Materials Science and Engineering B xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Sb_2MoO_6, Bi_2MoO_6, Sb_2WO_6, and Bi_2WO_6 flake-like crystals: Generalized hydrothermal synthesis and the applications of Bi_2WO_6 and Bi_2MoO_6 as red phosphors doped with Eu^{3+} ions

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ARTICLE INFO

Article history:
Received 10 September 2015
Received in revised form
20 November 2015
Accepted 8 December 2015
Available online xxx

Keywords:
Tungstate
Molybdate
Hydrothermal
Phosphor
Luminescence

ABSTRACT

Under hydrothermal conditions, a series of flake-like Sb_2MoO_6, Bi_2MoO_6, Sb_2WO_6, Bi_2WO_6 with the Aurivillius structure have been prepared controllably. It reveals that the initial molar ratios of $SbCl_3$-to-NaOH (or $BiCl_3$-to-NaOH) in the reaction system ($SbCl_3$-Na_2MoO_4, $BiCl_3$-Na_2MoO_4, $SbCl_3$-Na_2WO_4, and $BiCl_3$-Na_2WO_4) play important roles in the determination of product phases. Besides, properly changing the content of NaOH involved can produce some unexpected phases such as orthorhombic Sb_2O_3 and tetragonal $Bi_{12}O_{17}Cl_2$. Moreover, substituting Bi^{3+} with Eu^{3+} at the A site is readily carried out because of their same valence states together with the similar ion radii. Consequently, the as-prepared Bi_2WO_6 and Bi_2MoO_6 samples have been doped with Eu^{3+} ions also under hydrothermal conditions to prepare the phosphors, which possess excellent red characteristics in terms of excitation and emission measurement. The present synthesis protocol has opened up an intriguing but effective avenue for producing antimony/bismuth-based materials, also exhibiting the potential application of red phosphors.

1. Introduction

As is well known, two-dimensional (2-D) nanoscale crystals, especially with atomic thickness, possess only in one axis and have infinite length in the plane, which makes them emerge as important new materials primarily due to their unique properties and potential applications in areas of optics, electronics and catalysis [1,2]. To largely fabricate 2-D nanocrystals as we desire, several kinds of solution-phase synthetic methods were documented [3]. In particular, in case of crystals possessing intrinsically layered structures, properly modulating the kinetic factors such as reaction temperature, solvent species and reagent concentration can result in 2-D nanostructures such as the excellent examples of graphene [4] and layered double hydroxides (LDHs) [5]. On the other side, certain kinds of surfactants (also known as structure modifier) are indispensable especially toward the kinetically induced anisotropic growth from molecular precursors for producing advanced shapes of nanocrystals since selective adhesion of surfactants can not only induce elongation along a specific axis but it can also induce compression along other axes [6,7]. For example, the alkanethiol molecules strongly adsorbed on the {001} faces of Cu_2S can markedly lower the surface energy, and thus 2-D Cu_2S nanodiscs occur [8].

Bismuth mixed oxides with the Aurivillius structure represented as $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (A = Ca, Sr, Ba, Pb, Bi, Na, K and B = Ti, Nb, Ta, Mo, W, Fe) possess unique layered structures by the perovskite slabs of $(A_{n-1}B_nO_{3n+1})^{2-}$ sandwiched between $(Bi_2O_2)^{2+}$ layers [9], as shown in Fig. 1, commonly giving rise to interesting physical properties such as ferroelectrics [10], catalytic behavior for organics [11], oxygen ion conductors [12]. Clearly, Bi_2WO_6 and Bi_2MoO_6 are the simplest members of these oxides with $n = 1$.

As an important set of visible-light active photocatalysts, Bi_2WO_6 and Bi_2MoO_6 nanocrystals as well as their self-assembled superstructures have been especially highlighted for environmental purification, water splitting and photocatalytic performance. For the case of Bi_2WO_6 sample, hierarchical flower-like hollow microspheres [13], porous nanosheets [14], and 1-D nanostructures [15] have been produced by the solvothermal process, solution-phase followed with calcination treatment, and electrospinning method, respectively. Regarding the case of Bi_2MoO_6, solvothermal method has been implemented for producing various kinds of flake-like

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http://dx.doi.org/10.1016/j.mseb.2015.12.003
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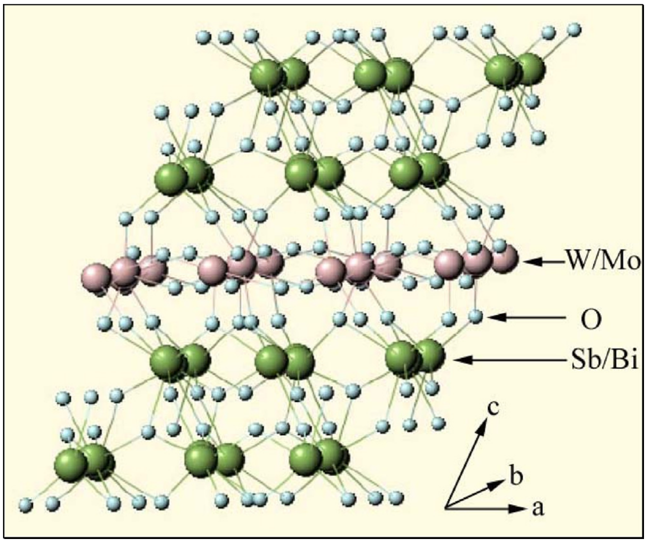

Fig. 1. Schematic depiction of A_2BO_6 (A = Sb, Bi and B = W, Mo) possessing Aurivillius structure.

microstructures [16], hollow microspheres [17–19]. Interestingly, Bi_2MoO_6 nanosheet-built frameworks were prepared by using MoO_3 nanobelts as the growth templates and molybdate source [20]. Besides, Sb_2WO_6, crystallizing in the triclinic system, is built up by $[WO_4]_n$ layers of WO_6 octahedra sharing corners, as in the simplest Aurivillius phase Bi_2WO_6, sandwiched by two $[Sb_2O_2]_n$ layers [21]. Regarding the crystal structure of Sb_2MoO_6, MoO_6 octahedra share corners and build sheets with the $[MoO_4]_n$ composition, which are separated by $[Sb_2O_2]_n$ layers [22,23]. Sb_2MoO_6 has been proved to be efficacious as organic catalyst for example in the field of sulfoxidation of thioethers [24] and selective oxidation of isobutene to methacrolein [25]. As for the preparation of Sb_2WO_6 and Sb_2MoO_6 samples by solid state method, rigorous experimental techniques such as high reaction temperature, vacuum or inert atmosphere are usually required [25,26], except for the recent reports on hierarchical architectures of Sb_2WO_6 [27,28]. However, as much as we know, few reports concerning the solution-phase method such as hydrothermal method has been documented in the literature on the systematical preparation of Sb_2MoO_6, Bi_2MoO_6, Sb_2WO_6, Bi_2WO_6 samples in a controllable manner without complex apparatuses or harsh conditions.

On the other hand, rare earth ions doping inorganic phosphors have attracted extensive attention owing to their remarkable luminescent properties and applications, commonly referring as of lamp industry, radiation dosimetry, X-ray imaging, and color display [29]. Trivalent europium (Eu^{3+}), as an efficient red luminescent activator, has been widely studied in terms of its electronic transitions from the lowest $^5D_0$ excited state to ^7F_J (J = 0, 1, 2, 3, 4) ground state, strongly depending on their local environments in host lattices [30]. Interestingly, bismuth compounds can serve as the host material for phosphors, because Bi^{3+} ions can be replaced partly by rare earth ions, which can absorb outer energy, efficiently transferring from Bi^{3+} to rare-earth ions [31]. To date, using Bi_2MoO_6 as the host material, various kinds of dopants have been utilized, mostly including Er^{3+}/Yb^{3+} [32], Ce^{3+} [33], Eu^{3+} [34], Sm^{3+} [35]; whereas, the host of Bi_2WO_6 is rarely employed as phosphor host when doping with Eu^{3+} [36,37]. Thereby, further investigating the doping of Eu^{3+} ions into Bi_2MoO_6 and Bi_2WO_6 samples together with their luminescent properties is also quite intriguing but necessary for red phosphor applications.

Herein, a series of antimony/bismuth based tungstate/molybdate samples have been prepared under hydrothermal conditions. The initial molar ratios of $SbCl_3$-to-NaOH (or $BiCl_3$-to-NaOH) in the reaction system were studied in detail, clearly revealing that the phase of final products strongly depend on them. In addition, the as-prepared Bi_2MoO_6 and Bi_2WO_6 samples were doped with Eu^{3+} ions to prepare the corresponding phosphors, whose luminescent properties were also studied.

2. Experimental

All chemicals are of analytical grade and used as received without further purification. In this work, for the sake of obtaining a series of Sb_2MoO_6, Bi_2MoO_6, Sb_2WO_6, and Bi_2WO_6 samples, all experiments were carried out in a 50 mL Teflon-lined stainless steel autoclave at 180 °C for 12 h by simply adjusting the initial molar ratios of $SbCl_3$-to-NaOH (or $BiCl_3$-to-NaOH) while keeping the initial molar ratio of $SbCl_3$-to-Na_2MoO_4 ($BiCl_3$-to-Na_2MoO_4, $SbCl_3$-to-Na_2WO_4, or $BiCl_3$-to-Na_2WO_4) as 2:1.

2.1. Typical hydrothermal procedure for preparing Sb_2MoO_6 sample

$SbCl_3$ (2 mmol) and $Na_2MoO_4{\cdot}2H_2O$ (1 mmol) were in turn added into 20 mL distilled H_2O under magnetic stirring, resulting in dark green precipitates. After being stirred for 20 min, aqueous solution (20 mL) containing 4 mmol NaOH was gradually poured into the above suspension. Next, the above suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was then sealed and kept at 180 °C in an electrical oven. After 12 h, the resulting dark green product was filtered off, washed with distilled water and absolute ethanol for several times, and then dried under vacuum at 60 °C for 6 h.

Similarly, light yellow Bi_2MoO_6, grass green Sb_2WO_6, and light cyan Bi_2WO_6 samples were obtained by properly changing the initial molar ratios of $SbCl_3$-to-NaOH (or $BiCl_3$-to-NaOH).

To obtain Bi_2WO_6:Eu^{3+} (or Bi_2MoO_6:Eu^{3+}) phosphors, 0.04 mmol $Eu(NO_3)_3$ prepared by dissolving Eu_2O_3 powders in concentrated HNO_3 solution was added into the above mentioned suspension while keeping other reaction parameters unchanged.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku Max-2200 with Cu Kα radiation. Field emission scanning electron microscopy (FESEM) images were taken with a Hitachi S-4800 scanning electron microscope. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images were performed with a JEOL 2100F unit operated at 200 kV. Photoluminescent (PL) analysis was conducted on a Hitachi F-4500 spectrophotometer with Xe lamp at room temperature.

3. Results and discussion

X-ray diffraction (XRD) technique is an effective tool to determine the phase, crystallinity and purity of samples prepared under various conditions. Previously, we presented a straightforward but effective solution-phase method (*i.e.* hydrothermal process) for the selective synthesis of BiOCl, $BiVO_4$ and δ-Bi_2O_3 nanocrystals by simply manipulating the reaction temperature and the $BiCl_3$-to-NaOH molar ratio in the reaction system of $BiCl_3$-NH_4VO_3-NaOH [38], in which we found that the $BiCl_3$-to-NaOH molar ratio (*i.e.* the content of NaOH in solution) is extremely crucial for the determination of final products.

In present work, we emphatically studied the effect of various $SbCl_3$-to-NaOH molar ratios upon the product phases in the

Please cite this article in press as: Z.J. Zhang, X.Y. Chen, Mater. Sci. Eng. B (2016), http://dx.doi.org/10.1016/j.mseb.2015.12.003