IONISING RADIATION ATTENUATING BISMUTH PIGMENTS OF HIGH NIR REFLECTANCE

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ABSTRACT

According to most of the notifications submitted to ECHA under CLP regulations, hazards have not been classified for bismuth oxides, these therefore being a sustainable basis for pigment production (1). Moreover, X-ray attenuation depends on the atomic number (Z), density and thickness of the X-ray absorbing material, lead (Z=82) being the traditional attenuator. However, the use of lead as traditional protection material is limited owing to its toxicity, which is why the use of Bi (Z=83) may be an alternative, it being possible to introduce it in pigment form (2,3). Bismuth oxide, Bi₂O₃, has five crystallographic polymorphs of which phase a (monoclinic $P2_1/c$) of low temperature and phase δ (defective fluorite-type) of high temperature are stable; the other three phases are only stable at high temperature. However, on being doped with appropriate ions, through incorporation of ions such as $M = Y^{3+}$, Zr^{4+} , Eu^{3+} , Nb^{5+} , they appear as metastable phases at room temperature. This study analyses ceramic pigments with high NIR reflectance and a high X-ray attenuation coefficient and compares them with V-zircon turquoise and Pr-zircon yellow: (a) yellows of bismuth oxide modified with Zr (tetragonal *P-421c*) (4), (b) yellows and greens of BiNbO₄ (a-BiNbO₄ orthorhombic Pnna) doped with Cr (5), (c) yellows and turquoise of BiVO₄ (monoclinic I2/b) doped with Ca and Cr (6), as well as (d) composites of yellow solid solutions of Bi,Ce in tetragonal zirconia (P42/mmc) and of Bi,Zr in ceria (cubic Fm-3m).

1. INTRODUCTION

Most of the notifications submitted to ECHA under CLP regulations have not classified hazards for bismuth oxides, these therefore being a sustainable basis for pigment production (1). Moreover, X-ray attenuation depends on the atomic number (Z), density and thickness of the X-ray absorbing material, lead (Z=82) being the traditional attenuator. However, the use of lead as traditional protection material is limited owing to its toxicity, which is why the use of Bi (Z=83) may be an alternative, it being possible to introduce it in pigment form (2,3).

Indeed, Figure 1 shows the radiation absorption by the material that follows a kinetic equation of the first order:

$$\frac{dI}{dx} = -\mu I \qquad (Eq. 1)$$

where μ is the coefficient of linear absorption. It may be observed (Fig. 1) that the variation of the total mass attenuation coefficient ($\mu_m = \mu/\rho$ where ρ is the density of the material) with scattering consistent with the ionising radiation energy of the phases a-Bi₂O₃, a-BiNbO₄ and BiVO₄ compared to that of elementary lead (2) is similar. For example, if a BiVO₄ yellow pigment (density 6,1 g/cm³ and mass absorption coefficient μ_m =5 cm²/g versus 5,55 of elementary Pb at radiation of 100keV (2)) is glazed at 8% in a borosilicate glass frit (μ_m =0,16 cm²/g at 100keV) yielding a deep yellow vitreous coat of density 2,7 g/cm³, the linear coefficient of attenuation μ of the vitreous coat, assuming the mass coefficients to be additive (con w_i the mass fraction of component i), is:

$$\frac{\mu}{\rho} = \sum w_i \frac{\mu_i}{\rho_i} = \frac{\mu}{2.7} = (0.08.5 + 0.92.0.16) = 0.55; \mu = 1.48 cm^{-1} \text{ (Eq. 2)}$$

Integrating Equation 1, the thickness of mean attenuation $D_{1/2}$ that halves radiation intensity is 4,7 mm:

$$I = I_0 e^{-\mu \alpha}$$
, $I / I_0 = 1/2 = e^{-\mu D_{1/2}}$, $D_{1/2} = \ln 2/\mu = 0.693/1.48 = 0.47 cm$ (Eq. 3)

Table 1 details the same values calculated for the three bismuth compounds compared with that of Pb.



Figure 1. Variation of mass attenuation coefficient μ_m with ionising radiation energy (3).

| Compound | a-Bi ₂ O ₃ | a-BiNbO4 | BiVO ₄ | Pb |
|-------------------------------------|----------------------------------|----------|-------------------|------|
| $\mu_m(cm^2/g)$ of the compound (3) | 5,16 | 3,57 | 3,78 | 5,55 |
| µ(cm⁻¹) | 1,51 | 1,17 | 1,10 | 1,6 |
| D _{1/2} (mm) | 4,6 | 5,9 | 5,7 | 4,3 |

Table 1. Coefficients of linear absorption μ and mean attenuation thickness $D_{1/2}$ calculated for vitreouscoats with 8% compound at 100 KeV radiation.

This paper analyses the following systems as ceramic pigments of high NIR reflectance with high X-ray attenuation coefficient and they are compared with commercial Pr-Zircon, V-Zircon and Cr_2O_3 pigments: (a) yellows of bismuth oxide modified with Zr (tetragonal *F-421c*) (4), (b) yellows and greens of BiNbO₄ (a-BiNbO₄ orthorhombic *Pnna*) doped with Cr (5), (c) yellows and turquoise of BiVO₄ (monoclinic *I2/b*) doped with Ca and Cr (6), as well as (d) composites of yellow solid solutions of Bi,Ce in tetragonal zirconia (*P42/mmc*) and of Bi,Zr in ceria (cubic *Fm-3m*) (7).

2. EXPERIMENTAL.

So-called cool pigments are pigments of high reflectivity in the near infrared (NIR, 780-2100 nm), protecting a building with a cladding envelope of high reflectivity from infrared rays with interesting environmental improvements, such as significant saving in building thermal conditioning (HVAC) and mitigation of the urban heat island effect (8).

The total solar reflectivity (R) of a surface is measured by the UV-Vis-NIR (300-2500 nm) diffuse reflectance spectrometry technique in relation to the standard solar spectrum (total fraction of reflected solar energy under previously described standard atmospheric conditions). The solar spectrum used is that of the American Society for Testing and Materials (ASTM G173-03, 2003). Using this method, the total solar reflectivity of surface, R, is calculated from Equation 4.

$$R = \frac{\int_{300}^{2500} r(\lambda)i(\lambda)d\lambda}{\int_{300}^{2500} i(\lambda)d\lambda}$$
(Eq. 4)

where $r(\lambda)$ is the measurement of spectral reflectance at each wavelength of the studied surface and $i(\lambda)$ is the spectral irradiance at the wavelength considered of the standard solar spectrum of the American Society for Testing and Materials (ASTM G173-03, 2003) (9).

In the ceramic samples, the precursors with a particle size of 0.3-5 μ m, supplied by ALDRICH, were mixed and mechanically homogenised in an electric grinding mill (20000 rpm) for 5 min. The mixture was fired at the corresponding temperature and dwell time. The powders were glazed at 5% in a monoporosa frit (1080°C) and in the cases of interest in a twice-fire frit (1050°C). The samples were characterised by the following techniques:

a) The powder samples were characterised by X-ray diffraction of randomly oriented powder in a Siemens D5000 diffractometer with Cu K_a radiation in the range 10-70°2 θ , scan speed 0.05 °2 θ /s, time constant 10 s, and conditions of 40 kV and 20 mA. The powders yielded vitreous pieces with glazes at 5% by weight in twice-fire frit (1050°C) and monoporosa frit (1080°C).

b) The colorimetric characterisation of the vitreous plates was made by measuring the colour parameters $L^*a^*b^*$ according to the CIE (Commission International de l'Eclairage) methodology using a Jasco V670 spectrometer, with D65 illuminant and 10° observer. In this method, L* measures lightness (100=white, 0=black), and a* and b* measure chroma (-a*= green, +a*= red, -b*= blue, +b*= yellow) (10).

c) Total solar reflectance (R) of the surface was assessed by the UV-Vis-NIR (300-2500 nm) diffuse reflectance spectrometry technique in relation to the standard solar spectrum, with a Jasco V670 spectrometer, of the powder samples and vitreous pieces in accordance with the above method.

3. RESULTS AND DISCUSSION

3.1. YELLOWS OF BISMUTH OXIDE MODIFIED WITH ZR

Figure 2 shows the appearance of bismuth oxide pigments modified with Zr (Bi_{2-x}Zr_{3x/4}O₃, x=0,4 and x=1,5) with their respective X-ray diffractograms. The sample with low Zr content (x=0,4) crystallised the phase Bi_{7.38}Zr_{0.62}O_{12.31} (SG *P-41c*) at 800°C/3h producing orange colorations that did not resist the vitreous coat. The sample rich in Zr x=1,5 did not react at this temperature (it only exhibited peaks associated with α -Bi₂O₃ and with colourless monoclinic zirconia (m-ZrO₂). However, at 1000°C, a tetragonal phase (SG *P-41c*) of the solid solution Bi_{7.38}Zr_{0.62}O_{12.31} crystallised together with m-ZrO₂ and yellow colorations that did not resist the vitreous coats, although in alkyd paint, they reached yellow colorations and high NIR reflectance (Fig.2). The value of the mean attenuation thickness D_{1/2} (Eq. 3) was estimated at 4-6 mm for 100keV radiation with 10% pigment addition in alkyd paint.

3.2. CR-BINBO4 YELLOWS AND GREENS

Bismuth niobates are good ionic conductors, photocatalysts, and materials with high-k dielectric constant. The orthorhombic polymorph of a-BiNbO₄ is stable at temperatures below 1020°C and the triclinic polymorph (β -BiNbO4) above 1020°C to its melting point (1240°C); classically, the transformation to the triclinic form at 1020°C is considered irreversible, but Zhou et al. observed that both BiNbO₄ phases could be stable in different temperature regions. Indeed, preparation by the ceramic route from Nb(V) and Bi(III) oxides, doping with chromium calcined a 1000°C/3h, produced green powders in which the predominant crystalline form was a-BiNbO₄ and that glazed at 3% in the twice-fire frit (1050°C) exhibited yellow-orange colorations of moderate strength (L*a*b*=71,2/2,9/21,2) (Fig. 3). The reflectance values were high though the moderate colour strength did not make them significant.

3.3. YELLOWS AND TURQUOISE OF BIVO₄ **DOPED WITH CA AND CR**

 $BiVO_4$ is a broadband semiconductor that has exhibited promising behaviour as a photoelectrochemical (PEC) anode for the photoelectrochemical decomposition of water and production of so-called green H₂, which has also been studied as a photocatalyst in solar photocatalytic applications (6). $BiVO_4$ exists in four polymorphs: orthorhombic, zircon-tetragonal structure, monoclinic, and tetragonal. Although the orthorhombic phase is the most common phase in nature, (pucherite mineral), they have not been synthesised in the laboratory.



Figure 2. Pigments ($Bi_{2-x}Zr_{3x/4}O_3$, x=0.4 and x=1.5) with their respective X-ray diffractograms and application at 10% in alkyd paint with their diffuse reflectance spectrum. CRYSTALLINE PHASES $S(Bi_{7.38}Zr_{0.62}O_{12.31})$, $B(a-Bi_2O_3)$, $M(m-ZrO_2)$



Figure 3. Bi(Cr_{0,05}Nb_{0,95})O₄ pigments calcined at 1000°C/3h



Figure 4. (*Ca_xBi_{1-x}*)*VO*₄ *pigments* 600°C/3*h*.

BiVO₄ synthesis at low temperature produces the zircon-tetragonal phase with a bandgap of 2.9 eV which, at 528 K, transforms into the monoclinic phase, reversible to tetragonal by adjusting the temperature. In these crystal structures, V is coordinated by four atoms of O in tetrahedral coordination and each Bi is coordinated to eight atoms of O from eight tetrahedral units of different VO₄. The only difference between t-BiVO₄ and m-BiVO₄ is that the polyhedrons VO₄ and BiO₈ in t-BiVO₄ are symmetrical, whereas those of m-BiVO₄ are not, both being indirect semiconductors with a bandgap between 2,3 and 2,4 eV (6). Fig. 4 shows the results of the doping with calcium and in Fig. 5 of that with chromium, adding different mineralisers.

With calcium (Fig. 4), yellow powders were obtained with high strength that mainly crystallised the monoclinic phase (m-BiVO₄ in Fig. 4), though residual peaks of cubic Bi_2O_3 and calcium pervanadate also appeared. The glazing in vitreous coats did not produce colour, though in alkyd paint at 10% they produced deep yellow colorations and high NIR reflectance (L*a*b*=75,2/2,1/46,2 and R_{Vis}/R_{NIR}/R 30/64/47). The entry of Ca into the solid solution did not produce additional bands in the UV-Vis-NIR spectrum, though it increased background absorption in the NIR with x (Fig. 4).

The results obtained with chromium (Fig. 5) indicate the obtainment of yellow powders (example: $L^*a^*b^*=51.5/9.3/31.8$ for the unmineralised sample) with presence of BiVO₄ monoclinic (space group *I2/b*) and very weak residual peaks of shcherbianite (V₂O₅) that disappeared in the XRD on washing (Fig. 6).

The UV-Vis NIR spectra of the powders (Fig. 7) exhibited bands at 380, 450 nm with an inflection point in the blue (495 nm, $E_q=2,50$ eV) associated with BiVO₄, and another band with lower strength and maximum at 700 nm (inflection point at 740 nm, $E_q=1,68$ eV) associated with chromium entry into the lattice. No absorptions in the infrared were observed for the unmineralised sample, but the mineralised ones exhibited a continuous absorption, particularly in borate mineraliser 3. The glazings in the monoporosa or twice-fire frit exhibited bands at 280 nm of charge transfer associated with the vitreous coats themselves and bands at 500, 600, and 700 nm (inflection point 740 nm, $E_q=1,68$ eV) associated with chromium and stronger in the twice-fire frit that induced a more turquoise colour (more negative b*) in these samples. The glazed samples displayed no NIR absorptions (unlike the classical turguoise of vanadium in zircon with strong absorption bands in the 1400-1600 nm range with L*a*b*=66.6/-14.7/-18.3 compared to 53.8/-5.8/- 8.9 for the best turquoise, in this case in the twicefire frit), exhibiting NIR reflectance values exceeding 60% (R_{Vis}/R_{NIR}/R=40/65/52 compared to 33/55/44 for vanadium-zircon)(8). Mineralisation did not produce more turquoise results, and E_q as well as R_{NIR} decreased with mineralisation.

| REF | 3%NH₄Cl (<u>min</u> 1) | 3 <u>%(</u> 3NaF.2MgF ₂ .Li ₂ CO ₃ (min 2) | 2 <u>%(</u> CaCO ₃ .KCl)+1% (NaF.Na ₄ B ₂ O ₇) (min 3) | | | |
|-------------------------|-------------------------------------|--|--|--|--|--|
| L*a*b* 51.5/9.3/31.8 | 52.9/5.7/32.9 | 45.5/3.5/23.8 | 42.6/4.7/25.1 | | | |
| 54.8/-5.8/-4.9 | TWICE-FIRE 1050°C 55.2/-8.3/-6.2 | 54.0/-4.0/3.8 | 50.4/-8.3/-3.7 | | | |
| | Washed samples | | | | | |
| 46.0/10.5/34.7 | 49.3/6.6/37.2 | 41.3/4.9/22.1 | 39.8/4.3/24.5 | | | |
| 66.9/-8.2/-2.6 | MONOPOROSA 10 67.8/-7.0/-2.1 | 80ºC 64.8/-7.8/-1.4 | 65.6/-8.4/-1.1 | | | |
| 53.8/-5.8/-8.9 | TWICE-FIRE 10509 54.9/-6.2/-7.3 | C 49.3/-8.2/-0.7 | 49.6/-9.4/-8.1 | | | |

Figure 5. Appearance of the powders ($600^{\circ}C/3h$) in a binocular magnifying glass (x40) ($Cr_{0,4}Bi_{0,6}$)VO₄ and of the glazed samples with the indicated mineraliser



Figure 6. XRD of unmineralised $(Cr_{0,4}Bi_{0,6})VO_4$ (600°C/3h, the peaks are associated with monoclinic $BiVO_4$



Figure 7. UV-Vis-NIR spectra of the samples.

3.4. COMPOSITES OF YELLOW SOLID SOLUTIONS OF BI,CE IN TETRAGONAL ZIRCONIA AND OF BI,ZR IN CERIA.

Furukawa et al. (7) describe yellow pigment preparation based on the $Ce_{1-x}Zr_xBi_yO_{2-y/2}$ solid solution: indeed, starting with Pr-CeO₂ solid solutions (8), which involves modification of the charge transfer band from O_{2p} to Ce_{4f} owing to the entry of dopants, other dopants like Bi or Zr may be expected to have a similar effect. $Bi_{0.1}Ce_{0.45}Zr_{0.34}O_3$ compositions were prepared by the reference ceramic route CE from the oxides, as well as an ammonia coprecipitation route CO from nitrates that, dissolved in water in the proportions of the designed composition, are coprecipitated by controlled addition of ammonia to pH 7, in addition to two MOD (Metal Organic Decomposition) routes involving complexing with polycarboxylate acids (oxalic and citric, respectively) added to the nitrate solution in the proportion sum of metals:polycarboxylate acid =1:1. In the CO and MOD routes, the precipitates obtained by adding ammonia to pH 7 were dried at 110°C and in the case of the MOD powders they were subjected to a charring process of 500°C/1h. The three samples were then calcined at 1300°C/6h.

Figure 8 shows the results ($L^*a^*b^*$ and reflectances) obtained with the powders and with the glazing in the twice-fire frit. Figure 9 depicts the X-ray diffraction of representative samples, as well as the UV-Vis-NIR diffuse reflectance spectra of the powders and the glazings.

| POWDERS 1300ºC/6h CE | со | MOD (OXALIC MOD (| (CITRIC) |
|--|----------------|---------------------|-------------|
| L*a*b*=80,8/-8,9/42,1 | 77,1/-6,4/46,8 | 78,7/-5,5/48,4 77,8 | 8/-6,6/45,5 |
| 3% in twice-fire frit (1050ºC) L*a*b*=81,8/-6,9/32,2 | 78,8/-5,4/36,5 | 80,8/-4/47,4 78,9/- | 5,6/38,5 |

Figure 8. Yellow pigments of solid solutions of Bi,Ce in zirconia (P42/mmc) and of Bi,Zr in ceria (Bi_{0.1}Ce_{0.45}Zr_{0,34}O₃)



Figure 9. XRD of the powders (Bi_{0.1}Ce_{0.45}Zr_{0,34}O₃) and UV-Vis-NIR spectra of the powders and twice-fire frit glazings.

The powders exhibited yellow colorations with c*=42,1 for the ceramic sample and higher values in the colloidal samples, reaching c*=48,4 in the sample with oxalic acid. This difference was associated with the presence of residual peaks of very low strength of monoclinic zirconia (m-ZrO₂, Fig.9) in the case of the CE sample. In contrast, in the colloidal samples the reaction had been completed and only the tetragonal zirconia and cubic ceria phases were detected. The powders displayed the typical UV-Vis-NIR reflectance spectrum of a semiconductor with an associated charge transfer band centred at about 400 nm and absorbance inflection point between 460 and 500 nm with a bandgap measured by the Tauc method between 2,70 eV for CE and 2,48 eV for the MOD (CITRIC) sample. This behaviour caused very high NIR reflectance (between 73 and 76%), conforming to cool pigment characteristics. Comparison of these powders with industrially optimized commercial Pr-zircon (L*a*b*=82,7/2/58.8, $R_{Vis}/R_{NIR}/R=55/70/63$) (8) revealed that the colour tended to green in this case and the values of b* were 10 points lower, but the comparison held up both in colour and in NIR reflectance.

The same occurred on glazing in the twice-fire frit (1050°C), in which the best result obtained the sample MOD(OXALIC) (L*a*b*=80,8/-4/47,4, in $R_{Vis}/R_{NIR}/R = 56/76/66$) Pr-zircon (L*a*b*=79,0/1,4/54,2, compared to $R_{Vis}/R_{NIR}/R=50/75/63$) also tended to green (b*=-4) and exhibited 7 points of yellow component b* (8). The UV-Vis-NIR spectra of the glazed pieces in Figure 9 indicate semiconductor behaviour with two charge transfer bands, one being in the strongest UV centred at 300 nm associated with the vitreous coat that overlapped that of the less strong pigment and exhibiting an inflection point at about 500 nm with bandgap values of 2,48 eV. The presence of Ce (Z=58) and in particular of Bi (Z=83) allowed the mean attenuation thickness D_{1/2} to be estimated at 6-7 mm for 100keV radiation with an 8% pigment addition to vitreous coats.

4. CONCLUSIONS

The present study has analysed ceramic pigments with high NIR reflectance and high X-ray attenuation coefficient associated with the presence of Bi (Z=83) and compared them with V-zircon turquoise and the Pr-zircon yellow:

(a) yellows of bismuth oxide modified with Zr (tetragonal *P*-421c): at 1000°C the tetragonal phase $Bi_{7.38}Zr_{0.62}O_{12.31}$ crystallised together with monoclinic ZrO_2 with yellow colorations that did not resist the vitreous coats, though in alkyd paint it reached yellow colorations and high NIR reflectance. The estimated value of the mean attenuation thickness $D_{1/2}$ was 4-6 mm for 100keV radiation with a 10% pigment addition in alkyd paint.

(b) yellows and green of $BiNbO_4$ (a- $BiNbO_4$ orthorhombic *Pnna*) doped with Cr: at 1000°C/3h, green powders were produced in which the predominant crystalline form was a- $BiNbO_4$ and glazings at 3% in the twice-fire frit (1050°C) exhibited yellow-orange colorations of moderate strength with high reflectance values that the moderate colour strength did not make significant.

(c) yellows and turguoise of BiVO₄ (monoclinic I2/b) doped with Ca and Cr: with calcium yellow powders with high strength were obtained, which crystallised the monoclinic phase, mainly (m-BiVO₄), though residual peaks of cubic Bi₂O₃ and calcium pervanadate also appeared. The glazing in vitreous coats did not produce colour although in alkyd paint at 10% they produced deep yellow colorations and high NIR reflectance (L*a*b*=75,2/2,1/46,2 and $R_{Vis}/R_{NIR}/R$ 30/64/47). The entry of Ca into the solid solution did not produce additional bands in the UV-Vis-NIR spectrum, though it increased NIR background absorption. On the other hand, chromium yielded yellow powders with the presence of monoclinic $BiVO_4$ and very weak residual peaks of shcherbianite (V₂O₅) that disappeared on washing. The UV-Vis NIR spectra of the powders exhibited bands at 380, 450 nm with an inflection point in the blue (495 nm, $E_0=2,50$ eV) associated with BiVO₄ and another band of lower maximum strength at 700 nm (inflection point at 740 nm, $E_q=1,68$ eV) associated with chromium entry into the lattice. The glazings in monoporosa or twice-fire frit exhibited charge transfer bands at 280 nm associated with the vitreous coats themselves and bands at 500, 600, and 700 nm (inflection point at 740 nm, $E_q=1,68 \text{ eV}$) associated with chromium and stronger in the twice-fire frit that induced a more turguoise colour (more negative b*) in these samples. The glazed samples exhibited no NIR absorptions (unlike the classic turguoise of vanadium-doped zircon with strong absorption bands in the range 1400-1600 nm and L*a*b*=66.6/-14.7/-18.3 compared to 53.8/-5.8/-8.9 of the best turquoise, in this case in the twice-fire frit) displaying NIR reflectance values above 60% (R_{Vis}/R_{NIR}/R=40/65/52 compared to 33/55/44 for vanadium-zircon). Mineralisation did not produce more turquoise results and E_q, as well as R_{NIR}, decreased with mineralisation.

(d) composites of yellow solid solutions of Bi,Ce in tetragonal zirconia and of Bi,Zr in cubic ceria: the powders displayed yellow colorations for the ceramic sample and higher values in the colloidal samples, reaching $c^*=48,4$ in the sample with oxalic acid, and they exhibited the typical UV-Vis-NIR reflectance spectrum of a semiconductor with a bandgap of 2,70 eV for CE and 2,48 eV for sample MOD(CITRIC). This behaviour caused very high NIR reflectance (between 73 and 76%), conforming to cool pigment characteristics.

On comparing the powders and glazings in vitreous coats with the industrially optimized commercial Pr-zircon, the colour was observed to tend to green in this case and the b* values were 10 points lower, but the comparison held up in both colour and NIR reflectance. The presence of Ce (Z=58) and above all Bi (Z=83) allowed the mean attenuation thickness $D_{1/2}$ to be estimated at 6-7 mm for 100 keV radiation with 8% pigment addition to vitreous coats.

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