

A New Mechanism of Thermochromism for Silica Sol-gel Materials

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Summary. In this contribution we provide evidence for thermochromic colour changes unique to silica based materials formed at low temperature by the sol-gel process. The mechanism requires the matrix and the dopant to interact in order to produce the observed colour changes. The materials formed have potential application as temperature sensitive light filters, visual temperature indicators, self-diagnostic labels for electronic devices and infrared recording media.

Keywords. Sol-gel process; Thermochromism; Copper complexes.

Introduction

A compound is termed “thermochromic” if a change in optical absorbance occurs as temperature changes. This loose definition encapsulates a highly varied range of chemical and physical reasons for the colour change [1, 2]. The thermochromic transition may be classified as “continuous” (gradual change with temperature) or discontinuous (sudden change at specific temperature) and may be reversible or irreversible. Thermochromic compounds of general formula $[M(L_3)][M'Cl_4]$ where M is Cu, Co or Ni, M' is Zn, Pd or Sn and L is phenanthroline, bathophenanthroline or dipyridine are known [3–5]. Thermal treatment leads to ligand exchange reactions with changes in coordination geometry that are associated with colour changes in the range 160–320°C depending on the complex type. Transition metal salts of diamines with the general formula $M(N,N\text{-diethylenediamine})_2(X)_2$ where M is Ni or Cu and X is an anion (usually a bulky one such as ClO_4^- or BF_4^- may also exhibit thermochromism [6–8]. The reasons for thermochromic behaviour include motion of the in-plane ligands [8] and dehydration/rehydration, particularly for complexes of copper and nickel with chlorides [9].

The limiting factor in commercial application of inorganic thermochromic compounds is their poor physical characteristics as most are crystalline solids.

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An alternative approach is to use a carrier phase as a vehicle for the temperature sensitive dopant. The low temperature processing conditions used in the preparation of sol-gel materials [10] allows the incorporation of such high temperature intolerant compounds into a porous ceramic material which may then be used in the form of a thin film coating, monolith or powder. The composite material will have the physical and mechanical properties of a glassy ceramic and yet retain the optical properties of the thermally sensitive dopant. With potential application as infra-red recording media, temperature sensitive light filters, optical temperature sensors and self-diagnostic labels for microchips these currently valueless compounds may be of commercial value when present in a sol-gel matrix. It should be noted that films of VO_2 and doped $M_x\text{VO}_2$ (M ; W(VI), Nb(V), Ti(IV), Cr(III) and Al(III)) prepared by the sol-gel method [11] and silica gels doped with silver colloids [12] show thermochromic behaviour.

Results and Discussion

In this communication we present results obtained using a simple diamine complex salt, diaquabis(1,2-propanediamine)copper(II) chloride as the dopant in a silica matrix prepared by the acid catalysed alkoxide route. Diaquabis(1,2-propanediamine)copper(II) chloride is a deep purple crystalline solid that on heating to 90°C for 30 minutes becomes deep blue [9]. The colour change is reversible on cooling in air but may be preserved by storage in a dessicator at room temperature. The colour change is explained by a thermal dehydration step followed by coordination of chloride groups to the Cu(II) ion, Fig. 1. (Evidence from FarIR analysis (band due to Cu–Cl bond at 358 cm^{-1}) [13] and thermogravimetric analysis (loss of weight equivalent to 2 moles of water per mole of copper at the temperature required for the colour change), data not presented).

Silica sol-gel materials prepared with the complex at 0.2 wt% Cu were a very pale green colour. Heating for 1 hour at 90°C gave a bright yellow glass that reverted to pale green on exposure to air. The yellow colour could be preserved in a dessicator. Prolonged heating at 90°C (approximately 24 h) resulted in a deep green colouration. Exposure of the glass to air at this stage resulted in a light blue glass. The deep green colour could also be preserved in a dessicator. Heating of any of these coloured glasses to 150°C for 1 hour resulted in an orange/brown coloured

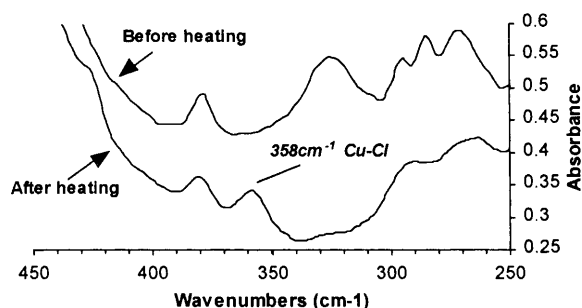


Fig. 1. Far infra-red spectrum of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2](\text{Cl})_2$ before and after thermal dehydration

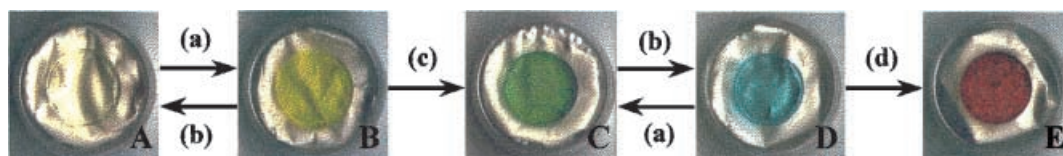


Fig. 2. Thermochromic transitions in 0.2 wt% Cu, $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2](\text{Cl})_2$ doped sol-gel material (a) heated to 90°C for 1 hour, (b) rehydrated in air, (c) heated to 90°C for 24 hours, (d) heated to 150°C for 1 hour

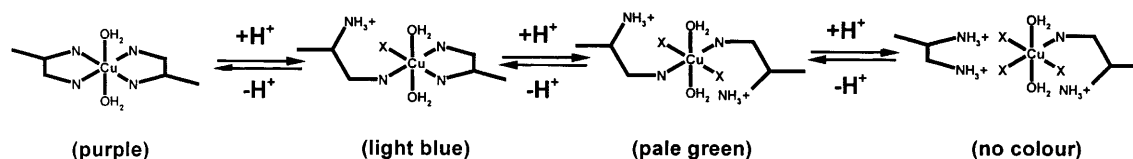


Fig. 3. Reaction of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2](\text{Cl})_2$ with acid

glass which did not subsequently change colour. This scheme of colours is shown in Fig. 2.

In order to understand the colour changes observed when the copper complex was incorporated into the alkoxide derived silica sol-gel material further studies were made of the complex.

A solution of the complex is purple but addition of stoichiometric amounts of acid lead to colour changes from purple to pale blue (1 complex : 1 HCl), pale green (1 complex : 2 HCl) and colourless (1 complex : 3 HCl). These changes can be explained by successive protonations of the nitrogen ligands. Infrared analysis of a pale green crystalline product obtained from solutions of the complex in the presence of 2 equivalents of hydrochloric acid provided evidence for the presence of $\text{C}-\text{NH}_3^+$ groups, data not presented. The ligands marked X in Fig. 3 are unknown but are suggested to be weaker field donors than the original diamine.

Some of the colours presented by the doped sol-gel materials can be understood by comparison with data obtained for the complex alone. The pale green colouration of the as prepared doped sol-gel glass suggests the presence of the doubly protonated complex with both the glass and the crystalline complex reversibly converting to a yellow material after a brief thermal treatment at 90°C . The yellow glass is suggested to contain the doubly protonated complex where the water groups have been replaced by chloride ions. A similar mechanism for this colour transition has been noted for the commercially available cobalt doped silica gels. There is no equivalent to the dark green glass colour nor the orange/brown glass colour in the colour chemistry of the complex alone. The light blue glass has a very similar visible spectrum to that of the blue, singly protonated complex, Fig. 4 and is suggested to contain the singly protonated complex. Significantly, the light blue complex contains three nitrogen atoms coordinated to the metal ion whereas the pale green complex contains two nitrogen atoms coordinated to the metal ion.

On extended thermal treatment (90°C for 24 hours as opposed to 90°C for 30 minutes) followed by a prolonged re-exposure to air the number of coordinated nitrogen ligands around the central copper(II) ion increases from 2 to 3. The data

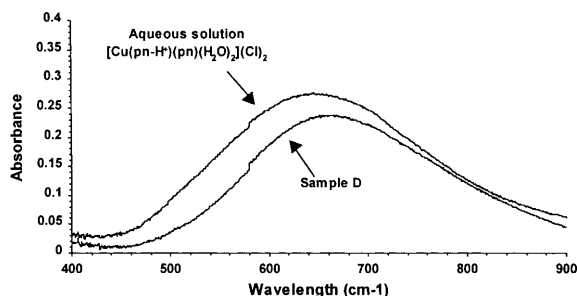


Fig. 4. Comparison of the optical spectrum of sample (d) with a 1 complex : 1 HCl ratio aqueous solution

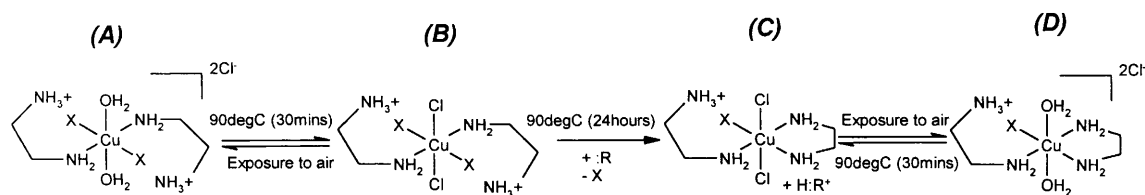


Fig. 5. Proposed structures of complexes in the silica sol-gel material; R = external proton acceptor in the matrix, X = unknown ligand

suggest that a proton is lost from an $-\text{NH}_3^+$ group on the complex during the extended thermal treatment and re-exposure to the atmosphere. In accordance with the other colour changes observed on mild thermal treatment, the change from dark green to light blue would be anticipated to involve only a change in coordination of water and chloride ions. Therefore the transition to the deep green colour is probably due to an irreversible intermolecular proton transfer to an acceptor in the matrix which would also be manifest in the light blue glass obtained on prolonged exposure of the dark green glass to air. These changes are clearly not possible for the complex alone and represent a new form of thermochromism involving the thermochromic compound itself in conjunction with its matrix. The irreversible change to orange/brown on heating to 150°C cannot as yet be explained although it is not due to the partial decomposition of the complex or any residual organics remaining in the glass. Proposed structures for the copper(II) complexes present in the coloured glasses are given in Fig. 5. The transition from yellow, structure (B) to dark green, structure (C) is a novel transition requiring both dopant and matrix to interact at the molecular level.

Further studies will utilise other thermochromic complexes to explore the generality of the mechanism and use EPR spectroscopy to validate the structures of the molecular species suggested to be present in the differently coloured glasses.

Experimental

Synthesis of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2](\text{Cl})_2$

Stoichiometric amounts of 1,2-propanediamine were added dropwise to a 1 M solution of copper(II) chloride in a 50 : 50 mixture of ethanol and diethylether at 60°C and stirred for 30 min. The solution

was cooled with ice and the purple precipitate filtered under suction and washed with diethylether. To attain a natural level of hydration the complex was heated to 100°C for 1 h and left to rehydrate in air for 24 h.

Preparation of doped silica sol-gel materials

0.2 wt% Cu silica sol-gel materials were prepared by dissolving 0.012 g of complex in 10.23 cm³ of dry ethanol (95% ethanol dried by refluxing over magnesium) and adding this to 10 cm³ of tetraethoxysilane (Aldrich, 99%). 3.165 ml of 0.2 M HCl was added and the mixture stirred for 1 h. 5 cm³ aliquots of the mixture were pipetted into four plastic petri-dishes (35 mm diameter, 10 mm deep, from BDH) and covered with NescoTM film. Four equally spaced holes were punctured in the film using a syringe needle and the dishes placed in an oven at 40°C. The mass of the samples was monitored daily until constant. To prevent extensive cracking, samples were initially heated from 25°C to 45°C at 0.5°C/min and held at constant temperature for 24 h to remove excess moisture in the silica pores. The temperature was then raised rapidly to 90°C with no further cracking.

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