



Thermochromics: A Temperature Sensitive Smart Material

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Abstract

Thermochromism is the ability of substance to change color due to a change in temperature. Thermochromic materials have recently attracted great attention due to their controllable and rich physicochemical properties. In this short review we have discussed the origin and application of different types of thermochromic material from pure organic compound to pure inorganic compound.

Keywords: Thermochromism, Physicochemical Properties, Thermochromic Materials

1. Introduction

Why do we use Sun-Glass? What is the Science behind the ‘Mood Ring’? These two examples of accessories come in the genre of chromic material. Chromic materials are the materials that undergo various colour changes through alteration of electron density (π or d electron) of a substance caused by the influence of external stimuli. In most of the cases the colour change is reversible and controllable. Depending upon the nature of external stimulus, chromic phenomena are named using the suffix *chromism* preceded by a prefix which is used to describe the stimulus giving rise to the colour change. Like thermochromism is associated to external stimuli heat, photochromism is associated with light, ionochromism occurs due to exchange of ions, electrochromism is related with electric potential as stimuli, solvatochromism deals with solvents, vapochromism is influenced by vapours and in mechanochromism mechanical actions works as external stimuli. Table 1 provides a comprehensive list of chromic phenomena and the responsible stimuli [1-3].

Table 1: Stimulus associated with classification of Chromic material

Stimulus	Chromic phenomenon
Heat	Thermochromism
Light	Photochromism
Electric Current	Electrochromism
Solvent	Solvatochromism
Vapour	Vapochromism
Mechanical action	Mechanochromism
Magnetic Field	Magneto chromism
Pressure	Piezochromism

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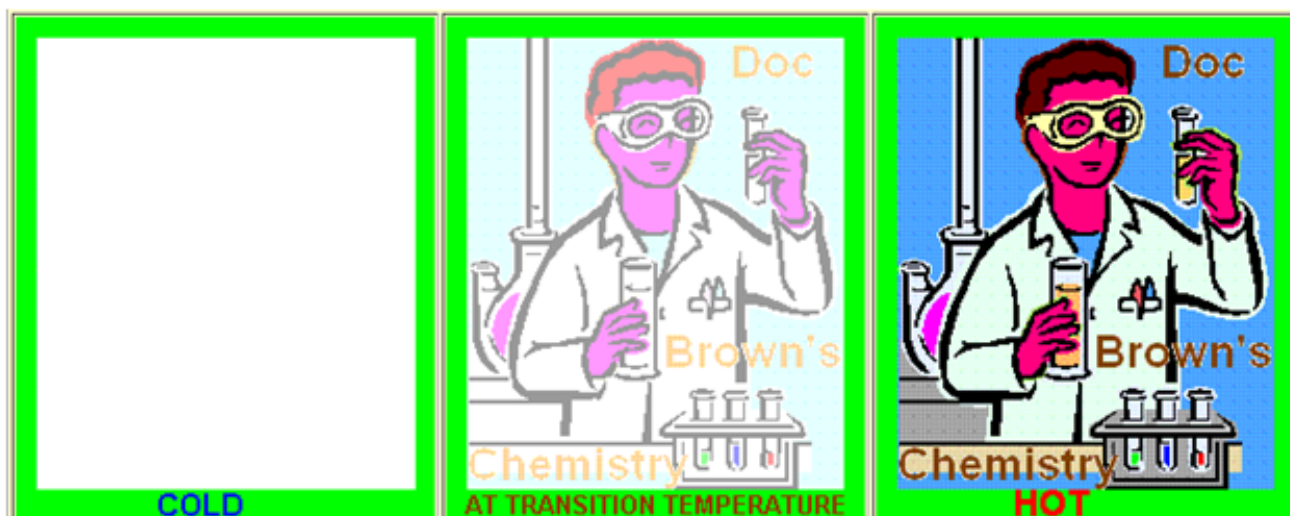


Figure 1: Paint or print of a picture image on a mug and then coating the image with a thin layer of a plain coloured thermochromic pigment paint. At room temperature (COLD) it appears nothing (left picture) pouring a hot drink into it, at a certain transition temperature e.g. 35°C, the plain layer thermochromic pigment begins to become transparent. Eventually the fully coloured image is then seen (Middle picture). Fully coloured image is seen in hot condition (right picture). Retrieved from ref 4.

Materials of different origin such as dyes and pigments, conjugated conducting polymers, inorganic oxides, organic molecules etc show chromic phenomena. There are multiple applications of such Chromic Materials. Some of the applications are already developed to the technological level and are commercialized successfully whereas some are in the developmental stage. Examples of successful realistic application of chromic materials include Industrial temperature indicator [5-6], Photo-chromic windows,[7] Smart Windows (a device combination of Solar Cell and Electrochromic Windows), Electrochromic Displays [8], Molecular Switches, Memories [9,10] and so on. High end technology like ophthalmics [11], thermometry [12], electronics and biomedicine [13] also uses different chromic phenomena based on application.

In this short review we will emphasize on the most versatile chromic phenomenon, Thermochromism. Different mechanisms of thermochromism will be discussed along with their potential applications.

2. Basic property of thermochromic material

The fundamental property which is responsible for thermochromicity of a material is the change in colour (reversible or irreversible) due to fluctuation in temperature or heat (as a stimulus)(Figure 1). Primarily, a reversible color change is considered to be necessary for thermochromism. However, there are significant applications of thermochromic materials in which an irreversible change is required and therefore, irreversible thermochromism is often included in topics. For an easier approach we generally identify reversible thermochromism as simply “thermochromism” and wherever irreversible reaction takes place we specify it as “irreversible thermochromism”.

3. Choice of materials for Thermochromic behaviour

3.1 Organic material

According to the view of Organic Chemistry, thermochromism is frequently observed in substances due

to structural and chemical modifications i.e. resonance, extended conjugation, tautomeric equilibrium, stereoisomerism between two crystal structures, formation of free radicals, ring opening reactions which is influenced by temperature changes.[14-16] Such structural and chemical changes alter the delocalized π -electronic structure of the molecule, giving rise to the dramatic changes in colour. [17] In the following section, we represent a short description of different organic materials that have this unique property of the rmochromicity.

- Crowded ethenes: These are a class of organic compounds which have two polycyclic aromatic rings separated by a double bond (Figure 2). For example: bianthrone and dixanthylene. At room temperature, two cyclic rings stay out of plane for steric crowding and show their individual properties. However, at elevated temperature, the central double bond becomes weak and electron density of the π -bond gets delocalized over two cyclic rings to acquire a planar arrangement. The enhanced coplanarity leads to π -bonding conjugation over the whole molecule, decreasing the absorption energy which ultimately leads to the colour change[18].

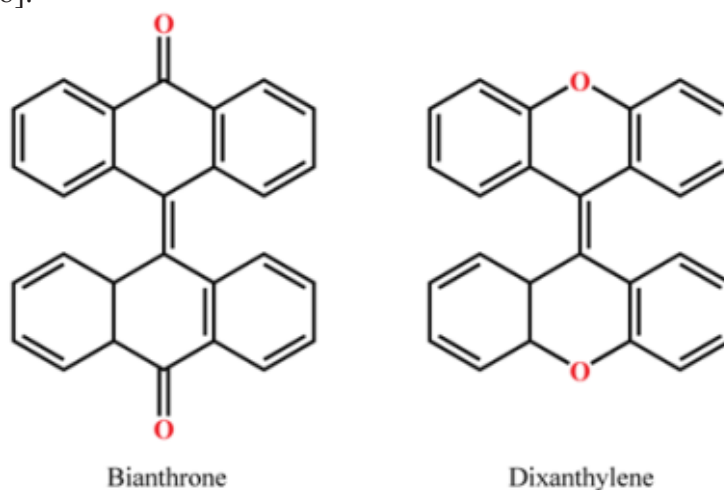


Figure 2: Structures of some crowded ethenes.

- In general, *enol-imine* form and *keto-enamine* form of a Schiff Base co-exist in equilibrium. An elevated temperature promotes the intramolecular tautomerisation reaction to occur. The keto-enamine form has a more extended π -bonding structure than the parent enol-imine due to the electronic rearrangement. It reduces the energy of electronic transitions of the π -electrons and changes the colour of the compound (Figure 3) [19,20].

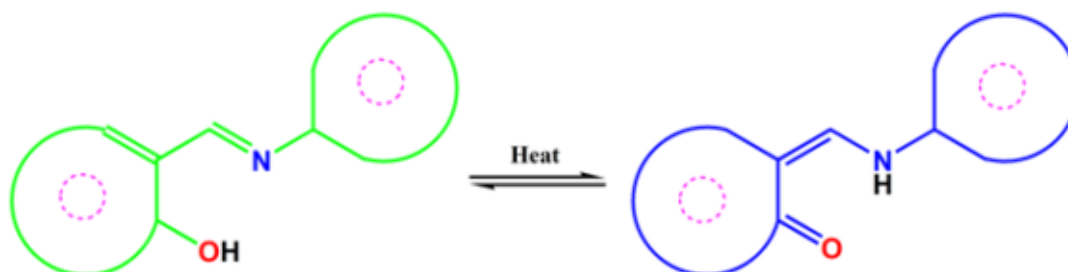


Figure 3: Schiff base fall under a category of compounds which exhibit the keto-enol equilibrium responsible for thermochromism. The cyclic part denotes different aromatic system.

Spiro compounds: These types of compounds fall under another important category which show thermochromicity. It includes triarylmethane dyes (TAM dyes), fluoran dyes, spiropyrans, spironaphthalenes, and spirooxazines.[21-26] The conversion of the sp^3 spiro carbon centre to an sp^2 carbon centre give rise to their thermochromic behaviour. On conversion to the sp^2 carbon centre, π -bonding electron density of the molecule can become delocalized over a larger portion of the molecule through extended conjugation and resonance, yielding electronic transitions which fall in the visible region of the electronic spectrum, producing visible colour (Figure 4).

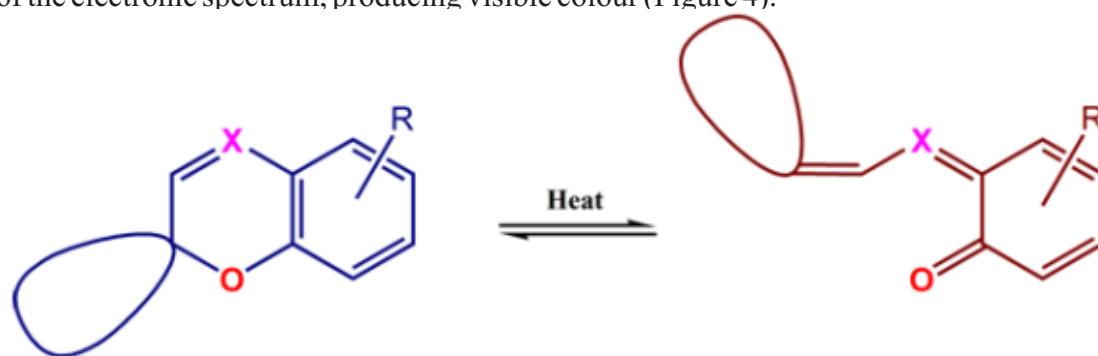


Figure 4: Tautomeric ring-opening equilibrium between the spiropyran (SP) form and the merocyanine (MC) form of a spiro compound. When X = CH, spiropyrans; X = N: spirooxazines.

Fluorans, crystal violet lactones, and spiro pyrans are acid sensitized dyes which undergo ring opening rearrangements to develop the colour. These compounds are extensively used as colorant in textile industry [27-29].

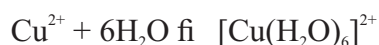
3.2 Inorganic material

In this section, we will now focus on inorganic mechanistic pathways for thermochromism of different compounds. Generally, such color change happens due to the changes in ligand geometry, crystalline phase, number of solvent molecules in coordination sphere. But the reasons behind it changes from one compound to another.

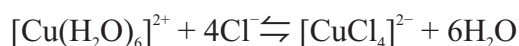
Different thermochromic materials and their applications are as follows:

In solid state, copper chloride hexahydrate is blue in colour but on heating above temperature 60°C , its color changes to green. The chemistry behind the observed thermochromism phenomenon is the conversion of the octahedral structure of hexahydrate complex of copper salt to tetrahedral chloro complex due to the loss of water of crystallization molecules upon heating (Figure 5).

At room temperature, copper is present at the centre of the octahedral complex: hexaaquacopper(II) complex,



And on heating, it gets converted into tetrachlorocuprate(II) complex.



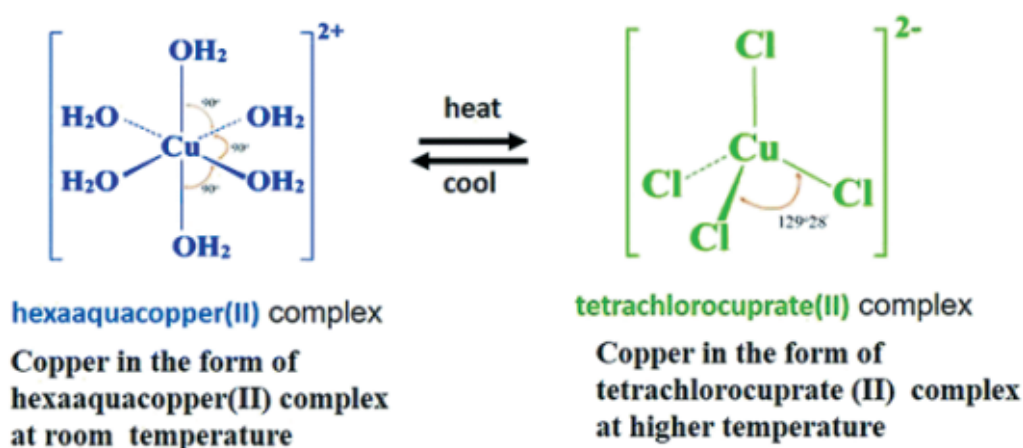


Figure 5: Structural change on heating $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

This simple chemistry is used to design reversible thermochromism based temperature sensor in an organic–inorganic composite system using Polyethylene dioxythiophene–polystyrene sulphonate (PEDOT:PSS) polymer [30].

Vanadium dioxide (VO_2) is one of most promising “smart and intelligent materials” which are sensitive to temperature due to the thermochromic mechanism. Vanadium dioxide has two stable polymorphs: the monoclinic and rutile (VO_2 (M/R)) depending on the temperature (Figure 6). As temperature increases, these two forms undergo reversible first order metal-to-insulator transition (MIT) at nearly 68°C in a sharp and reversible manner. The structural switch-over from monoclinic VO_2 (M) form (low temperature) to rutile VO_2 form (R) (high temperature) occur accompanied by a dramatic change in its near-infrared optical properties (Figure 7). At low temperature region, the monoclinic VO_2 form behaves like a semiconductor, which allows large amount of solar light to be absorbed or transmitted through. As the reaction temperature exceeds the transition temperature (T_c), VO_2 behaves like a metal, which reflects the radiation at near-infrared (NIR) region. Infrared region contains the nearly half of the heat energy carried by solar light. Above T_c , the material reflects infrared radiation. Yet, below T_c , it is transparent, which is crucial in its application as a thin film coating for “intelligent” architectural glazing [31].

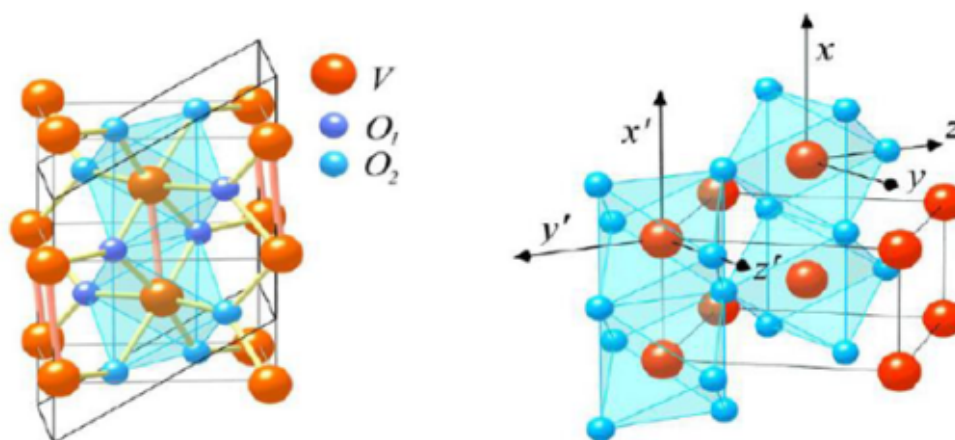


Figure 6: Crystal structures of Vanadium dioxide (VO_2) in Monoclinic (left) and Rutile (right) form observed in lower and higher temperature. Retrieved from ref 32.

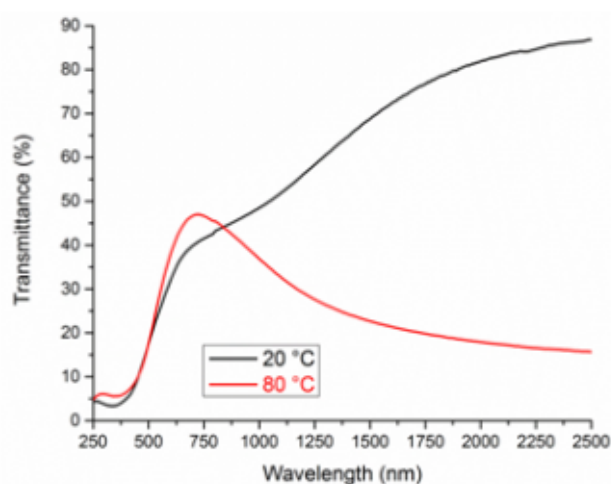


Figure 7: Typical VO₂ thermochromic performance below and above T_c.

Due to this novel characteristic, VO₂ becomes a promising base material for a coating of windows in equatorial region to reduce the inner temperature of the house [33].

Another mechanism of thermochromism is Order-disorder phase changes. The compound Cu₂HgI₄ is thermochromatic. It reversibly changes color with alteration in temperature. At low temperatures, this compound is bright red, and at high temperatures it is dark brown. At the low-temperature form, the Cu⁺ and Hg²⁺ ions are arranged in separate alternating layers, packed between layers of I ions (Figure 8). At the high-temperature form, the I ions occupy the same positions as before, but the metal ions now randomly occupy all the tetrahedral holes in the iodide array. This conversion of one crystal form to another form takes place sharply at temperature 700C. The Metal-Metal charge transfer appears to be the most likely reason for the evolution of colour. The d-d transition and Metalfi Ligand transition are ruled out due to d¹⁰ configuration of Hg²⁺ and π-acceptor property of chloride respectively [33, 34].

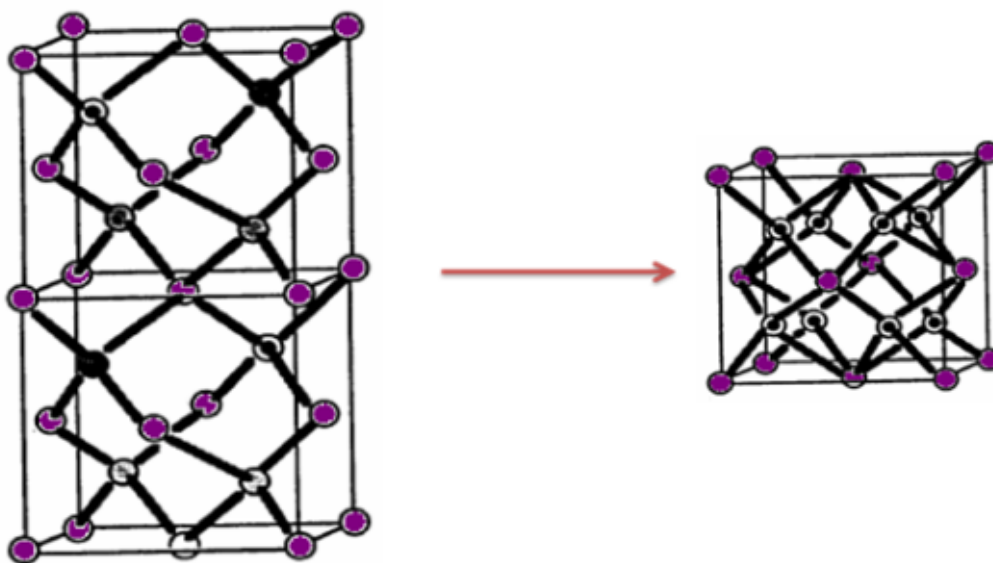


Figure 8: The structure of ordered low temperature(left) and randomly distributed high temperature(right) form of Cu₂HgI₄. Violet ball= I, filled black ball= Hg²⁺, scattered black ball = Cu⁺.

Cr-doped Al_2O_3 , usually known as ruby, are another class of inorganic materials that depicts thermochromism. The color change of the Cr-doped Al_2O_3 can be explained based on the crystal field theory of transition metal complexes. The origin of colors of such transition metal complexes are because of the electronic transitions between the d-orbitals, splitted under the electric field of the ligands. The origin of the pink color of the Cr-doped Al_2O_3 is the splitting of the d-orbitals of Cr^{3+} which gives rise to the electronic transition ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_1\text{g}$ (410–461 nm), and ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_2\text{g}$ (561–600 nm). At low temperatures, doping of a Cr^{3+} in the crystal lattice of Al_2O_3 occurs by squeezing it into the octahedral cage of O^{2-} ions, which is too small. At elevated temperatures, the chemical bonds in this compound expand due to enhanced molecular vibration, and the Cr^{3+} ions instead of being squeezed become more relaxed and regains proper green color as of pure Cr_2O_3 . The change of ligand field strength in lieu of change of Cr- O distance at high temperature is thus the origin of such kind of thermochromism. [35,36]

Some nickel based coordination complexes like dichlorobis (triphenylphosphine) nickel(II) and $[\text{R}_x\text{NH}_{4-x}]_2\text{NiCl}_4$, (where R = alkyl or aryl group) shows thermochromism due to structural isomerism. The mechanism for the thermochromism observed in the later complexes involves a change in geometry and coordination numbers from an octahedral (CN = 6) to a tetrahedral (CN = 4) geometry (Figure 9). The possibility that the thermochromism involves a five-coordinate nickel(II) complex can be ruled out on the basis of the experimental results obtained, as well as for stereochemical reasons. In case of former complex different colour in temperature is due to the equilibrium between square planar and tetrahedral geometry [37,38].

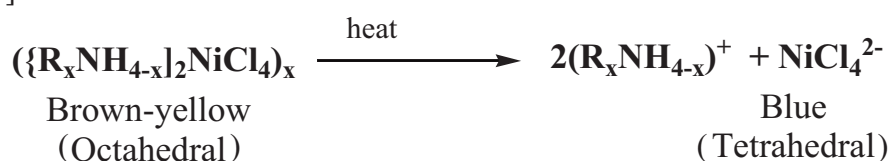


Figure 9: Change in geometry induced thermochromism in quaternary nickel complex.

4. Conclusion

Altogether we can conclude that thermochromism is a colour changing phenomena due to temperature changes. Thermochromism is frequently observed due to structural and chemical modifications. At molecular level, the colour change happens due to the change in ligand geometry, crystalline phase, number of solvent molecules in coordination sphere. In solid state of copper chloride hexahydrate, the thermochromism phenomenon happens due to the conversion of the hexahydrate complex of copper salt to tetrahedral chloro complex, because of the loss of water of crystallization molecules with heating. This logic was involved in designing reversible thermochromism based temperature sensor using Polyethylene dioxythiophene–polystyrene sulphonate (PEDOT:PSS) polymer. The Vanadium dioxide co-exists as two polymorphs: the monoclinic form and rutile form (VO_2 (M/R)) depending upon the temperature. Above T_c , the material reflects infrared radiation but below T_c , it is transparent, which is crucial in its application as a thin film coating for “intelligent” architectural glazing, coating for windows. Cu_2HgI_4 is thermochromatic due to Metal-Metal charge transfer. Cr-doped Al_2O_3 (Ruby) is another class of inorganic material that depicts thermochromism. The color change of the Cr-doped Al_2O_3 (Ruby) can be explained from the basis of crystal field theory of transition metal complexes.

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