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Bulk and Thin Films of Bismuth Vanadates Prepared from Hybrid Materials Made from an Organic Polymer and Inorganic Salts

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A new precursor route for the preparation of bulk oxides and thin films of bismuth vanadates is proposed. The method involves the thermal treatment under air and mild conditions of hybrid organic−inorganic precursors, made from a zwitterionic salt-free polymer matrix and selected inorganic species. Monoclinic $BiVO_4$ was obtained in the form of bulk oxide by calcination of the powdered homogeneous hybrid materials at 600 °C, from precursors containing Bi and V in stoichiometric amounts. In the same way, thermodiffractometry studies performed on a hybrid material exhibiting a Bi/V molar ratio of 2 revealed that the ionic conductor γ-$Bi_4V_2O_{11}$ phase can be stabilized under very soft thermal conditions (300 °C). Additionally, thin films of yellow monoclinic $BiVO_4$ were for the first time fabricated, by thermal treatment of the same hybrid polymeric precursors deposited on quartz substrates by spin coating, using a layer-by-layer technique. The presence of the target phase at the surface of the plates was confirmed by X-ray diffraction as well as UV−vis measurements.

Introduction

Advanced inorganic materials, and in particular multicomponent oxides, are currently prepared via the precursor route. This pathway exhibits different advantages compared to the standard ceramic route, mainly the implementation of rather soft temperatures to produce the oxide. Subsequently, a control on the structure, morphology of particles, dispersion of the different metals, etc. is also sometimes possible. For example, methods based on the decomposition of precursors containing an organic additive like EDTA and its derivatives,[1] citrate gels,[2] or oxalates[3] were successfully implemented. Other organic precursors can be envisaged, too, to stabilize phases exhibiting interesting properties in a more efficient way. Recently, we proposed an original pathway to multicomponent oxide materials which are produced by thermal treatment of hybrid organic−inorganic materials. The organic precursor was an ordered and regular poly(ampholyte) matrix able to interact with the metal ions.[4] This approach was for the first time applied to the preparation of nickel and cobalt molybdate catalysts[5] and subsequently optimized.[6] In that context, a further objective was to check the versatility of this new synthetic method for the preparation of other kinds of oxide phases, produced in other forms. Our choice was oriented to the Bi−V−O system, for different reasons. This system is discussed for potential applications in numerous advanced technological and scientific fields. Many different crystalline phases of various stoichiometries have been reported,[7,8] among which the most stable and well-characterized are $BiVO_4$ and $Bi_4V_2O_{11}$. The $BiVO_4$ phase exhibits different polymorphs. First, the orthorhombic phase occurs naturally as a mineral, but this form is difficult to produce by classical laboratory routes. Next to this phase, the synthesis under low-temperature conditions produces the tetragonal structure, whereas high-temperature preparation gives the monoclinic form.[9] In addition to the catalytical applications of this compound as a catalyst in oxidation reactions,[10] $BiVO_4$ exhibits electronic and ionic conductivity, particularly at high temperatures. This phase is also frequently reported as an efficient yellow pigment for high-performance lead-free paints,[11,12] and its photochromism has been investigated in detail.[13] $Bi_4V_2O_{11}$ [14,15,16]

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is mainly studied for its dielectric, pyroelectric, and ferroelectric properties. Three main crystallographic polymorphs have been identified as the α-, β-, and γ-phases. The γ-$Bi_4V_2O_{11}$ phase exhibits fascinating ionic conducting behavior and can be readily used in lithium batteries.[17] Various attempts have been performed to stabilize this phase at room temperature and to improve the ionic conductor performances by a doping strategy using different metals such as Zn,[18] Na and Pb,[19] Ti, Zr, and Sn,[20] La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy,[21] Cu,[22] or Ca,[23] leading to the so-called BIMEVOX family of materials. Modification of Bi−V−O materials by other elements such as F for example was also reported.[24] $Bi_4V_2O_{11}$ can also be easily reduced,[25] leading to the phases $Bi_4V_2O_{10.66}$ ($Bi_6V_3O_{16}$) and $Bi_4V_2O_{10}$. Noteworthy, the Bi−V−O phases described before are commonly prepared in the form of bulk oxides by implementing standard preparation techniques such as the ceramic route or mechanical milling methods,[26] involving Bi_2O_3 and V_2O_5 as reactants. Some examples of the preparation of Bi−V−O films on various substrates are also reported in the literature. Techniques involving metallo-organic precursors[27] and coating-pyrolysis processes,[28,29] successive layer-by-layer deposition of simple Bi and V inorganic salts in solution,[30] or chemical vapor deposition[31] have been successfully used. In the same way, the preparation of Bi−V−O films doped with other metals by pyrolysis of sol−gel coatings was also reported.[32] In this context, this work presents a new route to prepare such Bi−V−O phases (including bulk oxides and thin films), involving the thermal treatment of hybrid precursor materials made from an organic polymer matrix and inorganic salts. For these studies, poly[*N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride-*alt*-(4′-methyl-piperazinyl)-4-oxo-2-butenoic acid] was selected as a polymer matrix, mainly due to its convenient synthesis and to its full water solubility throughout the whole pH window.[6] Research efforts were mainly focused on the preparation of the most commonly used phases from this large family of Bi−V−O compounds, namely, $BiVO_4$ and $Bi_4V_2O_{11}$. Because monoclinic $BiVO_4$ is commonly used as inorganic yellow pigment, the preparation of this phase in the form of thin films was envisaged. The conditions for preparation and stabilization of the second material, namely, $Bi_4V_2O_{11}$, were studied in order to obtain this phase in the form of its bulk γ-phase, which exhibits promising ionic conductivity properties. Additionally, we were interested to see if this new synthetic method exhibits advantages compared to more conventional preparation routes.

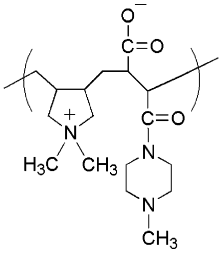

Figure 1. Zwitterionic copolymer used.

Experimental Section

Materials. All chemicals were analytical grade and used without further purification. Bismuth(III) nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) was purchased from Fluka Chemie. Ammonium vanadate (NH_4VO_3) was supplied from Merck. Ammonia (25 wt % in water) was purchased from Applichem. Nitric acid (65 wt % in water) was supplied from Fluka Chemika. Sulfuric acid (>98%) was purchased from Fisher Scientific. Hydrogen peroxide (35 wt % in water) was supplied from Acros Organics. Water was first purified using an Elgastat Maxima system (resistance: 18.2 MΩ). Quartz plates (Suprasil), glass plates (24 × 40 mm, Vel), and cover glasses (25 × 25 mm, Corning Labware and Equipment) were used as substrates for the deposition of the hybrid materials and the preparation of the oxide films. Syringe filters (PTFE, porosity 0.45 μm, Alltech) served for filtering the precursor solution before coating. Calcination experiments (500 or 600 °C, air atmosphere) were mainly carried out using the quartz substrates, due to the insufficient thermal resistance of the glass plates employed.

Methods. TGA curves were recorded on a Mettler-Toledo 851e thermogravimetric analyzer, applying a heating rate of 10 °C min^{-1} under air. UV−visible (UV−vis) measurements were performed on a Varian Cary 5E, using background correction and subtraction of the signal from the substrates. X-ray diffractograms (XRD) were taken with a Siemens D-5000 diffractometer, using the Cu Kα line ($\lambda = 0.1541$ nm). Samples in the form of powders were analyzed on standard supports made from Si monocrystals. Scanning electron microscopy (SEM) was performed with a Gemini DSM 982 digital scanning microscope, coupled with an energy-dispersive analyzer for complementary EDX measurements. The hybrid materials were analyzed by deposition of Cr at the surface of the samples using plasma, to increase their conductivity and enable the analysis. Elemental analysis was performed at the University College of London, UK.

Preparation of the Polymer Matrix. The synthesis of the precursor copolymer (namely, poly[*N*,*N*-dimethyl-*N*,*N*-diallylammmonium chloride-*alt*-(4′-methyl-piperazinyl)-4-oxo-2-butenoic acid], Figure 1), is described elsewhere.[6] The sodium content in the matrix was checked by ICP-AES in order to exclude contamina-

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tion of the hybrid blends by residual inorganic salts from the matrix and was found to be 0.01%. Similarly, contamination by chloride was found to be absent, according to elemental analysis.

Preparation of the Hybrid Organic−Inorganic Materials. In a typical experiment, 50 mg of polymer was dissolved in 20 mL of water by stirring at room temperature. The appropriate amounts of aqueous solutions (pH = 1, adjustment with nitric acid) of the inorganic species (namely, 0.019 M $Bi(NO_3)_3{\cdot}5H_2O$ and 0.039 M NH_4VO_3) were added in order to reach the desired molar ratio of metal ion(s) per repeat units of the copolymer. The pH value was then adjusted by adding the appropriate amount of 0.1 M aqueous NH_3 or HNO_3. After stirring for 1 h, water was removed from the precursors under vacuum, according to a standard lyophilization technique, after freezing the solutions in liquid nitrogen, yielding yellowish, finely divided powdered hybrid materials.

Preparation of the Bulk Oxides. The bulk oxide materials were prepared from the corresponding homogeneous hybrid materials, made by incorporation in aqueous solution (pH = 1, HNO_3 medium) of the inorganic precursors (namely, 0.019 M aqueous $Bi(NO_3)_3{\cdot}5H_2O$ and 0.039 M aqueous NH_4VO_3) into the polymer matrix (namely, poly[*N*,*N*-dimethyl-*N*,*N*-diallylammmonium chloride-*alt*-(4′-methyl-piperazinyl)-4-oxo-2-butenoic acid]), to reach the desired Bi/V molar ratio. Calcination of these materials under air flow (1 $L{\cdot}min^{-1}$, heating rate of 10 $°C{\cdot}min^{-1}$ up to 600 °C and then 5 h at 600 °C) produced $BiVO_4$ and $Bi_4V_2O_{11}$ powders.

Preparation of Thin Films on Glass or Quartz Supports. *Preparation of Substrates.* Quartz and glass plates were first sonicated in ethanol and both types of substrates were cleaned for 30 min in a piranha mixture [H_2SO_4/H_2O_2 1:2 (v:v)] (*Caution! Piranha solution is extremely corrosive and reacts violently with organic compounds*), left at ambient temperature, then thoroughly washed with ultrapure water.

Preparation of a Precursor Solution for Coating. Copolymer (649 mg), 485 mg of $Bi(NO_3)_3{\cdot}5H_2O$, and 117 mg of NH_4VO_3 were dissolved in the minimum amount of H_2O/HNO_3 (65 wt %) solutions [99:1 (v:v), 20:80 (v:v), and 60:40 (v:v), respectively]. The three solutions were mixed and pure water was added to reach a total volume of 25 mL of yellowish solution. The solution was not stable with time (the color turned green after about 1 h under air) and a fresh mixture had to be prepared before each series of coatings.

Film Coating. The films were cast by placing some drops of filtered precursor solution on a cleaned support, which was spun to 1000 rpm for 10 s (typical conditions, depending on the substrate; acceleration rate: 1000 $rpm{\cdot}s^{-1}$) using a conventional spin coater. The plate was then preheated at 200 °C. The process was repeated several times, from 1 to 20 cycles. The quartz plates were finally treated in an oven at 500 or 600 °C under air (1 $L{\cdot}min^{-1}$, heating rate of 10 $°C{\cdot}min^{-1}$ up to 500 or 600 °C and then for 30 min at 500 or 600 °C).

Results and Discussion

Preparation and Characterization of Bi−V Bulk Oxides Obtained from Hybrid Organic−Inorganic Precursors. *Solution and Solid-State Studies.* First, miscibility tests were carried out in order to establish appropriate conditions to obtain homogeneous solutions of the copolymer and the inorganic species generated in solution from NH_4VO_3 and $Bi(NO_3)_3{\cdot}5H_2O$. Homogeneous solutions were only obtained from the salt-free polymer and the metal salts in water under strong acidic conditions, namely, by adding 0.1 M aqueous HNO_3. Under such pH conditions, and in agreement with the Pourbaix diagram, vanadium (+V) is present in solution in the form of the oxocation VO_2^+ (actually, $[VO_2(H_2O)_4]^+$), so that the two metals are present as cationic species. A yellow precipitate forms rapidly when the pH value was increased to about 2 by adding 0.1 M aqueous NH_3.

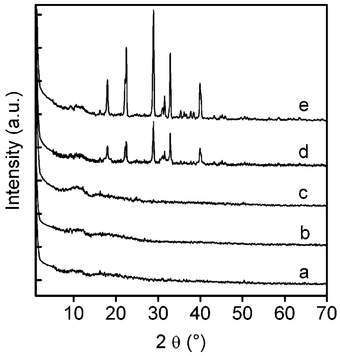

Figure 2. XRD patterns of hybrid materials made from the polymer and $Bi(NO_3)_3{\cdot}5H_2O$ incorporated jointly with NH_4VO_3, as a function of the pH of the precursor solution: pH = 0.5 (a), 1 (b), 1.5 (c), 2.5 (d), and 8 (e). Relative amounts: 0.5 mol of metals/mol of repeat units of copolymer.

To prepare homogeneous hybrid mixtures from the copolymer and the selected inorganic salts, the homogeneity of the materials in the solid state was screened. After lyophilization, the hybrid blends were analyzed by XRD. Figure 2 illustrates the diffractograms of some materials, as a function of the pH of the precursor solution. The presence of sharp lines in the diffractograms of the solids prepared at pH values of 2.5 and 8 suggests that a part of the inorganic salt(s) does not interact with the matrix, but forms a separate phase. Attempts were made to indentify this phase by using the JCPDS data file, but without success. However, under harsh acidic conditions (namely, pH values of 0.5, 1, and 1.5), homogeneously mixed amorphous precursors were obtained, as seen by the XRD patterns of the materials. Under these pH values, and in agreement with the Pourbaix diagram of vanadium, all metals in solution are present in the form of cations in the precursor solution. In the same way, the carboxylate moieties of the copolymer are assumed to be mainly protonated under the strongly acidic conditions. For that reason, the formation of homogeneous blends in the solid state can be explained in this case by a rearrangement of negatively charged counterions around the cationic organic and inorganic species, which enables the full dissociation of the metals in the matrix.

Additionally, scanning electron microscopy (SEM) was used to determine the morphology of the particles. Figure 3 displays a typical SEM micrograph of one hybrid homogeneous material. This picture is representative for all compounds analyzed in the context of this study, namely, whatever the homogeneity. Particles visualized on micrographs of all samples (homogeneous as well as inhomogeneous) exhibit various morphologies, including crystals of various shapes, revealing a typical fibrous structure for all the particles, whatever the pH of preparation of the precursor solution that is considered.

The thermal decomposition of the polymer matrix and the formation of the oxide phase were followed by thermogravimetric analysis (TGA). Figure 4 displays the TGA curves of the matrix and of a hybrid material made from $Bi(NO_3)_3{\cdot}5H_2O$ incorporated jointly with NH_4VO_3, in a molar ratio

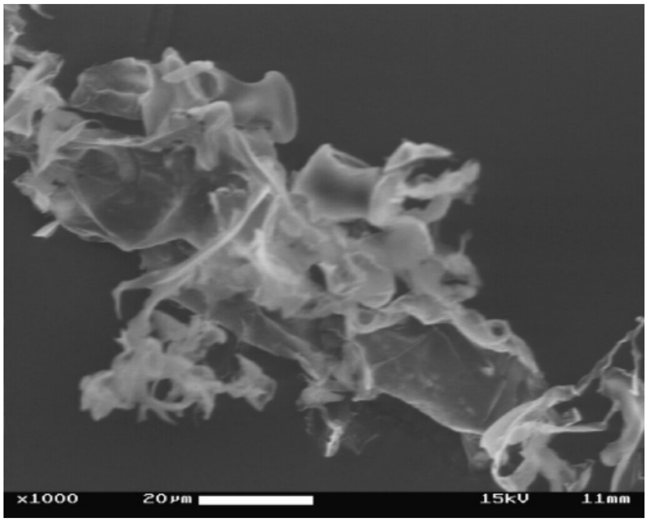

Figure 3. SEM micrograph (magnification: 1000×) of a hybrid powdered material made from the copolymer matrix and containing $Bi(NO_3)_3{\cdot}5H_2O$ jointly with NH_4VO_3, prepared from precursor solutions whose pH was adjusted to 1.

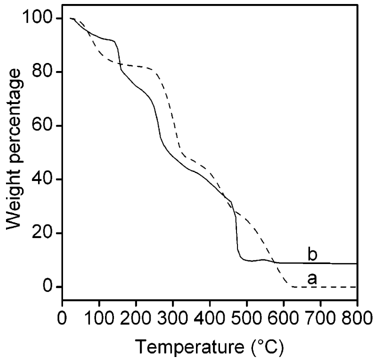

Figure 4. TGA curves under air of the salt-free copolymer matrix (a) and of a hybrid blend made from the copolymer and $Bi(NO_3)_3{\cdot}5H_2O$ incorporated jointly with NH_4VO_3 (b); relative amounts: 0.5 mol of metal ions/mol of repeat units of polymer.

Bi/V of 1. All curves exhibit a first slow weight loss, which is partially attributed to the dehydration of both the polymer matrix and the hybrid precursor. This is followed by different steps, corresponding to the pyrolysis of the matrix, combined with the degradation of the ammonium and nitrate counterions and the formation of the expected oxide phase in the case of the hybrid material. The weight becomes stable from ~640 °C (polymer) and ~500 °C (hybrid mixture) on and is stable up to 800 °C. Because the pyrolysis of the matrix is complete, and as the residual weight corresponding to the hybrid material matches well with the value calculated on the basis of the formation of the corresponding vanadate phase, results from the TGA measurements suggest that, in the case of the hybrid material, the main calcination product consists of $BiVO_4$. The milder conditions needed to calcine the hybrid material by comparison with the polymer matrix can be explained by the presence of large amounts of nitrate which act as oxidant and accelerate the decomposition of the organic compounds. Moreover, the presence of the metal ions might add up the effect, by catalyzing the oxidation of the polymer.

Preparation and Characterization of Bi−V Oxide Materials. According to the solid-state studies, and to the thermal behavior of the hybrid precursors, all the inorganic oxide materials described in the following were prepared according to the same procedure. Mixing of the polymer and inorganic salts in aqueous solution at a pH value of 1, and subsequent lyophilization, produced homogeneous hybrid organic−inorganic materials in the form of powders. To ensure complete pyrolysis of the organic polymer matrix and to favor the formation of the crystalline phases, the final products were obtained upon calcination of the precursors under an air flow of 1 L/min at 600 °C. This temperature is higher than the limiting decomposition temperature of the hybrid mixtures determined by TGA.

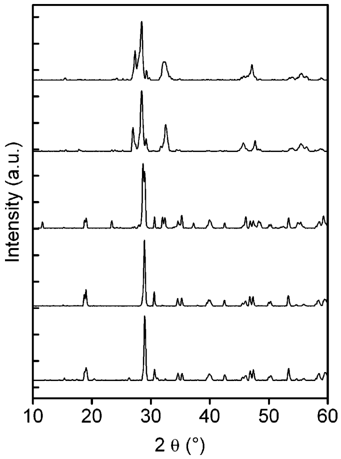

Figure 5. Diffractograms of the material obtained by calcination at 600 °C of hybrid mixtures made from the salt-free copolymer matrix and $Bi(NO_3)_3{\cdot}5H_2O$ incorporated jointly with NH_4VO_3, as a function of the molar ratio Bi/V (from bottom to top: Bi/V = 0.5, 1, 2, 4, 6). Relative amounts: 0.5 mol of metal ions per mol of repeat units of copolymer.

In agreement with the literature, different Bi−V−O phases can be prepared, depending on the molar ratio Bi/V in the precursor. Consequently, in the multicomponent oxide, the nature of the final phase obtained was screened as a function of the Bi/V ratio in the precursor material. The structure of the final materials was systematically checked by XRD measurements, by comparison with the JCPDS files of the expected phases. Figure 5 illustrates representative diffractograms in the 2θ range 10°−60° of the materials prepared by incorporation of different amounts of Bi and V species in the precursor hybrid materials (namely, molar ratios Bi/V equal to 0.5, 1, 2, 4, and 6), obtained upon calcination at 600 °C under air. In the case of precursors containing a large excess of Bi (Bi/V = 4 or 6) or of V (Bi/V = 0.5), the final materials always consist in a mixture of different phases. Incorporation of excess V compared to the equimolar amount (Bi/V = 0.5 rather than 1) leads to the formation of a mixture of monoclinic $BiVO_4$ (JCPDS file 14-068), which can be for example unambiguously identified by the presence of a characteristic intense line around 18.8°, jointly with other compounds. Among these compounds, VO_2 and V_2O_3 (JCPDS files 82-1074 and 84-0318) can be identified by the presence of some of the most pronounced lines of their XRD patterns at 2θ values around 15° and 33° for example. In contrast, Bi_2O_3 (JCPDS 76-1730) appears to be the major phase obtained when large amounts of Bi are engaged (Bi/V = 4, 6). Under stoichiometric conditions, the pure $BiVO_4$ phase appears in the form of its monoclinic polymorph (JCPDS file 14-0688). Finally, a mixture of monoclinic

Table 1. Residual C, H, and N Contents for the Prepared Materials after Heating at 600 °C, as a Function of the Bi/V Molar Ratio in the Precursor

Bi/V	% C	% H	% N
0.5	0.08	0	0
1	0.24	0	0
2	0.08	0	0
4	0.08	0	0
6	0.19	0	0

$BiVO_4$ and $Bi_4V_2O_{11}$, probably in rather similar amounts as judged from the intensity of the signals, is obtained for a molar ratio Bi/V of 2. For example, lines at about 18.8°, on one hand, and at 11.1° and 23.1°, on the other hand, can be unambiguously identified. However, additional signals indicate the presence of other phase(s) in the sample. This is probably Bi_2O_3 or related compounds, in agreement with the stoichiometries of the two main products obtained and of the inorganic salts engaged, as suggested by the line at about 27.5°. Noteworthy, the formation of the monoclinic $BiVO_4$ phase in this case is in agreement with the literature data. Indeed, this phase is commonly obtained by thermal treatment at rather high temperatures,[9] as is the case here. The chemical purity of the phases, namely, if the vanadates obtained by calcination are really free of organic contaminants, was checked by elemental analysis on the basis of the residual C, H, and N contents in the samples. Table 1 summarizes the results corresponding to the set of materials considered before. The values demonstrate that the residual carbon content is in all cases well below 0.3 %. Therefore, despite the use of a carbon-rich polymeric precursor, the amount of residual carbon in the final materials after calcination is quite low. This means that the preparation method is particularly well-suited for preparation of vanadate phases in a pure form. Because the potential applications of the $Bi_4V_2O_{11}$ phase are particularly promising, the stability of this material was studied as a function of the temperature, to determine the optimal conditions for its formation and stabilization. Figure 6 displays the X-ray thermodiffractograms recorded under air in the temperature interval from ambient temperature to 800 °C of a hybrid material containing $Bi(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3, with a molar ratio Bi/V of 2. Diffractograms were recorded at every 100 °C. The diffractograms of the material recorded at room temperature and 100 °C do not exhibit any line indicative of inorganic crystals. This observation provides a further piece of evidence of the full integration of the inorganic species in the polymer matrix, as discussed before. From about 200 °C, sharp lines corresponding to the formation of a Bi−V phase appear. This phase is characterized by marked lines for instance at about 11.1°, 23.1°, 27.5°, or 55.1°, which are typical of any $Bi_4V_2O_{11}$ phase. The absence of lines which are characteristic of the $BiVO_4$ phase (for example, at about 18.8°), even after magnification of the concerned zone, proves that the $Bi_4V_2O_{11}$ phase produced is not contaminated by a $BiVO_4$ phase (monoclinic: JCPDS 14-0688; tetragonal: JCPDS 14-0133; orthorhombic: JCPDS 85-1730). The nature of the polymorph that was obtained was identified in agreement with the corresponding JCPDS files (the orthorhombic α-phase or the tetragonal β- or γ-phases; JCPDS files: 41-0575, 44-0357, and 44-0358, respectively). As described previously in the case of the preparation of similar materials by using another synthetic route,[14] the absence of a splitting of the lines and of superlattice signals in the diffractograms suggest that the γ-phase is obtained. However, when the calcination temperature is increased from 300 to 800 °C, the intensity of the lines corresponding to $Bi_4V_2O_{11}$ decreases. Simultaneously, new lines appear which are characteristic of the $BiVO_4$ phase, for example, near 18.8°, 28.2°, or 34.1°. Pure $BiVO_4$ is stabilized up to 800 °C, even if the presence of other compounds in small amounts is not excluded, due to the stoichiometry of the metals engaged. The stabilization of the γ-$Bi_4V_2O_{11}$ phase at low temperature is not surprising, as the transitions $\gamma \rightarrow \beta \rightarrow \alpha$ by increasing the temperature from 400 to 650 °C, and then cooling to 500 °C, were already reported.[14] However, the present results differ from other observations, which evidenced the progressive transformation of the precursors to $BiVO_4$, and then to $Bi_4V_2O_{11}$, for example, by increasing the ball-milling time,[15] thus providing more energy to the system. In the same way, the synthesis of this phase via the "chelate" route by using precursors made from EDTA or related compounds can only be performed at high temperature (750 °C) and long annealing times (53 h).[33] In the present case, the stabilization of this phase at low temperature can be attributed to a particular effect due to the use of a polymeric matrix as unconventional organic precursor. However, more information is needed to clarify that point.

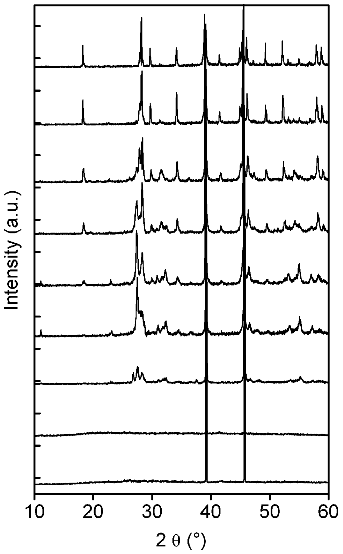

Figure 6. X-ray thermodiffractograms under air (from bottom to top: 25, 100, 200, 300, 400, 500, 600, 700, 800 °C) of a hybrid material made from the salt-free copolymer matrix and $Bi(NO_3)_3{\cdot}5H_2O$ incorporated jointly with NH_4VO_3. Relative amounts: 0.5 mol of metal ions/mol of repeat units of copolymer, Bi/V molar ratio = 2. The two peaks at 2θ values of about 39° and 46° correspond to typical reflections of the Pt support used for the in situ calcination experiments.

Preparation and Characterization of Thin Films of Bi−V−O Materials Made from Hybrid Precursors. Following the successful preparation of $BiVO_4$ in the form of powders, our new synthetic approach was explored in preliminary experiments to prepare Bi−V−O thin films. The films were grown on glass or on quartz supports. The supports were carefully pretreated by a standard procedure,[34] in order to

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(33) Lambrecht, M.; Wullens, H.; Devillers, M. Unpublished results.

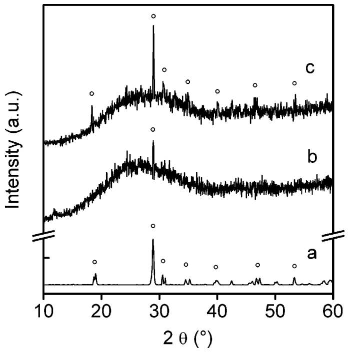

Figure 7. XRD patterns of $BiVO_4$ phases prepared by calcination of hybrid blends made from the polymer matrix and $Bi(NO_3)_3$·$5H_2O$ incorporated with NH_4VO_3 (relative amounts: 0.5 mol of metal ions/mol of repeat units of polymer, Bi/V molar ratio = 1): (a) bulk oxide; (b) film grown on quartz by 10 successive deposition cycles; (c) film grown on quartz by 15 deposition cycles (calcination temperature: 500 °C). (°) denotes the position of the most intense reflections that can be isolated in the diffractograms, and corresponding to the monoclinic $BiVO_4$ phase, in agreement with the JCPDS file.

clean the substrates and to increase their hydrophilicity. The precursor film was deposited just after cleaning, to control the whole process, and to avoid contamination of the substrates during storage. It was carried out by spin coating of the precursor solution containing the polymer matrix and the inorganic salts (namely, $Bi(NO_3)_3$·$5H_2O$ and NH_4VO_3) in stoichiometric ratio (Bi/V = 1), under acidic conditions (pH = 1, aqueous HNO_3 medium). After spin coating, the samples were dried in air (about 200 °C), and the process was repeated several times. Because of the insufficient thermal stability of glass substrates, quartz plates were selected for the calcination experiments. They were heated at 500 or 600 °C in air, to remove the organic component according to the TGA data, and to favor the formation of the crystalline phase at the surface of the plates.

The thin films were characterized after calcination by XRD. Figure 7 displays the typical XRD patterns of films grown on a quartz plate by 10 and 15 deposition cycles. It also compares them with the diffractogram of a bulk sample of monoclinic $BiVO_4$ obtained from the same kind of hybrid organic−inorganic materials as precursors (namely, the same preparation conditions and the same organic and inorganic precursor materials). The diffractogram of the film made from 15 deposition cycles exhibits lines which are in agreement with the formation of crystalline monoclinic $BiVO_4$ at the surface of the plate. In the case of a film grown from 10 deposition cycles, however, only the most intense reflection from $BiVO_4$ (around 28°) could be dectected in the diffractogram. From these data, it seems that contamination by other crystalline compounds present in large amounts and made from Bi or V was avoided during the fabrication process.

Since the plates were transparent, UV−vis spectra of the films in the simple transmission mode could be recorded. Figure 8 illustrates a representative spectrum of a $BiVO_4$ film grown on quartz and characterized by 12 deposition cycles. Even if no clearly resolved bands were detected, the spectrum exhibits two shoulders, at about 320 and 405 nm.

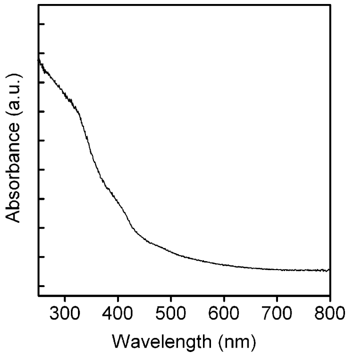

Figure 8. UV−vis spectrum of a $BiVO_4$ film growth on a quartz substrate by 12 successive deposition cycles, upon calcination at 500 °C of the hybrid blend made from salt-free copolymer matrix and $Bi(NO_3)_3$·$5H_2O$ incorporated jointly in the matrix with NH_4VO_3 (relative amounts: 0.5 mol of metal ions/mol of repeat units of polymer, Bi/V molar ratio = 1).

The shape of this spectrum and the position of the bands agree with related data from the literature, namely, the UV−vis spectrum of a $BiVO_4$ film grown on a glass substrate and prepared by decomposition of metallo-organic precursors.[29] In that case, the values of the maxima of the bands were 415 and 320 nm. In agreement with the literature,[35] the bands are attributed to charge-transfer transitions involving the vanadate component, on one hand, and Bi and V centers, on the other hand.

Conclusions

The preparation of Bi−V oxides was undertaken by using a new approach involving an appropriate organic polymer, bearing functional groups, and acting as matrix for the inorganic species. Homogeneous hybrid particles could be prepared by incorporation of bismuth nitrate and ammonium vanadate in solution under acidic conditions, and subsequent lyophilization. These particles were used as precursors for the preparation of bismuth vanadates. XRD and TGA measurements combined with elemental analysis data showed that the thermal treatment of these hybrid organic−inorganic materials under soft conditions in air favors pyrolysis of the polymeric matrix, and the formation of crystalline bismuth vanadate phases. More particularly, monoclinic $BiVO_4$ was obtained easily in the form of bulk oxide. In the same way, the γ-$Bi_4V_2O_{11}$ phase, which is known as a very efficient ionic conductor, was stabilized under rather soft conditions, too. This clearly demonstrates the particular interest of the new preparation route described compared to more standard procedures for the preparation of such phases. Subsequently, thin films of $BiVO_4$ deposited on quartz were prepared in the same way, by simple spin coating of the hybrid precursor made from the organic polymer matrix and the inorganic species, followed by thermal treatment of the homogeneous hybrid film. This demonstrates the real versatility and easy applicability of the method in the case of the preparation of multicomponent oxides in different forms.

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