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Synthesis and Characterisation of Nano crystalline Neodymium Nickelate ($NdNiO_3$) Powders using Low Temperature Molten Salt Technique

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Abstract

The ultrafine neodymium nickelate ($NdNiO_3$) powders have been prepared by molten flux method using oxide precursors. The synthesized materials were characterised using XRD, FTIR, CHNS, EDAX and EPR analytical techniques. The morphology of the synthesized crystals were scrutinized using scanning electron microscopy (SEM). The XRD analysis has shown that the synthesized crystal has possessed cubic structure. FTIR spectrum exhibits the absorption bands for the Nd-O stretching vibration and Ni-O bands at different wave lengths. The CHNS analysis presents the impurities level in the synthesized compound. EDAX analysis gives the concentration of Nd, Ni and O ions in the compound. The lone pair of electron state is identified from the EPR spectrum. The SEM micrographs depicts the presence of fine crystallites with assorted morphology. The average particle size of the powders is ranging between 25-35 µm. From the above studies, it has been concluded that pure crystals of $NdNiO_3$ compound can be synthesized by low temperature molten salt technique.

Keywords: Molten salt synthesis, neodymium nickelate, XRD, FTIR, SEM.

Introduction

Perovskite ABO_3 materials are of worldwide interest because of their very interesting properties, such as ferroelectric, magnetic, optical and colossal magnetoresistance[1], high-Tc superconductivity[2], non-volatile memory effects[3]. Thermoelectric devices have been used in broad areas such as refrigerators and in cooling units for fiber junctions in optical fiber communication technology[4]. Their crystal structure consists of corner sharing BO6 octahedra with the A ion in a high co-ordination site. The relative ionic radii of A^{m+} or B^{n+} (m+n = 6) give rise to 'distorted' perovskite structures with cubic symmetry. Tungsten trioxide exhibits a cubic perovskite like structure based on the corner sharing of regular octahedra with the oxygen atoms at the corner and the tungsten atoms at the center of each octahedron[5]. A variety of transition and non transition metal ions can be substituted either fully or partially in A and B sites. This gives rise to an extraordinary range of phenomena such as ferroelectricity, superconductivity, high temperature ionic conductivity, a variety of magnetic ordering etc[6].

In recent years cerium-based catalysts have been investigated since they find potential applications for the treatment of exhaust gas from automobiles to their use in methanol formation[7,8] the water gas shift reaction[9,10] acetone hydrogenation, alkadiene hydrogenation[11] and catalytic oxidation of CO[12] and of light hydrocarbons[13-15] CdS thin films have been prepared by diverse techniques: sputtering, vacuum evaporation, spray pyrolysis, electrodeposition and chemical bath deposition (CBD)[16]**.** Copper selenide is an interesting metal chalcogenide semiconductor material. It has a number of applications in solar cells, super ionic conductors and photo-detectors[17]

Nanosized metal oxide particles can be synthesised by a variety of methods, including chemical gas phase growth methods such as chemical vapor deposition (CVD), sol-gel processing and reverse micelle[18] laser pyrolysis[19] self-assembly templating[20], electrochemical synthesis[21] metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxial, and plasma synthesis[22,23]. Photodegradation of phenol in presence of UV light using semiconductor metal oxides (such as ZnO, SnO_2, Fe_2O_3, CdO, TiO_2 etc) is an efficient technique in wastewater treatment[24]. Molten salt synthesis is one of the most versatile techniques to prepare highly ordered complex oxide materials. The molten salts are used as the reaction medium for the reactants dissolution and product precipitation. Studies have shown that the products obtained from molten salts are influenced by the synthesis conditions, such as the type of salt used, the annealing temperature, the temperature ramp rate, the precursor composition and the solubility of the reactive constituents in the molten salt etc[25-27].

The molten salts rendered homogeneous distribution and high intimacy of the reactive components at the atomic scale in the initial mixture of precursor salts. Hence, the diffusion distance and the rate of the reactive species in molten melts are modified and an efficient material transport is enabled to meet the minimal kinetic requirement for the reaction[28-30]. Generally the starting materials for molten salt synthesis are inorganic compounds such as sulfates, chlorides and oxides, which are

blended with the alkali metal nitrates, chlorides, carbonates, hydroxides as a powder mixture before heating to the reaction temperature. Many complex oxide materials have been synthesized by molten salt technique [31-34]. Even though, many soft chemical routes have been attempted, only few studies have been made on the synthesis of $NdNiO_3$ compounds using molten flux method. Hence, an attempt has been made on the preparation of $NdNiO_3$ by this method.

Material and Methods

Reagent-grade chemicals like neodymium oxide (Nd_2O_3), nickel oxide (NiO) were used as the starting materials. They were obtained from Merck India Ltd, Bombay. Appropriate amount of chloride salts such as sodium chloride (NaCl) and potassium chloride (KCl) were used as the flux. They were thoroughly ground using a mortar and pestle and were placed in a high density alumina crucible. The mixture was then heated in an electrical resistance furnace at 900^0C for 12 hrs. The heating rate was 200°C per hour for all the experiments.The resulting reaction mixture was cooled to ambient temperature. The contents were removed from the crucible and washed with hot water for several times. The unreacted neodymium, nickel, alkaline salts were removed by treating with these solvents. The residual powders were dried in a vacuum oven at 50°C for 1 hour and cooled to room temperature. The method of synthesis is presented in the form of a flow chart and shown in figure 1. Finally free flowing black powders were obtained and they were characterized for their physicochemical properties.

The purified powders were characterized by XRD (Philips 8030 X-ray diffractometer) to identify the phase purity of the compound. The unit cell lattice parameters were obtained by the Least-square fitting method of the d-spacing and the hkl values. Fourier transform infrared (FTIR) spectroscopy was used to study the structure coordination of the calcined powders using Perkin Elmer UK paragon-500 spectrophotometer. To record the spectrum, each sample was mixed with KBr, ground in to fine powder and made into pellet. It was then examined in the wave number ranging from 400-4000 cm^{-1}. Carbon, hydrogen, nitrogen, and sulphur contents of the samples were assessed using an elemental analyzer Vario EL III-Germany Instrument. Electron spin resonance (ESR) spectroscopical analysis was performed using microwave frequency 9.857403 GHz with fields corresponding to about ~ 6500.000G sweep width using a Bruker Bio Spin Gmbh EPR spectrometer. The morphology of the synthesized powders was examined by a Scanning Electron Microscope (SEM)-JSM-3.5 CF, Japan JEOL make.

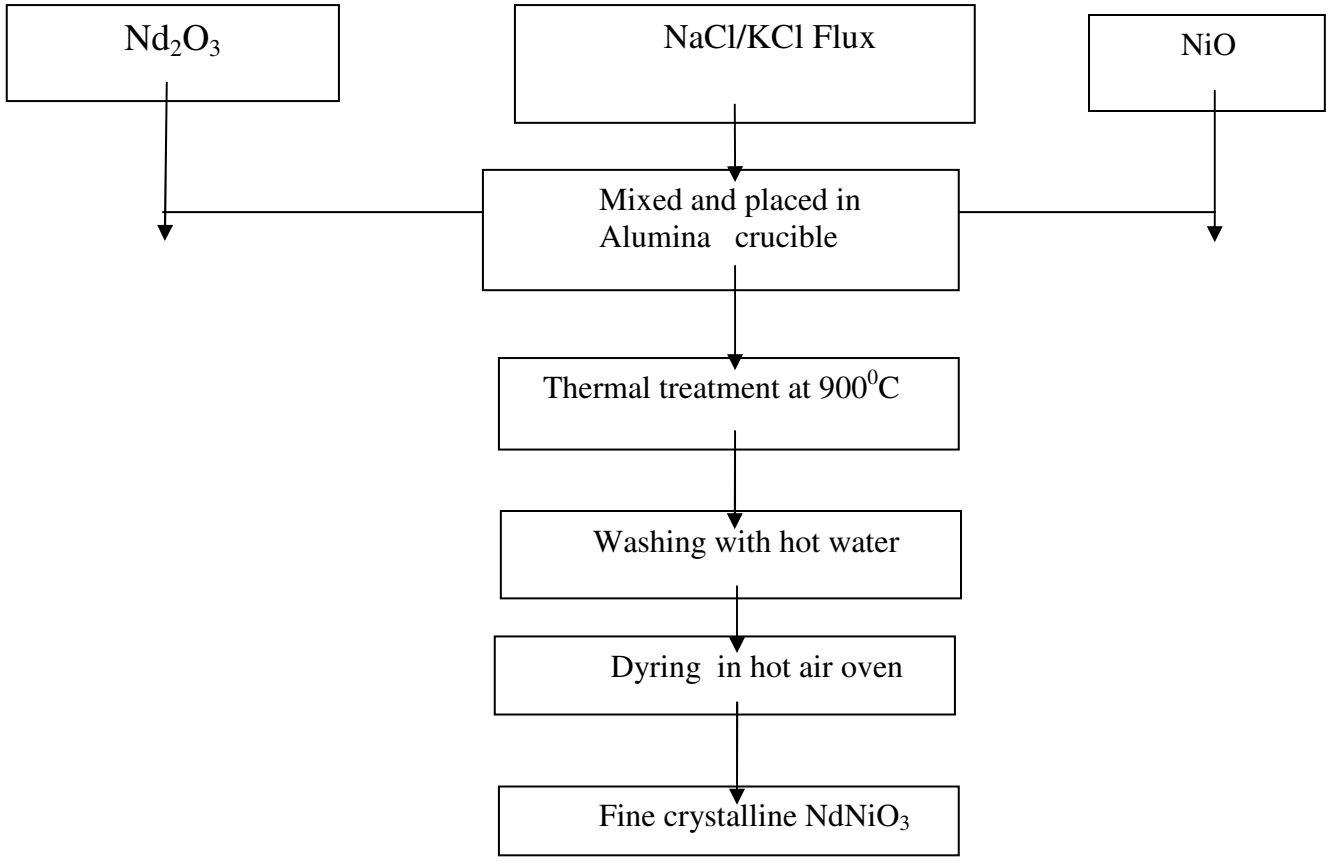


Figure -1
Flow chart for the preparation of $NdNiO_3$ compound

Results and Discussion

The XRD data of the synthesized crystals are presented in figure 2. The lattice constant values are determined using the equation, $1/d^2= h^2/a^2 +k^2/b^2 +l^2/c^2$

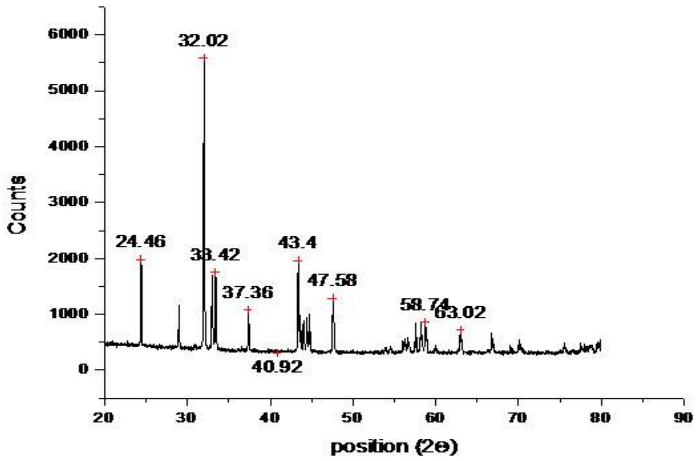


Figure-2
X-ray diffraction spectrum of $NdNiO_3$

All the XRD peaks are indexed assuming a orthorhombic structure. The calculated lattice parameter values are in good agreement with the reported values. The d spacing values of calcined powders are well matched with the XRD pattern of NdNiO3. The average crystallite size of the products was determined from the XRD patterns according to the Scherrer's equation $D = 0.9\lambda / \beta\cos\theta$. The average crystallite size is ranging between 85-100nm.

Fourier transform infrared (FTIR) spectroscopical analysis: FTIR spectrum recorded for the neodymium nickelate compound and presented in figure 3. The transmittance band appeared at 3462 cm^{-1} may be attributed to the O-H stretching vibration of water molecules as reported in the literature[35]. The bands seen between 1364 to 1707 cm^{-1} are related to the coordination of the Ni^{3+}cations as reported by Fernades et al.[36]. The transmittance bands in the wave length region of 3434-3404 cm^{-1} are responsible for the formation of the single phase $NdNiO_3$compound. The bands noticed at higher wavelength region may be assigned to the Ni-O bands.

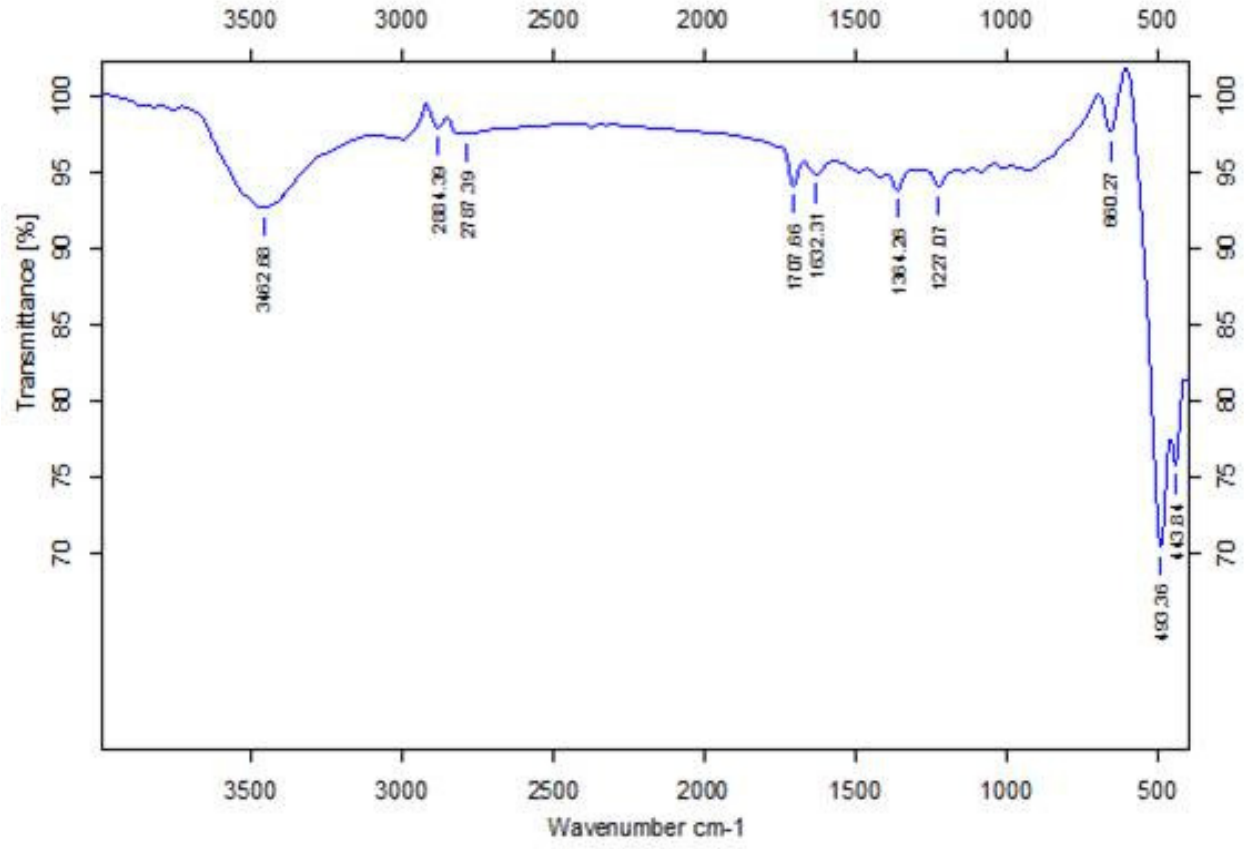


Figure-3
FTIR spectrum of $NdNiO_3$ compound

Carbon, hydrogen, nitrogen and sulfur (CHNS) analysis: The results on the CHNS analysis are presented in table 1. From the table, it is noticed that the compound has associated with some minor impurities such as C, H and S.

Table -1
Chemical analysis of the compound of $NdNiO_3$

Compound	C (%)	H (%)	N (%)	S (%)
$NdNiO_3$	0.167	0.035	0.000	0.067

Energy dispersive X-ray analysis (EDAX): The elemental analysis of the synthesized compound was performed using energy dispersive x-ray analysis technique. Figure 4 represents the EDAX profile of Nd, Ni and O of the synthesized $NdNiO_3$ compound. The results on the EDAX analysis are presented in Table.2. The spectrum exhibits the constituent elements are in appropriate weight percentage.

Table-2
EDAX analysis data

Compound	Nd (wt%)	Ni (wt%)	O (wt%)
$NdNiO_3$	57.84	32.04	10.12

Electro paramagnetic resonance (EPR) studies: The paramagnetic resonance spectrum of the $NdNiO_3$ is presented in figure 5. From the EPR spectrum, it is noticed that the value of g factor is g=2, which represents the paramagnetic entities present in the parent compound. The lone pair electron state is identified from the spectrum. It is also revealed that the position of the signal is very close to the value expected for uncorrelated spins with the gyromagnetic factor Nd^{3+}. Ni^{2+} dipolar interactions.

Ultra-violet spectroscopic studies: Figure 6 shows the UV-Visible spectrum of the synthesized $NdNiO_3$ compound. A broad absorption band is noticed at 340 nm in the spectrum represents the Ni-O and Nd-O absorption bands. From the spectrum, the band gap of the material is determined using the formula E = hυ and found to be 5.84 eV.

SEM analysis: The morphological features of the synthesised powders were obtained by means of scanning electron microscopy. Figure 7(a) and 7(b) show the scanning electron micrographs of NdNiO3 compound obtained by molten salt Synthesis (MSS) route. The crystals have shown an assorted plate like particle morphology. The average particle size of the powders is ranging between 25-35 μm.

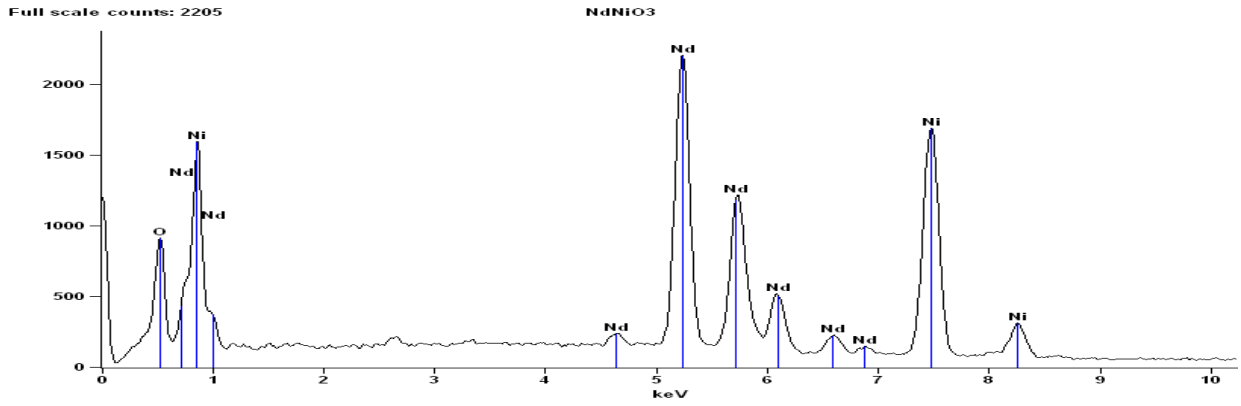


Figure-4
EDAX profile of Nd, Ni, and O in $NdNiO_3$

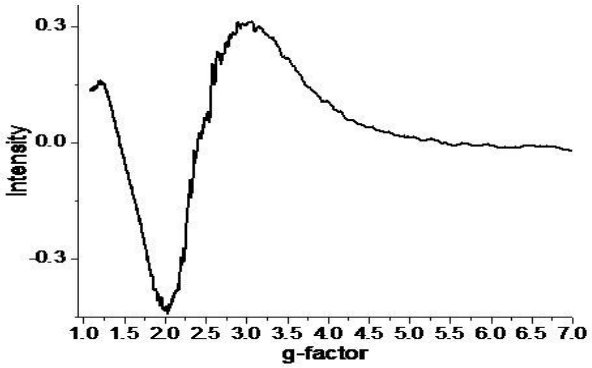


Figure-5
EPR spectrum of $NdNiO_3$compound

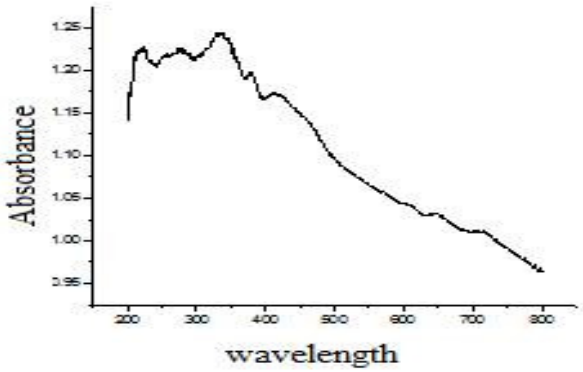
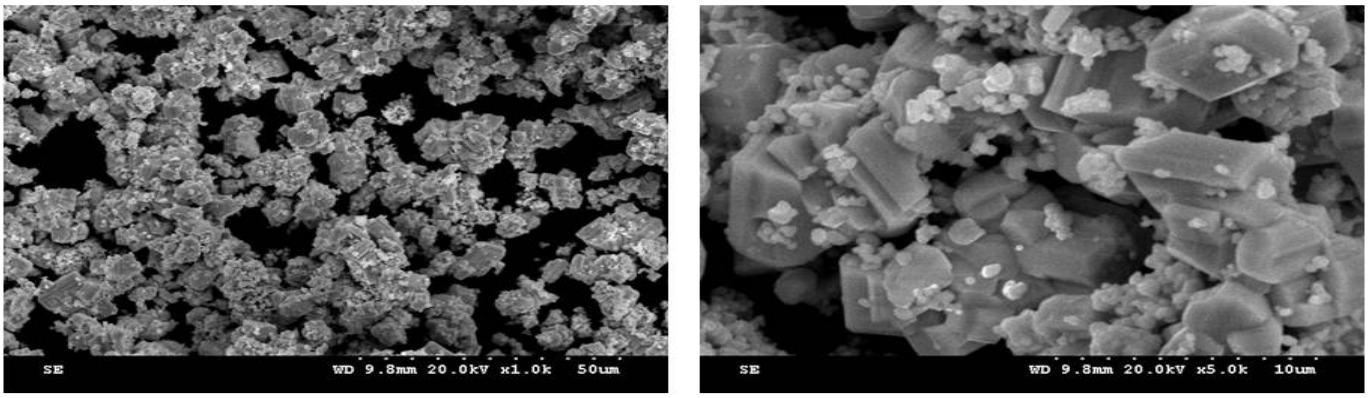


Figure-6
UV-Visible spectrum of $NdNiO_3$ compound



(a) (b)

Figure-7
(a) and (b) SEM image of $NdNiO_3$

Conclusion

Fine crystalline $NdNiO_3$ powders are successfully synthesized using low temperature molten salt technique. The XRD analysis confirms that the compound has the cubic structure. FTIR spectrum reveals the Nd-O, Ni-O band positions in $NdNiO_3$ compound. CHNS analysis shows the compound has minor impurities such as carbon, hydrogen and sulphur. From the UV reflectance spectrum, the band gap value is determined and found to be e_g = 5.84 eV. The EPR spectrum reveals that the value of g factor is g=2. The SEM image reveals that the particles have assorted crystal morphology. The average particle size is found to be 20 - 35 μm. From the above studies, it has been concluded that the fine crystalline neodymium nickelate compound can be synthesized by low temperature molten salt technique.

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