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Spectroscopic comparison of UV-VIS electronic transitions of Cr ions in solution, sol and Xerogel silica matrices

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ABSTRACT

Electronic transitions and the oxidation state of Cr ions have been investigated in two complexes ($CrCl_3.6H_2O$ and $Cr(NO_3)_3.9H_2O$). These complexes were dissolved in (water and ethanol) and doped in silica using sol-gel technique. The molar ratio of TEOS: H_2O: Ethanol is 1:10:15.3 with pH value = 1 at 60°C. The Racah parameter (B), ligand field strength (Δ) and nephelauxetic ratio $\beta = B/B_o$ has been calculated for Cr^{3+} ions in solution, Sol and Xerogel. The samples were heated with temperatures ranging from 60 to 600°C. The UV-visible spectra indicated that, during the increase of heat treatment, there is a change in the chromium species from Cr^{3+} to Cr^{6+} and Cr^{5+}. The conversion of $Cr^{3+} \rightarrow Cr^{6+}$ was promoted for the samples of concentrations $> 10^{-3}$ M while the conversion of $Cr^{3+} \rightarrow Cr^{5+}$ was promoted for the samples of concentrations $< 10^{-3}$ M

KEYWORDS

Spectroscopy;
Sol-gel;
Cr ion.

INTRODUCTION

The sol gel technologies were developed during the past 40 years as an alternative for the preparation of glasses and ceramics at considerably lower temperatures. The initial system represents a solution where different polymerization and polycondensation processes lead to the gradual formation of the solid phase network[1,2]. The first row transition metal ions[3] have been utilized for this purpose. The stabilization energy of Cr^{3+} ion is a maximum in the specific type of octahedral symmetry environment, which can be described as a regular octahedron possessing a centre of inversion. The strength of the crystal field, Δ (10Dq), is characterized by the energy difference between the $^4A_2$ and $^4T_2$ states. Figure 1 is the Tanabe-Sugano diagram for Cr^{3+} which is very well known by spectroscopists[4].

The chrome ions are very interesting for optical spectroscopy and laser physics[5]. For example, Cr^{3+} in inorganic glasses is used as an active medium for tunable solid state lasers[6], and sensitizers of Nd-laser[7]. Cr^{5+}[8] and Cr^{6+}[9] have also been shown to be luminescent even at room temperature which might be interesting for tunable solid state lasers in the visible range. Chrome ion has been incorporated in the SiO_2 network following a sol-gel routine. Several optical spectroscopic studies in this field have been reported[6-12]. The main aim of this study is to investigate the electronic transitions (allowed and forbidden) of chrome ion samples which were prepared by sol gel technique in different concentration and different phases: solutions, sol, Xerogel using UV absorption spectra, FTIR, and magnetic susceptibility techniques. And finally to verify is the chrome ions cooperated in silica network at different annealing temperatures.

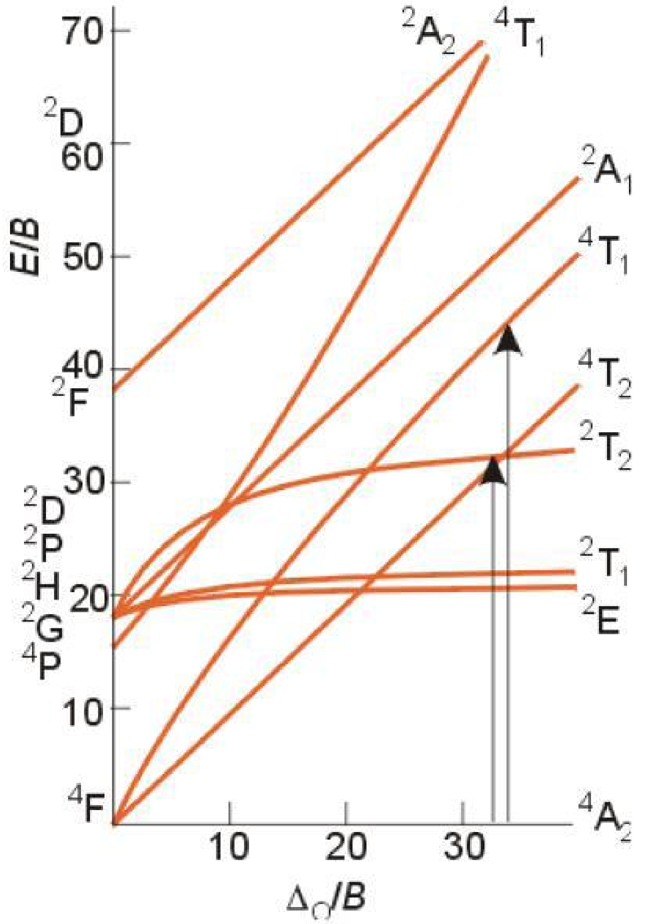

Figure 1 : The Tanabe-Sugano diagram showing energy levels E/B of the Cr3+ ion in an octahedral crystal field as a function of the crystal field[4].

EXPERIMENTAL PROCEDURE

The flow chart of the preparation of samples is shown in Figure 2.

The spectroscopy study requires basically transparent and free crack samples, so that many samples prepared with different sol gel parameters {R-molar ratio, pH, ageing temperature T} at different concentrations.

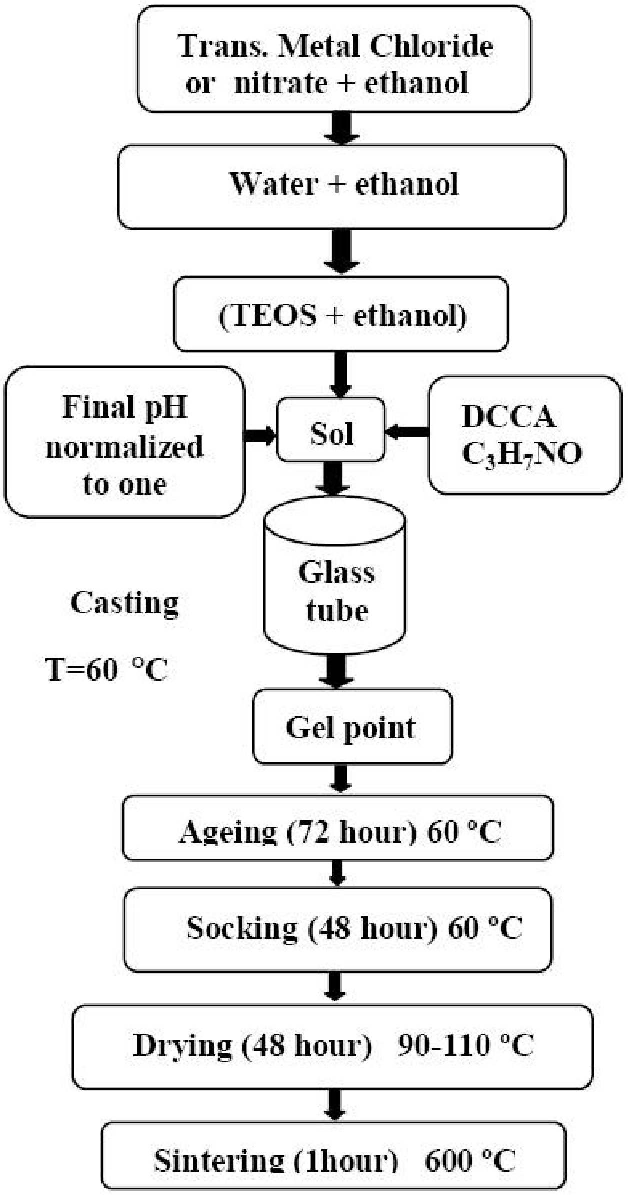

Figure 2 : The flow chart of the overall process of preparing Xerogel

Different R-molar ratios, of alkoxide /water, (2, 5, 10, 24.7 and 61.8) were used at specific pH, ageing temperature (T) and concentrations. In this work the R-molar ratios which achieve the above requirements were (2, 5, 10) while the other higher values of R gave opaque Xerogel samples. This may be attributed to the increase of the chance of condensation which produces less cross-linked samples. We have adopted the ratio 10 among them to get minimum gelling time. To get more exact value of R the chromium salts were dissolved in ethanol instead of water. The pH value has been normalized to unity because of two reasons:

Firstly; in order to get a maximum transparency, since the other samples became semi opaque and the samples became totally opaque for pH > 4.

Secondly since the $Cr^{6+} \rightarrow Cr^{3+}$ conversion proceeds with the decreasing of pH value[13] and we preferred that Cr^{3+} ion to be present rather than other oxidization states of Cr ions. The ageing temperature has been chosen to be 60ºC to get optimum polymerization with minimum gelling time. So the optimum value for R, pH and T which were adopted in this work are 10, 1 and 60°C 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 concentration > 10^{-1} M. At concentration < 10^{-3} M, the forbidden transitions have never been observed. Hence the Cr^{3+} concentrations adopted in this work were (10^{-1}-10^{-3}) M. All the employed concentrations were increasing ten times after drying to 600 ºC due to shrinkage. The absorption spectra at room temperature were measured using double beam UV-1650PC Spectrophoto-meter supplied by Shimadzu Corporation (Kyoto, Japan). And infrared absorption spectra, in the range of 400 to 1200 cm^{-1} measured using FTIR spectrophotometer (model IRPRESTIGE-21, supplied by Shimadzu). The magnetic susceptibility has been also measured by using Magnetic Susceptibility Balance (model MSB-MK1).

RESULTS AND DISCUSSION

The absorption spectra of Cr $(NO_3)_3.9H_2O$ in H_2O for different concentrations are shown in Figure 3.

The observed transitions in these spectra: are $(t^3_{2g})\ ^4A_{2g} \rightarrow (t^2_{2g}e_g)\ ^4T_{2g}$ denoted as (υ_1) at 576 nm (= Δ), transition $(t^3_{2g})\ ^4A_{2g} \rightarrow (t^2_{2g}\ e_g)\ ^4T_{1g}$ denoted as (υ_2) at 412 nm and another UV band at 307 nm which may be attributed to the charge transfer[14].

The weak shoulder observed at ~ 670 nm apparently corresponds to the spin forbidden transition $^4A_{2g} \rightarrow {}^2E_g$ as illustrates by doted arrow in Figure 3.

The third Cr^{3+} electronic transition is (υ_3) $(t^3_{2g})\ ^4A_{2g} \rightarrow (t_{2g}\ e_g^{\ 2})\ ^4T_{1g}$ (p), it can be predicated using Lever's method[15] to be at ~ 40798.4 cm^{-1} (245 nm). This transition is not notice clearly in Figure 3, because of its very weak intensity, which may be attributed to its nature, where it is belong to the two electron jump.

Figure 4 illustrate a magnified view of figure 3, where the peak absorbance of (υ_3) can be seen noticeably which is around 245 nm at concentration of $(1\times 10^{-2}$ M). When the ion concentration increases a red shift occur in the position of the peak, due to concentration effect. The congruency between the theoretical and experimental value of the peak position (245 nm) may give us good insight about the optimum value of concentration of Cr ions in the starting recipe yielding best Cr^{3+} solution.

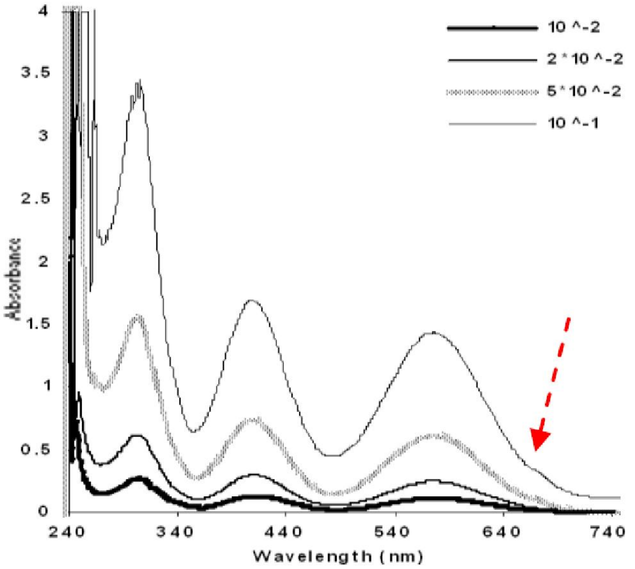

Figure 3 : The absorption spectra of Cr^{3+}in solution of Cr $(NO_3)_3.9H_2O$ dissolved in water for different molar concentrations.

All other peaks have negligible shift with concentration.

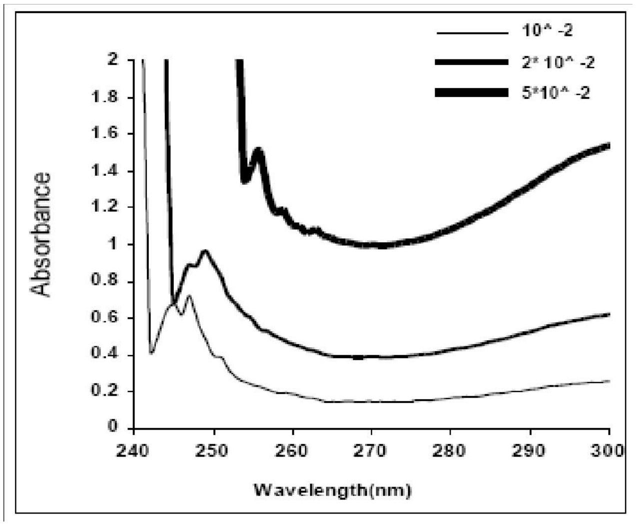

Figure 4 : The transition (υ_3) of Cr $(NO_3)_3.9H_2O$ dissolved in water.

From figure 5 and TABLE 1 one can see that; at a fixed concentration (10^{-1} M) and starting from chromium nitrate ion dissolved in water.

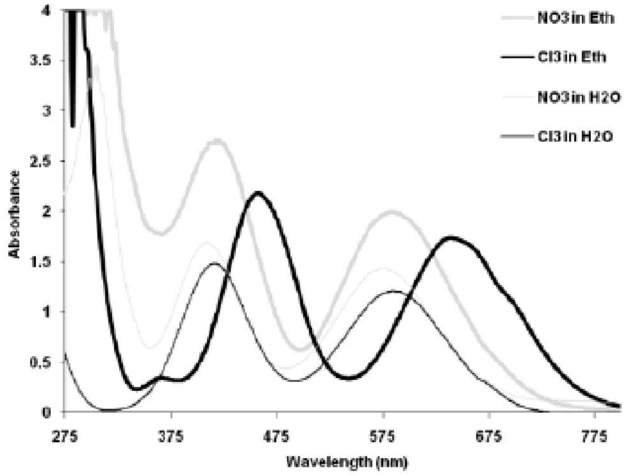

Figure 5 : Illustrate a comparison between the absorption spectra of Cr^{3+} in two complexes in water and ethanol at concentration of 10^{-1} M.

The absorption peaks are slightly red shifted when the solution changed from water to ethanol, which may ascribe to the decreasing in the ligand field strength in ethanol compared to that in water. Whereas, there are large shifts occur in the case of chromium chloride at the same condition, this may indicate that, ligands generating a stronger ligand field going from chloride to nitrate. One possible explanation to this behavior is that the narrowing of ionic radii from Cl to NO_3 causes the bonding between the ligand and the metal central ion to increase in strength of the filed.

TABLE 1 : The electronic transitions of Cr^{3+} ion in $CrCl_3.6H_2O$ complex solution

Transitions	In water λ (nm)	In ethanol λ (nm)
$(t^3_{2g})^4A_{2g} \rightarrow (t^3_{2g})^2Eg$	671	700
$\rightarrow (t^3_{2g})\ ^2T_{1g}$	-----	-------
$\rightarrow (t^2_{2g}e_g)\ ^4T_{2g}$	590	645
$\rightarrow (t^3_{2g})\ ^2T_{2g}$	----	-----
$\rightarrow (t^2_{2g}e_g)\ ^4T_{1g}$	420	459
$\rightarrow (t_{2g}e_g^2)\ ^4T_{1g}(p)$	-----	------
(Belong to Cr^{6+})		368

According to the υ_1 values in the two complexes, the results confirm that the spectrochemical series of NO_3 > Cl which is obvious[16].

The intensity of both peaks in ethanol solvent sample is higher than that in water solvent samples. This may be attributed to the deference in the polarity of the two solvent.

There is another weak band appears at 368 nm (27173.9 cm^{-1}), only in the sample of chromium chloride dissolve in ethanol. The presence of this band together with those at (640 nm & 460 nm) could be attributed to the presence of Cr^{+6} together with Cr^{3+}.

In general, the polarity of the solvent of Cr salt in the sol gel process is playing a significant rule on the starting material oxidation state and increasing the absorption cross section.

The absorption spectra of the Sol phase which were carried out after one hour of mixing, confirm that the transitions are similar to that of solution except that the absorbance here is lower. This may due to the reduction in the Cr^{3+} ions concentration, because of the addition of (TEOS, H_2O, C_2H_5OH, HCl and C_3H_5NO) beside H_2O and C_2H_5OH which are produced during the condensation process as a byproducts in sol-gel process.

All the absorption peaks in sol are blue shifted compared to that in ethanol solution and red shifted compared to that of water solution. This may be attributed to the relaxation because of dilution effect.

The observed transitions of Cr ion in $CrCl_3.6H_2O$ and $Cr(NO_3)_3.9H_2O$ for Xerogel samples at 60 °C after 5 days are summarized in TABLE 2.

TABLE 2 : The electronic transitions of Cr^{3+} in Xerogel

Transitions from $(t^3_{2g})^4A_{2g}$	*nitrate* λ nm	*Chloride* λ nm
$\rightarrow (t^3_{2g})\ ^2Eg$	691	692
$\rightarrow (t^3_{2g})\ ^2T_{1g}$	632	630
$\rightarrow (t^2_{2g}e_g)^4T_{2g}$	595	600
$\rightarrow (t^3_{2g})\ ^2T_{2g}$	465	472
$\rightarrow (t^2_{2g}e_g)T_{1g}$	420	422
$\rightarrow (t_{2g}e_g^2)\ T_{1g}$ (p)	--------	---------

The transitions in Xerogel are more obvious than in solution and in Sol. The absorbance increases after 12 days of drying at 60 °C, which may be attributed to the increase of the concentration due to the solvent evaporation.

There is also a little red shift in the absorption peaks.

TABLE 3 gives the Racah parameter (B), ligand field strength (Δ) and nephelauxetic ratio $\beta = B / B_o$

which have been calculated for Cr^{3+} ions in solution, Sol and Xerogel.

TABLE 3 : Some measured & calculated spectroscopic parameter of Cr compounds

	$CrCl_3.6H_2O$		
	H_2O	Ethanol	Xerogel
υ_1 cm^{-1}	16949	15503	16666
υ_2 cm^{-1}	23809	21786	23697
$B(cm^{-1})$	689	631	7167
? /B	24.61	24.57	23.26
$\beta=B/B_0$	0.750	0.687	0.7801
	$Cr(NO_3)_3.9H_2O$		
υ_1 cm^{-1}	17361	16949	16807
υ_2 cm^{-1}	24272	23753	23810
$B(cm^{-1})$	690	681	710
? /B	23.26	24.88	23.66
$\beta=B/B_0$	0.752	0.742	0.774

Where B_0 is Racah parameters for gaseous ion =918 cm^{-1} for Cr^{+3}

One can notice from this table that β has a maximum value in the Xerogel and this may mean that there is a reduction in the covalence bonding between Cr^{+3} ion and the ligands. The e_g electrons will become σ anti-bonding and will therefore spend some of their time near the ligands.

While the t_{2g} electrons may become π bonding or anti-bonding (depending upon the nature of ligands) and will also spend some time near the ligands. In other words a small amount of the σ and π electron density on the metal may be transferred onto the ligands. Such delocalization will increase the mean distance between the d electrons and thereby reducing B. Central field covalency perhaps contributes the major part to the reduction of B in transition metal complexes. We believe that, this behavior may give evidence that Cr^{3+} ion forms bonds in the silica network, yielding a weakness in the bond between Cr^{3+} ion and the ligands. To confirm the above conclusion we have measured the FTIR absorption spectra of the samples which have been dried for 12 days at 60 °C as shown in figure 6.

The appearance of the bands at ~ 550 and 650 cm^{-1} support our conclusion. Since these bands have been observed by others and were ascribed to Cr^{3+} in Cr_2O_3[17].

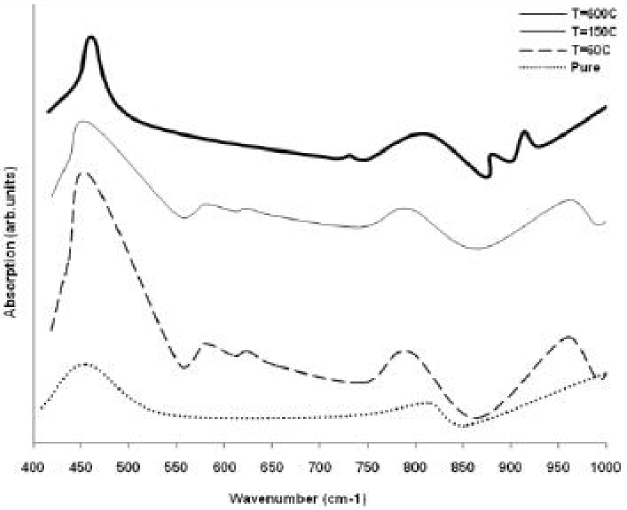

Figure 6 : FTIR absorption spectra of pure and the Cr nitrate samples which have been dried for 12 days at 60 °C, 150 °C and 600 °C.

The absorption spectra of Cr nitrate at concentration (2×10^{-2}M) for solution and Xerogels dried at 60, 120 and 600 ºC are shown in Figure 7.

This figure shows that; at 120 ºC the absorption band at about 400 nm starts to diminish due to the oxidation of carbon incorporated to the Xerogel network. And approximately at about 200 ºC the absorption band ~ 600 nm begins to diminish too.

Whereas, up to 200–250 °C the number of defects is increasing due to the carbon impurity incorporating in the structure during the drying process of the gels forming (-O -C -O-) and/or (- Si - C-) bonds[10].

When the temperature increases to 600 ºC, the sample became orange-red and transparent and the absorption band at about 600 nm, which is assigned to Cr^{3+} Figure (7, 8), as well as the 550 and 650 cm^{-1} Figure (6)bands are completely disappeared. Therefore; the chromium ions Cr^{3+} may be converted to Cr^{6+} (dichromate ion $Cr_2O_7^{2-}$).

This indication could be confirmed by the measurement of mass susceptibility ($X_{g)}$ of the sample using Magnetic Susceptibility Balance[18]. The result of this test confirms that this material is diamagnetic. In other words the electron configuration of this ion is $3d^0$, which belongs to Cr^{6+}.

Further proof can be achieved by FTIR measurements, as shown in Figure 6, where two absorption bands appeared at ~ 700 and 900 cm^{-1}, of the samples dried at 600 ºC. These bands were assigned to $Cr_2O_7^{2-}$ [19]. While the bands at ~ 550 and 650 cm^{-1} which be-

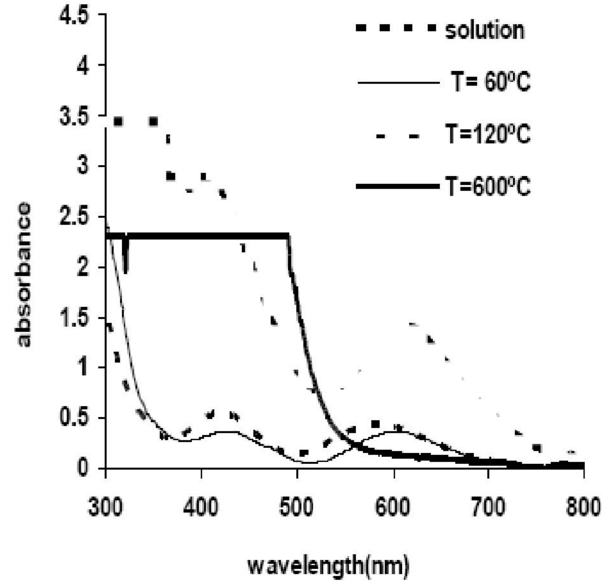

Figure 7 : The absorption spectra of Cr^{3+} in Cr $(NO_3)_3.9H_2O$ ($2x10^{-2}$M) for different temperatures

long to Cr^{3+} in Cr_2O_3 disappeared. This gives further evidence that Cr^{3+} ions have been converted to Cr^{6+}.

Whereas the appearance of the band around 919 cm^{-1}, which is assigned to the bridging Cr-O-Si stretching bond[19], gives a support that the Cr ions are not capturing inside the pores, but they have been incorporated in the silica network via sol gel procedure.

Figure 8 Shows the absorption spectra of Cr $(NO_3)_3.9H_2O$ in Xerogel at concentration of (10^{-3}M) dried at 60, 120 and 600 °C. There are two absorption bands at ~350 and at ~ 450 nm which arise due to the formation of Cr^{5+}. The origin of the bands at ~350 nm and ~ 450 nm were related to the splitting of the energy level ^2D of the Cr^{5+}in the octahedral crystal field into two levels: the ground state $^2T_2$ level and the excited state ^2E level [10, 20].

Due to low symmetry component of the distorted crystal field, the ^2E state may further split giving rise to the absorption bands at ~ 350 nm and ~ 450 nm.

However, it has been also argued that the origin of these two bands is due to the transition $^2T_2 \rightarrow {}^2E$ of Cr^{5+} but in tetrahedral sites[8]. Similar results have been obtained for $CrCl_3.6H_2O$.

The conversion of $Cr^{3+} \rightarrow Cr^{6+}$ was promoted for the samples of concentrations > 10^{-3} M (see figure 7) while the conversion of $Cr^{3+} \rightarrow Cr^{5+}$ was promoted for the samples of concentrations < 10^{-3} M (see figure 8).

So the starting Cr ion concentration is the essential factor which may identify the oxidation state of the final product in the sol gel routine.

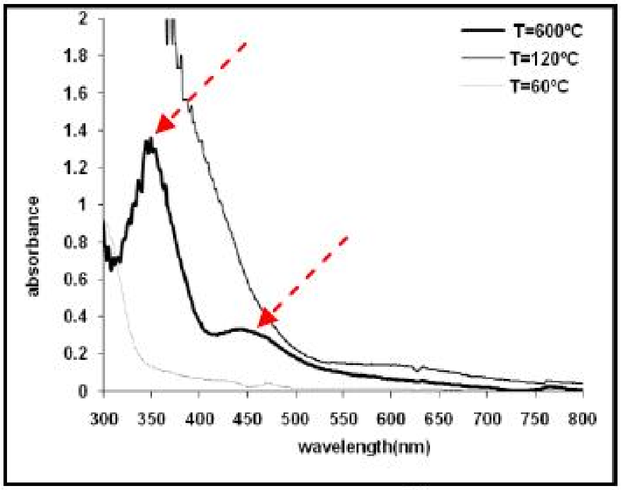

Figure 8 : The absorption spectra of Cr^{+3}inCr$(NO_3)_3.9H_2O$ Xerogel (10^{-3}M) for different temperature

The measured XRD verify that, as expected, all prepared sample keep their amorphous structure, included the samples heated to 600 °C.

CONCLUSIONS

The presence of Cr ions in Xerogel samples depends on the final pH of the sol and the annealing temperatures. The ligand field strength (Δ) for chromium in silica network was found to be intermediate, hence the spectrochemical series is $\Delta_{H2O} > \Delta_{silica} > \Delta_{Ethanol}$. And the nephelauxetic ratio β was found to have a maximum value in Xerogel. Cr^{3+} is the preferable oxidation state of the chromium ion up to annealing temperatures around 200°C. The absorption peak around 600 nm, which is assigned to Cr^{3+}, begins to diminish above this temperature. The oxidation states of the chromium, which were obtained after annealing to 600 °C, were found to depend on chromium concentration. So, in the present work, for the samples of concentrations = 10^{-3}M, the Cr^{5+} is the preferable oxidation state, while for concentrations > 10^{-3}M, the Cr^{6+} is the preferable state.

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