Spectroscopic study of UV-VIS electronic transitions of Ni^{2+} ions in different phases of Sol- Gel process

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دراسة طيفية للأنتقالات الالكترونية (UV-VIS) لأيون النيكل Ni $^{2+}$ لمختلف أطوار عملية صول جل (Sol-Gel)

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Qussay Mohammed Salman

Laser Physics Department, College of science for women, University of Babylon ,
Babylon, (IRAQ) E-mail:qusay_63@yahoo.com

ABSTRACT

Allowed and forbidden Electronic transition of Ni^{2+} ions have been investigated in solution, sol and Xerogel .Two complexes NiCl$_2$.6H$_2$O and Ni(NO$_3$)$_2$.6H$_2$O) have been dissolved in (water and ethanol) and doped in silica matrices using sol-gel technique. The molar ratio of TEOS: H2O: Ethanol which adopted in this study were 1:8:12 of PH value = 1 at 60°C. It is found that up to 150°C the Xerogel samples as well as in sol and solution Ni^{2+} ions have octahedral symmetry. The Racah parameter (B) and ligand field strength (Δ) has been calculated for Ni^{2+} ions in solution it is found Δ /B=0.85, while in silica matrices ligand field strength has been increased to be greater than 0.9 .It also found that absorbance peaks also have red shift with increasing draying time .

Key words : Ni^{2+} ions, Sol-Gel glasses , spectroscopy

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الخلاصة

الانتقالات الالكترونية المسموحة والممنوعة طيفيا لأيون   Ni $^{2+}$ تمت متابعتها خلال مراحل عملية الصول جل حيث تم اذابة المركبين NiCl$_2$.6H$_2$O   و   Ni(NO$_3$)$_2$.6H$_2$ في كلا من الماء والكحول ومن ثم أجراء تطعيم في مصفوفات سليكا باستخدام تقنية sol-gel . ان النسبة المولارية لكل من TEOS: H2O: Ethanol   المعتمدة في هذا البحث هي 1:8:12 وقيمة PH هي 1 عند درجة حرارة 60°C . وقد وجد ان ايون   Ni $^{2+}$ في نماذج Xerogel المحضرة وحتى درجة 150°C وكذلك في طور sol وكذلك المحاليل يمتلك تناظر ثماني .   وقد تم حساب معامل Racah (B) وكذلك شدة المجال الليكاند(Δ)لأيونNi^{2+} في المحاليل حيث وجدت Δ /B=0.85 بينما في مصفوفات سليكا كانت قيمته اكثر من 0.9 . وجد في هذا البحث كذلك ان قمم الامتصاصية يكون لها انحراف باتجاه الاطوال الموجية الطويلة بزيادة زمن التجفيف للنماذج.

الكلمات المفتاحية : ايونNi^{2+} , صول جل زجاج , أطياف

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I. INTRODUCTION.

Sol-gel technique is widely have been used to prepare different of mixed-metal oxides, nanomaterials and organic-inorganic hybrids materials by incorporating different cations or molecules in a silica host [1–5]. An important characteristic of the sol-gel process is the possibility of controlling all stages, which occur during the passage through molecular precursor to the final product. Over the last few decades Sol-gel methods prepared successfully different garnets, aluminates, cobaltates and superconductors [6 – 8].

Nickel oxide films were have been deposited from mixtures of nickel nitrate, [Ni(NO3)2.6(H2O)], in alcohol or ethylene glycol C$_2$H$_6$O$_2$ [9,10] solutions but the stability of nickel nitrate during heat processing limited its use to finite applications. The use of nickel sulphate heptahydrate NiSO$_4$.7H$_2$O with addition of several other compounds has been also studied. More studies confirm that the heat treatment is very effective parameter [11–14]. The same effect has been found for coating with sols of nickel chloride (NiCl2.6H2O) in ethylene glycol and butanol for the deposition process of NiOxHy thin films [15, 16]. The addition of tetraethoxysilane (TEOS) to the alcoholic mixture of anhydrous halide showed to be a suitable procedure, to prepare electrochromic Ni-based thin films, the results have also shown that coatings have been more

hardness, better adhesion and maintaining rather high[17]. another Mixture of nickel nitrate with ethylene glycol and tetraethoxysilane was also suggested [10].

The requirement to enhance solid-state lasers, optoelectronic communication devices, and optical quality of the materials has increase the interest in activator doped glass. Glass ceramic (GC) materials are one of the most important hybrid optical materials required which can be produced by controlling the nucleation and crystallization of glass. This type of nanocomposite materials can be used as hosts for activators ions so they can combine the advantages of both glass for it is easy made and doped crystal as optical activity [18].

In this paper the electronic transitions for both allowed and forbidden of Ni^{2+} ion (d^8) have been investigated. According to the Tanabe-Sugano diagram Figure 1 for Ni^{2+} , the strength of the crystal field, $\Delta(10Dq)$, is determined by the energy difference between the $^3A_{2g}$ and $^3T_{2g}$ states, also other states clearly in the diagram which is very well known by spectroscopists[19]. The samples which prepared by sol gel technique have been studied in different phases :solutions , sol, Xerogel and glasses by using UV-VIS absorption spectra, Finally verifying the Ni^{2+} ions cooperated in silica network at different annealing temperature.
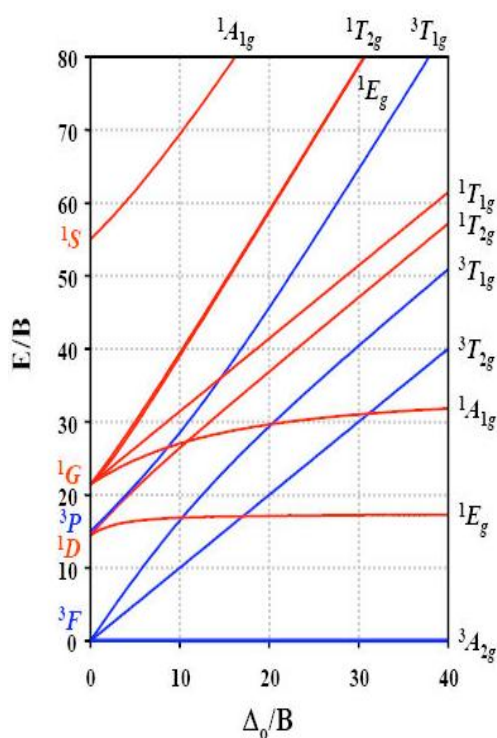

Figure (1) Energy level diagram for a d^8 ion in octahedral ligand fields . [19]

II. EXPERIMENTAL METHOD.

In order to have spectroscopy study the samples should be basically transparent clearly and free crack, so many samples have prepared with different sol gel parameters { pH ,R- molar ratio, ageing temperature T} at different concentrations of Ni ions.

Different R-molar ratio, of water/alkoxide, (2, 5, 8, 10, 25 and 60) were used at specific pH, ageing temperature (T) and Ni ion concentration. To get more exact value of R, the chromium salts were dissolved in ethanol instead of water. The final pH value has been modify to one (pH=1) in order to get a maximum transparency [20], since the other samples became quasi opaque and the samples transfer totally opaque for value of pH greater than four.

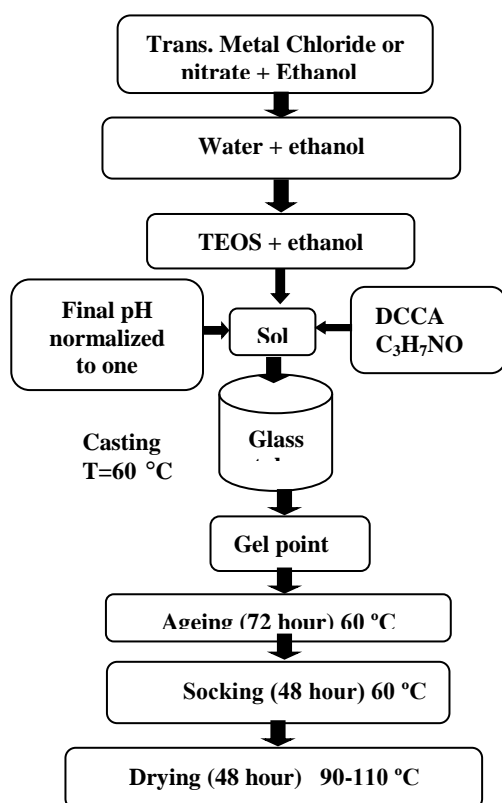The schematic diagram for preparing samples is shown in Fig.2.

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┌───────────────────────────┐
│ Trans. Metal Chloride or  │
│    nitrate + Ethanol      │
└───────────────────────────┘
              │
┌───────────────────────────┐
│      Water + ethanol      │
└───────────────────────────┘
              │
┌───────────────────────────┐
│      TEOS + ethanol       │
└───────────────────────────┘
              │
┌──────────┐   ┌─────┐   ┌──────────┐
│ Final pH │   │ Sol │◄──│   DCCA   │
│normalized│──►│     │   │ C₃H₇NO   │
│  to one  │   └─────┘   └──────────┘
└──────────┘      │
  Casting      ┌─────┐
  T=60 °C      │Glass│
               └─────┘
                  │
┌───────────────────────────┐
│         Gel point         │
└───────────────────────────┘
              │
┌───────────────────────────┐
│   Ageing (72 hour) 60 °C  │
└───────────────────────────┘
              │
┌───────────────────────────┐
│   Socking (48 hour) 60 °C │
└───────────────────────────┘
              │
┌───────────────────────────┐
│  Drying (48 hour) 90-110 °C│
└───────────────────────────┘
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Figure (2) Schematic diagram of preparing Xerogel samples

The ageing temperature has been chosen to be 60ºC to get optimum polymerization at minimum gelling time. So the optimum value for R, pH and T which were employed in this work are 8, 1 and 60^oC respectively. N, N dimethayl formamide (C_3H_7NO) was used in this work as drying control chemical additive (DCCA). In our study, saturation occurs at Ni ion concentration about 10^{-1} M, while at concentrations lower than 10^{-3} M the forbidden transitions have never been observed. Hence the Ni^{2+} concentrations adopted in this work were (10^{-1}-10^{-3}) M. All the employed concentrations were increasing ten times after drying to 200 ºC due to the contraction phenomena. Room temperature absorption spectra were measured using double beam UV-VIS -2700 Spectrophotometer supplied by CECIL company.

III. RESULTS AND DISCUSSION.

Two complexes ($NiCl_2.6H_2O$) & ($Ni (NO_3)_2.6H_2O$) are dissolved in water & ethanol. Fig. (3) shows absorbance spectra of $NiCl_2.6H_2O$ dissolved in H_2O for different concentrations .
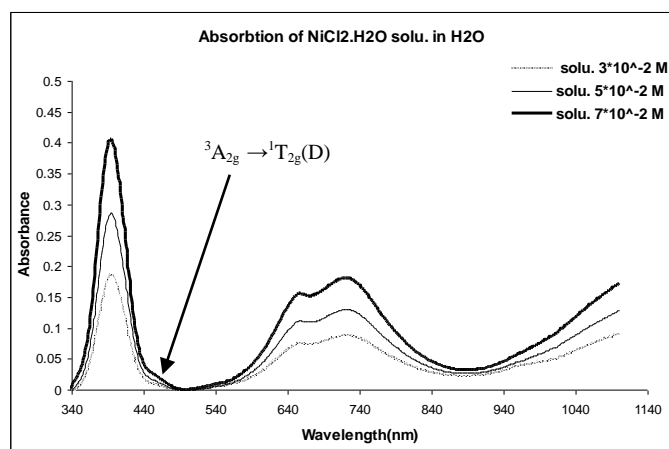

Figure (3)

The transition v_2 ($^3A_{2g} \to {}^3T_{1g}$) is observed at 726nm(13774.104cm^{-1}) and the transition v_3 ($^3A_{2g} \to {}^3T_{1g}$ (p)) which has more intensity Than (v_2) at 398nm (25125.628cm^{-1}). So ratio of two allowed transition $v_3/v_2 \approx 1.824$ by using Level method [19] obtain Dq/B=0.9, so the first transition v_1 ($^3A_{2g} \to {}^3T_{2g}$) and B can be calculated to be at 8347.941cm^{-1} , 927.544cm^{-1} respectively.

When dissolved NiCl2.6H2O complex in Ethanol as in H_2O there's also Three transitions observed v_2 at 760nm (13157.89cm^{-1}) and transition v_3 at 410nm(24390.24cm^{-1}) Also spin-forbidden transition has observed at 700(nm) which attributed to $^3A_2 \to {}^1E(D)$,while the transition $^3A_2 \to {}^1E(D)$ is not observed in ethanol solution . There is also another absorption peak in concentration 10^{-1}M at 283nm which may be referred to the charge transfer (C.T) fig.(4) spectra this transition not clear in other concentration.
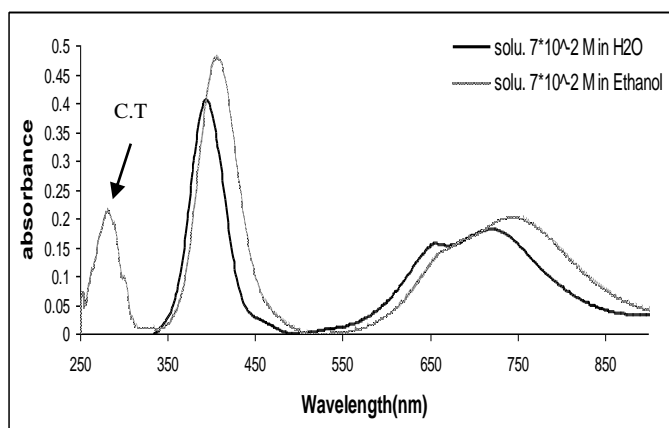

Figure (4) The absorption spectra of $NiCl_2.6H2O$ in Water and Ethanol

as in H_2O, B and Δ can be calculated by using Level method Dq/B=0.85 obtain v_1=7739.93cm^{-1} and B=910.58cm^{-1} , comparison between The two solvent it is easily noticed the absorbance in Ethanol is more than in H_2O ,the absorption Peak in Ethanol have red shifted fig.(4) which indicating a decrease in ligand field strength.

The absorption spectra of Ni^{2+} in the complex ($Ni(NO_3)_2.6H2O$) dissolved in water at several concentrations are shown in Figure (3-6).

The transition (v_2) is observed at 724nm($13812.154cm^{-1}$) and the transition (v_3) which has more intensity Than (v_2) observed at 394nm($25380.710cm^{-1}$).

spin-forbidden transition has observed also in this solution at 655(nm) which attributed to $^3A_2 \rightarrow {}^1E(D)$ Fig. (5), another spin-forbidden transition has observed at 355nm which attributed to $^3A_2 \rightarrow {}^1A_{1g}$ which belong to (^1G) state Fig. (5).
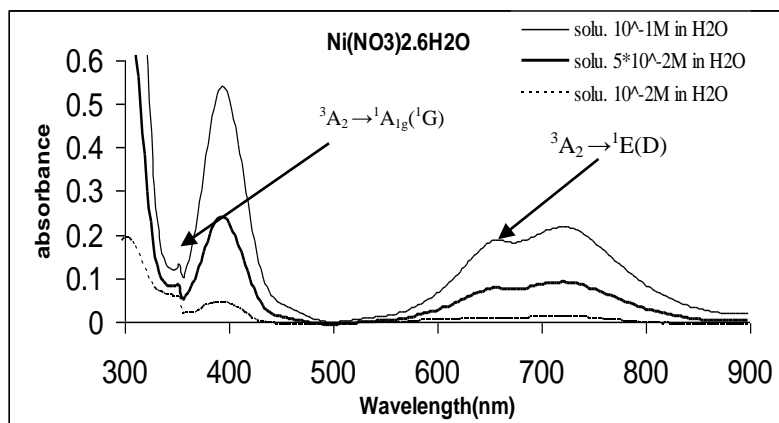
Figure (5) The absorption spectra of Ni(NO3)2.6H2O in water

Fig.(6) illustrates the absorption spectra of Ni^{2+} in the two complex ($Ni(NO_3)_2.6H2O$) and $NiCl_2.6H_2O$ which are dissolved in water comparison between The two solvent it is easily noticed the absorbance of Ni^{2+} in $NiCl_2.6H_2O$ is more than in $Ni(NO_3)_2.6H2O$, it is also noticed the absorption Peaks in $NiCl_2.6H_2O$ have red shifted which indicating a decrease in ligand field strength . Nickel (II)complexes appears in this work to be ($Cl^- < NO_3^-$) .
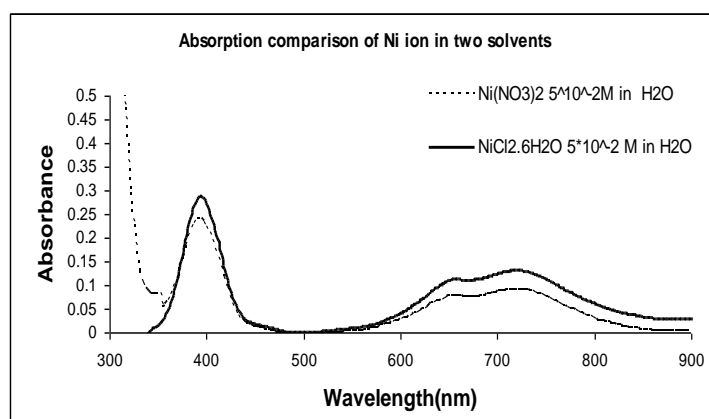

Figure (6) The absorption spectra of Ni(NO3)2.6H2O and
$NiCl_2.6H_2O$ in water

Fig.(7) shows the absorption spectra of $NiCl_2.6H_2O$ SOL for different concentrations as in the solution there are mainly three transitions observed their intensity were lower than that in solution and this may be attributed to decreasing of the concentration of Ni^{2+} after adding (H_2O, TEOS, DMF, Ethanol, and HNO_3) in sol gel process. The two absorption peaks were shifted toward short wavelength compared to that of ethanol solution, which may be explain by increasing in the $\Delta(10Dq)$ in sol compared to that in ethanol solution.
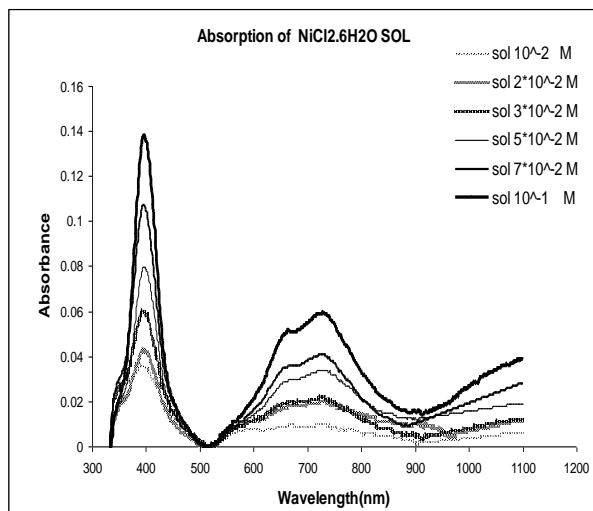

Figure (7). The absorption spectra of
$NiCl_2.6H_2O$ SOL

The transitions observed are $^3A_{2g} \rightarrow ^3T_{1g}$ (v_2) at 735 nm and the third transition
$^3A_{2g} \rightarrow ^3T_{1g}$ (p) (v_3) at 400nm. Also there is a spin-forbidden transition $^3A_2 \rightarrow ^1E(D)$ observed at 665nm so the transitions in Sol has blue shifted compare to the solution due to increasing in the $\Delta(10Dq)$.

Fig.(8) shows the absorption spectra of $NiCl_2.6H_2O$ Xerogel for different concentrations after 6 days, The transition $^3A_{2g} \rightarrow ^3T_{1g}(v_2)$ is observed at ~735nm ($13605.44cm^{-1}$) and the transition $^3A_{2g} \rightarrow ^3T_{1g}(p)$ (v_3) at~397nm ($25188.91cm^{-1}$) which have a little red shift with concentration increasing .Also there are forbidden transitions observed in the samples at(765,630, 472)nm in addition to $^3A_2 \rightarrow ^1E(D)$ at ~ 670nm.
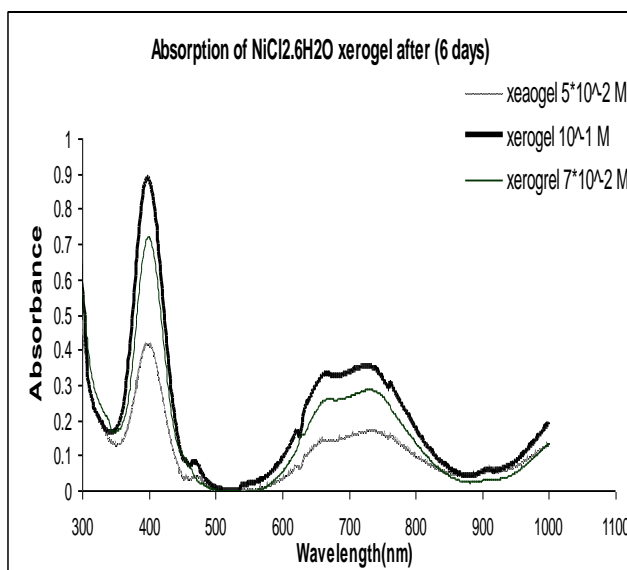

Figure 8. The absorption spectra of $NiCl_2.6H_2O$ Xerogel for different
concentrations after 6 days

It is very clear the absorption Peaks of Ni^{+2} ions in Xerogel have shifted towards short wavelength compare to that in solution Fig.(9) which may be explain by increasing in strength of ligand field strength in silica matrices, so it can be calculated Dq/B in Xerogel is greater than 0.9
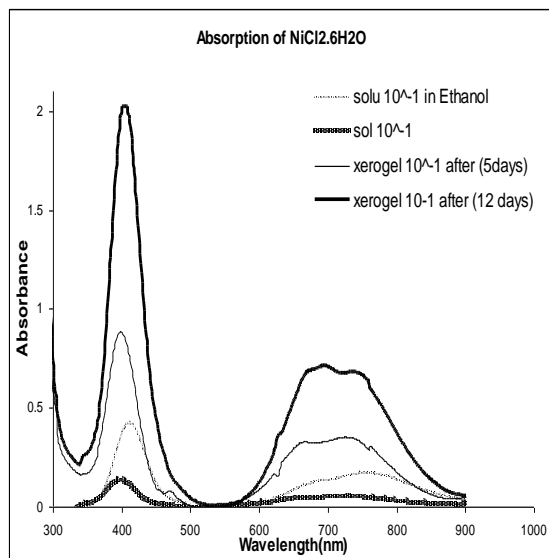

Figure 9. The absorption spectra of Ni^{+2} ions in solution , Sol and Xerogel of complex $NiCl_2.6H_2O$

Fig.(10) shows the absorption spectra of $NiCl_2.6H_2O$ Xerogel for after 6, 12 and 30 days,. the samples have the same transitions with the red shift for all transitions,
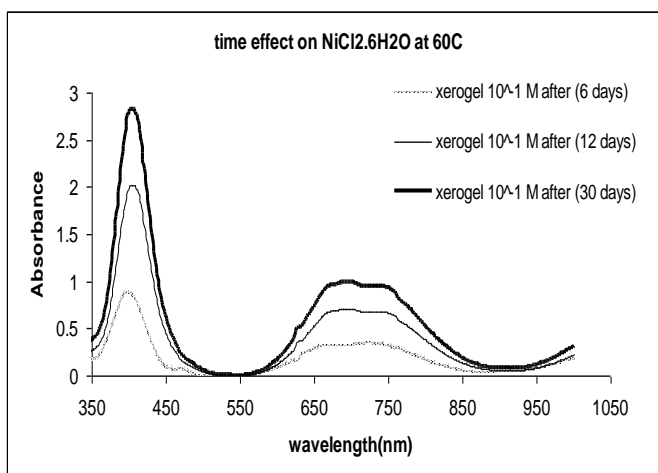

Figure 10. The absorption spectra of Ni^{+2} ions Xerogel after 6, 12 and 30 days of complex $NiCl_2.6H_2O$

also the increases in concentrations causes red shift Fig.(11) shows this shifted for peak around 400nm for different concentrations.
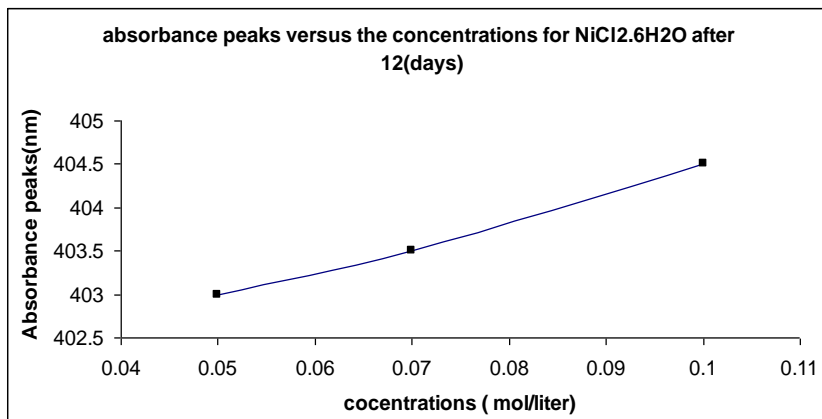

Figure 11. *illustrated the shift of absorbance peaks versus the concentrations for NiCl$_2$.6H$_2$O after 12 days*

Fig.(12) shows the absorption spectra of NiCl$_2$.6H$_2$O Xerogel for different temperatures, The absorbance increases as temperatures arise from 60^oC to 150^oC. The intensity of transition (ν_3) is more than (ν_2) for all temperatures ,also the separation between two transitions $^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ at~700nm and the forbidden transition $^3A_2 \rightarrow {}^1E(D)$ at~ 660nm become more obviously when temperature arise from 60 ^oC to 150^oC . There is also a shoulder at 630nm may attribute to forbidden transitions.
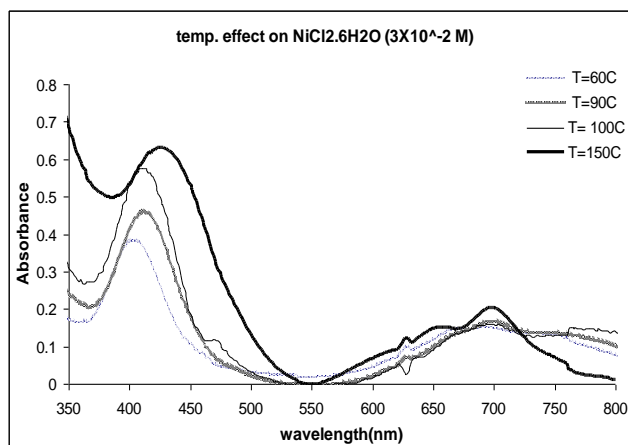

Figure 12. absorption spectra of Ni^{+2} ions in NiCl$_2$.6H$_2$O Xerogel for different temperatures

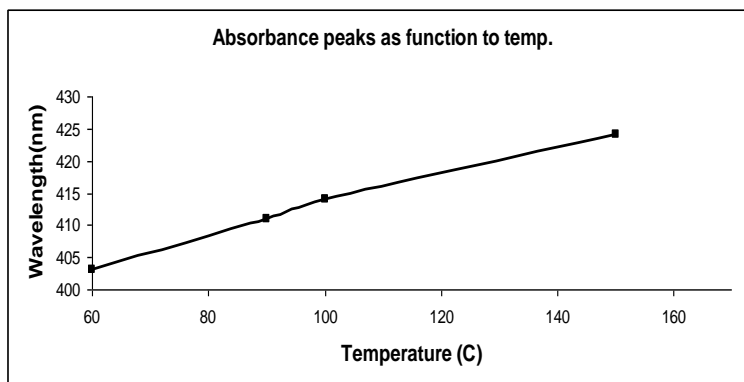The absorbance peak of the transition (v_3) have red shift with temperatures increases as show in Fig.(13).

Figure 13. absorbance peak of Xerogel for transition (v_3) as function of temperature

IV. CONCLUSIONS

Our studies show that Ni^{2+} ion in the two complexes $NiCl_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$) have octahedral symmetry in solution (Ethanol & water),sol and xerogel up to 150^oC. the absorption Peaks of Ni^{+2} ions in silica matrices of Xerogel have shown blue shifted compare to that in solution and Sol , so the ligand field strength (Δ) increasing , also (Δ) has shown increasing in nitrate compare to chloride. Also the absorbance peaks after 12 and 30 days have red shift in Xerogel compare with same sample after 6 days. the absorbance spectra show the Ni^{2+} ion have cooperated in silica matrices in all drying conditions (temperature & drying time).

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