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Chemical bath deposition of cerium doped $BiVO_4$

Márcia C. Neves[a], Marian Lehocky[c], Rosário Soares[b], Lubomir Lapcik Jr.[c], Tito Trindade[a,*]

[a]*Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal*
[b]*The Central Analysis Laboratory, University of Aveiro, 3810-193 Aveiro, Portugal*
[c]*Institute of Physics and Material Engineering, Faculty of Technology in Zlín, Tomas Bata University in Zlin, Czech Republic*

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Abstract

The preparation of Ce doped $BiVO_4$ coatings on glass, by the thermal treatment of aqueous solutions containing a bismuth (III) ethylenediaminetetra-acetate chelate, vanadium (V) and cerium (III) species, is described here. The influence of cerium content on the colour properties of the coating was investigated. The coatings consist on morphological well-defined particles forming dense monolayers.

Keywords: Bismuth vanadate; Pigments; Coatings; Deposition process

1. Introduction

High-performance coatings require pigments with outstanding properties, which is difficult to obtain with lead or cadmium free formulations. Due to the toxicity of these heavy metals, there has been interest in searching for alternative premium quality pigments. Although high priced, bismuth (III) vanadate ($BiVO_4$) is a non-toxic yellow pigment which has been considered as a very interesting alternative [1]. The extension of the colour pallet of $BiVO_4$ is a factor that will increase the commercial competitiveness of this pigment. Besides application as a pigment [1], $BiVO_4$ has other interesting properties such as ferroelasticity [2], ionic conductivity [3] and photocatalytic activity [4].

Recently, we have developed a new synthetic method to produce morphologically well-defined $BiVO_4$ coatings on glass [5]. The deposition temperatures used are lower (<100 °C) than those employed in the traditional production process [1] and involves the thermal treatment of homogeneous solutions containing soluble Bi(III) complexes in which the ligand ethylenediaminetetra-acetate (EDTA) acts as a metal sequestering agent, to avoid the spontaneous precipitation of $BiVO_4$. In order to obtain colour modifications in $BiVO_4$, the deposition of this pigment on glass in the presence of a cerium(III) salt was investigated and is reported here.

2. Experimental

A typical solution for deposition of uniform $BiVO_4$ coatings on glass was prepared as follows.

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* Corresponding author. Fax.: +351-234-370-084.
E-mail address: ttrindade@dq.ua.pt (T. Trindade).

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$Bi(NO_3)_3.5H_2O$ (98%, Aldrich) and $Ce(NO_3).6$ H_2O (99%, Aldrich) (in total 1.25 mmol) were added to 10 ml of a buffered aqueous solution ($[Na_2HPO_4] = [NaH_2PO_4] = 0.1$ mol.dm^{-3}), according to the amounts shown in Table 1. Ethylenediaminetetracetic acid disodium salt (Pronolab) (2.50 mmol) was then added to this solution and the milky suspension formed was stirred for 10 minutes. To this suspension 5 ml of a buffered aqueous solution ($[Na_2HPO_4] = [NaH_2PO_4] = 0.1$ moldm^{-3}) containing $NaVO_3$ (Merck) (2.50 mmol) was added. The final suspension has a ($Bi^{3+} + Ce^{3+}$):EDTA: $NaVO_3$ stoichiometric ratio of 1:2:2 and the pH was adjusted to 8 using NaOH 1 mol dm^{-3}. A clear solution was then obtained by heating with vigorous stirring. At this time, stirring was stopped and a microscope glass slip (22 mm×20 mm) was introduced vertically into the reaction vial and kept standing at the required temperature and time. Finally the glass slip was taken out of the solution, washed thoroughly with distilled water and dried under a nitrogen stream. The glass slips were previously treated using chromosulfuric acid, followed by immersion in 30 ml of NH_4OH/H_2O (1:1) and heated to boiling. At this stage the heating was stopped and 15 ml of H_2O_2 was added. The substrates were then rinsed with distilled water and then with HPLC acetone.

2.1. Characterization

The visible diffuse reflectance spectra of the coatings were recorded on a Jasco V-560 UV/VIS spectrophotometer, using MgO as the reference. The CIELab coordinates were obtained from a Datacolour 3890 using the Datamatch software. X-ray powder diffraction (XRD) was performed on the coatings deposited on glass substrates, using a Philips X'Pert instrument operating with Cu-K$_\alpha$ radiation ($\lambda = 1.54178$ Å) at 40k V/50mA. Scanning electron microscopy (SEM) images were obtained using a FEG-SEM Hitachi S4100 microscope operating at 25 kV.

Table 1
Relative amounts of Ce and Bi used in the preparation of the coatings

%Ce	m(Bi(NO$_3$).5H$_2$O)		m(Ce(NO$_3$).6H$_2$O)	
	n(mmol)	wg(mg)	n(mmol)	wg(mg)
0	1.250	606		
0.5	1.244	603	0.006	2.71
1	1.238	600	0.012	5.43
1.5	1.231	597	0.019	8.14
2	1.225	594	0.025	10.86

3. Results and discussion

Colour changes were observed in $BiVO_4$ coatings deposited from a chemical bath in which distinct Ce(III) contents were used. For all samples, the $BiVO_4$ coatings were strongly adherent to the glass surfaces. Table 2 shows the effect of the increasing content of Ce(III) on the hue of the $BiVO_4$ coatings for a typical time of deposition. The CIELab data shows that the hue of the $BiVO_4$ coatings shifted from yellow to orange-red as the amount of Ce(III) present in solution increased. Accordingly, the reflectance spectra shown in Fig. 1

Table 2
Effect of the increasing content of Ce(III) (in the chemical bath) on the hue of the deposited $BiVO_4$ pigments (time of deposition = 16 h)

% Ce	*L**	*a**	*b**
0	68.08	16.52	42.32
0.5	65.80	18.95	35.86
1	62.91	21.29	29.90
1.5	57.50	23.05	24.00
2	55.67	23.67	21.80

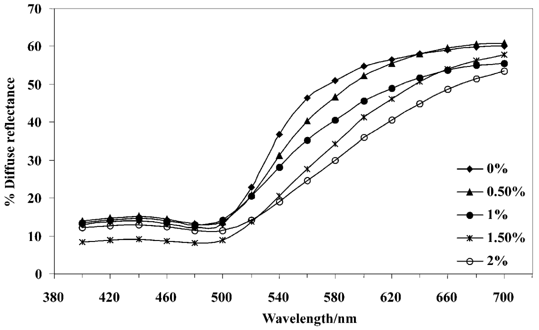

Fig. 1. Visible diffuse reflectance spectra of $BiVO_4$ coatings for different Ce(III) content in the starting solutions (time of deposition = 16 h).

for the $BiVO_4$ coatings show a red shift of the optical band edge and a decrease of the reflectance as the amount of Ce(III) increases. These colour modifications are possibly related to an increasing incorporation of Ce(III) into the $BiVO_4$ lattice. The ionic radii of Bi^{3+} and Ce^{3+} are 1.17 Å and 1.14 Å, respectively. Hence, in principle, the substitution of Bi^{3+} by Ce^{3+} is a favorable process although the moderate temperatures used in the synthesis do not favour an extensive isomorphous substitution. In a typical ICP analysis performed on $BiVO_4$ samples, it was found that the coatings have ca. 10% of Ce(III) in relation to the amount present in the chemical bath.

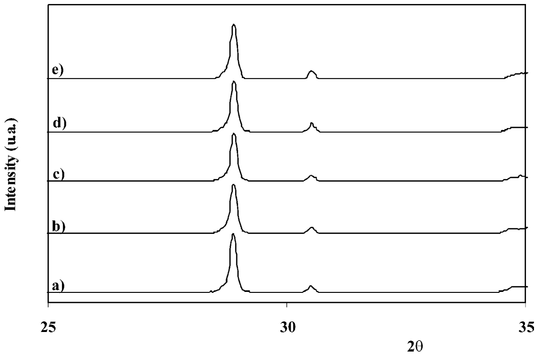

Fig. 2. XRD patterns for $BiVO_4$ coatings prepared using different Ce(III) content in the starting solutions: (a) 0% (b) 0.5% (c) 1% (d) 1.5% (e) 2%.

Fig. 2 shows the X-ray powder diffraction of $BiVO_4$ coatings prepared in the presence of different amounts of Ce(III), for the same time and temperature of deposition. The monoclinic phase of $BiVO_4$ is present for all the samples which were prepared using the chemical bath deposition method reported here. Using the XRD data, a variation of the volume of the unit cell from 309.5 to 311.5 $Å^3$ was calculated. The slight shifts

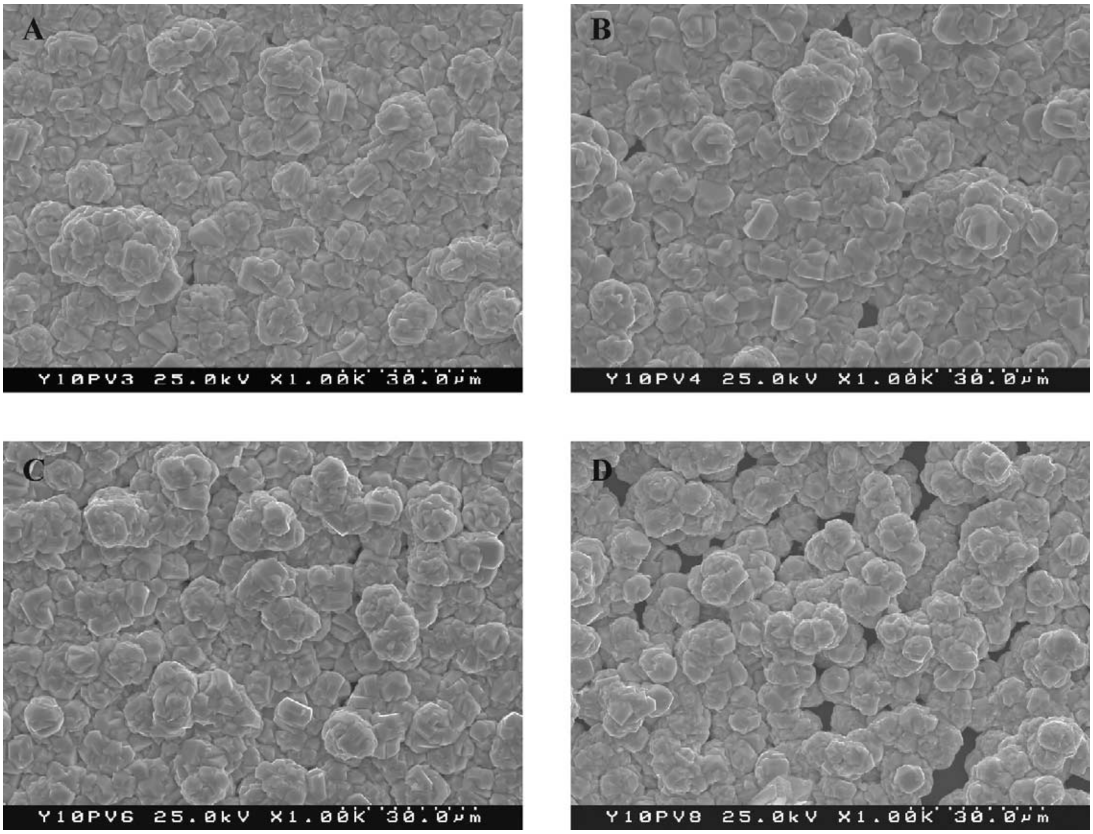

Fig. 3. SEM images of Ce doped $BiVO_4$ coatings on glass: (a) 0% (b) 0.5% (c) 1% (d) 1.5%.

observed (Fig. 2) in the XRD reflection peaks reveal that the colour modifications occurring in Ce doped $BiVO_4$ coatings just require small amounts of the foreign cation.

The SEM images of $BiVO_4$ coatings obtained from chemical bath with different cerium contents are shown in Fig. 3. The $BiVO_4$ coatings consist in morphologically well-defined micrometric particles although distinct of those reported previously and obtained for different experimental deposition parameters [5]. The microparticles are evenly spread on the substrate forming a dense layer (*ca.* 13 μm). The SEM images (Fig. 3) show for all the samples analysed, that the coatings are formed by round associations (typically less than 15 μm in diameter) of smaller $BiVO_4$ particles. There are no noticeable morphological differences within the several samples containing distinct amounts of Ce(III). This result confirms that the colour modifications observed for the coatings are due to cerium doping on the $BiVO_4$ lattice rather than to differences on the particle morphology.

In summary, a new method has been devised to modify the characteristic yellow hue of $BiVO_4$ coatings to orange-red. This method involves moderate temperatures and the incorporation of small amounts of Ce(III) in the crystalline lattice of monoclinic $BiVO_4$. The final coatings consist in morphologically well defined microparticles forming dense monolayers.

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