J Mater Sci (2009) 44:1412–1415
DOI 10.1007/s10853-009-3258-5

LETTER

Synthesis and characterization of nanoscaled $BiPO_4$ and $BiPO_4$:Tb

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Received: 25 July 2008 / Accepted: 8 January 2009 / Published online: 4 February 2009

$BiPO_4$ has been claimed for several aspects of technical application, including catalysis [1, 2], orthophosphate ion sensing by means of a quartz-crystal microbalance [3], as well as coprecipitation and separation of radioactive actinides [4, 5]. Especially for catalysis $BiPO_4$ is a promising candidate and has been used, e.g., for a reduction of butyraldehyde to *n*-butanol [6]. Moreover, $BiPO_4$ has been denoted as a host lattice for incorporation and luminescence of rare-earth ions [7, 8]. Structurally, $BiPO_4$ has been described with three different modifications, whereof the monazite-type structure is thermodynamically most favored [9–11]. On the nanoscale, rod- or wire-type $BiPO_4$ has been recently synthesized via sonochemical [12] and CVD [13] methods. Interestingly, spherical shapes with uniform size and a low degree of agglomeration have not been addressed, yet.

In this study, a polyol-mediated synthesis has applied to realize $BiPO_4$ nanocrystals. The underlying concept of synthesis—a multidentate and high-boiling alcohol as the liquid phase (so-called polyol)—has been widely used already [14–17]. In a typical recipe, diethylene glycol (DEG, 100 mL, 99%, Acros) as the polyol was placed in a 250 mL beaker. BiI_3 (1.2 g) was added and dissolved at 60 °C (solution 1). In addition, 260 mg $NH_4H_2PO_4$ were dissolved in 4 mL deionized H_2O (solution 2). Solution 2 was added to solution 1 under vigorous stirring, resulting in an immediate nucleation. After 2 min the suspension was rapidly heated to 160 °C and kept there for 1 h; thereafter the suspension was left to cool to room temperature. To separate the solid material, ethanol (100 mL) was added and the suspension centrifuged (15 min, 25000 rpm). Thereafter, the colorless fine powder was resuspended in ethanol and centrifuged twice in order to remove all DEG and remaining salts. Finally, the product was dried under reduced pressure (10^{-3} mbar, 1 h, 70 °C). Nanoscale $BiPO_4$:Tb (1 mol%) was realized by addition of 100 mg $Tb(NO_3)_3 \cdot 6\,H_2O$ to BiI_3. Fractions of the final product were calcinated in a chamber furnace in air at 750 °C (5 min) and 800 °C (40 min) in order to study temperature-driven crystallinity, degree of agglomeration, as well as luminescence.

As-prepared $BiPO_4$ was characterized by dynamic light scattering (DLS, Malvern Instruments Nanosizer ZS), scanning electron microscopy (SEM, Zeiss Supra 40 VP, samples deposited on silicon and sputtered with Pt), X-ray powder diffraction (XRD, Stoe Stadi P system, Ge-monochromatized Cu-K_α radiation), Fourier-transform infrared spectroscopy (FT-IR, Bruker Vertex 70 FT-IR), and thermogravimetry (TG, Netzsch STA409C, nitrogen atmosphere). Photoluminescence (PL) was recorded with a Jobin Yvon Spex Fluorolog 3 equipped with a 450 W Xe-lamp and double grating excitation and emission monochromators. The quantum yield was measured by comparison to $LaPO_4$:Ce,Tb (45 mol%, 15 mol%) as a standard lamp phosphor (Philips, particle size: 4–8 µm, quantum yield: 86% of Tb^{3+}-related emission at $\lambda_{excitation} = 254$ nm) [18].

Particle size, particle shape, and degree of agglomeration of as-prepared $BiPO_4$ were validated for powder samples as well as for redispersed material. SEM (Fig. 1a) displays very uniform and non-agglomerated particles with a mean diameter of 33(12) nm. This mean diameter was gained based on a statistical evaluation of about 100 particles. DLS analysis of redispersed $BiPO_4$ in DEG results in a

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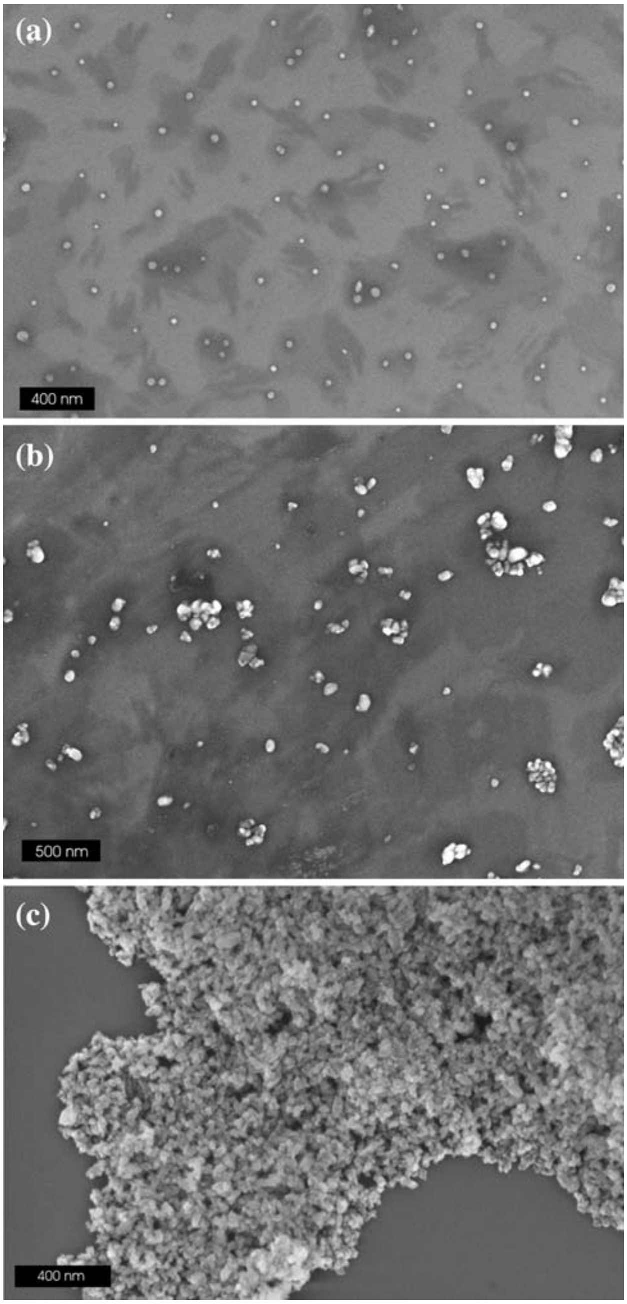

Fig. 1 SEM images of the as-prepared $BiPO_4$ particles (**a**) as well as subsequent to calcination at 750 °C (**b**) and 800 °C (**c**)

hydrodynamic diameter of 37(7) nm (Fig. 2). This value confirms the presence of non-agglomerated particles as well as the particle size as given by SEM. Furthermore, the specific surface of as-prepared $BiPO_4$ powders was verified via nitrogen adsorption. Based on the BET-method (Brunauer-Emmett-Teller) a value of 36 $m^2\ g^{-1}$ was determined. Considering a bulk density of $\rho = 6.323\ g\ cm^{-3}$ [19], a particle diameter of about 26 nm was deduced, which again is in accordance with the above results.

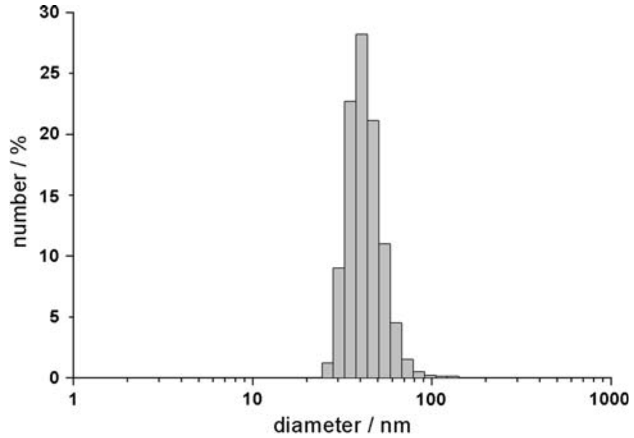

Fig. 2 Dynamic light scattering of $BiPO_4$ resuspended in DEG

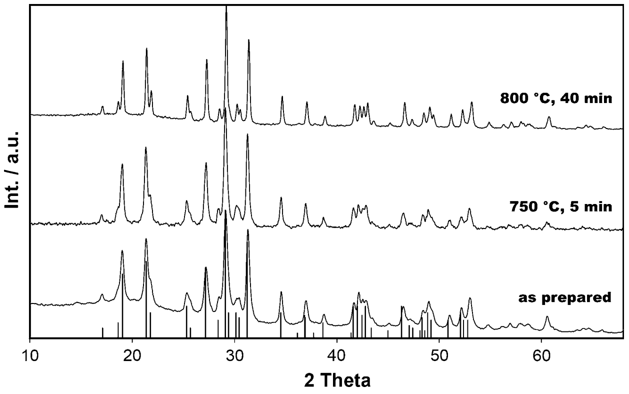

Fig. 3 X-ray powder diffraction of $BiPO_4$ nanoparticles (ICDD-No. 15–767 as a reference)

Chemical composition and phase purity of nanoscaled $BiPO_4$ were investigated by XRD as well as by FT-IR. To this end, XRD analysis of washed and dried powder samples exhibits broadened reflections, which match with monazite-type $BiPO_4$ (Fig. 3). Based on Scherrer's equation, the particle diameter was calculated to 34 nm for the (120) reflection ($2\Theta = 29.1°$). This crystallite size is in good agreement to the primary particle diameter stemming from SEM and DLS. FT-IR spectra are very comparable to reference data of bulk $BiPO_4$ (Fig. 4: $\nu(PO_4)$: 1150–850 cm^{-1}, $\delta(PO_4)$: 650–550 cm^{-1}) [10]. Based on former investigations, additional vibrations at 3650–3350 cm^{-1} (ν(O–H)), 2950–2800 cm^{-1} (ν(C–H)), 1600–1550 cm^{-1} (δ(O–H)), and 1250 cm^{-1} (ν(C–O)) can be related to DEG and H_2O adhered on the particle surfaces [20, 21]. TG of solid powders showed a weight loss of 1% in two steps. A first weight loss of 0.7% starts at 40 °C and is completed at about 120 °C. A second step occurs with a weight loss of 0.3% between 260 °C and 400 °C. The first step can be attributed to the evaporation of surface-bound water and ethanol; the second step is due to the loss of DEG on the particle surface. It is interesting to note that differential

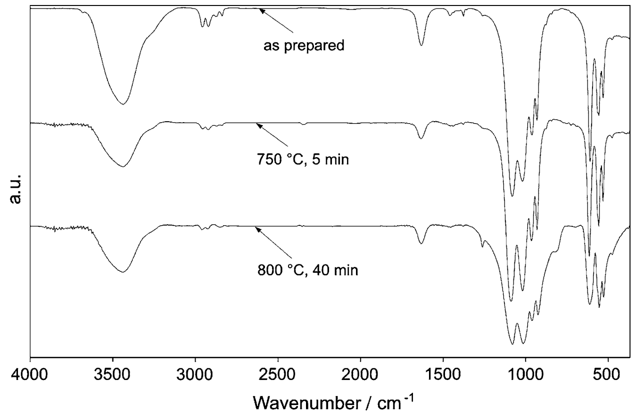

Fig. 4 FT-IR spectra of $BiPO_4$ nanoparticles

thermal analysis does not show any thermal effect up to 800 °C, although exothermal transformation to the monoclinic high-temperature form was described in literature to occur at about 600 °C in case of bulk $BiPO_4$ [9–11]. This difference might be due to kinetic effects. Concordantly, the residue of TG analysis with XRD analysis shows the monazite-type modification, too (Fig. 3).

Aiming at luminescence, $BiPO_4$ nanocrystals were codoped with 1 mol% Tb^{3+}. Excitation and emission spectra show characteristic Tb-related transitions (Fig. 5) [22]. This is excitation via strong $4f^85d^0 \rightarrow 4f^75d^1$ transition as well as via weak transitions is within the 4f-manifold of Tb^{3+}. Emission is dominated by $^5D_4 \rightarrow {}^7F_J$ relaxation. By comparison to $LaPO_4$:Ce,Tb as a reference exhibiting very similar luminescent processes, the quantum yield of as-prepared $BiPO_4$:Tb was measured to 2% [18]. Note that the host lattice is inactive to luminescence at room temperature due to well-known concentration quenching of Bi^{3+} [23]. By calcination at 750 °C for 5 min the emission intensity as well as the quantum yield (12%) was significantly increased. XRD analysis still proves the presence of the monazite modification (Fig. 3); FT-IR spectra of the calcinated powder only show a decrease of DEG- and water-related vibrations (Fig. 4). After short-timed calcination, BET analysis with 16 $m^2\ g^{-1}$ suggests a certain agglomeration, which is confirmed by first small agglomerates visible on SEM images (Fig. 1b). With a mean diameter of 39(14) nm (SEM) and 30(4) nm (DLS) $BiPO_4$:Tb is nevertheless nanoscaled and can still be redispersed in DEG or ethanol. Increasing duration and temperature of calcination to 40 min at 800 °C results in an even higher quantum yield (23%). However, significant agglomeration of nanoscaled particles is now observed considering SEM images (Fig. 1c) and the values of specific surface (0.3 $m^2\ g^{-1}$). As a consequence, redispersion of $BiPO_4$:Tb is not possible any more.

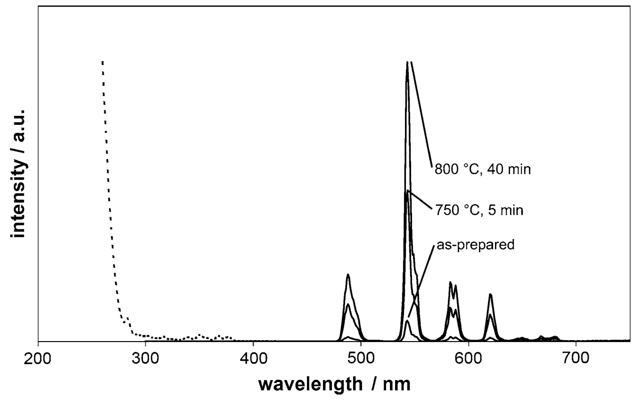

Fig. 5 Excitation and emission spectra of $BiPO_4$:Tb ($\lambda_{exc.} = 254$ nm, $\lambda_{em.} = 542$ nm)

In summary, nanoscale $BiPO_4$ was firstly gained via a polyol-mediated synthesis, resulting in non-agglomerated and very uniform particles, about 30 nm in size. Tb-codoped $BiPO_4$ nanocrystals show intense emission of green light. The underlying quantum yield was increased to 12% by short-timed calcination (700 °C, 5 min), which still allows for redispersion.

Acknowledgements The authors are grateful to the DFG Center for Functional Nanostructures (CFN) at the University of Karlsruhe for financial support.

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