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Rare-earth and tungsten oxynitrides with a defect fluorite-type structure as new pigments

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Abstract

The thermal nitridation in flowing ammonia of different rare-earth tungstates leads to new oxynitride compositions in which the +VI oxidation state of tungsten can be kept. From the tungstates Re_2WO_6, fluorite-type oxynitrides are prepared as brown-colored powders of the general composition $A_4X_{6.6}$ (A=cations, X=anions) intermediate between the CaF_2 (A_4X_8) fluorite and Mn_2O_3 (A_4X_6) bixbyite stoichiometries. Starting from the tungstates $Re_{14}W_4O_{33}$ and Re_6WO_{12} which have a defect fluorite-type structure, a progressive substitution of nitrogen for oxygen within the anionic network is shown to be possible with the formation of two oxynitride solid solution domains ranging from $A_4X_{7.33}\square_{0.67}$ and $A_4X_{6.85}\square_{1.15}$, respectively, to $A_4X_6\square_2$ in both cases. The color of the nitrided powders changes continuously from white to yellow with the nitrogen enrichment as a function of the nitridation temperature and time, and the diffuse reflectance spectra confirm that the absorption edge is progressively shifted towards higher wavelength values. These observations can be explained by a decrease in the energy band gap, as nitrogen gives with cationic elements more covalent bonds than oxygen. So, this progressive N^{3-}/O^{2-} anionic substitution gives access to a new class of pigments with, in addition, the possibility to tune the absorption edge position to a precise value.

Keywords: Oxynitride; Rare earth tungstate; Defect fluorite structure; Pigment

1. Introduction

The market for colored pigments has changed in recent years due to environmental problems caused by the use of inorganic pigments based on heavy metals or certain transition metals. This study is motivated by the development of new colored pigments in the field of nitride-type compounds. Introduction of nitrogen N^{3-} within oxide anionic subnetworks results in modifications of properties. Among them, the color is particularly affected by the more covalent bond character induced by a nitrogen/oxygen substitution [1].

A commonly used method to synthesize nitride-type compounds consists of a thermal ammonolysis of oxides [2,3]. At $T \geq 823$ K, NH_3 decomposes into active species which can both reduce and nitride to form oxynitrides and nitrides. In this paper, rare earth tungstates have been reacted at different temperatures with flowing ammonia.

Among the numerous ternary oxide compositions of the Re–W–O system [4,5], the three stoichiometries Re_2WO_6 (Re/W=2), $Re_{14}W_4O_{33}$ (Re/W=3.5) and Re_6WO_{12} (Re/W=6) have been particularly studied. The tungstates $Re_{14}W_4O_{33}$ and Re_6WO_{12} have both a defect fluorite structure so they can be formulated $A_4X_{7.33}\square_{0.67}$ and $A_4X_{6.85}\square_{1.15}$, respectively, according to a fluorite-type formulation. The oxides $Re_{14}W_4O_{33}$ have a rhombohedral or pseudo-rhombohedral symmetry, whereas the symmetry of the oxides Re_6WO_{12} depends on the rare-earth element: cubic or pseudo-cubic from La to Pr, pseudo-tetragonal from Nd to Gd, and rhombohedral from Tb to Lu and for Y [6]. The latter compounds show a structural analogy with the mixed-valent binary oxide Pr_7O_{12} [7–9] as well as the ternary oxide Y_6UO_{12} [10]. Their crystal structure can be described by the model presented in Fig. 1: seven cubes sharing edges are considered, the central cube being occupied by W^{6+} cations and containing two vacancies located on its main diagonal. The six other cubes surrounding this central $[WO_6\square_2]$ cube contain the Re^{3+} cations and only one vacancy. The rhombohedral unit cell is defined by the heavy solid line. Diot et al. [11] have recently performed a complete determination of the crystal structure of Ho_6WO_{12} and Y_6WO_{12}, and confirmed that the Re^{3+} cations are sevenfold coordinated while the W^{6+} cations are sixfold coordinated.

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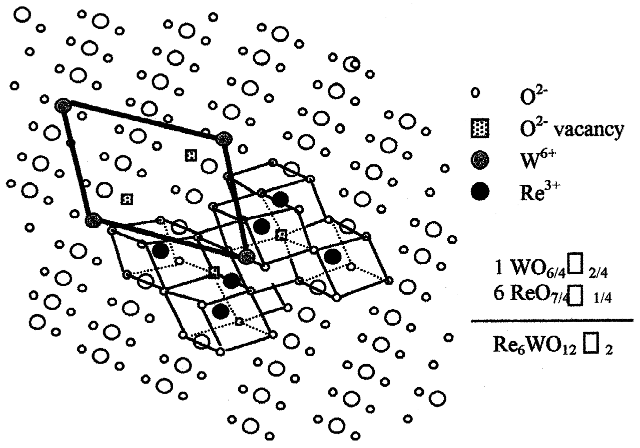

Fig. 1. Structural model for the tungstates Re_6WO_{12} with a rhombohedral symmetry.

The thermal nitridation in flowing ammonia of the above-mentioned rare-earth tungstate compositions gives rise to new oxynitrides in which the +VI oxidation state of tungsten can be maintained. Those ionic–covalent oxynitrides have colors depending on their nitrogen content which can be controlled as a function of the nitridation conditions.

2. Experimental

2.1. Precursors

The starting ternary oxides Re_2WO_6 (Re=Nd→Yb, Y), $Re_{14}W_4O_{33}$ (particularly with Re=La, Sm, Y, Ho) and Re_6WO_{12} (particularly with Re=Nd, Sm, Y, Ho) were generally prepared by direct combination of rare earth sesqui-oxide Re_2O_3 and tungsten oxide WO_3 powders. The samples were first heated at 800°C in an open air furnace in order to totally combine the tungsten oxide, and therefore to avoid any subsequent sublimation. After regrinding, the samples were heated in air in the range 1100–1300°C until a single phase compound was obtained. The phase purity was checked by X-ray powder diffraction.

2.2. Thermal ammonolysis

Nitridation reactions were carried out by heating the rare earth tungstates under ammonia flow (NH_3 flow rate: 30–40 $l\ h^{-1}$) in the range 600–1000°C (heating rate: 10°C min^{-1}).

2.3. Characterization

X-ray diffraction powder patterns were obtained with a Siemens D500 spectrometer using the monochromatic Cu $K\alpha_1$ radiation.

Time-of-flight (TOF) neutron powder diffraction experiments were performed using the medium resolution diffractometer Polaris at the ISIS spallation source.

The nitrogen content of the nitrided powders was determined as N_2 by thermal conductivity measurement with a LECO analyzer calibrated with pure 99.995% N_2 gas, and also as NH_3 by a previously described chemical method [2,12]. Those two methods gave comparable results.

Diffuse reflectance spectra were collected using a dual beam UV-vis-near IR spectrometer (Perkin-Elmer Lambda 900). The absolute reflectance of the samples is compared with a ‘Spectralon’ standard (Labsphere Cie) which reflects 100% of the light in a 250–2500 nm range. The spectra are represented in a 250–800 nm range. The CIE *La*b** color coordinates (*L*, brightness axis; *a**, green–red axis; *b**, blue–yellow axis) were deduced from the diffuse reflectance spectra. For some samples the results were compared with colorimetric data from a Pacific Spectrograd BYK–Gardner colorimeter. The two methods gave comparable results except for the brightness which is underestimated when deduced from diffuse reflectance spectra.

3. Results

3.1. Synthesis and crystallographic data

3.1.1. Re/W=2

By ammonolysis at 800°C of the tungstates Re_2WO_6 (Re=Nd→Yb, Y) brown-colored oxynitride powders are prepared and characterized as defect fluorite-type compounds, with the general composition $A_4X_{6.6}\square_{1.4}$ (A=cations, X=anions) [13]. No composition domain has been characterized as a function of the nitridation temperature or time. The above composition $A_4X_{6.6}\square_{1.4}$ (more precisely $Re_{2.67}W_{1.33}O_{3.8}N_{2.8}\square_{1.4}$) is about halfway between the CaF_2 (A_4X_8) fluorite and Mn_2O_3 (A_4X_6) bixbyite stoichiometries. The corresponding X-ray diffraction powder pattern is compatible with the *Fm-3m* space group with a cubic unit cell parameter ranging from $a=5.383(1)$ Å for Re=Nd to $a=5.164(2)$ Å for Re=Yb. Considering such a unit cell, it is necessary that the Re and W atoms occupy the same 4*a* position (0, 0, 0), in spite of a quite different ionic radius, as well as O and N the same 8*c* position (1/4, 1/4, 1/4).

Neutron powder diffraction experiments have been performed to detect a possible superstructure. Data were collected for the two Re=Yb and Re=Y compositions. A structure refinement in the *Fm-3m* space group suits well with the experimental data, however a too high value of the anion isotropic displacement parameter is observed, indicative of a more complex solution. An explanation could be a slight displacement of the anions out of their

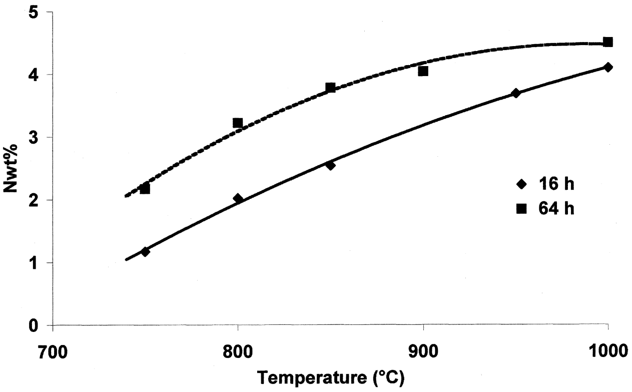

Fig. 2. $Ho_{14}W_4O_{33-3x}N_{2x}$ compositions: nitrogen enrichment as a function of the nitridation temperature, for nitridation times of 16 h and 64 h.

ideal position as has already been shown by Horiuchi et al. [14] in stabilized cubic zirconia $Zr(Y)O_{1.862}\square_{0.138}$.

3.1.2. Re/W=3.5 and 6

Thermal nitridations of the tungstates $Re_{14}W_4O_{33}$ and Re_6WO_{12} carried out at temperatures ranging from 700 to 1000°C give rise to new oxynitride compositions in the Re–W–O–N system, respectively formulated $Re_{14}W_4O_{33-3x}N_{2x}$ and $Re_6WO_{12-3y}N_{2y}$. The amount of incorporated nitrogen progressively increases as a function of the nitridation temperature and time (Fig. 2), while the corresponding X-ray diffraction powder patterns show few evolutions. In most cases, an enlargement of the diffraction peaks and a slight shift of their position can be only noticed (Fig. 3). On the other hand, when nitriding the rhombohedral oxides Re_6WO_{12} (studied here for Re=Ho and Y) a continuous modification of the X-ray diffraction powder pattern is observed as more nitrogen is incorporated, and, for the highest nitrogen content, the symmetry is cubic.

In all cases, the progressive substitution of nitrogen for oxygen within the anionic network gives rise to oxynitride solid solution domains, while the amount of anionic vacancies increases, according to the equation: $2N^{3-} + 1\square = 3O^{2-}$. For the two considered tungstate stoichiometries, the composition ranges from $A_4X_{7.33}\square_{0.67}$ to $A_4X_6\square_2$ (Re/W=3.5), and from $A_4X_{6.85}\square_{1.15}$ to $A_4X_6\square_2$ (Re/W=6). The same limit formulation $A_4X_6\square_2$ obtained in both cases (more precisely $Re_{3.11}W_{0.89}O_{3.4}N_{2.6}\square_2$ and $Re_{3.43}W_{0.57}O_{4.3}N_{1.7}\square_2$, respectively) corresponds to a bixbyite-type stoichiometry. In the bixbyite structure, each cation occupies a cubic site formed by six anions and two vacancies regularly distributed either along the diagonal of a face or along the main diagonal of the cube.

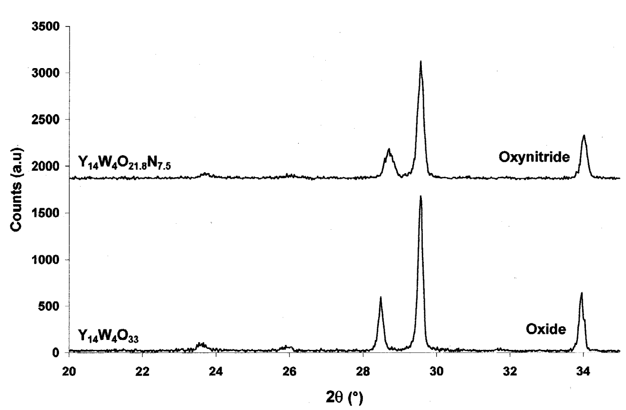

Fig. 3. X-ray diffraction powder patterns of the tungstate $Y_{14}W_4O_{33}$ and a corresponding oxynitride composition.

The X-ray powder diffraction pattern of the oxynitrides $Ho_{3.43}W_{0.57}O_{4.3}N_{1.7}\square_2$ and $Y_{3.43}W_{0.57}O_{4.3}N_{1.7}\square_2$ can be indexed, respectively, with the cubic unit cell parameter $a=5.2737(6)$ Å and $a=5.2770(4)$ Å. The holmium composition has been studied by neutron powder diffraction and refined in the *Fm-3m* space group. However, as for the above Re/W=2 defect fluorite oxynitrides, the result is not totally satisfactory due to an abnormally high value of the anion isotropic displacement parameter.

For the largest rare earth elements La and Nd a reduction of the tungsten +VI occurs, as shown by the black color of the nitrided powders, when the nitridation is carried out above 900°C. An observation by optical microscopy shows a heterogeneous character of those powders. This reduction phenomenon, which is more particularly associated to the highest nitrogen contents, can be explained by an incompatibility between La^{3+} or Nd^{3+} and a sixfold coordination resulting from the increasing proportion of vacancies.

3.2. Color as a function of the nitrogen enrichment

3.2.1. Re/W=2

Whatever the rare earth element, the oxynitride powders are brown-colored. For example, the CIE *La*b** color coordinates of $Yb_{2.67}W_{1.33}O_{3.8}N_{2.8}$ are $L = 25$, $a^* = 8$ and $b^* = 5$ (colorimeter data).

3.2.2. Re/W=3.5 and 6

For Re/W=3.5 and Re=Ho, Sm, Nd, Y, the color of the nitrided powders changes continuously (and globally) from pale yellow to yellow and brown as a function of the nitrogen enrichment. The diffuse reflectance spectra confirm that the absorption edge is progressively shifted towards higher wavelength values. A comparable shift is observed for Re/W=6 and Re=La, Y (Fig. 4), Ho, Sm, where the color globally changes from pale yellow to yellow and finally khaki.

The localized contribution of 4f–4f transitions disrupts more or less the color range, depending on the rare earth element. For instance, for Re=Nd, the color is so much modified that the resulting oxynitrides are green. Holmium brings an orange component while for samarium the matrix contribution predominates. The khaki color observed for some Re/W=6 compositions might be due also to a black

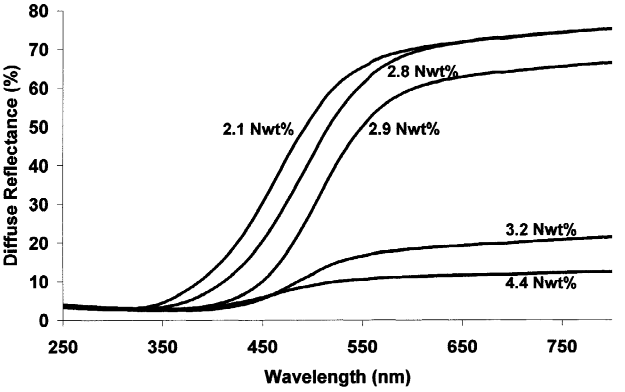

Fig. 4. Diffuse reflectance spectra of oxynitride powders with the general composition $Y_6WO_{12-3x}N_{2x}$.

Table 1
CIE *La*b** coordinates of three oxynitride compositions and the industrial pigment $BiVO_4$[a]

Compound	*L*	*a**	*b**
$Sm_6WO_{8.3}N_{2.5}\square_{3.2}$	75	4	60
$Y_6WO_{9.1}N_{1.9}\square_{3.0}$	74	4	56
$Sm_{14}W_4O_{23.4}N_{6.4}\square_{6.2}$	81	−2	64
$BiVO_4$	76	−4	81

[a] All these data are deduced from diffuse reflectance spectra.

component beside the yellow one, as suggested by the intensity decrease of the diffuse reflectance for high nitrogen contents.

Among all these new oxynitride compositions, some are really interesting for application as yellow pigments. Table 1 gathers the CIE *La*b** coordinates for three of them in comparison with $BiVO_4$. Fig. 5 represents diffuse reflectance spectra of $BiVO_4$ and $Sm_{14}W_4O_{23.4}N_{6.4}\square_{6.2}$.

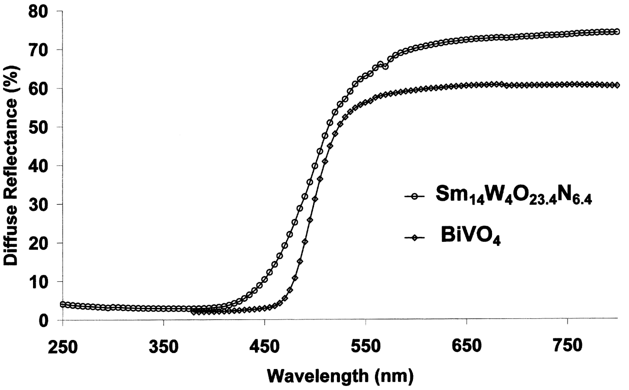

Fig. 5. Diffuse reflectance spectra of $BiVO_4$ and $Sm_{14}W_4O_{23.4}N_{6.4}\square_{6.2}$.

4. Conclusion

New oxynitride compositions with a defect fluorite-type structure have been synthesized by a thermal ammonolysis of rare earth tungstates. The brown-colored powders resulting from the nitridation of the oxides Re_2WO_6 have a fixed composition and the general formulation $A_4X_{6.6}\square_{1.4}$ (A = cations, X = anions). In contrast, nitridation of the fluorite-type tungstates $Re_{14}W_4O_{33}$ and Re_6WO_{12} at different temperatures and for various times gives rise to two oxynitride solid solution domains ranging from $A_4X_{7.33}\square_{0.67}$ and $A_4X_{6.85}\square_{1.15}$, respectively, to a $A_4X_6\square_2$ limit bixbyite-type stoichiometry. The progressive nitrogen enrichment induces a continuous variation of color of the nitrided powders, as confirmed by the shift of their absorption edge towards higher wavelength values observed by diffuse reflectance technique. This new oxynitride family is promising for utilization as novel colored pigments, with, in addition, the possibility to tune the absorption edge to a precise value.

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