Optical properties of rare-earth oxides and oxynitrides, ... towards "second generation" UV absorbers

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Abstract

"Second-generation" UV-blocking materials are needed. Using the fluorite-type rare-earth tungstates R_6WO_{12} as starting reference compounds, anionic or cationic substitutions were achieved in (R,R')-(W,Mo)-(O,N) systems, thus delimiting large solid solution domains. The continuous shift of the absorption edge in diffuse reflectance spectra towards lower energy values makes it possible to tune it at the required value of 3.1 eV (400 nm), with in several cases a steep enough slope. Attempts were also carried out in perovskite (A,R)-Ti-(O,N) systems (A = alkaline-earth, R = rare-earth) to isolate suitable oxynitride compositions.

Keywords: UV-absorber, absorption edge, optical properties, oxynitride.

Introduction

It is well known that UV radiations can cause irreversible damages to organic materials, human tissues included. The so-called "UV B" (wavelengths within the range 280-320 nm) are the most energetic, that often results in short term effects (sunburns). However, the "UV A" (320-400 nm), about which one has not cared for a long time, are not so harmless because of cumulative effects. So, an effective protection in the whole UV spectrum is more than necessary for outer applications. The filtering system can be incorporated into the material to be protected (plastics) or can cover it (varnish, skin protection).

To date, inorganic anti-UV are not totally satisfactory. Mainly TiO_2-based, rutile or anatase phase, they are often not effective at high wavelengths and engender whitening phenomena due to the high value of their refractive index (rutile: n = 2.72, anatase: n = 2.5) [1]. Potential challengers, with lower indices, are ZnO (n = 2.2) and CeO_2 (n = 2.05) whose absorption edge is also close to 400 nm (or 3.1 eV), the frontier between the UV part and the visible part of the electromagnetic spectrum.

The powder morphology is a crucial parameter which has to be adapted to each case. In particular, to avoid whitish aspect, nanosized particles are needed for TiO_2, while sizes of about 100 nm are sufficient for ZnO or CeO_2.

Furthermore, a major drawback of these "first-generation" UV-absorbers is their photocatalytic activity: under irradiation they generate oxidizing species which induce secondary reactions at the surface of the host matrix, with noticeable degradation.

The purpose of this study is to finalize the preparation of "second-generation" UV-blocking materials which are effective for the whole UV spectrum. A good candidate for such an application should satisfy the following specifications:

1/ absorption of all radiations with $\lambda < 400$ nm

2/ transmission of all the lower energy radiations

3/ as a consequence of 1) and 2), a steep absorption edge, as much as possible, defining the spectral selectivity

4/ a low refractive index in the Visible (however, a high refractive index in the UV gives a maximum opacity)

5/ no photocatalytic activity.

Modification in the chemical composition of a solid is often accompanied by changes in its physical or chemical properties. In case of a progressive modification inside a solid solution domain, it is possible to conceive new materials with properties particularly well fitted for

given applications by adjustment of the composition. Considering the optical absorption properties of semi-conducting compounds, a slight modification in composition can affect the width of the bandgap (and the position of the absorption edge) through a modification of the electronic structure.

In this paper, two types of solid solutions have been studied. Large composition domains have been evidenced in fluorite-type systems R-(W,Mo)-(O,N) (R = rare earth) [2] and in perovskite-type systems (A,R)-Ti-(O,N) (A = alkaline-earth) by involving cationic and/or anionic substitutions. In the case of fluorites, starting from a rare-earth tungstate absorbing in the UV, the width of the bandgap can be decreased to 3.1 eV (400 nm) by modifying the position either of the valence band (N/O substitution) or of the conduction band (Mo/W substitution). In the case of perovskites, N^{3-} substituting progressively for O^{2-} in a titanate $ATiO_3$ induces an increase in the anionic formal charge which can be compensated, according to a cross-substitution principle, by a trivalent rare-earth cation replacing the divalent alkaline-earth. Such a substitution results in a shift of the absorption edge towards higher wavelengths and in the possibility to adjust it to 400 nm.

Experimental

Preparation of rare-earth-based oxide precursors by the ceramic method has shown limits regarding homogeneity and reactivity of the products. Single phases are often difficult to prepare in a pure state and the difficulty increases with multinary oxides, as numerous other compositions are potentially accessible.

Several *chimie douce*-type processes have been developed to prepare oxide powders in order to improve their quality (purity, chemical homogeneity, etc..) and also their reactivity. Herein, the "amorphous citrate" route was preferentially used to synthesize oxide precursors. It involves citric acid as a complexing agent and is not, strictly speaking, a classic sol-gel process in the sense that no gel is formed by a metal-oxygen-metal network, but rather from

metal-organic complexes which yield after calcination ultrafine reactive powders with a good chemical homogeneity. The principle consists in preparing a solution containing the complexed cations in the desired ratios, afterwards the solution is evaporated until formation of a viscous liquid. A progressive heating to 250°C follows, then a calcination up to 500-600°C to get rid of all organics. The citrate route can be generalized to a large number of compositions which cannot be obtained via traditional methods. The use of citric acid presents several advantages such as formation of very stable solutions of more or less complex stoichiometries. The cation stoichiometry being the same in the solution and in the powdered residue, *a priori* any designed composition may be easily and rapidly obtained by this aqueous process.

Nitridation reactions were carried out in an alumina boat containing the oxide precursor powder placed inside an alumina tube through which ammonia gas flowed at a rate of 30-40 $l.h^{-1}$. The temperature was raised in the range 500-1000°C, depending on the precursor and system studied.

XRD powder patterns were recorded using a Philips (PW 3710 X'PERT) diffractometer operating with Cu K_α radiation (λ = 1.5418 Å). Nitrogen and oxygen contents were determined with a LECO TC-436 analyser using the inert gas fusion method, nitrogen as N_2 by thermal conductivity measurement, oxygen as CO_2 by infrared detection. Diffuse reflectance spectra were collected using a UV-Visible Varian Cary 100 spectrometer in which the absolute reflectance of the sample is compared with a "spectralon" standard (Labsphere Cie).

Results and discussion

Our first approach of solid solutions has concerned the systems R-(W,Mo)-(O,N), more particularly the rare-earth tungstates R_6WO_{12}. Y_6WO_{12} is a representative term of this anion-

defect fluorite-type series ($Y_6WO_{12}\square_2$ or $Y_{3.43}W_{0.57}O_{6.85}\square_{1.15}$), giving a white powder absorbing at 3.65 eV.

● Thermal ammonolysis of Y_6WO_{12} between 500 and 800°C for different times forms a series of oxynitrides with a defect fluorite-type structure [3,4]. The progressive anionic substitution of nitrogen for oxygen according to:

$$2N^{3-} + 1\square = 3O^{2-}$$

reaches the nitrogen-rich limit composition $Y_{3.43}W_{0.57}O_{4.3}N_{1.7}\square_2$. It is accompanied by a continuous shift of the absorption edge from 3.65 to 2.36 eV, as a consequence of an increased covalent character that leads to a decrease in the optical bandgap value (Table 1, Fig. 1). Hence, it is possible, by adjusting the nitrogen content, to obtain an oxynitride composition cutting off exactly at 3.1 eV. The nitrogen incorporation causes a decrease in the maximum of diffuse reflectance. Besides, less steep than for the starting oxide, the slope of the absorption edge does not change with nitrogen content. However, the spectral selectivity is not good enough for anti-UV application.

Table 1. $Y_6WO_{12-3x}N_{2y}$ oxynitrides synthesized from an oxide precursor issuing from the citrate route.

NH_3 treatment	**wt% N**	**Fluorite-type formulation**	**Colour**
500°C/5h	0.4	$Y_{3.43}W_{0.57}O_{6.63}N_{0.17}$	white
550°C/5h	1.2	$Y_{3.43}W_{0.57}O_{6.23}N_{0.40}$	yellow
600°C/60h	2	$Y_{3.43}W_{0.57}O_{5.77}N_{0.74}$	yellow
800°C/15h	2.9	$Y_{3.43}W_{0.57}O_{5.31}N_{1.03}$	mustard yellow

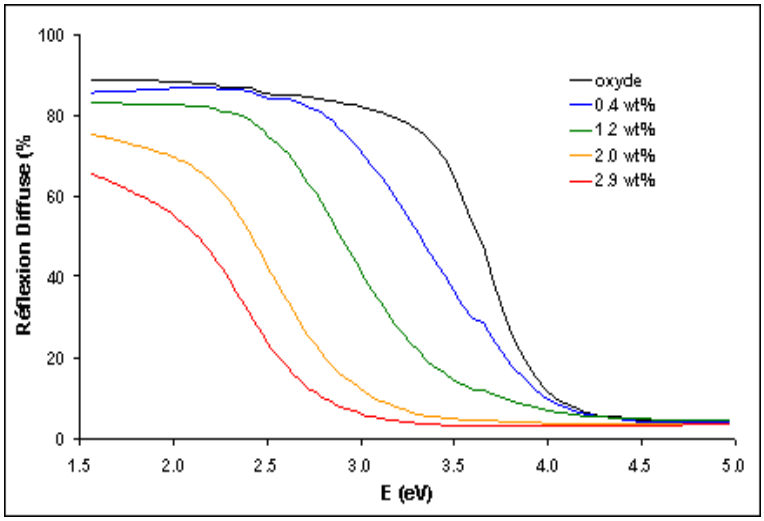

Fig. 1. Diffuse reflectance spectra of several $Y_{3.43}W_{0.57}O_{6.86-3x}N_{2x}$ ($0 \leq x \leq 0.52$) compositions.

● As molybdenum is more electronegative than tungsten, the energy level of the 4d(Mo) orbitals is lower than that of the 5d(W) orbitals. Consequently, a progressive cationic substitution of Mo for W induces a shift of the absorption edge, from 3.65 eV for Y_6WO_{12} to 2.80 eV for Y_6MoO_{12} (Fig. 2). The non linear variation law of the optical bandgap along the solid solution suggests that the 4d(Mo) and 5d(W) levels form two bands relatively distinct from each other [2]. We have succeeded in preparing an intermediate composition cutting off precisely at 3.1 eV. Moreover, after powder annealing, a steep absorption edge could be observed, giving a spectral selectivity of 0.49 nm, comparable to 0.29 nm for TiO_2 nanorutile). Consequently, $Y_6W_{1-x}Mo_xO_{12}$ compositions with x ~ 0.8-0.85 seem to be attractive materials for anti-UV purposes, as they have in addition a low refractive index (n ~ 2) [5]. Electron energy loss spectrometry (EELS) measurements, which are capable of distinguishing absorption from diffusion, are now in progress.

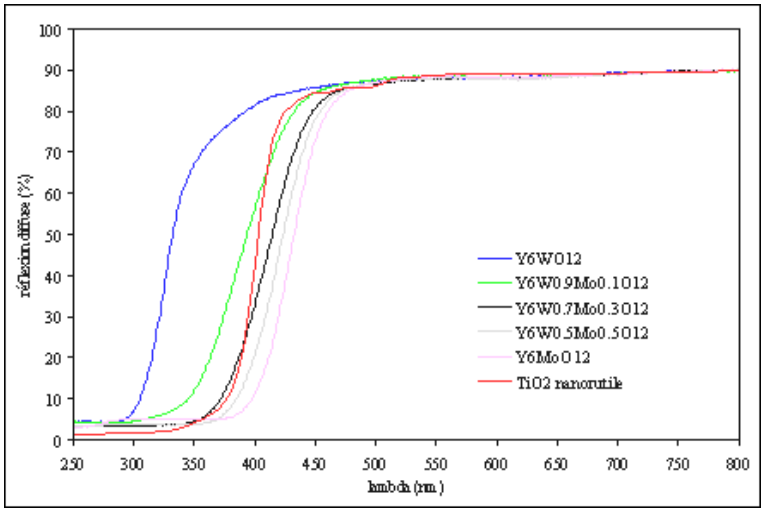

Fig. 2. Diffuse reflectance spectra of $Y_6W_{1-x}Mo_xO_{12}$ compositions, compared with TiO_2 nanorutile.

This study is funded, in particular, by the French Ministry of Trade and Industry under the acronym AUVIB [6]. The project aims at emerging new varnish and wood stain formulations containing stable UV-absorbers, in order to prevent or limit wood photodegradation.

Our second approach of solid solutions has concerned domains ranging between two perovskite-type limits: a white oxide $ATiO_3$ (A = Ca, Sr, Ba), absorbing in the UV, and a strongly coloured oxynitride $RTiO_2N$ (R = La, for ex.) [7]. Applying the cross-substitution principle:

$$R^{3+} + N^{3-} = A^{2+} + O^{2-}$$

we have attempted to synthesize intermediate compositions showing an absorption edge located between those of the two limits of the solid solution domain.

As illustrated in Fig. 3, the powder colour acts as an excellent first indicator to estimate the width of the bandgap and, consequently, the corresponding absorption edge position.

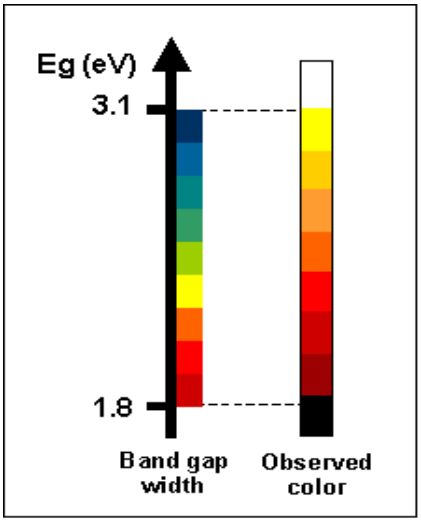

Fig. 3. Colour of the oxynitride powder as a function of the bandgap energy value.

The (Sr,La)-Ti-(O,N) system has been first chosen. Thermal ammonolysis of corresponding oxide compositions between 800 and 1000°C evidences a perovskite-type solid solution domain along the whole range comprised between $LaTiO_2N$ [7] and $SrTiO_3$. $Sr_{1-x}La_xTiO_{3-x}N_x$ oxynitride compositions have been synthesized particularly for x = 0.05; 0.10; 0.25; 0.50; 0.75 (Table 2). The absorption properties change progressively when decreasing x, the powder colour going from red-brown (x = 1: $LaTiO_2N$) to yellow (x = 0.10). The yellow colour of the $Sr_{0.90}La_{0.10}TiO_{2.90}N_{0.10}$ composition corresponds to an absorption edge located at around 500 nm, a lower x value is therefore necessary. However, the powder corresponding to x = 0.05 shows after ammonia treatment an undesired yellow-green colour, indicative of a black component and of a reduction phenomenon of Ti^{IV}, which is no more totally stabilized under the used reducing ammonia synthesis conditions. This would indicate that the inductive effect of strontium ions is weaker than that of lanthanum ions.

Table 2: Colour of nitrided powders in the (Sr,La)-Ti-(O,N) system.

Cationic composition	**Observed color**
LaTi	red brown
$Sr_{0.25}La_{0.75}Ti$	red
$Sr_{0.50}La_{0.50}Ti$	orange
$Sr_{0.75}La_{0.25}Ti$	yellow orange
$Sr_{0.90}La_{0.10}Ti$	yellow
$Sr_{0.95}La_{0.05}Ti$	yellow green
SrTi	white

This study, still in progress, focuses now on the different possibilities to modify the alkaline-earth/rare-earth couple, and also the (alkaline earth + rare-earth)/titanium ratio, in order to enhance the inductive effect and thus stabilize Ti^{IV} during thermal ammonolysis.

Conclusion

The amorphous citrate route proves its efficiency to prepare multinary oxide compositions. By this way, we have succeeded in modifying optical absorption properties by adjusting both oxide and oxynitride chemical compositions. Potential oxide UV-absorbers have been isolated. Preliminary results of a study of their photocatalytic activity (phenol photodegradation test) [8] are encouraging. Another aspect concerns optimization of the performances of oxynitride compositions, especially the steepness of the absorption edge. In all cases, the powder morphology is an important parameter to be controlled before envisaging an industrial opening for these oxide and oxynitride materials.

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