples NiO(400 °C), NiO(500 °C), NiO(700 °C) and NiO(1100 °C) were then prepared. X-ray diffraction was conducted with the help of the Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation (0.154 nm) in the angle range 10°–90°. Thermo gravimetric analyses (TGA) was done to classify the stoichiometry of the samples and to obtain the oxygen content of the samples. In our experiment, TGA with the top-of-the-line METTLER TOLEDO ultra-micro balance with unique built-in calibration weights ensures with an accuracy of 0.1 μg .

3. Results and discussions

3.1. X-ray diffraction analysis

XRD analysis, which is the most useful technique for identification of crystalline structure, was employed to investigate the crystallinity and purity of the solid product obtained by thermal conversion in air of the poly-nuclear coordination compounds. The XRD data of nickel oxide sample prepared at different temperature is shown in Fig. 1, which shows the presence of the characteristic peaks for NiO at 2θ in the range of 10° – 90°, in accordance with JCPDF File 78-0643. The lattice parameters were obtained from the following relationship analytically: $\sin^2\theta = C(h^2 + k^2 + l^2)$, where $C = \lambda^2/4a^2$. The results of the X-ray structural analysis are given in Table 1 for one of the representative samples sintered at 400 °C. Our analysis indicates good agreement between Bragg's reflection peaks obtained from analytical analysis data and the structural data of with JCPDF File 78-0643. This indicates that the NiO sample obtained by thermal conversion in air of the polynuclear coordination compounds, revealed the NiO with face-centered cubic phase, also known as the bunsenite structure (lattice constant a of cubic unit cell, 0.4177 nm). For others samples, there was also no appreciable deviation in structural data within the limit of accuracy of analytical method. No other additional peaks corresponding to other phases were emerged, suggested NiO phase is stable.

Further, the mean crystallite size of the NiO sample can be calculated using Sherrer formula: $L = k\lambda/\beta\cos(\theta)$, where L is the crystallite size, k is the Sherrer constant, usually taken as 0.89, λ is the

Table 1. Crystallographic data using analytical analysis for NiO samples.

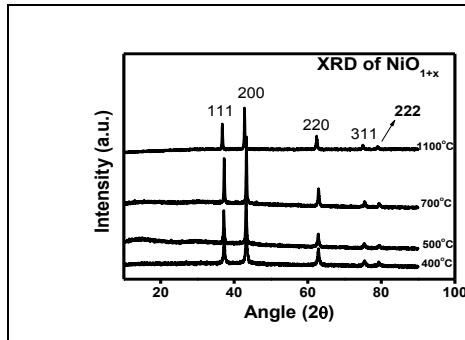
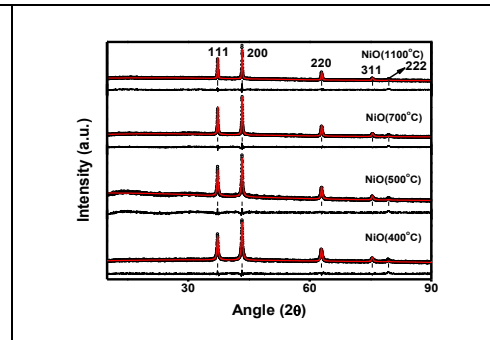
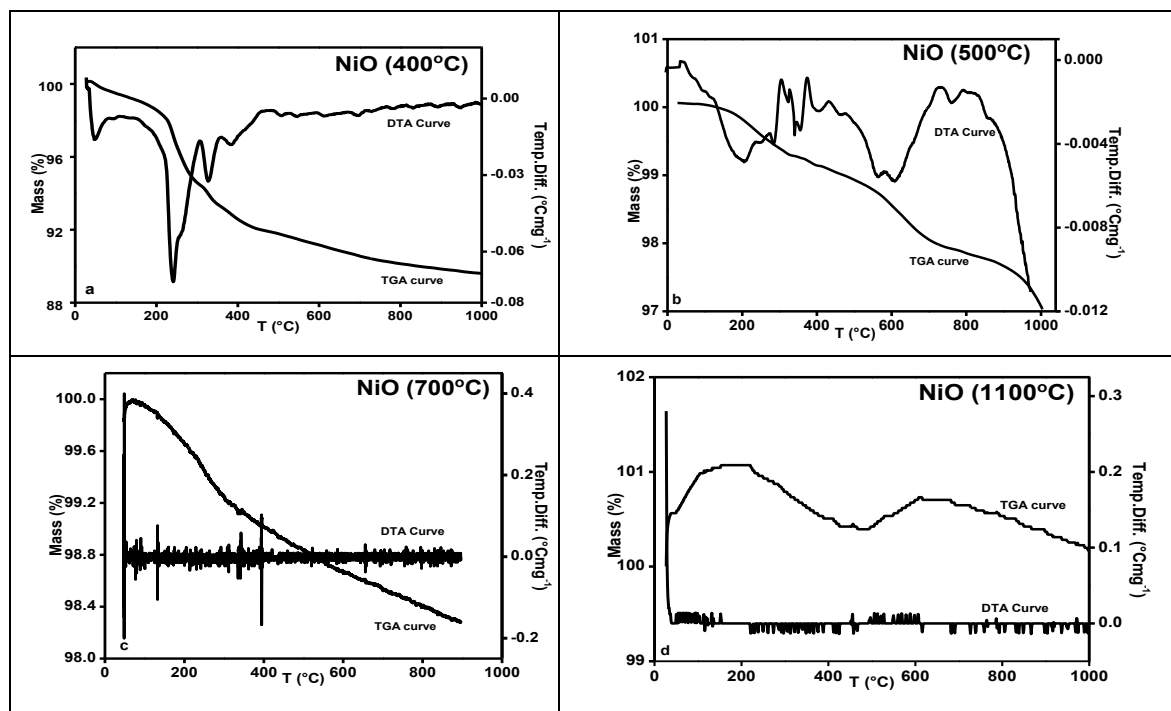
Intensity (%)	2θ	$\sin^2 \theta$	$h^2 + k^2 + l^2$	C	(hkl)	$a(\text{\AA})$	$\bar{a}(\text{\AA})$
61.69	37.279	0.1022	3	0.034	(111)	4.1772	4.1775
100	43.472	0.1365	4	0.034	(200)	4.1727	
44.83	62.901	0.2722	8	0.034	(220)	4.1772	
15.68	75.416	0.3741	11	0.034	(311)	4.1772	

Table 2. Rietveld parameters of different NiO samples.

Compounds	$a(\text{\AA})$	V ($\text{\AA}^3$)	Rf factor	Bragg's R-factor	R_p	R_{wp}	R_e	χ^2	$L(\text{nm})$
NiO (400 °C)	4.176	72.82	2.39	3.94	24	16.7	14.9	1.261	240
NiO (500 °C)	4.174	72.74	4.44	4.33	29.6	19.6	16.7	1.381	290
NiO (700 °C)	4.172	72.64	4.04	4.51	22	15.8	13.3	1.416	350
NiO (1100 °C)	4170	27.58	20.4	31.7	56.3	37.4	22.3	2.673	460

Table 3. Calculated excess oxygen present in different samples.

Samples→	NiO (400 °C)	NiO (500 °C)	NiO (700 °C)	NiO (1100 °C)
Excess oxygen %	7.8	2.8	1.2	0

**Figure 1.** X ray diffraction pattern of non stoichiometric NiO**Figure 2.** Rietveld refinement of x-ray diffraction of non-stoichiometric NiO.**Figure 3.** TGA and DTG curves of NiO samples prepared at different temperature

wavelength of the x-ray radiation (0.154056 nm for Cu K α), and β is the full width at half maximum (FWHM) of diffraction peak measured at 2θ . The deduced values of crystallite size of the analyzed NiO samples are reported in Table 2, which indicates that as the sintering temperature of precursor increases the crystallite size of NiO also increases.

We have also performed Rietveld refinements for all the samples using Fullprof software. Fig.2 shows the refinement profile of all the samples and the various parameters obtained from refinement data are given in Table 2. It can be concluded that the crystal parameters obtained from analytical calculation from XRD graph and fitting the curve by Rietveld refinement corroborates each other.

3.2. Thermogravimetric analysis (TGA)

TGA measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. In order to establish the estimation of excess of oxygen, TGA was performed on the samples prepared at different temperature. In present investigation, the weight of the non-stoichiometric oxygen is obtained directly by obtaining the weight loss. The thermo-gravimetric (TG) curve and its differential curve (DTG) are shown in Fig. 3 for NiO (400 °C). It is clear from Fig. 3 that a very sharp peak is present between 200 and 300 °C on the DTG curve, which is a measure of amount of excess oxygen released in the heating process. The corresponding weight loss reflects desorption of oxygen in non-stoichiometric sample. On the other hand, the peak below 100°C is due to the evaporation of the physically bound water in the sample and does not contribute in the estimation of excess oxygen. Further, it is noted that, for NiO (500 °C) and above samples, the reduction of mass with temperatures decreases and is found to be negligible above NiO (600 °C) sample as shown in Fig. 3 by TG and DTG curves. Consequently, composition ratio of O/Ni is equal to 1 for above the NiO (700 °C) sample and crystallizes with Ni deficiency, establishing stoichiometry in nickel oxide. The weight percentage of excess oxygen is tabulated in Table 3. From above TG curves it is clear that as the temperature of preparation of sample increases the stoichiometry of the sample changes and at above 600 °C the excess oxygen present in the sample completely evolved out from the sample and becomes stoichiometric.

4. Conclusions

Nickel oxide of various stoichiometry were prepared by using a simple and inexpensive thermal decomposition technique at different sintering temperatures. The XRD studies show that all the nickel oxide samples were crystallize in cubic phase. Thermogravimetric analysis of samples prepared at different temperature indicates that as sintering temperature of precursor increased, the stoichiometry of the sample changes, the samples which prepared at low temperature have more excess oxygen as compare to sample prepared at higher temperature.

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