

COBALT (II) ENVIRONMENT CHARACTERIZATION IN SOL-GEL THERMOCHROMIC SENSORS

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Abstract: Optical absorption and magnetic properties of silica sol-gel monoliths doped with cobalt starting from different precursors and water/1-propanol molar ratios are investigated. Structure characterization of the sol-gel by X-ray near-edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy corroborate that oxidising state of cobalt is Co^{2+} . Furthermore the Co^{2+} first neighbors are O atoms displaying a temperature transition from octahedral to tetrahedral coordination. The doped monoliths show thermochromic sensor activity ranging from 10 to 50 °C, which is related to the environment of Co^{2+} ions. The magnetic susceptibility also varies with Co^{2+} ions environment due to changes in the orbital contribution to the magnetic moment. Thus, we achieve a better understand about environment of the Co^{2+} ions in the gel matrix and explain their reversible temperature behavior in spite of the rigid state of the host matrix.

Keywords: Sol-gel, sensor, thermochromic, cobalt chloride

Introduction

Most recent advances in technology have favoured the research and development of smart sensors with numerous applications [1]. Specially, temperature has become an important variable to be measured or controlled [2]. Temperature monitoring with smart optical, wireless devices is convenient for many applications such as conservation of historical artworks in places of limited access [3], for food industry, mainly during transport [4] or previously to consume [2], for the monitorization of water in fish farmers or nurseries [5], etc.

The sol-gel process is a chemical technique for the preparation of metal oxide materials at room temperature. Normally, starting from a hydro-alcoholic solution with typical precursors as metal alkoxides (*sol*) a three-dimensional amorphous network with M-O-M or M-OH-M bonds (*gel*) after hydrolysis and polycondensation is obtained. The drying process serves to remove the solvent from the gel and further thermal treatment helps to continue the polycondensation process [6]. Gels are ideal matrices to act as host for sensing purposes in contrast to liquids which are highly instable and evaporate. Moreover, solids are too rigid, avoiding interactions with the external environment that decrease the sensitivity (in addition to the difficulties to incorporate organic matter into solid matrices). In the last decades, sol-gel materials have demonstrated their utilities for the encapsulation of molecules preserving their properties and showing reversible behaviour to external stimuli [7-9]. Several studies on the influence of additives, like surfactants [10,11] or capping agents [12] into sol-gel matrices, have shown the interaction between dopant - host matrix and the modification of the gel properties due to this interaction.

It is well known that the incorporation of cobalt into a variety of glassy and crystalline matrices provides them with interesting optical and magnetic features, which strongly depend on the ionic state and coordination of cobalt. Thus, in this research we have prepared sol-gel monoliths starting from different precursors doped with Co^{2+} ions with thermochromic properties. Actually, optical properties of Co^{2+} in water/alcohol mixtures show two coordinations, tetrahedral and octahedral, which display bluish and pinkish coloration respectively [13]. A specific study of the optical and magnetic properties of the thermochromic resulting material is performed. Furthermore, to clarify and confirm the exact structure and near cobalt environment, which allows sensibility and reversibility to temperature changes of this material, X-ray absorption spectroscopy is used. Both X-ray Absorption Near Edge Structure (XANES) and X-ray Absorption Fine Structure (EXAFS) spectroscopies are helpful techniques for structural studies of materials (coordinations, nature of chemical bondings, symmetries) [14,15], including Co- doped matrices [16].

Experimental

Sensors synthesis. All chemicals were used as received without further purification. Alkoxides and alkyl-alkoxides: tetraethylorthosilicate 99.0 % (TEOS), tetramethylorthosilicate 99.0 % (TMOS), methyl-trimethoxysilane 98.0 % (MTMOS), diethoxy-dimethyl-silane 96.0 % (DEDMS), 3-Trimethoxysilyl)propyl methacrylate 98.0 % (MAP), and 3-glycidoxypropyltrimethoxysilane 97.0 % (GLYMO), were purchased from Fluka. Cobalt chloride salt (1.0000 g) having a purity of 98.0 % from Fluka was dissolved in 2.5 ml of distilled water. An aliquot of 125 μl was added to a pre-hydrolyzed sol which contains the corresponding alkoxide and water with molar ratios of 1.0 : 6.9, 7.4, 7.9, 8.4, 8.6, 8.9, 9.1 and 9.4. 1-propanol purchased from Aldrich

was used as solvent in a molar ratio alkoxides: alcohol of 1.0 : 12.4, 10.3, 8.2, 6.2, 5.1, 4.1, 3.1 and 2.1. Total volume of prepared sols was 3.0 ml. They were transparent and showed colours from light pink to intense blue. After 5 min they were cast into cuvettes and hermetically sealed to avoid solvent evaporations. Table 1 shows the chemical composition of the prepared sensors.

Optical characterization. Optical absorption spectra were measured over the wavelength range 300 – 800 nm with a Shimadzu 3100 double-beam spectrophotometer, equipped with an integrating sphere. VIS spectra of the sensors were recorded each 10 °C from 10 to 60 °C. In order to fit the sensors to the corresponding temperature, they were previously immersed into a water thermostatic bath for 15 min.

Characterization and structural study of the Co environment. The X-ray absorption spectroscopy of near edge structure (XANES) and the Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy were performed on synchrotron radiation from beam line BM25 (Spanish-SPLine CRG) at the European Synchrotron Radiation Facilities, ESRF. XANES and EXAFS spectra were collected at room temperature in absorption mode using an ionization chamber as detector system. Samples for analysis were placed into aluminium holders and covered with kapton film. XANES spectra were collected at the Co k-edge between 7600 eV and 7850 eV at a step increment of 0.2 eV. The spectra were handled and normalized using the IEFIT code.

Magnetic properties. Susceptibility of the samples was calculated from magnetization curves measured at room temperature in a Vibrating Sample Magnetometer (LakeShore VSM model 7304). The applied magnetic field was varied from +1 T to -1 T and the

susceptibility was calculated from the slope of the magnetization curve after subtracting the contribution from the sample holder.

Results and discussion

Co^{2+} ion in its neutral state has a $3d^7$ electron configuration. In aqueous solution it shows a pink pale colour. Deconvolution of the absorption spectra was resolved in two overlapping Voigt Amp shapes with centres at 2.386 eV (520 nm) and 2.620 eV (472 nm) (Fig. 1 a). The iterative fitting yielded to a coefficient of determination $r^2 = 0.999$ ($r^2 = 1 - [\text{sum of squares of residuals}]/[\text{sum of squares about the mean}]$). This absorption is attributed to an octahedral coordination of Co^{2+} ions (each Co^{2+} ion is surrounded for 6 H_2O molecules). The main electronic transition involved is ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$. Nevertheless, the level ${}^4\text{A}_{2g}$ is located near the level ${}^4\text{T}_{1g}(\text{P})$, that is why transitions from ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ are also possible in octahedral systems (see table 2) [13,17].

When Co^{2+} ions are dissolved in a non aqueous media, like ethanol, they show an intense blue colour with one main absorption band and two shoulders. Satisfactory deconvolution of the spectrum resolved three overlapping Voigt Amp shapes with centres at 1.859 eV (667 nm), 1.981 eV (626 nm) and 2.170 eV (571 nm) ($r^2 = 0.999$) (see Fig. 1 b). VIS transitions in Co^{2+} tetrahedral environments are approximately one order of magnitude higher than in octahedral ones and in this case, each Co^{2+} ion is surrounding by 4 molecules of alcohol [13]. The electronic transitions associated with these VIS absorptions are ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$, ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ respectively [16] and the shape of the bands are normally complex because some transitions to double excited states take place in the same region and are quite intense

due to the spin-orbit interactions attributed to a Jahn-Teller distortion of the structure or to an interaction of the L and S quantum numbers (see table 2) [18].

The visible absorption bands of Co^{2+} ions from the TM-4 sensor show Co^{2+} ions in both tetrahedral and octahedral coordinations (table 2). Nevertheless, the associated electronic transitions appear slightly shifted to higher wavelengths (lower energies) than from Co^{2+} ions in solution. This is due to a low splitting of the energy levels by the different coordination ligand fields. As Fig. 2 a and b show, at room temperature, the close similarity between the aqueous/alcoholic Co^{2+} solutions and the sol-gel spectra of sensors TM-2 and TM-6 indicates similarities in the coordination environments for Co^{2+} in both media. As suggested by Scherer [20], the sol-gel matrix provides a local aqueous micro-environment for the encapsulation of Co^{2+} ions within a silanol network. The sol-gel network is formed by amorphous tetrahedral of Si atoms, covalent bonded with four oxygen atoms in each vertex resulting in a three-dimensional structure. Then, Co^{2+} ions would be encapsulated with alcohol and water surrounding molecules. The presence of Si-O-Co bonding has not been confirmed, but also not discarded.

In conventional glasses doped with Co^{2+} , the energy levels splitting is in general higher for tetragonal coordination than in solution. In contrast for the octahedral coordination systems, the splitting of energy levels of Co^{2+} is lower than in aqueous-alcoholic solutions and the sol-gel sensor.

The liquid state is an ideal medium for Co^{2+} reversible character. However, when Co^{2+} ions are part of a conventional glass matrix they show non-reversible behaviour, although a rigid state is preferred for application later on. Silica sol-gel matrices doped

with Co^{2+} present a rigid state, and as it is demonstrated in this work, they show reversible thermochroism (Fig. 3).

Influence of the precursor. Sensors prepared with precursors: TMOS, TEOS, MTMOS, DEDMS, MAP and GLYMO and the same water/1-propanol ratio (6.2/8.4) were immersed for 15 min in a thermostatic bath, and UV-VIS spectra was recorded in steps of 10 °C. The maximum absorption intensity at 667 nm was collected for each sensor and plotted in the following calibration curves at the corresponding temperature (Fig. 4).

A matrix influence in the sensors which contain the same amount of Co^{2+} ions, water, 1-propanol and different precursor was noticed. Sensors MTM-4, DE-4 and MA-4 presented a high increment of absorbance in the 20 – 40 °C range, but they remained as liquid sols several months after their preparation. This was considered a practical disadvantage for their future use. TE-4 sensor needed four days for gelification. It presented small response time and a high increment in intensity of absorbance in the 20 – 40 °C range when it was just prepared, but after several weeks, the response time increases and the absorption increment between 20 and 40 °C decreases. Sensor GLY-4 showed pink colour in the whole range of temperature. Maybe Co^{2+} ions are surrounded by the alkyl rest of the alkoxide and it showed no interaction with water neither with 1-propanol molecules. Finally, TM-4 sensor showed response times of 15 min, gelification occurs 3h after preparation and it was usable several months after preparation [21]. TMOS matrix is compact and pores size is small compared to other precursors. Probably this was the reason of such high sensibility of Co^{2+} ions in this matrix [6]. Sensors TM-1 up to TM- 8 were selected as the appropriate for further tests.

In order to study the reversibility of the sensors some hysteresis cycles were performed. Absorbance after 15 min stabilization of each sensor immersed in the thermostatic bath was recorded in steps of 10 °C from 10 °C up to 60 °C and vice-versa. Results demonstrate that there is no significant hysteresis and thus, a complete reversibility of the TMOS sensor in the previous temperature range is found (Fig. 5).

Influence of the water/1-propanol ratio. Sensors prepared from the same precursor and different water / 1-propanol ratios, as indicated in the synthesis section, showed different colours from pale pink until deep blue. This indicates a main octahedral coordination of the Co^{2+} ions in the sensors TM-1 – TM-3, a main tetrahedral coordination in sensors TM-5 – TM-8 and a partial co-existence of both coordination states in sensor TM-4 of violet colour. Figure 2 a and b show the absorption spectrum of TM-2 and TM-7 sol-gel sensors at 20 °C. The spectra are similar in shape as spectra of Co^{2+} ions in water / 1-propanol solutions and indicates the co-existence of both coordination states in the sol-gel matrix depending on the sensors composition.

Influence of temperature. TM- sensors prepared with different water / 1-propanol ratios (from TM-1 up to TM-8) were exposed to temperatures between 10 and 50 °C and corresponding colour in the VIS region varied. Figure 2 c and d show optical responses of the sensor TM-4 as a function of temperature. The inset shows a detail of the ratio between the amplitude of absorption component at 1.859 eV and at 2.386 eV that indicates the progressively change of colour from pink to deep blue as temperature increases from 10 to 50 °C. Sensors with high water content (TM-1, TM-2 or TM-3) display pale pink colour when the temperature increases or differences in absorbance

are small to be observed with naked eye. The same occurred for sensors with high alcohol content (TM-6, TM-7 or TM-8), which remained deep blue colour when temperature increases.

The oxidising state and coordination of Co atoms was investigated by X-ray Absorption Spectroscopy. Figure 6 a shows the XANES spectra at the Co K edge. The position of the white line with the maxima at 7722 eV confirms that the oxidising state of Co ions is Co^{2+} in all the samples. Thus, a massive oxidation to Co^{3+} or a reduction to Co^+ can be discarded. However, the detailed analysis of the spectra (Fig. 6 b) shows that increasing the water content, there is an enhancement of the white line and a slight shift of the maximum toward larger wavelengths. Both features are indicative of scarce increase in the Co oxidising state.

Fig. 7a shows the radial distribution function obtained from EXAFS spectra. Fit of the data in the q space to a first shell of oxygen atoms lead to a bond distance of 2.11 Å slightly larger than the Co^{2+} -O bond distance [22,23]. Thus, oxygen water atoms locates around the Co atoms that will share part of the 3d electrons with oxygen atoms leading to the slight increase in oxidising state with water content detected by XANES. What it is important to notice from the results, is the absence of chloride ions in the first coordination shell of Co^{2+} atoms of the sol-gel sensors. Co-Cl distances have been reported at about 2.25 Å by other authors [24], which are not found in our experiments. The tetrahedral coordination [19] and the blue colour observed in the sol-gel sensors should not be associated with the presence of mixed complexes with chloride ions [19], such as $\text{Co}[\text{O}_3\text{Cl}]^{5-}$, but to the tetrahedral coordination of oxygen ions. The area of the first coordination shell is proportional to the number of first neighbours and therefore it

can give information about the coordination state of the Co ions. As Fig. 7 a shows, this area increases as the water content does, confirming the presence of more O atoms around the Co ions when there is more water present in the material. Changes from an octahedral coordination (6 first neighbours) to tetrahedral one (4 first neighbours) should reduce the area of the coordination shell in 33%, while the data in Fig. 7 exhibit only a decrease of 16%. The absorption of X-rays by the Co atoms can lead to a local heating that reduces the water content in the vicinity of the Co atoms which could account for this difference. Actually, consecutive measurements on the same sample exhibit a decrease in the area of the first shell that confirms the progressive degradation of the samples upon X-ray irradiation.

Renevier *et al.* [15] reported the presence of a pre-peak in their Co^{2+} tetrahedral coordinated samples and the absence of this pre-peak in the octahedral ones, as a sign of the symmetry. In our samples the pre-peak is observed in all the samples with a tendency to increase as the water content decreases. This confirms, in the irradiated samples, the presence of some Co in tetrahedral coordination.

Therefore, XAS experiments indicate that the water content modifies mainly the environment of the Co atoms with a scarce modification of the Co oxidising state, so the changes in the optical properties are mainly due to modification of the Co coordination in the gel.

All samples exhibit paramagnetic behaviour as expected for isolated Co ions in a diamagnetic matrix. The values of the magnetic susceptibility follow a complex behaviour as Fig. 8 illustrates. The susceptibility is maxima in sensors TM-1 and TM-7

and shows a local maximum for the TM-4 one. Considering that the curve seems to have a large dispersion of the data, the experiment was repeated three times with different samples of each sensor, getting the same curve in all cases. This behaviour can be understood as the combination of two factors: on the permanent magnetic moment of the involved atoms or ions and on how easy is this magnetic moment to be oriented by an external magnetic field. Taking into account these two factors, TM-1 and TM-7 are the sensors in which the environment surrounding the Co^{2+} ions has higher symmetry (octahedral in TM-1 and tetrahedral in TM-7). This higher symmetry means higher splitting in the electronic bands of the ions and thus, a higher magnetic moment leading to a higher value of susceptibility. The environment of the Co^{2+} ions is changing from octahedral to tetrahedral in the rest of the series. Therefore, Co^{2+} ions in sensor TM-4 are expected to be surrounded by a highly disordered and therefore, more isotropic environment. Although this fact supposes a lower value of the permanent magnetic moment, it is easier to be aligned by the external magnetic field due to the isotropic environment, which also makes the susceptibility to increase. That is why the value of the susceptibility of sensor TM-4 increases in the plot.

Summary

Sol-gel silica monoliths doped with Co^{2+} ions starting from different alkoxide precursors and water/1-propanol ratios have been prepared and characterized. The influence of the precursor, water and 1-propanol content has proved to be essential in the sensitivity and response of the sensor against temperature changes.

TMOS sol-gel matrix has proved to be versatile enough to preserve dopant Co^{2+} ions properties and modify the functionality of the obtained material. Prepared sensors have

proved to be thermochromic in the 10 - 50 °C range showing a colour change in the visible region of spectrum (from pale pink to intense blue). A rigid state sensor was aimed for its hanging during use. Reversibility without hysteresis was found in TM-4 and TM-5 sensors.

XANES measurements have provided detailed information about the oxidising state of the Co ions in the sol-gel matrix (o.s. = 2). The local environment or first neighbours from the TM-1 up to the TM-7 sensors have been O-atoms. EXAFS data resulted in a 2.11 Å Co-O bond distance. A reduction in the area of the first coordination Co shell is noticed as the number of oxygen atoms and thus the water content around each Co diminishes. In this way, a change from pink – violet – blue colour in the sensor indicates a transition from octahedral (6-O atoms) to tetrahedral (4-O atoms) state. A partial degradation of the gels was also noticed as a result of the X-ray interaction and heating of the sample.

Magnetic susceptibility measurements point out higher symmetry for sensors TM-1 and TM-7, almost with completely octahedral and tetrahedral coordination, respectively. Furthermore, higher sensibility to temperature changes was found and demonstrated by the local maximum value of the magnetic susceptibility of sensor TM-4, where the high isotropic environment favours the orientation of the external magnetic field.

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References

- [1] N. Kirianaki, Happy 5th, IFSA! (1999-2004 Activity Report), *Sensors & Transducers Magazine* 47 (9) (2004) 296-301.
- [2] H. Oda, Photostabilization of organic thermochromic pigments, Part 2: Effect of hydroxyarylbenzotriazoles containing an amphoteric counter-ion moiety on the light fastness of color formers, *Dyes and Pigments* 76 (2008) 400-405.
- [3] N. Carmona, E. Herrero-Hernández, J. Llopis, M.A. Villegas, Proceedings of Lacona 7, Lasers in the conservation of artworks, CSIC (Ed.), Madrid, 2008.
- [4] M.G. Baron, M. Elie, Temperature sensing using reversible thermochromic polymeric films, *Sens. Actuators B* 90 (2003) 271-275.
- [5] C. Fernández-Valdivielso, E. Egozkue, I.R. Matías, F.J. Arregui, C. Bariáin, Experimental study of a thermochromic material based optical fiber sensor for monitoring the temperature of the water in several applications, *Sens. Actuators B* 91 (2003) 231-240.
- [6] C.J. Brinker, G.W. Scherer, Sol-gel science. The physics and chemistry of sol-gel processing, Academic Press Inc., San Diego, 1990.
- [7] M.A. Garcia, S.E. Paje, M.A. Villegas, J. Llopis, Preparation and characterisation of calcein-doped thin coatings, *Appl. Phys. A* 74 (2002) 83-88.
- [8] J.M.J. Paulusse, D.J.M. van Beek, R.P. Sijbesma, Reversible switching of the sol-gel transition with ultrasound in rhodium(I) and iridium(I) coordination networks, *J. Am. Chem. Soc.* 129 (2007) 2392-2397.
- [9] S. Sivakumar, F.C.J. van Veggel, P.S. May, Near-infrared (NIR) to red and green up-conversion emission from silica sol-gel thin films made with La_{0.45}Yb_{0.50}Er_{0.05}F₃ nanoparticles, hetero-looping-enhanced energy transfer (hetero-LEET): A new up-conversion process, *J. Am. Chem. Soc.* 129 (2007) 620-625.
- [10] C. Rottman, G. Grader, Y. De Hazan, S. Melchior, D. Avnir, Surfactant-Induced modification of dopants reactivity in sol-gel matrixes, *J. Am. Chem. Soc.* 121 (1999) 8533-8543.

- [11] H. Frenkel-Mullerad, D. Avnir, Sol-gel materials as efficient enzyme protectors: preserving the activity of phosphatases under extreme pH conditions, *J. Am. Chem. Soc.* 127 (2005) 8077-8081.
- [12] M.A. Garcia, J.M. Merino, E. Fernández Pinel, A. Quesada, J. de la Venta, M.L. Ruíz González, G.R. Castro, P. Crespo, J. Llopis, J.M. González-Calbet, A. Hernando, Magnetic properties of ZnO nanoparticles, *Nanoletters* 7-6 (2007) 1489-1494.
- [13] F.A. Cotton, G. Wilkinson, *Advanced inorganic chemistry*, 4th Limusa (Ed.), México, 1986.
- [14] D. Carta, A. Corrias, G. Mountjoy, G. Navarra, Structural study of highly porous nanocomposite aerogels, *J. Non-Cryst. Solids* 353 (2007) 1785-1788.
- [15] H. Renevier, J.L. Hodeau, M. Marezio, A. Fontaine, A. Michalowicz, G. Tourillon, Local structure around the Co cations in $\text{YBa}_2(\text{Cu}_{1-y}\text{Co}_y)_3\text{O}_{6+x}$ ($0 < y \leq 0.06$) determined by x-ray-absorption spectroscopy, *Physical Review B* 47 (17) (1993) 11398-11410.
- [16] X.-C. Liu, E.-W. Shi, Z.-Z. Chen, H.-W. Zhang, L.-X. Song, H. Wang, S.-D. Yao, Structural, optical and magnetic properties of Co-doped ZnO films, *J. of Crystal Growth* 296 (2006) 135-140.
- [17] D. Sutton, *Electronic spectra of transition metal complexes*, McGraw-Hill Publishing Company Limited (Ed.), Maidenhead-Berkshire, England, 1975.
- [18] J.M. Fernández-Navarro, *El vidrio. Constitución, fabricación y propiedades*, Consejo Superior de Investigaciones Científicas y Sociedad Española de Cerámica y Vidrio (Eds.), Madrid, 2003.
- [19] A. Paul, A.N. Tiwari, Optical absorption of cobalt (II) and cobalt (III) in $\text{Na}_2\text{O-NaBr-B}_2\text{O}_3$ glasses, *Physics and Chemistry of Glasses* 15 (4) (1974) 81-85.
- [20] G. W. Scherer, Aging and drying of gels, *J. Non Cryst. Solids* 100, 1988, 77-92.
- [21] N. Carmona, E. Herrero-Hernández, J. Llopis, M.A. Villegas, Novel sol-gel reversible thermochromic materials for environmental sensors. *J. Sol-Gel Sci. Technol.* (2008) doi: 10.1007/s10971-008-1741-0.
- [22] C.C. Harrison, X. Li, Ultraviolet-Visible-Near-infrared and EXAFS Study of Coil Coordination Chemistry in Post-doped Silica Sol-Gel Glasses, *J. Chem. Soc. Faraday Trans.* 89 (22) (1993) 4115-4122.

[23] J. Choy, H. Jung, J. Yoon, Co K-edge XAS study on a new cobaltdoped- SiO₂ pillared clay, *J. Synchrotron Rad.* 8 (2001) 599-601.

[24] J.M. Rubin-Preminger, U. Englert, Halogen bonding in substituted cobaloximes, *Inorg. Chim. Acta* (2008) doi:10.1016/j.ica.2008.05.026

TABLES

Table 1. Chemical composition of prepared sensors.

Sensor name	Molar ratio			
	Alkoxide*	1-propanol	H ₂ O	CoCl ₂
TM-1	1.0 TMOS	6.9	12.4	0.1
TM-2	1.0 TMOS	7.4	10.3	0.1
TM-3	1.0 TMOS	7.9	8.2	0.1
TM-4	1.0 TMOS	8.4	6.2	0.1
TM-5	1.0 TMOS	8.6	5.1	0.1
TM-6	1.0 TMOS	8.9	4.1	0.1
TM-7	1.0 TMOS	9.1	3.1	0.1
TM-8	1.0 TMOS	9.4	2.1	0.1

* Other alkoxides used: TEOS (TE-), MTMOS (MTM-), DEDMS (DE-), MAP (MA-), GLYMO (GLY-).

Table 2. Maximum absorption wavelength of Co²⁺ ions in different media (nm).

$\lambda_{\text{abs max.}}$ (nm)	Co ²⁺ in solution*	Co ²⁺ in sol-gel TM-4 sensor	Co ²⁺ in glass**	Electronic transitions assigned
Octahedral field	473 (weak)	475 (weak)	592 (weak)	⁴ T ₁ (F) → ⁴ A ₂ (F)
	520	527	548	⁴ T ₁ (F) → ⁴ T ₁ (P)
Tetrahedral field	571	603	540	⁴ A ₂ (F) → ⁴ T ₁ (P)
	626	646	590	⁴ A ₂ (F) → ⁴ T ₁ (F)
	667	679	678 / 640	⁴ A ₂ (F) → ⁴ T ₂ (F)

* F.A. Cotton, G. Wilkinson (1986)¹³; D. Sutton (1975)¹⁷

** J.M. Fernández-Navarro (2003)¹⁸; A. Paul (1974)¹⁹

FIGURES

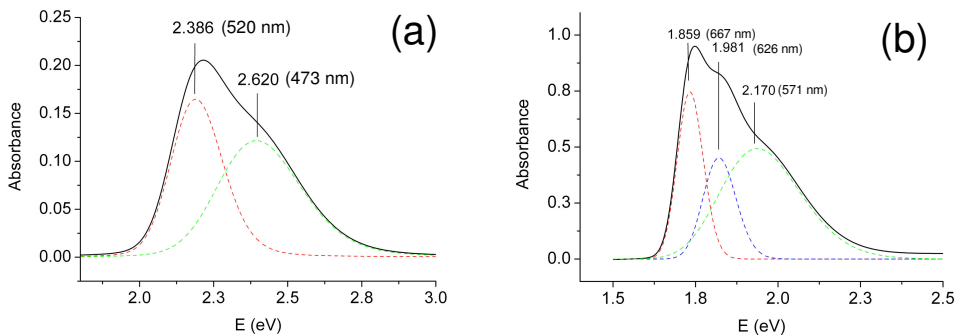


Fig. 1. Optical absorption spectra of a CoCl_2 solution in: (a) water and (b) 1-propanol.

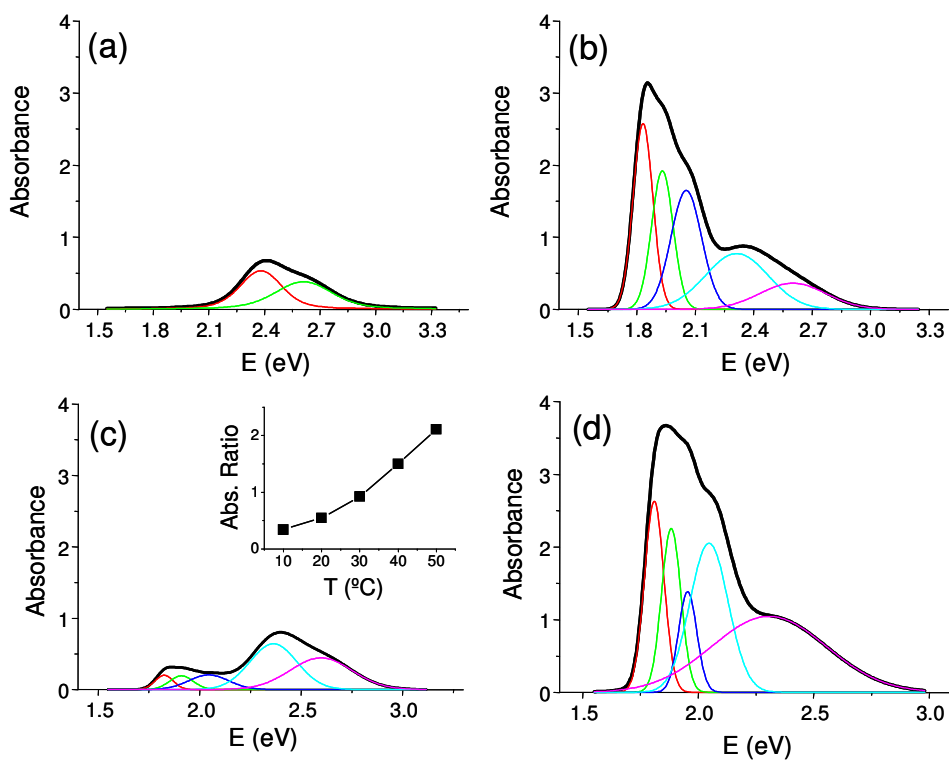


Fig. 2. Optical absorption spectra of sensor: (a) TM-2 and (b) sensor TM-6 at 20 °C; (c) sensor TM-4 after immersion in a thermostatic water bath at 10 °C and (d) 50 °C for 15 min. Inset shows the ratio between the amplitude of absorbance component at 1.859 eV and 2.386 eV for sensor TM-4.

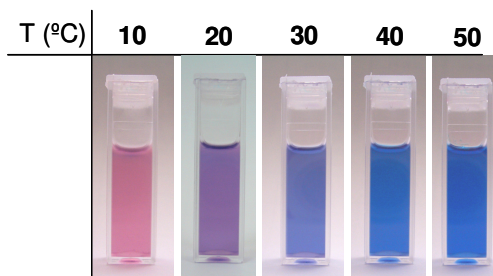


Fig. 3. Temperature sensor TM-4. Change of colour at temperatures from 10 to 50 °C.

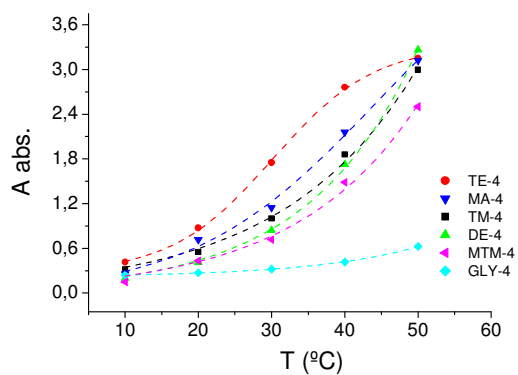


Fig. 4. Calibration curves for the sensor prepared from TMOS, TEOS, MTEOS, DEDMS, MAP and GLYMO as precursors and a water/1-propanol ratio of 6.2/8.4 as a function of the temperature.

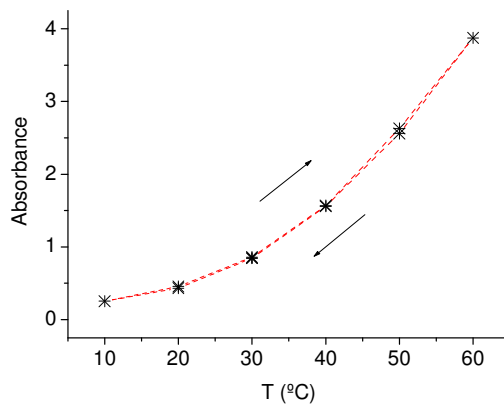


Figure 5. Hysteresis Cycle of sensor TM-4.

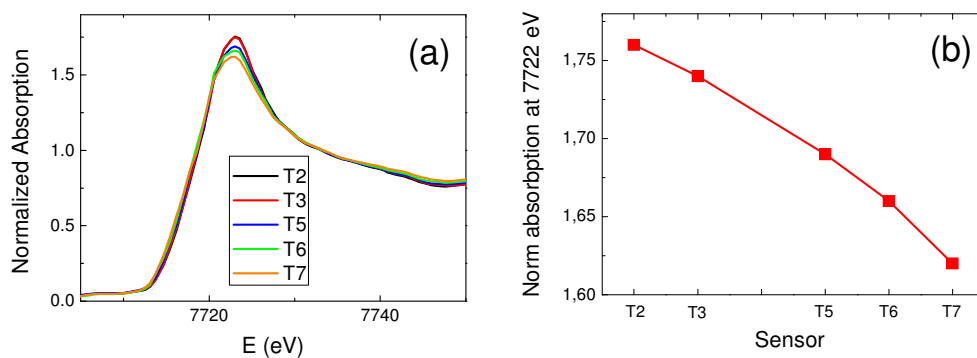


Figure 6. Samples TM-2, TM-3, TM-5, TM-6 and TM-7: a) normalized XANES spectra at the Co k-edge, and b) detail of the maximum absorption edge (7.722 keV) versus the sensor or water content.

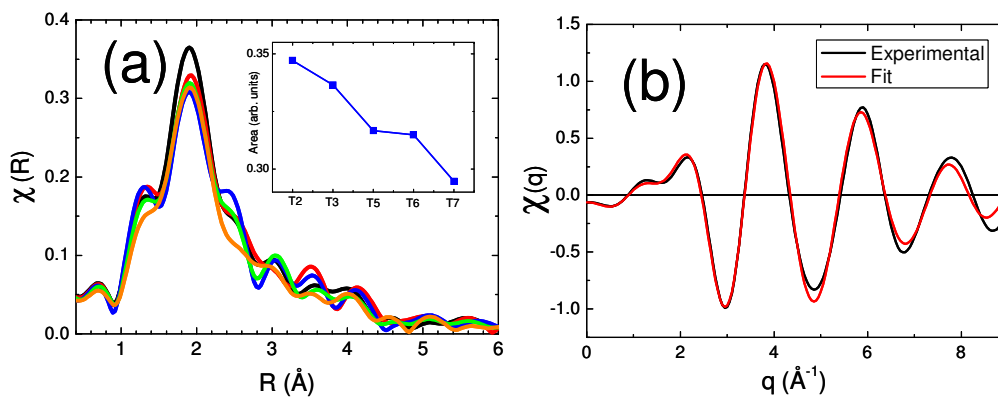


Figure 7. (a) Radial distribution function $\chi(R)$ (colour code identical to figure 7). Inset shows the area of the first coordination shell as a function of the sensor (b) Fit of the χ function in the q space with a tetrahedral coordination shell of oxygen atoms at 2.10 \AA .

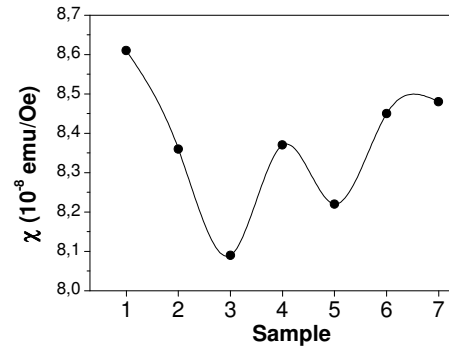


Figure 8. Paramagnetic susceptibility of the sensors TM-1 to TM-7 at room temperature.