Numerical Study of Thermo-Chromic Properties of VO_2-Polymer Composites Coatings Applied to Building Thermal Insulation

Omar Iken [#1], Rachid Agounoun[#], Miloud Rahmoune[#], Khalid Sbai[#], Amine Zoubir[#],
Rachid Saadani[#], Abdelali Rahmani[*]

[#] Laboratoire d'Etude des Matériaux Avancés et Applications (LEM2A), Université Moulay Ismail, Faculté des sciences, Ecole Supérieure de Technologie Meknès, Morocco

[1] omar.iken0@gmail.com

[*] Laboratoire d'Etude des Matériaux Avancés et Applications (LEM2A), Université Moulay Ismail, Faculté des sciences, Meknès, Morocco

***Abstract*— Kubelka-Munk (KM) (two-flux) model was computed to solve the radiative transfer equation. The transmittance and reflectance spectra were calculated for Vanadium dioxide (VO_2) particulate film embedded in a polymer matrix. Numerical results in this work show a high similarity with experimental results reported in literature. The influence of particles concentration and thickness on the absorption coefficient K and temperature dependence of VO_2 transmittance were verified. A comparison with a four-flux model confirms the exactitude of our results. Calculations were done in the 300-2500 nm solar optical wavelength range for several particles concentration values of 1, 0.5, 0.25 and 0.1 and several thicknesses for two values of temperature 22°C and 100°C under and above (VO_2) Transition.**

Keywords: Kubelka-Munk Model, Nanoparticles Concentration, Solar Modulation, VO_2 Thermo-chromic Properties.

I. INTRODUCTION

VO_2 is a thermo-chromic material which has the capacity to switch from an insulating state to a metallic state around a transition temperature of about $T_c = 68°C$ according to F.J. Morin et al. [1].

The insulating state of VO_2 is characterized by a high transparency to solar radiations of visible and near infrared spectrum, contrarily to the metallic state in which VO_2 becomes more reflective to the infrared spectrum. A change in the crystallographic structure of VO_2 is the cause of this Insulator/Metal transition. For low temperatures $T < T_c$, the VO_2 crystal lattice is monoclinic, therefore, inter-atomic distances V—O and V—V are relatively big and an energy gap between electronic bands is created, H.W. Verleur et al. [2]. With this gap, VO_2 behaves as a semiconductor (SC) material according to Goodenough [3]. From an optical point of view, empty sites in the (SC) crystal structure are much important, which explains the high transparency to solar spectrum especially to near infrared wavelengths; this part of the spectrum is known as the main heat energy transporter. For high temperatures $T > T_c$, the VO_2 crystal structure changes to quadratic geometry (rutile), where the inter-atomic distances become much smaller, thus the energy gap disappears and the crystal behaves as a metal. Optically speaking, for these temperatures, VO_2 reflects a big part of near infrared radiations.

The ability of this material to change its optical properties depending on temperature makes of it a good candidate for applications in buildings thermal insulation. Example of these applications is energy efficient windows based on VO_2 thin films proposed by C.M. Lampert et al. [4], M. Saeli et al. [5] and Y. Gao et al. [6], this application uses the principle of radiative thermal rectification to regulate heat transfer and energy consumption in buildings. So far, the use of VO_2 in these applications is blocked by two limitations. The first one is about the high value of the transition temperature that should be near to 25°C (comfort temperature), this problem has been solved by Tungsten (W) and Fluor (F) doped VO_2 with small concentrations according to W. Burkhardt et al. [7]. The second limitation is related to the high absorption in the visible region of the solar spectrum; this phenomenon has a negative influence on the luminance of VO_2 coated windows, we can overcome it by optimizing the concentration of the absorbing particles, this solution will be treated numerically in this paper. This problem does not affect the wall applications because there is no need for high luminance and here is an invitation to more researches in this direction.

VO_2 nanoparticles are characterized by their transmittance and reflectance. Those two spectra are highly dependent on particles absorption and scattering properties. In this work, we will focus on the influence of the absorption phenomenon generated by the narrow optical band gap in VO_2 according to C.G. Granqvist et al. [8]. The numerical model used here to calculate the transmittance and the reflectance of the nanocomposite is a Two-flux model based on Kubelka-Munk (KM) theory, this model is unable to solve the particles scattering part of the radiative transfer equation because of the acute anisotropic single scattering which requires a high accuracy M.Q. Brewster et al. [9]. This type of scattering is generated by particles with small dimensions (radii $r << \lambda$) considered as a low scattering condition by K. Laaksonen et al. [10].

The two-flux model is a simple method developed by P. Kubelka et al. [11] to solve the radiative transfer equation which describes light propagation through a scattering and absorbing media. This model considers two propagation directions with descendent (transmitted) and ascendant (reflected) light flux, those two flux include absorption and scattering interactions in the illuminated media, with K and S are respectively the absorbed fraction (absorption coefficient) and the scattered fraction (scattering coefficient) of light flux.

In this work, we present a numerical characterization of VO_2 Particulate film embedded in a polymer matrix using the (KM) theory. We show the influence of the matrix thickness and the particles concentration on the absorption coefficient K, scattering is neglected because of low accuracy in the two-flux model. We make a comparison with results computed by the four-flux model and with experimental results. We calculate the transmittance for two values of temperature under and above VO_2 transition temperature 22°C and 100°C to verify numerically thermo-chromism properties.

Theory section outlines the model used for our calculations, results section presents our findings discussed and compared with recent works. The last section recapitulates results and conclusions.

II. TEORY

We consider a transparent polymer matrix with x thickness containing VO_2 nanoparticles with an equivalent thickness $dx = 50nm$ (particulate film), see fig 1. This configuration is based on some recent experimental works Y. Gao et al. [6] and I.G. Madida et al. [12], which we are here trying to verify numerically.

The incident solar radiation is divided in two fluxes i(x) and j(x) with opposite directions. When the flux j(x) passes through VO_2 particles dx, a fraction is lost (-) by absorption Kj(x) and by scattering Sj(x), yet i(x) acquire (+) Si(x) by scattering. The same reasoning is applied in the opposite direction for i(x), thus the fraction (K+S)i(x) is acquired and Sj(x) is lost. This analysis leads to the following equations system:

$$\begin{cases} \frac{di(x)}{dx} = (K+S)i(x) - Sj(x) \\ \frac{dj(x)}{dx} = -(K+S)j(x) + Si(x) \end{cases} \qquad (1)$$

K and S are considered respectively as the KM phenomenological coefficients of absorption and scattering according to the new KM formulation reported by P. Emmel [13]. KM theory supposes a perfectly diffuse source; therefore, K can be related to the spectral extinction $k(\lambda, T)$ of the Beer-Lambert low. The relation between K and $k(\lambda, T)$ is demonstrated by photometric calculations:

$$K = 2.ln10.c.k(\lambda, T) \qquad (2)$$

Where "c" is the concentration of VO_2 nanoparticles, it has the same signification as the volume fraction $f = NV$ reported by K. Laaksonen et al. [10], it refers to the number of particles N found in a unit volume of the polymer matrix and V is the volume of a single particle.

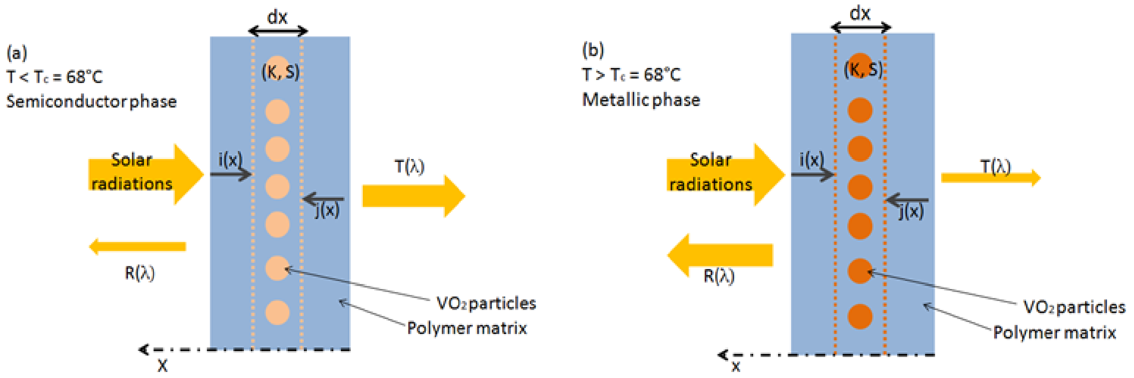


Fig. 1. Schematic diagram of the model used to calculate transmittance and reflectance spectra for a VO2 particulate film embedded in a polymer matrix.

The variation of this concentration has a big influence on the absorption rate; therefore a parametric study based on its variation would give optimal values of VO_2 nanoparticles concentration to overcome the high absorption localized in the visible spectrum.

Scattering coefficient S depends on the surface ratio between particles and polymer matrix, this ratio is considered as the scattering cross section which is related to the Beer-Lambert low through the total cross section formula, and thus S could be written as:

$$S = ln10.c.n(\lambda,T).\pi.r^2/(dx.L) \tag{3}$$

We consider spherical VO2 nanoparticles with radii "r". $dx \times L$ refers to the polymer surface containing VO_2 nanoparticles with refractive index "$n(\lambda,T)$". We fixed the radius value in 5 nm to verify low scattering condition $(r \ll \lambda)$; therefore, the scattering phenomenon is limited to the anisotropic single scattering with low intensity. Computing this type of low scattering requires high accuracy which is not possible with the KM method.

Our calculations are based on the matrix method represented by P. Emmel [13] as a new formulation of KM theory, thus equation (1) is written as:

$$\begin{bmatrix} \frac{di(x)}{dx} \\ \frac{dj(x)}{dx} \end{bmatrix} = \underbrace{\begin{bmatrix} K+S & -S \\ S & -(K+S) \end{bmatrix}}_{\text{M}} \begin{bmatrix} i(x) \\ j(x) \end{bmatrix} \tag{4}$$

Solutions of this differential equation are given by the exponential of the matrix M as:

$$\begin{bmatrix} i(x) \\ j(x) \end{bmatrix} = \exp[XM] \times \begin{bmatrix} i(x_0) \\ j(x_0) \end{bmatrix} = \begin{bmatrix} t & u \\ v & w \end{bmatrix} \times \begin{bmatrix} i(x_0) \\ j(x_0) \end{bmatrix} \tag{5}$$

With t, u, v and w are functions of the film thickness $X = (x - x_0)$, the absorption coefficient K and the scattering coefficient S, so we can write:

$$j(X) = \frac{v+wR_g}{t+uR_g}\,.i(X) \text{ And } R = \frac{j(X)}{i(X)} = \frac{v+wR_g}{t+uR_g} \tag{6}$$

Rg is the backing reflectance of the polymer matrix at x_0 with $R_g = j(x_0)/i(x_0) = 0.1$ considered as standard glass. After the determination of Eigen values $\alpha_1 = b.S$ et $\alpha_2 = -b.S$ and Eigen vectors:

$$e_1 = \begin{bmatrix} 1 \\ \alpha_1 = \frac{K+S-\sqrt{K^2+2KS}}{S} \end{bmatrix} and\ e_2 = \begin{bmatrix} 1 \\ \alpha_2 = \frac{K+S+\sqrt{K^2+2KS}}{S} \end{bmatrix} \tag{7}$$

Then the exponential of the matrix M can be written:

$$exp[XM] = V \begin{bmatrix} exp[\alpha_1 X] & 0 \\ 0 & exp[\alpha_2 X] \end{bmatrix} V^{-1} \tag{8}$$

$$V = \begin{bmatrix} 1 & 1 \\ (a-b) & (a+b) \end{bmatrix} and\ V^{-1} = \frac{1}{2b} \begin{bmatrix} (a+b) & -1 \\ -(a-b) & 1 \end{bmatrix} \tag{9}$$

With V is the transfer matrix, $b = \sqrt{a^2 - 1}$ and $a = (K + S)/S$

Transmittance and reflectance are given by:

$$T = \frac{b}{a\sinh(bSX) + b\cosh(bSX)}\ and\ R = \frac{1 - R_g(a - b\,coth(bSX))}{a + b\,coth(bSX) - R_g} \tag{10}$$

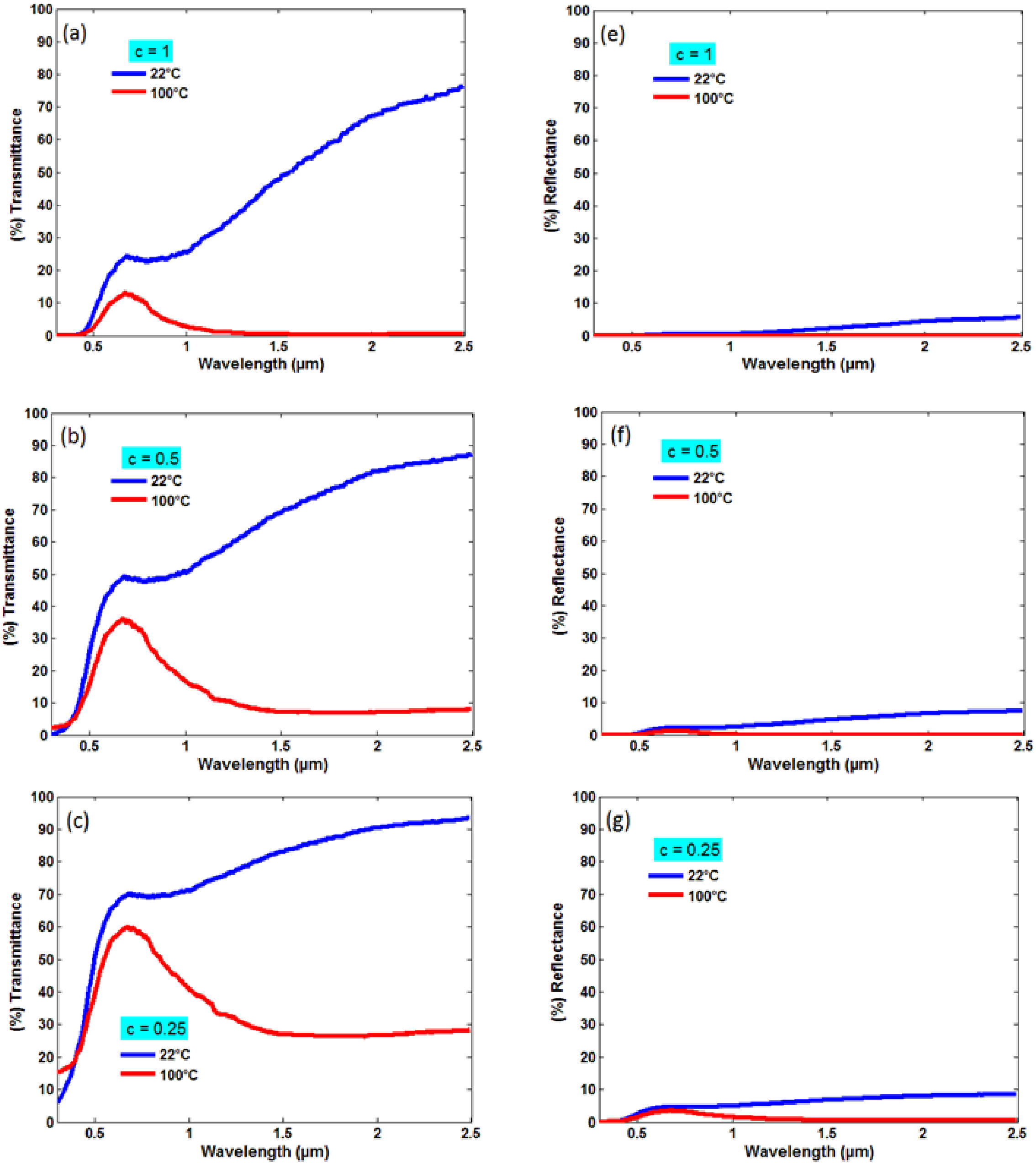
III. RESULTS AND DISCUSSION

We calculated the spectral transmittance and reflectance for several nanoparticles concentrations 1, 0.5, 0.25 and 0.1. Concentration is directly related to the degree of porosity of the particulate VO_2 film, the porosity decreases as the concentration increases. For high concentration (volume fraction near to 1), nanoparticles occupy the entire volume, thus, we obtain low porosity and high absorbance because of the high number of absorbing particles. As a result, the transmittance drop very clearly in the visible region, see (fig 2-a, 2-b). In the case of low concentration, porosity becomes more important and absorbance decreases, therefore, the transmittance increases considerably in the majority of the spectrum, see (fig 2-c, 2-d).

Our numerical results are in good agreement with experimental findings obtained by Gao et al. [6] for VO_2 particulate film deposited by polymer-assisted sol-gel process, especially between transmittance at $c = 0.5$ (fig 2-b) and transmittance of simples annealed at high temperatures for a long time. Annealing changes the particles ratio between the polymer and VO_2 because of polymer evaporation, which is equivalent to increasing the nanoparticles concentration.

Comparing our results to those calculated by K. Laaksonen et al. [10] using the four-flux method, we noticed a huge difference in transmittance for metallic state particularly in the infrared part of the spectrum with an increase in transmittance after a minimum at 1200 nm for the four-flux method, while in our results, the metallic state transmittance continue decreasing in infrared. This can be explained in two points. In one hand, there is a lack of accuracy of the two-flux method related to scattering phenomena produced by particles with small dimensions ($r \ll \lambda$). In the other hand, a morphological difference exists the between particulate films simulated in this work and nanoparticles studied in [10].

Another aspect that we can notice from our results is that the optical modulation ΔT which occurs at the transition between semiconductor and metallic state [14-18] depends on VO_2 concentration. ΔT For the concentration $c = 0.1$ at $\lambda = 2\mu m$ is about 37% (fig 2-d) while for $c = 0.5$ at the same wavelength the modulation is about 70% (fig 2-b). this dependence was found experimentally by I.G. Madida et al. [12] for a submicronic VO_2-PVP composite by modifying the relative mass ratio $C_{VO_2/PVP}$ which is the same as our "c" value, they reported that the higher is the relative mass ratio, the larger is the optical modulation and this is what we found numerically.



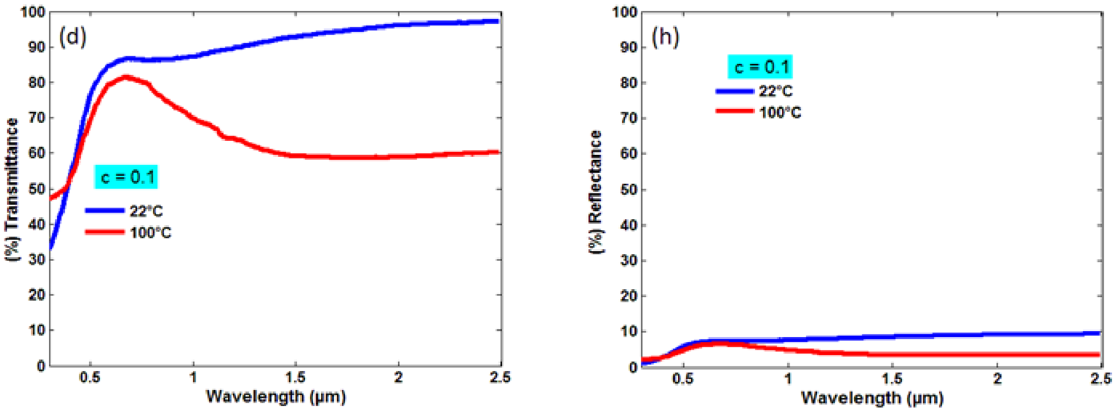


Fig. 2. Optical transmittance and reflectance spectra for four different VO2 particles concentrations at two temperatures 22°C and 100°C

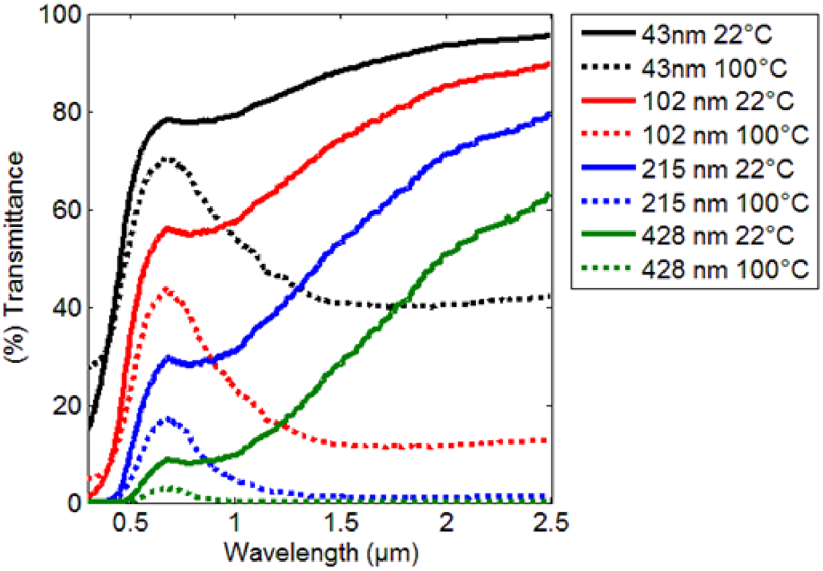


Fig. 3. Optical transmittance spectra for four different thicknesses of the VO2 particulate film at 22°C and 100°C.

In figure 3, we tried to see the impact of thickness on the thermo-chromic properties of the VO$_2$ particulate film. We fixed the concentration at a value of 0.2 and calculate the transmittance at 22°C and 100°C for thicknesses of 43 nm, 102 nm, 215 and 428 nm. We found that thickness has the same influence as concentration. The transmittance decreases as the thickness increases because the ratio $VO_2/Polymer$ tends to 1, so the absorption increases. We found also that the optical modulation across the VO$_2$ transition is highly dependent to thickness. For example, a 102 nm film exhibits a transmittance change of 72% at 2μm whereas a 43nm film shows a change of 52% at the same wavelength (see figure 3). The same behavior was noticed experimentally by Gao et al. [6] for VO$_2$ particulate films. The impact of thickness can be used as an adjustment tool for the optical modulation.

Refractive index $n(\lambda, T)$ and extinction coefficient $k(\lambda, T)$ employed in this study were measured at 22°C and 100°C by N.R. Mlyuka et al [20]. We were autorized to use this data by Mr. C.G. Granqvist.

IV. CONCLUSION

In the present work, we solved the radiative transfer equation in aVO$_2$ particulate film embedded in a polymer matrix using a two-flux method based on Kubelka-Munk theory. Transmittance and reflectance were calculated for several values of VO$_2$ particles concentration and thicknesses. In this study, we verified numerically the high dependence of absorption phenomena to particles concentration and thickness. We noticed that our results are in good agreement with experimental studies realized in the same context. We mentioned the difference between a two-flux and a four flux method regarding the scattering issue. We validated the fact that optical modulation at VO$_2$ transition depends also on the particles concentration and thickness. VO$_2$ coatings are considered as a reliable solution for buildings thermal insulation, it means that in winter, VO$_2$ allows having thermal gains inside buildings by letting the solar radiations enter and vice versa, in summer, VO$_2$ blocks the radiative heat transfer.

ACKNOWLEDGMENT

We are grateful to Mr C.G. Granqvist for his authorization to use data of refractive index and extinction coefficient measured by his team at 22°C and 100°C.

REFERENCES

[1] F.J. Morin. (1959) "Oxides which show metal-to-insulator transition at the neel temperature," Physical review letters (3), 34-36.

[2] Hans W. Verleur, A.S. Barker. Jr, C.N. Berglund, (1968) "Optical properties of VO_2 between 0.25 and 5 eV," Physical review 172 vol. 3, 788-798.

[3] J.B. Goodenough , "J. Solid state chem," Vol. 3, (1971), 490.

[4] C.M. Lampert, C.G. Granqvist (1990) "Large-Area Chromogenics: Materials and Devices for Transmittance Control," SPIE Institutes for Advanced Optical Technologies, Vol. 4 (SPIE Opt Engr Press, Bellingham, WA, USA).

[5] M. Saeli, C. Piccirillo, M.E.A. Warwick, R.Binions, "Thermochromic Thin Films: Synthesis, Properties and Energy Consumption Modelling," Materials and processes for energy: communicating current research and technological developments.

[6] Yanfeng Gao, Litao Kang, Zhang Chen and Hongjie Luo. (2011) "Solution processing of Nanoceramic VO_2 Thin Films for Application to smart Windows, Nanofabrication," Dr. Yoshitake Masuda (Ed.), ISBN: 978-953-307-912-7, InTech, Available from: http://www.intechopen.com/books/nanofabrication/Solution-processing-of-nanoceramics-vo2-thin-films-for-application-to-smart-windows

[7] W. Burkhardt, T. Christmann, B.K. Meyer, W. Niessner, D. Schalch, A. Scharmann. (1999) "W- and F-doped VO_2 films studied by photoelectron spectrometry," Thin Solid Films 345, 229-235.

[8] C.G. Granqvist, Yu-Xia Ji, J. Montero, Gunnar A Niklasson. (2016) "Thermochormic vanadium-dioxide-besed thin films and nanoparticles: Survey of some buildings-related advances" INERA Conference Vapor Phase Technologies for Metal Oxide and Carbon Nanostructures.

[9] M.Q. Brewster, C.L. Tien. (1982) "Examination of the Two-Flux model for radiative transfer in particular systems," Journal of Heat and Mass Transfer (12), Vol. 25, 1905-1907.

[10] K. Laaksonen, S.-Y. Li, S.R. Puisto, N.K.J. Rostedt, T. Ala-Nissila, C.G. Granqvist, R.M. Nieminen, G.A. Niklasson. (2014) "Nanoparticles of TiO_2 and VO_2 in dielectric media: Conditions for low optical scattering, and comparison between effective medium and four-flux theories," Solar Energy Materials and Solar cells vol. 130, 132-137.

[11] P. Kubelka. (1948) "New Contributions to the Optics of Intensely Light-scattering Materials. Part I," Journal of the optical society of America, Vol. 38, 448-457.

[12] I.G. Madida, A. Simo, B. Sone, A. Maity, J.B. Kana Kana, A. Gibaud, G.Merad, F.T. Thema, M. Maaza. (2014) "Submicronic VO_2-PVP composites coatings for smart windows applications and solar heat management," Journal of Solar Energy, Vol. 107, 758-769.

[13] P. Emmel. (2000) " Nouvelle formulation du modèle de Kubelka et Munk avec application aux ancres fluorescentes," Actes de l'Ecole de Printemps –le Pays d'Apt en Couleurs, Apt et Roussillon, France, 87-96.

[14] S.-Y. Li, G.A. Niklasson, C.G. Granqvist. (2010) "Nanothermochromics : Calculations for VO_2 nanoparticles in dielectric hosts show much improved luminous transmittance and solar energy transmittance modulation," J. App. Phys. Vol. 108.

[15] S.-Y. Li, G.A. Niklasson, C.G. Granqvist. (2011) "Nanothermochromics withVO_2-based core-shell structures: calculated luminous and solar optical properties," J. App. Phys. Vol. 109.

[16] S.-Y. Li, K. Namura, M. Suzuki, G.A. Niklasson, C.G. Granqvist. (2013) "Thermochromic VO_2 nanorods made by sputter deposition: growth conditions and optical modeling," J. App. Phys. Vol. 114.

[17] S.-Y. Li, G.A. Niklasson, C.G. Granqvist. (2014) "Thermochromic undoped and Mg-doped VO_2 thin films and nanoparticles: optical properties and performance limits for energy efficient windows," J. App. Phys. Vol. 115.

[18] Y.Zhou, A. Huang, Y. Li, S. Ji, Y. Gao, P. Jin. (2014) "Surface Plasmon resonance induced excellent solar control for VO_2@SiO_2 nanorods-based thermochromic foils," Nanoscale, Vol. 5, 9208-9213.

[19] J. Montero, Yu-Xia Ji, C.G. Granqvist, G.A. Niklasson. (2016) "Thermochromic light scattering from particulate VO_2 layers," Journal of Applied Physics, Vol. 119, 085302-1-6.

[20] N.R. Mlyuka, G.A. Niklasson, C.G. Granqvist. (2009) "Thermochromic VO_2-based multi-layer films with enhanced luminous transmittance and solar modulation," Phys. Status Solidi A, Vol. 206, 2155-2160.

AUTHOR PROFILE

Omar Iken is a Ph.D student at Moulay Ismail University. He received a first MSc. Degree in Photonics, Micro and Nanotechnologies and Time-Frequency from the University of Franche-Comté (France), and a second MSc. Degree in Instrumental Development for Micro and Nanotechnologies from the University of Lyon 1 (France). His Ph.D subject is about radiative thermal rectification applied to building thermal insulation. He is focused on thermo-chromic materials at nanoscale.

Rachid Agounoun is a senior lecturer at University Moulay Ismail, Morocco. He received the MSc. Degree (Magister) in mechanics and energetic system from the Université de Lorraine, Nancy, France and the Ph.D degree in science for engineers from the Université de Lorraine, Nancy, France. He is an active researcher at Thermal & Material Research Unit (advanced materials and energy system). His area of research includes Thermal Comfort, Building Thermal Simulation, renewable energy and Porous Media.

Amine Zoubir is a senior lecturer at University Moulay Ismail, Morocco. He received the MSc. Degree (Magister) in fluid mechanics from the University of Lyon 1 (France) and the Ph.D degree in Mechanics, Energetics, Civil Engineering and Acoustics of INSA Lyon (France). He is an active researcher at Thermal & Material Research Unit (advanced materials and energy system). His area of research are focused on the numerical modeling of convective heat transfer and around the diagnosis of energy performance in buildings.

Miloud Rahmoune is a full professor at Moulay Ismail University. He received his Msc. Degree in applied mechanics from Université Montpellier 2 (France) and his Ph.D. degrees in Mechatronics from Universit Montpellier 2 (France) and Universite´ Hassan II Mohammedia, in 1993 and 1996 respectively. His research interests include structural Dynamics, active control, and smart materials.

Khalid Sbai is a full professor since 2001 in Electronics. He received his M.sc. Degree in Electronics from Valencienne University (France) in 1996 and his Habilitation in Physics from Moulay Ismail University in 2008. His research interests include Structural studies, vibrational and electronic properties of carbon nanotubes.

Rachid Saadani is a senior lecturer at University Moulay Ismail, Morocco. Was born in Morocco in 1977. He received the MSc. Degree (Magister) in thermal and energetic system from the Universit Marne La Vallée, Paris Est, Paris, France and the Ph.D degree in science for engineers from the Universite´ Paris Est, Créteil, Paris. He is an active researcher at Thermal & Material Research Unit (advanced materials and energy system). His area of research includes Thermal Comfort, Building Thermal Simulation, renewable energy and Porous Media.

Abdelali Rahmani is a full professor at University Moulay Ismail, Morocco. He received the MSc. Degree in theoretical physics from the Universite´ Montpellier 2, France and the Ph.D degree in Materials science from the the Université Montpellier 2, France. He is the Director of Laboratory of Studies of Avanced Materials and Applications). His area of research includes Computational physics and nanomaterials.