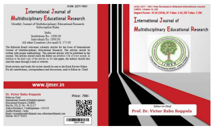


Cover Page

INTERNATIONAL JOURNAL OF MULTIDISCIPLINARY EDUCATIONAL RESEARCH
ISSN:2277-7881(Print); IMPACT FACTOR :10.16(2026); IC VALUE:5.16; ISI VALUE:2.286
Peer-Peer Reviewed, Refereed & Open Access International Journal - As per UGC Norms
(Fulfilled Suggests Parameters of UGC by IJMER)
Volume:15, Issue:6(1), June 2026
Scopus Review ID: A2B96D3ACF3FEA2A
Article Received: Reviewed: Accepted
Publisher: Sucharitha Publication, India
Online Copy of Article Publication Available: www.ijmer.in

SYNTHESIS METHODS AND THEIR INFLUENCE ON THE ELECTRICAL AND OPTICAL PROPERTIES OF NON-STOICHIOMETRIC NIO

Chouhan Aakanksha and Dubey Paras
Department of Physics
Sage University, Indore, Madhya Pradesh, India

Abstract:

Metal oxides are the subject of study that encompasses the design and synthesis of nanostructured thin films as well as engineering that demonstrates the multifunctional qualities that are required for the technology that is now in use. One of the distinguishing features of metal oxides is that they include a greater number of oxidation states of metal ions, each of which is capable of undergoing a transformation from one state to another. Furthermore, the oxide materials acquire a wide range of electronic characteristics, including superconductivity and the transition between metals and insulators, piezoelectricity, ferroelectricity, ferromagnetism, and magnetoresistance.All of these features of nickel oxide provide a perfect opportunity, and in this particular instance, non-stoichiometric nickel oxide was created using the thermal breakdown technique at a variety of sintering temperatures.

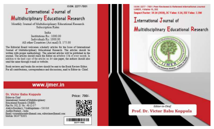
Keyword: Nickel Oxide, Non-Stoichiometric, Synthesis Methods, Electrical Properties, Optical Properties.

Introduction

In addition, the phase transitions, complex phases, and magnetic orientation changes of transition metal oxides (TMOs) are the subject of much research and investigation. Furthermore, oxides of graphene (GO) are an instant alternative to graphene for the production of flexible devices in the electronics sector (Wei et al. 2010).

It is the new features of integrated electronic devices made of oxides and semiconductors that are the most promising prospects for the development of information technology. In this thesis, the phase transitions of the metal oxide semiconductors of iron, cobalt, and nickel are examined for their potential uses in transformer core and super capacitor applications. The phase transitions are investigated under annealing conditions. It has been hypothesized that the creation of thin films of amorphous metal oxides, metal chalcogenides, and alloys can be accomplished through the use of Physical and Chemical Vapor Deposition methods. [1] The glass substrates have been transformed into alloys by the process of annealing at low temperatures. The surface mobility of the atoms is restricted when these circumstances are present, which results in the formation of a disordered structure. At low temperatures, however, amorphous structures are able to keep their phase, despite the fact that, according to thermodynamics, it was thought that only crystalline solids could have the stable structure. In order to achieve thermal equilibrium, the deposition of bulk materials involves melting and solidifying at temperatures that are higher than normal. The mobility of atoms is the cause for this, since it makes stable phases easier to achieve, which in turn promotes nucleation and further advancement of the growth process. Metal oxides, on the other hand, are characterized by metastable phases due to the sluggish movement of atoms in very viscous melts. However, the thin film technology has a difficult time achieving equilibrium, and as a result, it is characterized by annealing operations that take place at low temperatures.

An analysis of the known structures of transition metal oxides, which are described in Table 1.1, reveals that transition metal oxides may be found in a wide variety of crystal formations. In order to provide a graphic representation of all the many sorts of structures that may be found in these oxides, the categorization that is utilized in Table 1.1 was selected. This is done by raising the atomic number of the transition metal, which results in the oxides being stacked horizontally, just as in the periodic table. Because the oxidation state of the metal increases as we move down the column, the oxides that make up a group are organized in a vertical fashion inside the group.

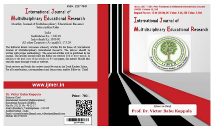


Several different synthetic approaches have been utilized in order to attain the goal of controlling the size, shape, and structure of transition metal oxides. [2] The solid state reaction pathway and thermal reduction are also techniques that may be utilized to get the bulk transition metal oxides. The yield of the metal oxide is dependent, in both of these procedures, on the precursors that are used as well as the temperature at which the synthesis is carried out [Kim et al., 1974]. For this kind of synthesis, the nitrate, carbonate, and chlorides are the most common components that are utilized. When it comes to the manufacture of polycrystalline solids from a combination of solid starting materials, the solid-state reaction approach is the method that is utilized the most frequently [West 2005]. The crystal structures of several common transition metal oxides are presented in Table 1.1. Solids do not react with one another at ambient temperature over typical time scales; thus, it is required to heat them to considerably higher temperatures. [3]

Sc_2O_3 c	TiO r* Ti_2O_3 cr TiO_2 t a, b	VO r V_2O_3 cr VO_2 t* VO_2 0r	Cr_2O_3 cr CrO_2 t CrO3 or	MnO r Mn_3O_4 sp* Mn_2O_2 cs* MnO_2 t*, and other	FeO r Fe_2O_3 Cr, sp Fe_3O_4 Sp	CoO r Co_3O_4 sp	NiO r	CuO s Cu_2O c	ZnO w
Y_2O_3 c	Z r O r ZrO_2 m, tet	NbO_2 r* Nb_2O_5 mt	MoO_2 m,(r*) MoO_3 I, or	TcO_2 m,(t) Tc_2O_7 Or	RuO_2 t	Rh_2O_3 cr* RhO_2 t	PdO s	Ag_2O c	CdO r
La_2O_3 mt	HfO_2 m	TaO_2 t Ta_2O_5 Or	WO_2 m,(t*) WO_3 m	ReO_2 m, (t) ReO_3 Cub(perovskite) Re_2O_7 or	OsO_2 t OsO_4 m	IrO_2 t	PtO_3 cub PtO_2 t	--	HgOor,and other

cris = cristobaiite. NaCl = rock sat, . W= wurtzile. C = C-M_20_3. CO=~ c orundum. SP =spinel. rui = rutile, a = anatase, b = bmoldte, mono = monoclinic, mt = multiple, I = layer, or = ortharhombic, mol = molecular, f = fluofie, tet = tetragonal, cub = cubic. (source: H.H kung,1989)

In order for the reaction to take place at a pace that is observable, the temperature must be between 1000 and 1500 degrees Celsius. According to West (2005), the feasibility and pace of a solid state reaction are dependent on a number of elements. These factors include the reaction circumstances, the structural features of the reactants, the surface area of the solids, the reactivity of the solids, and the change in thermodynamic free energy that is connected with the reaction. There is a group of processes known as thermal reduction that are based on the reduction of metal compounds (oxides, halides, and other compounds) to the corresponding metals by more active metals (aluminum, magnesium, and silicon, which for this purpose is considered to be a metal), and they are accompanied by the generation of heat. There are three different types of thermal reduction processes: aluminothermy, magnesiothermy, and silicothermy [Beliaev 1970]. These processes are divided according to the reducing metal. The production of solid materials from tiny molecules can be accomplished by a process known as the sol–gel phase. This technique is utilized in the production of metal oxides, particularly oxides of silicon (Si) and titanium (Ti), where it is very effective. The procedure entails the transformation of monomers into a colloidal solution (sol), which serves as the precursor for an integrated network (or gel) consisting of either discrete particles or network polymers [Brinker et al 1990]. Metal alkoxides are some examples of typical precursors. Both nanoparticles and bulk particles can be produced with the use of this approach.[4] When using the vapor phase growth method, which is usually carried out in a thermal furnace, it is essential to manage the reaction that takes place between the oxygen gas and the metal vapor source. A number of different approaches have been devised in order to accomplish this goal. These approaches include controlling the aspect ratio, diameter, and specific surface area of the product. The sputtering procedure is utilized in order to create thin films. Physical Vapor Deposition (PVD) is one of the coating processes that may be utilized, while sputtering is another approach that can be utilized [Andre 2000]. The sputtering technique for the deposition of thin films includes the introduction of a regulated gas, often argon, which is chemically inert, into a vacuum chamber. Additionally, a cathode is electrically energized in order to create a plasma that is capable of maintaining itself [Milton



2003]. There are a great number of other ways that may be utilized to synthesis transition metal oxides; the selection of appropriate methods is contingent upon the requirements.

Non-Stoichiometric

Non-stoichiometric compounds are any solid chemical compounds in which the number of atoms of the specific elements cannot be stated in a ratio of a tiny whole number. These compounds are often characterized by their lack of stoichiometry.

The atomic ratios are not expressed in this manner; rather, they are represented as tiny integers. The concept of a non-stoichiometric compound is connected to the Dalton law of multiple proportions. A conventional non-stoichiometric compound is defined as one that has a small and fixed composition and is represented in a small integer ratio among its atomic components. Non-stoichiometric compounds are also known as non-stoichiometric compounds. [5]

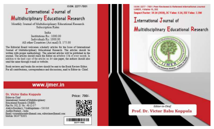
The atoms that are present in these compounds are precisely positioned at the places on the crystal lattice that correspond to them, and neither flaws nor impurities are permitted to leave the compounds.

WHAT IS NICKEL OXIDE

With an atomic number of 28, an atomic mass of about 58.69 grams per mole, and the ability to exist in a variety of oxidation states (0, 1+, 2+, 3+, and 4+), nickel is a metallic element that is hard, malleable, and silvery white in color. It is classified in Group VIIIB of the periodic table. [Ar] 4s2 3d8 is the symbol that represents the electrical configuration of nickel. At a photon energy of 2 eV, nickel has a melting temperature of approximately 1,453 degrees Celsius, a boiling point of approximately 2,732 degrees Celsius, and a refractive index of approximately 2.33. Almost all nickel compounds have a color that is either blue or green. It is possible to combine nickel with a wide variety of other elements, such as chlorine, Sulphur, and oxygen. Nickel is also capable of easily forming alloys with copper, zinc, iron, chromium, and other alloying elements. A great number of nickel compounds are easily dissolved in water, and the resulting colors are often green or blue. [6] In addition to its use in electrochromic devices, ceramic coloring, batteries, and catalysts for chemical processes, nickel compounds are also utilized in manufacturing. Nickel (II) oxide is a basic oxide that exists with the formula NiO. It has a face-centered cubic (FCC) rock-salt (NaCl) crystal structure and possesses octahedral Ni (II) and O2- sites. 'a', the lattice parameter, is comparable to approximately 4.1769 Å, and it is a member of the Fm3m space group. The non-stoichiometric form of NiO, which is characterized by a divergence of the Ni/O ratio from 1, is a typical occurrence. The presence of Ni-vacancies produced Ni3+ is a factor that contributes to the p-type conductivity of NiO. Approximately three to four electron volts is the band gap that exists between the O2p and Ni3d orbitals in NiO, which is a Mott-Hubbard insulator.[7] There are two primary hypotheses that are associated with the optical absorption in NiO. These theories include charge-transfer features, which include transitions from oxygen to nickel (p → d), and cationic transitions, which involve moving from d to d. However, there is still a lot of controversy over the insulating properties and optical transition of NiO. Because of its low cost potential and optical modulation, NiO is frequently used as an anodic coloring material (counter electrodes) in commercial electrochromic devices. This is due to the fact that it has been observed to fluctuate between about 77% and 35% in bleached and colored states, respectively.

REVIEW

In the process of determining the electrical and optical properties of non-stoichiometric NiO, a number of different synthesis processes play an important role. For example, the combustion synthesis method was discovered to be superior in terms of creating LaNiO perovskite powders that exhibited improved electrocatalytic activity (Zhi-An, 2008). These powders had high specific surface areas. In addition, the band structure technique, when paired with molecular dynamics cluster optimization, was able to provide insights into the optical properties of LiNbO3 crystals. These insights highlighted



the impact that non-stoichiometry has on the electro optics coefficient (Enas, Ali, 2023). Doped samples with better band gap energies and enhanced ionic conductivity were produced as a result of the synthesis of NiO nanostructures by co-precipitation procedures, which made them interesting candidates for applications in the field of photo electronics (María, T., 1999). The findings of these research collectively highlight the significance of synthesis methods in the process of tailoring the properties of non-stoichiometric NiO materials for a variety of industries and applications.[8]

The electrical and optical properties of non-stoichiometric NiO are considerably influenced by a variety of synthesis procedures using different techniques. The combustion synthesis of LaNiO perovskites yields a high electro catalytic activity that is comparable to that of platinum, which makes them appropriate for use in electrochemical devices (María, T., 1999). In addition to this, the band structure method combined with molecular dynamics optimization sheds light on the dependence of optical characteristics in LiNbO3 on variations in crystal composition (I.V., Kityk., 2001). The wet chemical production of NiO nanoparticles demonstrates that as the particle size increases, the intensity of the UV emission increases, and antiferromagnetic behavior is observed. Magnetic moment changes are attributed to surface cluster spins.(2017) Mohd., Arif., 2019. In addition, the optical conductivity of electro polished Nb samples is significantly higher than that of buffered chemically polished and as-received samples, despite the fact that there are substantial changes in the physical constants and the depth of electric field penetration. In the year 2017, Nageshwar Singh NiO's band gap energy and ionic conductivity are both improved when it is doped with copper and zinc, which makes it a good candidate for use in photo electronic applications. (Enas, Ali, 2023)

Research method

In this study, different documents that have been published between the years 2012 and 2022 were compiled and reviewed. [9, 10] A significant amount of research work was found in the form of journal articles, conference proceedings, press articles, book chapters and organizational reports. Through a screening process, the found documents were scrutinized first by the relevance of their titles and then by reviewing their abstracts and conclusions. The documents were then further refined by synthesizing the whole document and finally, the most relevant sources were selected for review.

Analysis

Synthesis of nonstoichiometric nickel oxide

The manner in which a chemical is prepared is a significant factor in determining the features that it possesses. Nonstoichiometric compounds, the composition and structure of which are known, are of great significance because of the distinctive optical, electrical, magnetic, thermal, and mechanical characteristics that they possess. The selection of a precursor for design and the customisation of materials with varying stoichiometry in order to achieve the desired level of performance are both topics that are of significant interest. It is possible to produce nonstoichiometric by employing a method that is both efficient and accurate in terms of controlling the composition, defect, and structure. In example, NiO samples of varying surface areas, colors, and degrees of nonstoichiometric can be created depending on the circumstances of preparation, the sintering temperature, and other factors. The preparation of nickel oxide can be accomplished using a variety of techniques, such as the chemical route, evaporation, sputtering, chemical deposition, and oxidation of nickel, sol-gel process, and thermal decomposition. One of the most common methods for powder preparation is the thermal breakdown technique, which is an endothermic process that is straightforward, inexpensive, and quick. [11]

Through the process of thermal breakdown of nickel nitrate hexahydrate, nonstoichiometric nickel oxide was successfully synthesized. In general, a sample of nickel oxide with a certain amount of oxygen (Ni1−δO) was produced by thermally decomposing about 5 grammes of Ni(NO3)2.6H2O in open air for a duration of three hours at a temperature of 400 degrees Celsius. The product that was obtained in this manner was unadulterated and without any extraneous mixing. [12] The formation of this exothermic reaction is not catalytic, and it does not require the presence of any other chemical in order to get started. At the end of the process of breaking down the precursor, the substance that is formed is nickel oxide and gaseous components, both of which are able to easily exit from the system. [13]In order to function properly, the decomposition mechanism of this process requires the bare minimum of time and temperature. The sample in question was referred to as NiO400. There were seven further samples that were created at temperatures of 500, 600, 700, 800, 900, 1000, and 1100 degrees Celsius. NiO500, NiO600, NiO700, NiO800, NiO900, NiO1000, and NiO1100 were the names given to each of these elements, in no particular order. [14]

Optical properties

One type of semiconductor that has a bread band gap is nickel oxide. Because of the presence of Ni+3ions within the oxide lattice, there is a charge transfer transition that occurs, which results in absorption in the visible area. The absorption edge is localized in the UV region. Several studies have made estimates on the amount of photon energy that NiO is able to absorb. Notwithstanding the fact that the refractive index of NiO is 2.33 at a photon energy of 2 eV, the gap energy value that has been reported for NiO falls somewhere in the region of 3.6 to 4 eV. There are localized Nickel 3d-bands that make up the valence band.[15] These bands have a width of 4.3-4.4 eV and are located approximately 2 eV above the Fermi level, which is –8.74 eV. The 3d states of nickel were linked with oxygen at the 2p band, which has a comparatively high energy of around 4–8 eV. The conduction band, on the other hand, is made up of several unoccupied states of nickel, including 3d, 4s, and 4p. Both of the primary ideas that have been presented to explain the optical absorption gap in NiO are as follows: either it is caused by a p→d transition in a single Ni atom, or it is caused by a d→ d transition in two adjacent Ni atoms in the lattice. [16]

Electrical properties

NiO exhibits the characteristics of a p-type oxide semiconductor and possesses a broadband gap energy. [17]A stoichiometry that is nominally pure NiO, which is seen in figure 1, is categorized as a Mott-Hubbard insulator due to its room temperature resistivity, which is on the order of 1013Ω-cm. numerous ideas have been developed in order to provide an explanation for the insulating properties of NiO. [18]These theories include the cluster theory, the chemical band approach, the band theory, and the localized electron theory. Notwithstanding the extensive theoretical and experimental research that has been conducted, the electronic structure of NiO continues to be a contentious topic. [19]

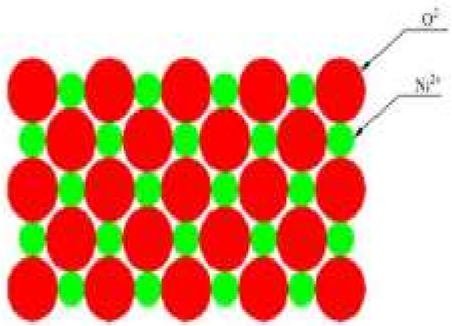


Figure 1: A schematic of pure stoichiometry NiO crystal [Wu. Hongbin, L.S. Wang1997].

In stoichiometry, NiO has a light green color. It has been determined that the presence of Ni+3ions is responsible for the black color of NiO. A charge compensation for nickel vacancies is provided by these ions, which are found in nickel oxide. [20] The fact that different samples have varying conductivities provides evidence that the influence of random impurities or lattice defects determines the extent to which conduction occurs. In defect nickel oxide, the presence of nickel vacancies, in addition to other impurities such as OH^-, has an effect on the electronic structure of the oxygen atom. This is seen by the presence of additional O1s peaks with a higher binding energy, as well as the conventional O1s peaks of oxygen in stoichiometry NiO. The presence of nickel vacancies or an excess of oxygen is thought to be responsible for the electronic conduction observed in non-doped nickel oxide. [21] When the active species of nickel and oxygen impact individually on the development of the film surface, the orientation of the film is often controlled by the orientation of O-2. This occurs in the ionic crystal of nickel oxide (NiO). The reason for this is because NiO does not possess the directivity of a combination between Ni+2 and O-2, and the radius of O-2, which is 0.140 nm, is greater than that of Ni+2, which is 0.069 nm. The size of the oxygen atom is so great that it is impossible for there to be a significant concentration of interstitial oxygen atoms in the structure. Because of this, there are vacancies in the typically occupied Ni sites, as seen in figure 2. [22]

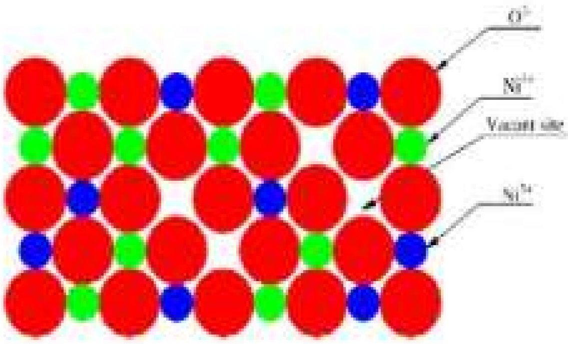


Figure 2: A schematic of pure non-stoichiometry NiO crystal [B. Sasi, 2007].

This is because to the excess of oxygen in NiO. However, in order to maintain the crystal's overall electrical neutrality, it is necessary to convert two Ni+2ions into Ni+3 for every Ni+2site that is unoccupied. It is possible to suggest that the Ni+3ions that were introduced into the crystal in this manner are positive centers that are able to move from one Ni+2 site to another. [23] The movement of an electron from a Ni+2 site to a Ni+3 site is analogous to the movement of a positive hole around the Ni+2 sites for the electron. The presence of an excessive amount of oxygen causes NiO to behave as a p-type semiconductor [B. Sasi, 2007].

Conclusion

Numerous Deviations from stoichiometry have a significant impact not only on the chemical characteristics of oxides but also on their physical qualities. The presence of foreign impurities in a solid has the potential to solidify a certain crystal structure that is present in the solid. Because of this, foreign metal ions, whether they are present as impurities or are doped on purpose, would also produce changes in the characteristics of these oxides that are able to be altered [Norbie 1987]. Because of this, stoichiometry is an essential component in the process of modifying the characteristics of transition metal oxide. Therefore, the scientists came to the conclusion that the difference in the infrared spectra of their various NiO samples cannot be solely attributed to the difference in their particle sizes. They also suggested that the actual geometrical shape of the particles and the possible shape distribution should be considered as significant factors in the interpretation of the infrared spectra of particles.

Reference

1. B. Sasi, Preparation and characterization studies of nanostructure nickel oxide and lithium doped nickel oxide thin films, PhD thesis, University of Kerala, 2007.
2. Boussafeur, Master thesis, Larbi Ben M "Hidi University Oum El-Bouaghi, (2012).
3. Chang, C. C. Shen and M. H. Hon, Ceramics Internet 29 (2003) 245.
4. Chigane M and Ishikawa M 1998 Faraday Trans. 94 3665

5. Enas, Ali, Ahmed, Alahsab., Abdullah, Ahmed, Ali, Ahmed., A.M., Abdulwahab. (2023). Synthesis, Structural, Optical and Electrical Properties of Pure and Doped NiO Nanostructures Prepared via The Co-precipitation Method. doi: 10.59167/tujnas.v8i1.1491
6. https://www.cef1.org (Fra DESS.old / dess_265 html).
7. I.V., Kityk., Malgorzata, Makowska-Janusik., M.D., Fontana., Michel, Aillerie., Farid, Abdi. (2001). Influence of Non-Stoichiometric Defects on Optical Properties in LiNbO3. Crystal Research and Technology, doi: 10.1002/1521-4079(200107)36:6<577::AID-CRAT577>3.0.CO;2-3
8. Iida Y and Ozaki S 1959 J. Am. Ceram.Soc. 42 219
9. Liu Y, Yang F, Yang X, Colloids Surf. A. Vol. 312, p. 219, 2008.
10. Lu AH, Salabas EL, Schuth F, Angew. Chem. Int. Vol. 46, p. 1222, 2007.
11. Lu JG, Chang P, Fan Z, Mater. Sci. Eng. R: Reports. Vol. 52, p. 49, 2006.
12. Mahaleh YBM, Sadrnezhaad SK, Hosseini D, J. Nanomater. p. 470595, 2008.
13. Makhlouf SA, J. Magn. Magn. Mater. Vol. 272, p. 1530, 2004.
14. Mallick P, Rath C, Rath A, Banerjee A, Mishra NC, Solid State Commun. Vol. 150, p.1342, 2010.
15. María, T., Colomer., Daniel, A., Fumo., José, R., Jurado., Ana, M., Segadães. (1999). Non-stoichiometric La(1 – x)NiO(3 – δ) perovskites produced by combustion synthesis. Journal of Materials Chemistry, doi: 10.1039/A902808K
16. Mohd., Arif., Amit, Sanger., Mohd., Shkir., Mohd., Shkir., Arun, Singh., Ram, S., Katiyar. (2019). Influence of interparticle interaction on the structural, optical and magnetic properties of NiO nanoparticles. Physica B-condensed Matter, doi: 10.1016/J.PHYSB.2018.09.023
17. Nageshwar, Singh., M.N., Deo., S, B, Roy. (2017). Optical investigation of niobium properties: Electrical- and physical constants. Physica C-superconductivity and Its Applications, doi: 10.1016/J.PHYSC.2017.05.008
18. Pramanik P and Bhattachraya S 1990 J. Electrochem.Soc. 137 3869
19. Soleimanpour, Synthesis, fabrication and surface modification of m,2013 onocrystalline nickel oxide for electronic gas sensors, PhD thesis, University of Toledo, 2013.
20. W.D. Callister, Fundamentals of materials science and engineering- An integrated approach. Second ed., USA: John Wiley & Sons, 2005.
21. Wu. Hongbin, L.S. Wang, A study of nickel monoxide (NiO), nickel dioxide (ONiO), and Ni(O2) complex by anion photoelectron spectroscopy, J. Chem. Phys., 1 (1997) P107
22. Z. Zhiwie, Oxygen reduction lithiated nickel oxide as catalyst and catalyst support, PhD thesis case Western Reserve university, 1993.
23. Zhi-An, Ren., S., Kuroiwa., Yoko, Tomita., Jun, Akimitsu. (2008). Structural phase evolution and superconductivity in the non-stoichiometric intermetallic compound niobium diboride. Physica C-superconductivity and Its Applications, doi: 10.1016/J.PHYSC.2008.01.001.