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Preparation of sub-micrometer $LnPO_4$ particles (Ln = La, Ce)

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Sub-micrometer $LnPO_4$ particles (Ln = La, Ce) are prepared by heating of $Ln(CH_3COO)_3 \cdot 2H_2O$ and $(NH_4)H_2PO_4$ in diethylene glycol (DEG) at 180°C. Based on this so-called polyol method, spherical $LnPO_4$ particles 30 to 180 nm in size can be realised. According to X-ray powder diffraction patterns, the phosphates turn out to be highly crystalline right after preparation. The particle size is investigated with scanning electron microscopy in the powder state as well as with laser diffraction methods in the DEG suspension. Furthermore, the agglomeration behaviour of the phosphate particles in DEG suspension after mixing with water and the properties of re-suspended powder material in water is studied.

1. Introduction

Sub-micrometer particles are of rapidly growing interest for fundamental research as well as for technical application. Photonic crystals, transparent solar cells as well as coatings are some important items worth mentioning [1–4]. Despite the fact that sub-micrometer sized materials show various interesting properties and although they are suitable for a wide area of applications, till now synthesis is concentrated on a limited number of materials. To a large extent oxides such as ZnO, Al_2O_3, SiO_2, TiO_2 or SnO_2 or ternary compounds, for instance $BaTiO_3$, have been investigated [1, 5–8]. Furthermore, with up-coming quantum dots, low band gap materials such as ZnS, CdS, CdSe have been examined [8–10]. However, with regard to more elaborate complex oxides, for instance phosphates, little is known [11–13]. Nevertheless, sub-micrometer metal phosphates can be very interesting concerning to flame-proofing agents, optical coatings or luminescent materials [14, 15].

With respect to the area of application mentioned above, it is often intended and attractive to apply non-agglomerated and highly crystalline metal phosphates as source of the material. Unfortunately, to gain materials crystallinity often a certain heat treatment is necessary which, on the other hand, normally favours agglomeration. In fact, an optimisation of the one or other requirement might contradict. Therefore, the need for careful selection of the experimental conditions is obvious. To this end, previous investigations aiming at nanoscale oxides have shown that the so-called polyol method is very attractive in order to realise crystalline and sub-micron sized particles [16, 17]. For the first time, the method is described here for the preparation of phosphates.

2. Experimental

A typical recipe for the preparation of nanoscale $LnPO_4$ (Ln = La, Ce) particles is as follows. 15.8 mmol $La(CH_3COO)_3 \cdot 2H_2O$ (99.9%, Aldrich) were filled in a round-bottomed flask. The solid was suspended in 50 ml diethylene glycol (99%, Merck) by rapid stirring. The suspension was heated for 1 h at 140°C. When it had become clear, 17.4 mmol $(NH_4)H_2PO_4$ (99%, Merck) diluted in 3 ml demineralised water were added. Afterwards, the solution was heated at 180°C for 4 h. After cooling to room temperature, the solid was separated by centrifugation. In order to remove diethylene glycol, the solid was twice re-suspended in ethanol and centrifuged again. Finally, the solid was dried 30 min at 60°C in a drying oven.

A Philips SEM XL30 equipped with a tungsten field emission gun was used for scanning electron microscopy (SEM). Samples were sputtered with carbon (300 Å). The investigations were carried out at room temperature applying a voltage of 15 to 25 kV. The spot size was 20 nm and the free working distance (FWD) 9 to 12 mm.

X-ray powder diffraction (XRD) was performed with a Philips vertical goniometer PW1050 with Bragg-Brentano-geometry. The diffractometer was equipped with a fixed divergence slit and a proportional counter. Cu K_α radiation was used and monochromatised by a secondary graphite monochromator.

Measurements of the particle size were performed based on laser diffraction techniques combined with polarisation intensity differential scattering. For this purpose a Coulter LS230 equipped with a laser (750 nm, 5 mW) and a PIDS lamp (tungsten-halogen, 150 lumens at 2,900 K) as well as 126 photodiode detectors was used.

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3. Results and discussion

$LaPO_4$ and $CePO_4$ are prepared based on the polyol method applying metal acetates and $(NH_4)H_2PO_4$ as precursor materials. By heating in diethylene glycol (DEG) colloidally stable suspensions of the phosphates are obtained. Solids contents up to 10 wt% can be realised. In order to characterise the materials, firstly, the solid is separated from the liquid. Scanning electron microscopy proves that indeed sub-micrometer and almost spherically shaped particles are formed (Fig. 1). The average diameter can be estimated to 110–140 nm in case of $LaPO_4$ and to 40 to 60 nm in case of $CePO_4$. Both ranges give also a representative picture of the particle diameter which can be realised with the polyol method. To this end, the concentration of the starting materials and the duration of the reaction are the most important parameters to control the particle size (Table I). Increasing the one or other parameter leads to enlarged particles. Moreover, also the type of precursor material and the reaction temperature have effect on the size as well as on the shape of the phosphate particles.

X-ray powder diffraction patterns prove that $LaPO_4$ and $CePO_4$ are well crystallised directly after the

TABLE I Influence of reaction parameters on the particle diameter of $LaPO_4$

Concentration		Temperature	Duration of heating	Particle diameter
(mmol La^{3+})	[mmol PO_4^{3-}]	(°C)	(h)	(nm)
7.6	9.6	180	2	30–35
15.8	17.4	180	2	90–100
20.1	21.2	180	6	160–180

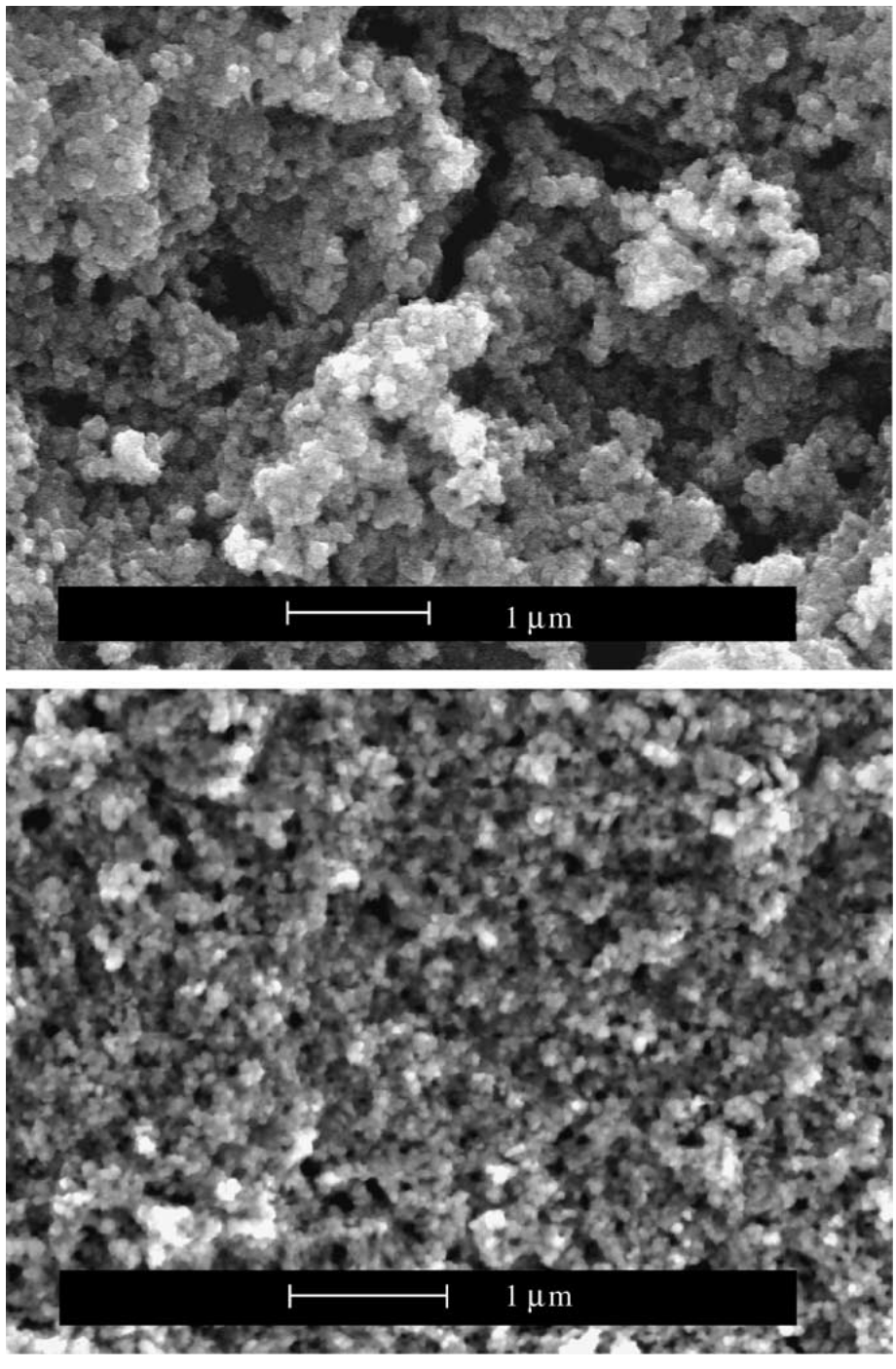

Figure 1 SEM photos of sub-micrometer $LaPO_4$ (top) and $CePO_4$ (bottom) particles.

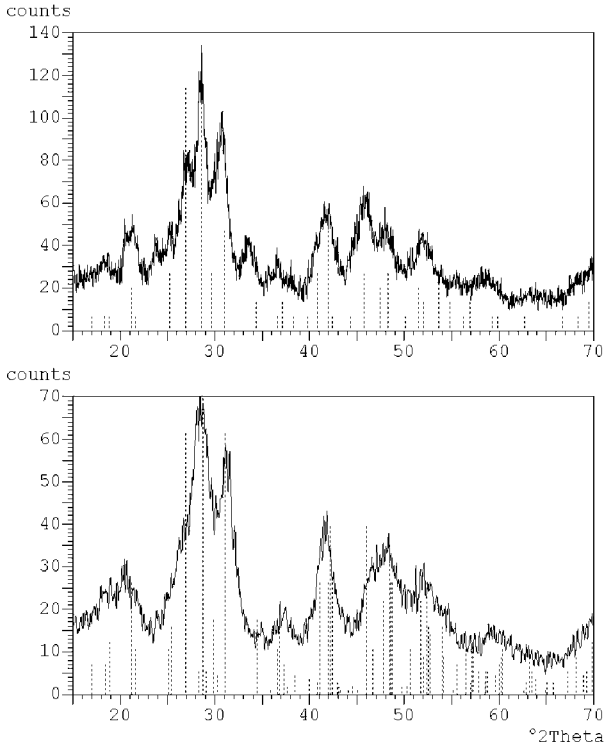

Figure 2 XRD patterns of sub-micrometer $LaPO_4$ (top, ICDD-ref. 35-0731) and $CePO_4$ (bottom, ICDD-ref. 32-0199) particles.

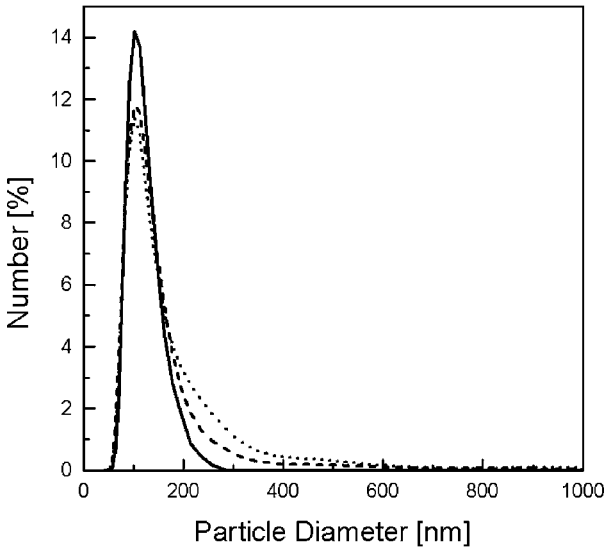

Figure 3 Particle size distribution of $LaPO_4$ particles in DEG (solid), H_2O (dashed) and resuspended powder in H_2O (doted).

synthesis with 180°C as the highest temperature applied (Fig. 2). Both phosphate materials are with the monazite type of structure. The results of differential scanning calorimetry and of thermal gravimetry point to the fact that a significant exothermic weight loss (about 3%) occurs between 220 and 300°C. In accordance with the boiling point of DEG (246°C [18]), this weight loss can be attributed to diethylene glycol remaining on the particle surface even after careful washing. Former investigations aiming at nanoscale oxides have shown that the DEG film being adhered on the particle surfaces is very important in order to limit the particle growth as well as to prevent the particles from agglomeration [16, 19].

In order to study the particle size distribution in suspension, laser diffraction techniques are applied. On one hand, a suspension of $LaPO_4$ in diethylene glycol is investigated as prepared. Here, a quite narrow size distribution is observed. The average particle size (d_{50}) is measured to be 116 nm (Fig. 3). This is in reasonable agreement with the findings of the SEM analysis and indicates that the DEG suspension indeed contains non-agglomerated, primary particles. Moreover, the particle size distribution is investigated while mixing the DEG suspension with water ($DEG : H_2O = 1 : 50$). Again, a very similar average particle diameter ($d_{50} : 124$ nm) is confirmed. A slight broadening of the particle size distribution towards larger particles tends to the fact that at least some agglomeration occurs. However, the agglomeration is much slower than it was found in case of nanoscale oxides particles such as Nb_2O_5 or $CoAl_2O_4$ [16, 20]. Finally, a $LaPO_4$ powder which was centrifuged off and washed is re-suspended in water applying an ultrasonic treatment. Afterwards, an average diameter (d_{50}) of 121 nm is detected which is again very similar to the as prepared DEG suspension. Again, a broadening of the size distribution curve occurs, indicating that some agglomerates still remain after the re-suspension or that again sleight agglomeration in water starts.

4. Conclusions

Nanoscale $LaPO_4$ and $CePO_4$ particles about 30 to 180 nm in size are prepared with the polyol method. The synthesis results in colloidal suspensions containing non-agglomerated phosphate particles in diethylene glycol. From these suspensions, the solid material can be separated via centrifugation. Residual diethylene glycol adhered on the particles surface is removed by heating of the powder to 400°C. The nanoscale phosphate powders are well crystallised and can easily be re-suspended, for instance, in water.

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