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X-ray diffraction line profile analysis of nanostructured nickel oxide: Shape factor and convolution of crystallite size and microstrain contributions

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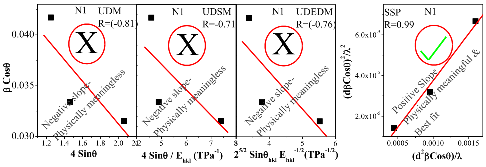
HIGHLIGHTS

- Extraction of size and microstrain contributions to XRD line broadening.
- Use of W-H and SSP methods to analyze crystallite size and microstrain.
- Analysis of Shape factor for explaining why SSP method is more suitable in the present case.
- Suitability of SSP method to deconvolute size and strain of small crystallites.
- Use of Rietveld refinement of the XRD pattern to reveal lattice expansion.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured nickel oxide is synthesized through a chemical route and annealed at different temperatures. Contribution of crystallite size and microstrain to X-ray diffraction line broadening are analyzed by Williamson-Hall analysis using isotropic and anisotropic models. None of the models perform well in the case of samples with smaller average crystallite sizes. For sample with crystallite size ∼3 nm all models show negative slope which is physically meaningless. Analysis of shape factor shows that the line profiles are more Gaussian like. Size-strain plot method, which assumes a different convolution of the crystallite size and microstrain contributions, is found to be most suitable. The study highlights the fact that the convolution of crystallite size and microstrain contributions may differ for samples and should be taken into account while analyzing the observed line broadening. Microstrain values show a regular decrease with increase in the annealing temperature.

1. Introduction

The physical and chemical properties of nanocrystalline materials are markedly different from those of single crystalline and coarse grained polycrystalline samples with the same average chemical composition [1]. Numerous studies on the structure-property correlations in nanostructured samples of varied types have appeared in the literature. Large surface areas to volume ratio and quantum size effects are the most important factors that determine the varied physical and chemical properties of nanocrystalline materials [1,2]. However, there are other factors such as lattice strain, compensation at the surface, non-stoichiometry, etc.,

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which could also contribute to the varied properties.

Lattice strain, which is one of the important structural parameters that could influence the physical properties, can be studied using X-ray diffraction (XRD) technique [3]. Two types of lattice strains are associated with nanocrystalline materials [4,5]. First kind extends over the entire lattice and is manifested as a shift in the position of the XRD peaks while the second kind extends only over a few lattice spacings and is often referred to as 'microstrain' or 'localized lattice strain' [6]. Microstrain originates due to the presence of defects such as vacancies or cores of vacancies in the lattice, excess fraction of grain boundaries, etc., and causes broadening of the XRD peaks [2,5–7]. Thus microstrain is a measure of the concentration of defects in the sample. In the case of systems such as nanostructured transition metal oxides where the presence, concentration and distribution of cation/anion vacancies could precipitously affect the physical and chemical properties, microstrain could be used as an indirect measure of the concentration of defects in the sample and hence could be a useful structural parameter for structure-property correlation [2,6].

From this discussion, it is clear that in the case of nanostructured samples, XRD line broadening could have contribution from both small crystallite size and microstrain [8]. A number of analytical methods are suggested for separating the crystallite size and microstrain contributions to the XRD line broadening, viz., Williamson-Hall method, Warren-Averbach method, Fourier method, Rietveld refinement, etc. [8–11]. Though full pattern refinement techniques are more rigorous, the execution is very complex due to a large number of control parameters and hence techniques such as Williamson-Hall analysis and Warren-Averbach procedures are often employed. Warren-Averbach method requires at least two orders of reflections along each crystallographic direction and when higher order reflections are weak and difficult to analyze Williamson-Hall method is employed [12]. Williamson-Hall method assuming uniform deformation (UDM) in all directions is computationally simple and can be implemented conveniently [8]. Also, the anisotropic nature of the elastic constants of the crystal can be incorporated in the Williamson-Hall analysis by using uniform deformation stress (UDSM) or uniform deformation energy density (UDEDM) models [8,12,13]. A number of reports on the Williamson-Hall analysis of nanostructured samples of different kinds have appeared in the literature in the recent past [6,12–23]. A perusal of these reports reveals that models which take into account the anisotropic nature of the crystal, viz., UDSM and UDEDM often more correctly model the system than the one which does not take the anisotropy into account viz., UDM [6,13–17,20]. Further, it was also noted that in the case of samples with smaller crystallite sizes, less than ~10 nm, the scattering of the points about the linear fit was markedly more, implying low value for correlation coefficient [3,19,20]. For samples with larger average crystallite sizes the correlation is usually very high [6,12].

Recently Madhu et al., had reported the Williamson-Hall analysis of nanocrystalline nickel oxide (NiO) samples synthesized through a wet chemical route with crystallite size in the range 33–50 nm and had inferred that the presence of both Ni^{2+} and O^{2-} vacancies contribute to microstrain [6]. It was shown that the microstrain values together with conductivity measurements/antioxidant activity could provide information on the relative concentration of Ni^{2+} and O^{2-} vacancies. In general, nanostructured NiO may contain both Ni^{2+} and O^{2-} vacancies and their relative concentration is important in determining the optical, electrical, magnetic, electrochemical, catalytic, etc., properties. Hence in the case of nanostructured NiO microstrain could be an important parameter in determining the structure-property correlation. This paper compares the performance of the isotropic and anisotropic models of Williamson-Hall analysis in the case of nanocrystalline NiO samples with average crystallite sizes in the range ~2–22 nm synthesized through chemical method. It may be noted that the size range is much smaller in comparison with previous reports [6]. A comparison of the performance of the different models (isotropic and anisotropic) in the case of samples with very small average crystallite size, < 10 nm is interesting. Size-strain plot analysis which is a modified form of the Williamson-Hall concept, assuming a different convolution of size and microstrain contributions to XRD line broadening, is also done and the performance is compared with those of the conventional isotropic and anisotropic models.

2. Experimental

Nanostructured nickel oxide (NiO) was synthesized through a two step process. In the first step, nickel carbonate precursor was synthesized through a controlled chemical precipitation route using nickel chloride ($NiCl_2 \cdot 6H_2O$) and ammonium carbonate (NH_4CO_3) as the starting materials and ethylene dinitrilo tetra acetic acid disodium salt (EDTA) as the stabilizer. All the chemicals used were of analytical grade and were used without further purification. The carbonate precursor was washed several times with distilled water and was dried in a hot air oven at 80 °C. In the second step, the finely powdered precursor was decomposed at 250 °C for 2 h in air ambience to get a loose powder of nanostructured NiO (sample code N1). The as prepared sample was annealed in air at different temperatures, viz., 350 (N2), 450 (N3), 500 (N4), 600 (N5), 700 (N6) and 800 °C (N7) for 1 h each. The sample codes given in brackets will be used for convenience in the results and discussions section.

The XRD patterns of the samples were recorded using a Philips X'pert Pro diffractometer with Cu kα ($\lambda = 1.54056$ Å) radiation in the 2θ range of 10–70°. The source was operating under an accelerating voltage of 40 kV with a tube current of 30 mA. Continuous scan was done with a scan step size of 0.08356° and time per step 39.95 s. Transmission Electron Microscopic (TEM) analysis of two representative samples N1 and N4 were carried out using a Philips CM-200 Transmission Electron Microscope.

3. Results and discussion

The XRD patterns of the samples are shown in Fig. 1 which can be indexed using JCPDS-ICDD Pattern number 47-1049 corresponding to NiO with cubic symmetry (space group-*Fm*3*m* (225)). The XRD lines are markedly broad indicating nanocrystalline nature. Further, the XRD lines become notably narrower with increase in the annealing temperature indicating an increase in the crystallite size. The as prepared sample (N1) is black in colour indicating nonstoichiometric nature with excess of uncompensated Ni^{2+} vacancies [24]. On annealing, the colour changes towards green and N7 is green indicating shift towards stoichiometry [24–28]. Thus, it is clear that on annealing together with an expected increase in the crystallite size there is a change in defect concentration and hence an analysis of the contributions of crystallite size and microstrain is interesting.

The full width at half maxima (FWHM), β_{obs} for each diffraction peak was estimated by a curve fitting routine assuming a pseudo-Voigt function for the line profile. Before analyzing the contributions of small crystallite size and microstrain to the XRD line broadening, the instrumental contribution to the line width of each peak must be estimated and subtracted [10,29,30]. For this the XRD pattern of standard silicon sample was recorded under identical conditions and the width due to instrumental factors for each diffraction peak of NiO, $\beta_{ins}(2\theta)$ was estimated by a method