BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 67 (71), Numărul 1, 2021
Secţia
CHIMIE şi INGINERIE CHIMICĂ

THERMOCHROMIC MATERIALS: OXIDES WITH APPLICATIONS IN INTELLIGENT TECHNOLOGIES

BY

GABRIELA ANTOANETA APOSTOLESCU, MIHAELA AURELIA VIZITIU, CORINA CERNĂTESCU, CLAUDIA COBZARU, RAMONA ELENA TĂTARU-FĂRMUŞ and NICOLAE APOSTOLESCU*

“Gheorghe Asachi” Technical University of Iaşi, Romania,
“Cristofor Simionescu” Faculty of Chemical Engineering and Environmental Protection

Received: January 25, 2021
Accepted for publication: March 15, 2021

Abstract. Many types of smart materials have been studied and developed in the late years, due to their applications in industry (military, aerospace, medical, construction). The possibilities to develop environmentally friendly products (*e.g.* reducing the cost of building maintenance by using construction materials / smart windows, pollution reduction by using photo-catalytic active materials) are also studied. This type of intelligent materials also includes thermo-chromatic materials, able to change their color with temperature variation. This paper presents the phenomenon of thermo-chromatism, the main classes of thermo-chromatic materials, with emphasis on oxide materials, methods of obtaining, their applications and the current state of research in the field of mechanisms of producing thermo-chromatic phenomena.

Keywords: thermochromic materials; organic-inorganic hybrid systems; VO_2.

*Corresponding author; *e-mail*: napostol@ch.tuiasi.ro

1. Introduction

Thermochromism is defined as a thermally induced transformation of a molecular structure, which determines a spectral change, usually of visible colour (but not necessarily). The stimulus can theoretically be any source of thermal energy (not only solar), and the resulting spectral change must not occur only in the range of visible light, but it can be any change in optical properties. This phenomenon can be reversible (the material returns to its original colour after cooling) or it can be irreversible.

Thermochromic behaviour can be obtained by various mechanisms, such as charge transfer, crystal field or any change in chemical structure. The characteristics of thermochromic materials are temperature memory functions, with potential important applications in the aerospace, military, anti-fake technology, construction, ophthalmology, fashion / cosmetics, security, sensors, optical memory and optical switches, paints, inks, plastics and textiles as indicators / sensors and in architecture, etc. but also in other areas. Differences of reversible thermochromism in systems where heat variation is the only cause of colour change, from systems where colour variation is induced by changes in the environment around the chromophore caused by heat, such as a change in pH value, should be made.

It is known that continuous thermochromism is a gradual change in colour as the temperature rises, and discontinuous thermochromism which corresponds to a sudden change in colour at a certain temperature or in a range of temperatures. This last phenomenon, which occurs mostly in the case of inorganic compounds, is essentially related to a solid-solid transition (change of coordination geometry around a metal centre, change of coordination number or ligands).

When the thermochromism of a molecular system results from the association with other chemical compounds (metal ions, protons, modification of the systems environment), this phenomenon is called thermo-solvato-chromatism.

Several classes of materials that exhibit the phenomenon of thermochromism are known. These are: thermochromic liquid crystals, organic dyes, in fact mixtures of leuco dyes with other suitable chemicals, displaying a colour change depending on temperature (usually between the colourless leuco form and the coloured form), polymers, inorganic materials (metal oxides, sulphides, halides, phosphates, mixed oxide-sulphide compounds) or complex combinations.

Because thermochromic phenomena usually occur without additional energy input (they take their energy from the environment), autonomous thermochromic materials are of great research interest and have presented great potential for multiple applications, as it shown in Fig. 1 (Abdullah *et al*., 2010; Guan *et al*., 2018; Jakovljevic *et al*., 2020; Mandal *et al*., 2019; Stasiek *et al*., 2002).

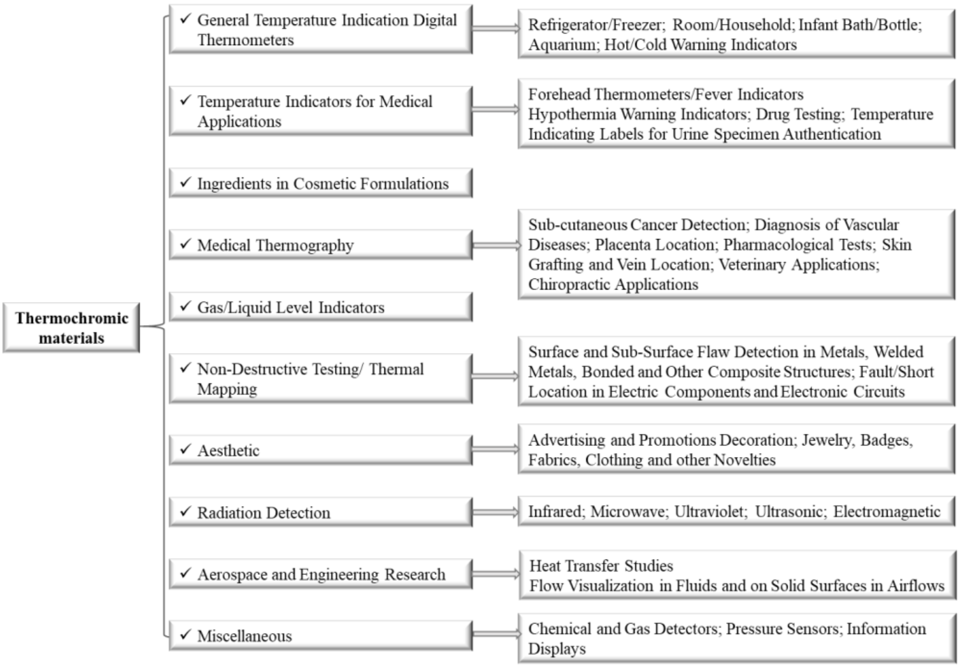

Fig. 1 – The main applications of thermochromic materials.

It is generally accepted that chromogenic dyeing involves the capture of electrons from inside the material in special lattice positions, usually in the anion (oxygen) free positions. Electronic excitation in thermochromism occurs through electron-photon interactions (Tomás *et al*., 2009).

2. Thermochromic Materials

2.1. Organic Thermochromic Materials

Several classes of organic materials with thermochromic properties are known; the colour changes due to the changes of the electronic properties (energy levels, electronic populations) of these materials' dependent on temperature variations.

2.1.1. *Thermochromic Liquid Crystals (TLC)*

Liquid crystals are anisotropic fluids that exist at the boundaries of the solid phase and the conventional, isotropic liquid phase. Thermochromic liquid crystals (TLC) react to temperature variations by changing their colour, their optical properties varying in a predictable and repeatable way.

Liquid crystals are generally named according to the formation mode (lyotropic ones are formed under the action of a solvent, thermotropic ones depend on temperature), those of interest on thermochromic properties being thermotropic liquid crystals (which, in turn, are classified as smectic, nematic or cholesteric). The term “cholesteric” derives from the fact that the first chemicals that showed the characteristic properties and structure of this particular type of liquid crystal were cholesterol esters. TLC-based temperature visualization is based on the property of these materials (cholesteric and chiral-nematic liquid crystals) to reflect colours at specific temperatures and specific viewing angles. The temperature-colour range depends on the composition of TLC and can be selected for values of about 0.5°C, in wide temperature ranges (from -30°C to over 120°C). As long as these TLC-s retain their physico-chemical properties (they are not damaged), the colour changes are repeatable and reversible, with a response time of approximately 10 ms, and can be accurately calibrated (Stasiek and Kowalewski 2002).

They have chiral (twisted) molecular structures and are optically active mixtures of organic chemicals.

TLC-s change colour by selectively reflecting incident white light. Conventional temperature-sensitive blends in thin films reflect bright, almost pure colours, changing from colourless (black, on a black background) to red colour at a certain temperature. As the temperature rises, they pass through the other colours of the visible spectrum. The colour changes are reversible, and the colour change sequence is reversed, on cooling. TLCs are commercially available in a variety of forms, including water-resistant or micro-encapsulated forms, with response times beginning with a few milliseconds.

Thus, Guan *et al*. (2018) synthesized (by the coacervation method) micro-encapsulated cholesteric liquid crystals, used as thermochromic materials in intelligent functional fibres, the thermochromic properties being closely related to particle size.

TLCs with selective reflection, with iridescent colour generating behaviour, based on (-) - menthyl group were obtained recently (Luo *et al*., 2019). TLCs used as thermal imaging tools in applications such as heat transfer, thermal flow visualization, microfluidic or electro-optical devices (Abdullah *et al*., 2010; Yan *et al*., 2018) and medical diagnosis (Bharara *et al*., 2006), TLCs with uses as thermochromic ink (Jakovljevic *et al*., 2020) are just a few examples of the diversity of applications of this class of materials.

2.1.2. *Thermochromic Polymers*

A series of polymers, sometimes doped with different compounds (oxides, sulphides, coordination compounds) have thermochromic properties and multiple practical applications. Among the best-known polymers with thermochromic properties are spiro-pyranes and poly-diacetylenes (PDAs).

Optical changes induced by temperature change are mainly due to the reduction of the effective length of the conjugate chain in the PDA system, which could be caused by twisting longer alkyl chains attached to the main chain of the PDA (Huo *et al*., 2017; Lee *et al*., 2016).

A possible mechanism to explain the thermochromism of diacetylenes was proposed by Mergu and Son, 2021, starting from the fact that diacetylenic monomers on UV irradiation turn into blue-coloured polydiacetylene which turns red in the presence of external stimuli (such as the heat). The “blue” flat shape has a continuous overlap of π electrons and a long conjugation length, and after applying the thermal stimulus, the stress accumulated during photo-polymerization is released by partially modifying the long alkyl chains that eventually twist the π orbitals to non-planar states, which reduces the effective length of the conjugation producing the transition from blue to red.

Maximum absorption (λ_{max}) of PDA in different phases is caused by polymer chain rearrangements due to steric repulsions and attraction forces (*e.g*., hydrophobic interactions and electronic π-π interactions) that occur as a result of thermal stimuli (Mergu and Son, 2021). The field of thermochromic polymers is vast and research in the field is booming (Cheng *et al*., 2018; Mandal *et al*., 2019; Sun *et al*., 2021).

2.2. Hybrid Organic and Organic-Inorganic Systems

The hybrid systems are of great interest mainly those which exploit the synergistic action of different organic phases (polymers - leuco-dyes or polymers - inorganic materials), effectively combining the specific properties of the component phases. Compared to traditional thermochromic materials, liquid crystal (LC) / polymer hybrid materials present advantages in terms of manufacturing process and easier processing. Thus, Liang *et al*. (2018) promoted a new soft thermochromic composite film (TS) based on polymeric / temperature sensitive liquid crystals (TLC) with a thermally induced phase transition between smectic state (SmA) and chiral nematic state (N*), with reversible transmittance starting from acrylic monomers (lauryl methacrylate, polyethylene glycol-di-acrylate (PEGDA 600) and hydroxy-propyl methacrylate) which was sandwiched between two transparent and conductive polyester substrates via capillary action.

Hybrid polymer materials - leuco dyes (methylene blue, crystal violet, etc.) have significantly higher thermochromic properties compared to those of simple polymers. Baron and Elie, (2003), Cheng *et al*., (2018) and recently Soreno *et al.*, (2020) synthesized a thermochromic material that exhibits reversible colour switching by simply mixing the methyl red dye with polydimethylsiloxane.

In addition to those presented above, there are known polymeric films of poly (methyl-methacrylate), poly-vinyl-pyrrolidone and poly (styrenebutadiene-styrene), doped with complex organo-boron combinations with fluoro-pyridyl-diketone ligands which also show thermochromic and acido-chromatic properties (Jimenez *et al*., 2020).

2.3. Inorganic Thermochromic Materials

Several classes of inorganic materials have thermochromic properties, such as transition metals oxides, sulphides, halides, phosphates, complex combinations or mixed oxide-sulphide compounds. For example, titanium dioxide, zinc sulphide and zinc oxide are white at room temperature, but when heated, they turn yellow. Similarly, indium (III) oxide is yellow and darkens to yellow-brown when heated.

2.3.1. *Metallic Oxides with Thermochromic Properties*

Thermochromic properties varying in a wide temperature range were found in the simple or mixed oxides of transitional elements but not only there. One of the most studied and used oxide is VO_2 (Chang *et al*., 2021).

The thermochromic properties of VO_2 derive from a phase transition from monoclinic (semiconductor, optically transparent) to tetragonal (metallic and thus optically reflective). The phase transition takes place at 67.8°C in femtoseconds. The behaviour can be attributed to changes in lattice patterns with temperature, resulting in a change in colour. The behaviour is similar to the phenomenon of polymorphism. The excitation of electrons followed by de-excitation with the release of energy in the form of photons may also be responsible for the colour change with temperature. In the monoclinic phase, V^{4+} ions form pairs along the c-axis, leading to alternation of short and long V-V distances of 2.65 Å and 3.12 Å. In comparison, in the tetragonal phase, the V^{4+} ions are separated by a fixed distance of 2.96 Å. As a result, the number of V^{4+} ions in the cell of the crystalline unit doubles from the tetragonal phase to the monoclinic phase.

Equilibrium morphology of VO_2: tetragonal particles are acicular, laterally limited by surfaces (110), which are the most stable termination planes. The surface tends to be oxidized relative to the stoichiometric composition, with oxygen adsorbed on the surface (110) forming vanadyl species. The presence of V^{5+} ions on the surface of VO_2 films was confirmed by X-ray photoelectron spectroscopy (Wang *et al*., 2017).

But VO_2 encapsulated in thin films of SiO_2, TiO_2, ZnO or Cr_2O_3 (Xie *et al*., 2021) present special thermochromic properties regarding their relatively high light transmission capacity and solar modulation), the material of the encapsulation coating modifying the optical performance of the thermochromic films due to the variation of the dielectric medium of the VO_2 nanoparticles.

Most applications of vanadium dioxide require its synthesis in the form of thin films, but several original forms of this material are mentioned for nanotechnology research such as nanoparticles and nanowires. VO_2 synthesis can be done by chemical processes (sol-gel process: the first step generally consists in synthesizing a V_2O_5 film using vanadium isopropyl-oxide precursors as $VO(OC_3H_7)_3$; then calcination in a reducing atmosphere or under low oxygen pressure; chemical vapor deposition (CVD) allows the deposition of epitaxial thin films on sapphire substrates (low pressure CVD) or polycrystalline thin films at atmospheric pressure); physical processes such as pulsed laser ablation deposition that makes possible to obtain thin films epitaxy on various monocrystalline substrates or electron beam irradiation evaporation - an electron beam irradiates a target of metallic vanadium and causes its evaporation; the synthesis is carried out in oxygen atmosphere and at substrate temperatures between 500 and 600°C. This technique allows the deposition of epitaxial films on substrates (Blagojevic *et al*., 2013; Kim *et al.* 2010; Kats *et al*., 2013; Pattanayak *et al*., 2018; Lee *et al*., 2017).

In_2O_3 is an amphoteric oxide of indium with applications in intelligent technologies (especially as a thermochromic material) it is yellow at low temperature, becoming yellow-brown when heated. In the form of a thin layer (film) is a light-transparent metal oxide (Korotcenkov *et al*., 2016). The crystalline form exists in two phases, cubic (bixbyite type) and rhombohedral (corundum type). Both phases have a bandwidth of about 3 eV. The rhombohedral phase is produced at high temperatures and pressures or when unbalanced growth methods are used.

The material obtained by the heating the combination of Cr_2O_3-Al_2O_3 has an exceptional thermochromic property, going from pink to grey or green in a temperature range of 25-600°C. The colour change is reversible and is dependent on the ambient temperature and the concentration of chromium; however, it is not depending on exposure time (Nguyen *et al*., 2017). Cr^{3+} ions replace Al^{3+} ions in Al_2O_3, the resulting material being Cr doped Al_2O_3 (ruby). If the chromium concentration in the compounds is low, the colour of the mixture is pink. At high concentrations of chromium, the colour of the compounds is green. The advantages of ruby are high heat resistance, high melting point, high mechanical strength, high transparency and excellent chemical stability. More importantly, the compounds may exhibit a remarkable phenomenon of reversible thermochromism. When heated, the colour of ruby changes from pink at low temperatures to green at high temperatures. This change is observed in a wide range of temperatures, from 200 to 900°C. The colour transition temperature threshold can be varied depending on the concentration of chromium doped in the Al_2O_3 lattice: 5% Cr_2O_3-95%Al_2O_3 changes from red to green at about 250°C, or 10% Cr_2O_3-90% Al_2O_3 changes from red to green / gray in the range 400-450°C.

Crystalline ZnO has the property of changing its colour (it is thermotropic) from white to yellow - green / reddish on heating (depending on temperature) and on cooling it returns to white. This colour variation is due to the formation of a non-stoichiometric oxide, by losing a small percentage of oxygen, for example for the temperature of 800°C, the formula is $Zn_{1+x}O$, where x = 0.00007 ($ZnO \leftrightarrow Zn_{1+x}O$). As a thermochromic material, it is used alone or in composite materials (Chanakul *et al*., 2013).

Ga-based oxides are reported as a new host for inorganic reversible thermochromic materials. Doping them with transition metals from "d" block is an effective way to control the electronic spectrum. The multi-coloured reversible thermochromic materials were prepared with $Er_3Ga_5O_{12}$ doped with Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} following a solid-state reaction at high temperature. Colour parameters depending on temperature were explored in the range of 20-460°C (Liu *et al*., 2019).

2.3.2. *Sulphides, Selenides and Other Compounds*

Besides the oxides, other classes of inorganic compounds have thermochromic properties (Cheng *et al*., 2018). Thus, sulphides, selenides, phosphates or complex combinations, simple or in hybrid structures have many practical applications. For example, MoO_3 films doped with ZnSe or CdS have been studied for the use in display devices (Tomás *et al*., 2009; Traiphol *et al*., 2009). The VO_2 / ZnS combination has applications in adaptive infrared camouflage (Ji *et al*., 2018) and Bismuth-containing multifunctional phosphate ($Mg_2Bi(PO_4)O_2$) has also been studied for thermochromic applications (Li *et al.*, 2020). Also, in the category of phosphates with thermochromic uses is $SrZr_4(PO_4)_6$ doped with V, Ca or Ba (Yanase *et al*., 2019). Some authors have studied the thermochromic properties of $BaCO_3$ doped with different percentages of Fe_2O_3 that allows the displaying of a large temperature range. Significant colour change is associated with decarbonation and the formation of mixed oxide of barium and the transition metal. The colour difference between the reagent mixture and the mixed oxide resulted is generally due to the increase of the oxidation state of the transition metal (Lataste *et al*., 2011).

Also, quite well studied are polycrystalline $CuMo_{1-x}W_xO_4$ solid solutions (Pudza *et al*., 2021), binuclear complex $Re_2(CO)_6(L)Br_2]$, with L= 1,2,4,5-tetrakis(diphenylphosphino)benzene (Petyuk *et al*., 2020) or tetrazole-functionalized iodo-cuprate (Yang *et al*., 2020).

3. Conclusions

Thermochromic materials are a new research topic, both in terms of synthesis methods, physical-chemical properties and, most importantly, practical applications. Often, the high transition temperature, the cost of these materials and the difficulties of synthesis limit the study of their possible applications. It is observed from the literature review, that in order to make the widespread use of these materials accessible, it is best to go for inorganic-organic hybrid materials, with specific dopants, which lower the transition temperature and improve the physical-chemical and mechanical properties.

REFERENCES

Abdullah N., Abu Talib Abd. R., Jaafar A.A., Amran M., Salleh M., Chong W.T., *The Basics and Issues of Thermochromic Liquid Crystal Calibrations*, Experimental Thermal and Fluid Science, **34,** 1089-1121 (2010).

Bharara M., Cobb J.E., Claremont D.J., *Thermography and Thermometry in the Assessment of Diabetic Neuropathic Foot: A Case for Furthering the Role of Thermal Techniques*, The International Journal of Lower Extremity Wounds, **5**, *4*, 250-260 (2006).

Baron M.G., Elie M., *Temperature Sensing Using Reversible Thermochromic Polymeric Films*, Sensors and Actuators B: Chemical, **90**, *1–3*, 20, 271-275 (2003).

Blagojevic V.A., Obradović N.N., Cvjeticanin N., Minić D.M., *Influence of Dimensionality on Phase Transition in* VO_2 *Nanocrystals*, Science of Sintering, **45**, *3*, 305-311, DOI: 10.2298/SOS1303305B (2013).

Chanakul A., Traiphol N., Traiphol R., *Controlling the Reversible Thermochromism of Polydiacetylene/Zinc Oxide Nanocomposites by Varying Alkyl Chain Length*, Journal of Colloid and Interface Science, **389**, 106-114 (2013).

Chang T., Zhu Y., Huang J., Luo H., Jin P., Cao X., *Flexible* VO_2 *Thermochromic Films with Narrow Hysteresis Loops*, Solar Energy Materials and Solar Cells, **219**, 110799 (2021).

Cheng Y., Zhang X., Fang C., Chen J., Wang Z., *Discoloration Mechanism, Structures and Recent Applications of Thermochromic Materials via Different Methods: A Review*, Journal of Materials Science & Technology, **34**, 2225-2234 (2018).

Guan Y., Zhang L., Wang D., West J.L., Fu S., *Preparation of Thermochromic Liquid Crystal Microcapsules for Intelligent Functional Fiber*, Materials and Design **147**, 28-34 (2018).

Huo J., Hu Z., He G., Hong X., Yang Z., Luo S., Ye X., Li Y., Zhang Y., Zhang M., Chen H., Fan T., Zhang Y., Xiong B., Wang Z., Zhu Z., Chen D., *High Temperature Thermochromic Polydiacetylenes: Design and Colorimetric Properties*, Applied Surface Science, **423**, 951-956 (2017).

Jakovljevic M.S., Kulcar R., Friskovec M., Lozo B., Gunde M.K., *Light Fastness of Liquid Crystal-Based Thermochromic Printing Inks*, Dyes and Pigments, **180** 108482 (2020).

Ji H., Liu D., Zhang C., Cheng H., VO_2*/ZnS Core-Shell Nanoparticle for the Adaptive Infrared Camouflage Application with Modified Color and Enhanced Oxidation Resistance*, Solar Energy Materials and Solar Cells, **176**, 1-8 (2018).

Jimenez R., Duarte F., Nuti S., Campo J.A., Lodeiro C., Cano M., Cuerva C., *Thermochromic and Acidochromic Properties of Polymer Films Doped with Pyridyl-β-Diketonate Boron(III) Complexes*, Dyes and Pigments, **177**, 108272 (2020).

Kats M.A., Romain B., Shuyan Z., Genevet P., Ko C., Ramanathan S., Capasso F., *Vanadium Dioxide as a Natural Disordered Metamaterial: Perfect Thermal Emission and Large Broadband Negative Differential Thermal Emittance*, Physical Review X, **3**, *4*, 041004, doi:10.1103/PhysRevX.3.041004 (2013).

Kim J., Ko C., Frenzel A., Ramanathan S., Hoffman J.E., *Nanoscale Imaging and Control of Resistance Switching in VO_2 at Room Temperature*, Applied Physics Letters, **96**, *21*, 213106 doi:10.1063/1.3435466 (2010).

Korotcenkov G., Brinzari V., Cho B.K., *In_2O_3- and SnO_2-Based Thin Film Ozone Sensors: Fundamentals*, Journal of Sensors, |Article ID 3816094 | https://doi.org/10.1155/2016/3816094 (2016).

Lataste E., Demourgues A., Salmi J., Naporea C., Gaudon M., *Thermochromic Behavior (400 < T°C < 1200°C) of Barium Carbonate/Binary Metal Oxide Mixtures*, Dyes and Pigments, **91**, 396e403 (2011).

Lee S., Hippalgaonkar K., Yang F., Hong J., Ko C., Suh J., Liu K., Wang K. Urban J.J., *Anomalously Low Electronic Thermal Conductivity in Metallic Vanadium Dioxide*, Science, **355**, *6323*, 371-374. doi:10.1126/science.aag0410 (2017).

Lee S., Kim J.-Y., Chen X., Yoon J., *Recent Progress in Stimuli-Induced Polydiacetylenes for Sensing Temperature, Chemical and Biological Targets*, Chemical Communications, **52**, *59*, 9178-9196 (2016).

Li J., Li H., Ding S., Wang Y., *Systemic Development of a Bismuth-Containing Multifunctional Phosphate for Field Emission Displays and Thermochromic Applications*, Chemical Engineering Journal, **381**, 122610 (2020).

Liang X., Chen M., Chen G., Li C., Han C., Zhang J., Zhang J., Zhang L., Yang H., *Effects of Polymer Micro-Structures on the Thermo-Optical Properties of a Flexible Soft-Mater Film Based on Liquid Crystals / Polymer Composite*, Polymer, **146**, 20, 161-168 (2018).

Liu H., Qi H., Yuan L., Wang B., Hou C., Feng S., *Design Principles for 3d Electron Transfer in a Ga-Based Garnet to Enable High-Performance Reversible Thermochromic Material Color Maps*, Chem. Mater., **31**, *3*, 1048-1056 (2019).

Luo C.-C., Wang X.-J., Han L.-J. Jia Y.-G., Ying S.-M., Wang J.-W., *Preparation, Structure and Optical Properties of Thermochromic Liquid Crystal Compounds Containing (−)-Menthyl with Selective Reflection*, Journal of Molecular Liquids, **275**, 241-250 (2019).

Mandal J., Jia M., Overvig A., Fu Y., Che E., Yu N., Yang Y., *Porous Polymers with Switchable Optical Transmittance for Optical and Thermal Regulation*, Joule **3**, 3088-3099 (2019).

Mergu N., Son Y.-A., *Design and Synthesis of Polydiacetylenes, and their Low Temperature Irreversible Thermochromic Properties*, Dyes and Pigments, **184** 108839 (2021).

Nguyen D.K., Lee H., Kim I -T., *Synthesis and Thermochromic Properties of Cr-Doped Al2O3 for a Reversible Thermochromic Sensor*, Materials, **10**, *5*, 476, https://doi.org/10.3390/ma10050476 (2017).

Pattanayak M., Hoque Md N.F., Zhaoyang F., Bernussi A., *Electrical Oscillation Generation with Current-Induced Resistivity Switching in VO_2 Micro-Channel Devices*, Science and Technology of Advanced Materials, **19**, *1*, 693-701, doi:10.1080/14686996.2018.1521249 (2018).

Petyuk M.Y., Berezin A.S., Bagryanskaya I.Y., Artyushin O.I., Brel V.K., Artemev A.V., *A Dinuclear Re(I) Tricarbonyl Complex Showing Thermochromic Luminescence*, Inorganic Chemistry Communications, **119**, 108058 (2020).

Pudza I., Kalinko A., Cintins A., Kuzmin A., *Study of the Thermochromic Phase Transition in $CuMo_{1-x}W_xO_4$ Solid Solutions at the WL_3-Edge by Resonant X-Ray Emission Spectroscopy*, Acta Materialia, **205**, 116581 (2021).

Soreno Z.V., Puguan J.M.C, Kim H., *Thermochromic Transition Analysis of Elastomer Prepared from Azo Dye-Siloxane Blend*, Materials Chemistry and Physics, **240**, 122297 (2020).

Stasiek J.A., Kowalewski T.A., *Thermochromic Liquid Crystals Applied for Heat Transfer Research*, Opto-Electronics Review, **10**, *1*, 1-10 (2002).

Sun S., Gao Y., Han N., Zhang X.X., Li W., *Reversible Photochromic Energy Storage Polyurea Microcapsules via in-situ Polymerization*, Energy, **219**, 119630 (2021).

Traiphol S.A., Arvizu M.A., Zelaya-Angel O., Rodríguez P., *Effect of ZnSe Doping on the Photochromic and Thermochromic Properties of MoO_3 thin Films*, Thin Solid Films, **518**, 1332-1336 (2009).

Wang C., Zhao L., Liang Z., Dong B., Wan L., Wang S., *New Intelligent Multifunctional SiO_2/VO_2 Composite Films with Enhanced Infrared Light Regulation Performance, Solar Modulation Capability, and Superhydrophobicity*, Science and Technology of Advanced Materials, **8**, *1*, 563-573, doi:10.1080/14686996.2017.1360752 (2017).

Xie Y.M., Zhao X.P., Mofid S.A., Tan J.Y., Jelle B.P., Yang R.G., *Influence of Shell Materials on the Optical Performance of VO_2 Coreeshell Nanoparticleebased Thermochromic Films*, Materials Today Nano, **13**, 100102 (2021).

Yan Q., Wei Z., Lin P., Cheng Z., Pu M., Huang Z., Lin W., *Polymer Stabilized Cholesteric Liquid Crystal Particles with High Thermal Stability*, Optical Materials Express, **8**, 6, 1537 (2018).

Yanase I., Oomori K., Kobayashi H., *Substitution Effect of V, Ca, and Ba on the Thermochromic Properties and Thermal Expansion of $SrZr_4(PO_4)_6$*, Ceramics International, **45**, *4*, 5001-5007 (2019).

Yang L., Zhou J., Fu L., *Thermochromic Luminescent Properties of a Tetrazole-Functionalized Iodocuprate without Cuprophilic Interaction*, Dyes and Pigments, **174**, 108039 (2020).

MATERIALE TERMOCROMATICE: OXIZI CU APLICAȚII ÎN TEHNOLOGII INTELIGENTE

(Rezumat)

În ultimii ani au fost studiate și dezvoltate multe tipuri de materiale inteligente, datorită aplicațiilor lor în industrie (militară, aerospațială, medicală, de construcții) și posibilităților de a dezvolta produse prietenoase cu mediul înconjurător (reducerea costului de întreținere clădirilor prin folosirea de materiale de construcție / ferestre inteligente, reducerea poluării prin utilizarea de materiale active fotocatalitic). În categoria materialelor inteligente se integrează si materialele termocromatice, capabile să își schimbe culoarea la variația de temperatură. În această lucrare este prezentat fenomenul de termocromatism, principalele clase de materiale termocromatice, cu accent pe materialele oxidice, metode de obținere, aplicațiile lor precum şi stadiul actual al cercetărilor în domeniu, privind mecanisme de producere a fenomenelor termocromatice.