



Solution synthesis of $Y_{1-x}Bi_xVO_4$ for optical applications

K. Hakouk^{a,b}, D. Giaume^a, P. Barboux^{a,*}, J. Sablayrolles^b

^a Laboratoire de Chimie de la Matière Condensée, CNRS UMR 7574, Chimie-Paristech, 11 rue Pierre et Marie Curie, 75005 Paris, France

^b Saint-Gobain Recherche, 39 Quai Lucien Lefranc, 93303 Aubervilliers, France

ARTICLE INFO

Article history:

Received 1 November 2011

Accepted 23 January 2012

Available online 1 February 2012

Keywords:

YVO_4 : Eu

$BiVO_4$: Eu

Film deposition

Bandgap engineering

ABSTRACT

Transparent luminescent $Y_{0.98-x}Bi_xEu_{0.02}VO_4$ ($0 < x < 1$) ceramic films have been prepared using a polymeric route and heat-treatment at 550 °C. A solid solution of zircon-type $Y_{1-x}Bi_xVO_4$ is obtained for x values below 0.5 whereas phase separation is observed above this limit. The absorption spectra of the films show a shift of the band edge towards high wavelength with the bismuth content, as theoretical calculi have predicted. Luminescence of the films under a UV excitation is typical of europium ion in the zircon structure. The poor correlation between absorption and excitation spectra at high bismuth content is coherent with desexcitation in localized states of valence band. However, the excitation wavelength could still be tuned from deep-UV to near-UV range by inserting bismuth in YVO_4 .

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Orthovanadates of trivalent metals show various optical applications. YVO_4 and other lanthanide vanadates are currently used as matrices for luminescent lanthanides [1] whereas $BiVO_4$ is a promising material for photocatalytic applications in the visible domain [2] or photoelectrochemical water decomposition [3]. All the properties of these materials rely on the position of the valence and conduction bands compared to the energy levels of luminescent doping rare earths or adsorbed molecules [4]. While the bandgap of YVO_4 lies in the deep-UV range at 3.8 eV, that of $BiVO_4$ lies at the edge of the visible range (2.9 eV). This last material can crystallize in three main structures, and depending on it, the bandgap changes. Previous works have already studied solid solutions in the system $Ln_{1-x}Bi_xVO_4$ [5–8] or in the system $Y_{1-x}Gd_xVO_4$ [9]. They have shown that increasing contents of Bi in zircon-type $Ln_{1-x}Bi_xVO_4$ up to $x=0.5$ shift the excitation bands down to low energy while the luminescence yield decreases. On the other hand, some works have reported the enhanced photocatalytic behavior of Ln doped monoclinic $BiVO_4$ [10,11]. The objective of this work is to deposit thin films of zircon-type $Y_xBi_{1-x}VO_4$ solid solutions doped with europium in order to modify the excitation spectrum of the Eu^{3+} ion luminescence. This allows the selective use of various visible solid-state lightning diodes (GaN-GaP) to obtain luminescence associated to the minimum of photocatalytic decomposition caused by deep UV [6].

In the literature, many different methods have been used to prepare vanadate films using solution techniques. Those techniques should allow an intimate mixing of all elements at the molecular level, thus enabling fast reactions at low temperature and homogeneous dispersion of the dopants. Methods use either dispersion of

nanoparticles, polymeric routes or sol gel methods. In the first option, the preparation of $BiVO_4$ nanoparticles can be obtained by ball milling [12], but controlled precipitation from nitrates and vanadates may be the most straightforward method to obtain nanoparticles of YVO_4 [13] or $BiVO_4$ [14,15]. Alternate methods such as hydrothermal synthesis [16], precipitation in confined systems such as microemulsions or nanocasting in a mesoporous silica matrix [17–19] can be used too. The polymeric routes [20] and similar methods such as the combustion methods [11,21] can be also used to form powders but they are more suited for thin films ceramic materials. The Pechini process using polymerization with citrate and ethylene glycol is probably the most versatile method [22–24] for this last purpose, although some alternative techniques have also been described such as Chemical Bath Deposition [25], ionic layer deposition [26], Metallo Organic Decomposition techniques [27], spray pyrolysis [28] and seed-mediated growth [29]. Finally, thin $Nd:YVO_4$ powders and thin films could also be synthesized by the sol-gel method using metal alkoxides in 2 methoxyethanol [30].

In this work we optimized a polymeric method based on condensation of beta-dicetones and hexamethylenetetramine to deposit transparent thin films of ceramics. The cationic species are chelated by the dicetones in the polymer [31]. These films have been used for comparing the absorption spectra with excitation spectra of $Y_{1-x}Bi_xVO_4$ doped with europium and opened a discussion on the origin of the optical properties.

2. Experimental section

2.1. Sample preparation and composition

2.1.1. Synthesis

Solutions for spin coating were prepared with chemical reagents (Aldrich chemicals) used as purchased. The metallic precursors

* Corresponding author.

E-mail address: philippe-barboux@chimie-paristech.fr (P. Barboux).

(yttrium acetate hexahydrate, bismuth nitrate and europium acetate pentahydrate) were first diluted in a water:acetic acid 1:1 mixture. The ratio of the elements was $0.98(1-x) \text{ Y} : 0.98 x \text{ Bi} : 0.02 \text{ Eu}$ [We call $M = \text{Bi} + \text{Y} + \text{Eu}$] ($M = 0.1 \text{ mol/L}$). x was varied from 0 to 1. Acetylacetone (1 mol/L) and hexamethylenetetramine, HMTA (1 mol/L) were added to the solution. A second solution was prepared by dissolution of NH_4VO_3 diluted in water at 0.1 M (1 equ.). The two solutions were mixed in equal volumes of 50 mL resulting in a M/V ratio of 1. The resulting solution was then heated under reflux (around 100°C) during 1 hour. It turned red and viscous (this is explained by the formation of a polyimine compound from condensation of amines and ketones). Half of the solution was dried in an oven at 150°C and calcined at various temperatures. Crystallization studies were performed using an X-ray powder diffractometer (X'Pert PRO, PANalytical) in the Bragg-Brentano geometry ($\text{Cu } \lambda(\text{K}_{\alpha\text{Cu}}) = 1.54056 \text{ \AA}$), on powders. Cell parameters refinements were performed with a linear model using the U-Fit software [32].

2.1.2. Film deposition

The second half of the solution was deposited by spin-coating onto soda-lime glass substrates of $10 \times 10 \text{ cm}^2$ for visual displays and onto $2 \times 2 \text{ cm}^2$ fused silica substrates for optical studies. A rotating speed of 2000 rpm was used during 30 seconds. The films were further calcined in the oven, at an appropriate temperature to obtain a well-crystallized film. The sequence was repeated three times to obtain a film thickness of 180 nm, as observed by Scanning electron microscopy.

2.1.3. Spectroscopic measurements

Transmission spectra of the powders and films within the range 200 nm–800 nm were obtained using a UV–vis Cary 6000 i spectrometer. Fluorescence properties were also characterized on a Fluorescence Spectrophotometer Cary Eclipse VARIAN. Emission spectra were recorded in the 550–750 nm range under an excitation at 280 nm, whereas excitation spectra were recorded in the 250–450 nm range using an emission wavelength of 619 nm. Internal bandpass filters were used in order to avoid the harmonics.

3. Results and discussion

3.1. Solid solution studies

X-Ray Diffraction patterns of the nominal $\text{Y}_{0.5}\text{Bi}_{0.5}\text{VO}_4$ composition have been performed after thermal post-treatment for one hour at different temperatures (Fig. 1). For temperatures below 550°C , multiphase materials are obtained. Those consist in a tetragonal distorted zircon-structure ($\text{Y}_{1-x}\text{Bi}_x\text{VO}_4$) that better crystallizes with temperature, and in a second monoclinic phase (BiVO_4) that disappears upon heating. Above 550°C , all the diffraction peaks are characteristic of the tetragonal zircon YVO_4 structure (space group $I4_1/amd$, JCPDS 04-007-8934), with a distorted cell. Bhattacharya et al. have reported that tetragonal BiVO_4 could be prepared by co-precipitation method at low temperature, but changed irreversibly into the monoclinic phase above 350°C [33]. Monoclinic BiVO_4 films with good photocatalytic properties could also be prepared by a citrate route at temperatures as low as 350°C [34]. However, in both cases, BiVO_4 remained in a monoclinic structure, even after a heating at 650°C . In our study, it seems that a zircon-type $\text{Y}_{0.5}\text{Bi}_{0.5}\text{VO}_4$ phase is obtained after a heating at 550°C with consumption of the monoclinic BiVO_4 . This higher temperature could be necessary due to the higher ionicity of YVO_4 compared with BiVO_4 . Because, our study was intended for applications to soda-lime glass that softens at moderate temperatures (600°C), it was

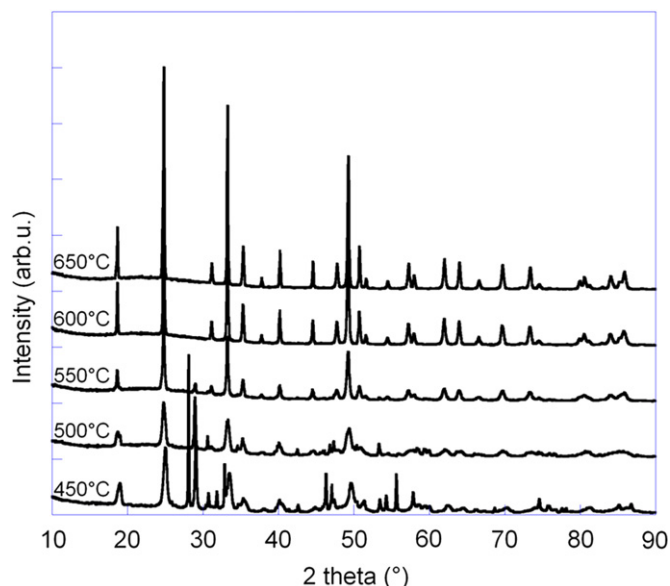


Fig. 1. X-Ray Diffraction patterns of the $\text{Y}_{0.5}\text{Bi}_{0.5}\text{VO}_4$ system after heat-treatment at 450°C , 500°C , 550°C , 600°C and 650°C .

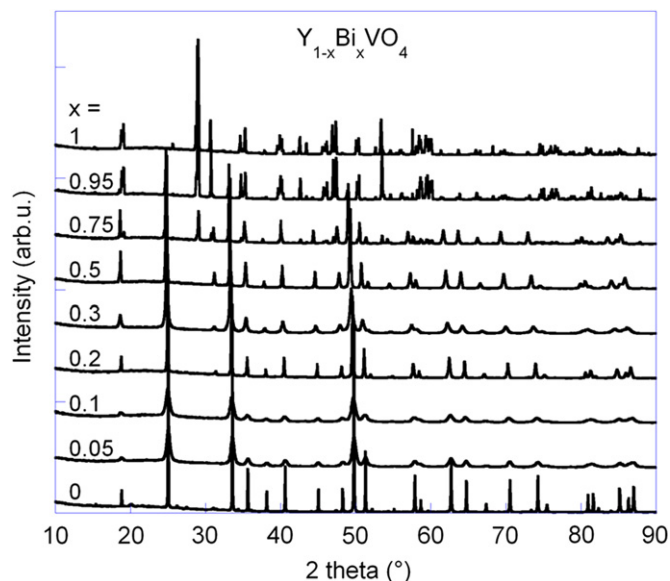


Fig. 2. X-Ray Diffraction patterns of the $\text{Y}_{1-x}\text{Bi}_x\text{VO}_4$ system post-treated at 650°C during 2 hours for $x = 0; 0.05; 0.1; 0.2; 0.3; 0.5; 0.75; 0.95$ and 1.

decided that a heat-treatment of one hour at 550°C was enough to reach well crystallized materials in the thin film geometry. But, one must point out that the following film study has been performed on pure silica substrates to avoid sodium diffusion or any parasitic reaction from an industrial glass.

Fig. 2 presents x-ray diffraction diagrams obtained on solid powders synthesized at 650°C for the $\text{Y}_{1-x}\text{Bi}_x\text{VO}_4$ samples with x varying from 0 to 1. The MVO_4 family crystallizes either with the tetragonal zircon structure (xenotime type) or the monoclinic structure depending on the size of the M ion [35]. For a bismuth content up to $x = 0.5$, a single phase is obtained, corresponding to the tetragonal zircon structure (space group $I4_1/amd$). This tetragonal structure consists of VO_4 tetrahedra sharing edges with MO_8 dodecahedra [36]. For $x = 0.75$, an additional diffraction pattern appears, which can be attributed to the monoclinic bismuth vanadate structure doped with yttrium (space group

Download English Version:

<https://daneshyari.com/en/article/5401558>

Download Persian Version:

<https://daneshyari.com/article/5401558>

[Daneshyari.com](https://daneshyari.com)