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Investigations of alkaline rare earth orthophosphates $M_3RE(PO_4)_2$

Lothar Schwarz*, Matthias Kloss, Annemarie Rohmann, Ute Sasum, Detlef Haberlandl

Institute of Physical Chemistry, Ernst-Moritz-Arndt-University Soldtmannstr. 23, D-17489 Greifswald, Germany

Abstract

A preparation route to synthesize rubidium and/or potassium rare earth double phosphate powders of the type $M_3RE(PO_4)_2$ (RE=La, Ce, Eu, Gd, Tb) as pure phases in a solid state reaction is described. The essential fact of the reaction is to make use of the low particle size of freshly precipitated rare earth phosphate $REPO_4.nH_2O$ as a starting material. Properties of the materials are described. © 1998 Elsevier Science S.A.

Keywords: FTIR; Lanthanum; Particle size frequency distribution; Phosphate; Potassium; Rare earth; REM; Rubidium; Solid solution; Solid state reaction; Thermal analysis; X-ray diffraction pattern

1. Introduction

Alkaline rare earth orthophosphates $M_3RE(PO_4)_2$ (M= Na, K, Rb; RE=La, Gd, Eu, Ce, Tb) and solid solutions like $K_3La_{1-x-y}Ce_xTb_y(PO_4)_2$ have already been described. These compounds were usually prepared from rare earth sesquioxides as powders by a solid state reaction via

$$6MHCO_3 + RE_2O_3 + 4(NH_4)_2HPO_4 \rightarrow 2M_3RE(PO_4)_2 + 6CO_2 + 5H_2O + 8NH_3 \quad (A)$$

or grown as crystals out of a flux of alkaline diphosphates. It was very difficult to synthesize pure phase $Rb_3RE(PO_4)_2$ powders by the above mentioned methods [1,2]. These double phosphates melt incongruently at about 1000°C. A formation of the $M_3RE(PO_4)_2$ double phosphates using monazite type compounds as a starting material is not to be expected due to the melting temperatures of these phosphates at about 2000°C, for instance for $LaPO_4$ $\vartheta = 2072 \pm 20$°C [3]. From a thermodynamic point of view, powders of pure double phosphate phases can not be formed by cooling melts of mixtures of the starting materials. Therefore we tried to find a preparation method using other rare earth phosphates as starting materials.

2. Experimental

Starting materials of high purity (Rare earth nitrates or oxides, 99.999%; Aldrich Corp./Steinheim) were used. Rubidium dihydrogen phosphate RbH_2PO_4 was prepared by precipitation [4]. Determination of particle size frequency distribution was carried out by a Fritsch particle sizer, type Analysette 22. Thermogravimetry (TG) and Differential Thermoanalysis (DTA) were conducted by the equipment SETARAM TGDTA 92 (heating rate: 10 $K\,min^{-1}$.; reference material: α-alumina). FTIR measurements in KBr technique were recorded by a PERKIN ELMER System 2000 spectrometer from 4000 to 400 cm^{-1}. REM photographs were produced by Digital Scanning Microscope DSM 940A C.Zeiss/Oberkochen, X-ray diffraction pattern by HZG4 of Feinmechanik Freiberg/Germany.

3. Results

Attempts were made to synthesize rubidium and/or potassium rare earth double phosphates (RE=La, Ce, Eu, Gd, Tb) corresponding to

$$MH_2PO_4 + M_2CO_3 + REPO_4.nH_2O \rightarrow M_3RE(PO_4)_2 + CO_2 + H_2O. \quad (B)$$

We used freshly precipitated rare earth orthophosphate hydrates $REPO_4\ .nH_2O$, for example $LaPO4.(0.6)H_2O$, as starting materials. Both grain size distribution measurements and REM photographs demonstrate the very small particle size of these phosphates. The grain size increases by agglomeration during the drying process of the precipitate (Fig. 1). Nevertheless, REM pictures show that one of the remarkable features of these products is their large

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*Corresponding author.

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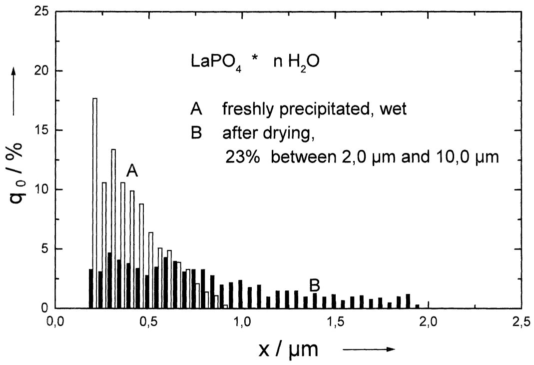

Fig. 1. Particle size frequency distribution of $LaPO_4.nH_2O$.

surface (Fig. 2). The X-ray diffraction pattern confirms that the $LaPO_4.nH_2O$ we prepared crystallize in the hexagonal rhabdophane structure [5]. It was converted into the monazite-type structure [5] by heating at 1000°C.

Blinc et al. [6] found by thermoanalysis at high temperature a phase change in tetragonal RbH_2PO_4 crystals at 86°C as a result of a quasi-irreversible transition to a monoclinic modification . As is shown in Fig. 3, the decomposition of the rubidium dihydrogen phosphate, accompanied by heat flow peaks at about 220°C and between 280°C and 350°C, occurs as a multistep reaction. This conclusion corresponds to the results of the FTIR absorption spectra, shown in Fig. 4. The typical FTIR spectrum of an orthophosphate which is found at room temperature (characteristic for PO_4 tetrahedra: stretching frequencies ν_s and ν_{as} between 850–1150 cm^{-1}, and deformation frequencies δ_s and δ_{as} between 400–550 cm^{-1}), changes step by step into that of a typical chain phosphate [7,8].

The X-ray diffraction pattern as well as FTIR absorption spectra of the final products confirm that the new preparation route type B at 930°C leads to the expected pure-phase compounds of the type $M_3RE(PO_4)_2$. This type of compounds has been prepared using one or more of the lanthanum or lanthanide elements from cerium to terbium. Furthermore, we could show that the system $M_3La(PO_4)_2$ forms a complete mixed crystal series of rubidium/potassium lanthanum double phosphates (Fig. 5; monoclinic structure (SG $P2_1/m$; $Z=2$)).

The band gap values of double phosphates determined by measurements of VUV reflectance and excitation spectra, which we recently reported, support the above conclusions [9,10].

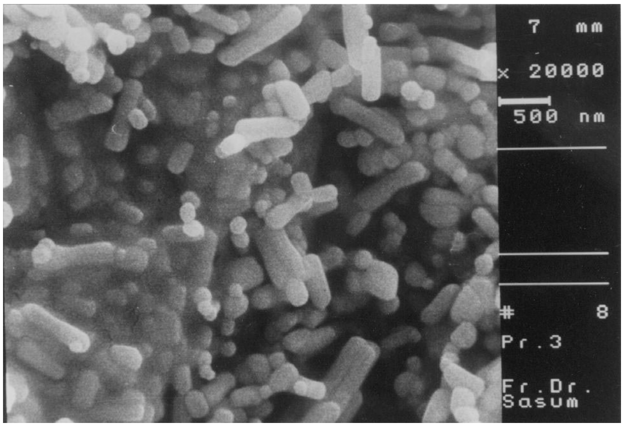

Fig. 2. REM photograph of $LaPO_4nH_2O$.

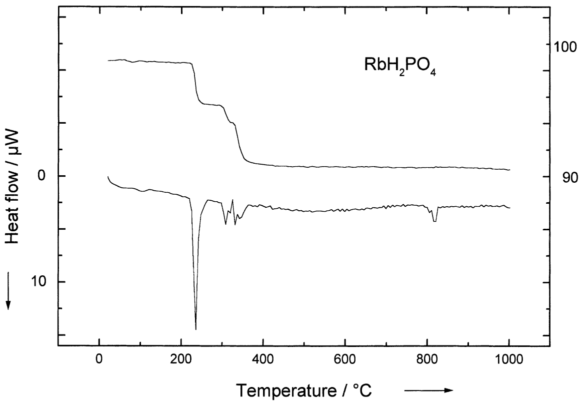

Fig. 3. Thermoanalysis of the precipitated RbH_2PO_4.

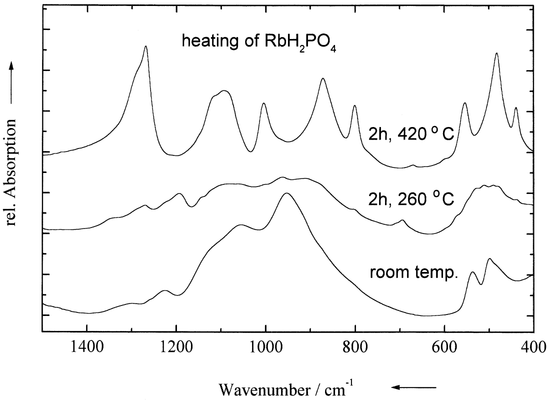

Fig. 4. FTIR absorption spectra of heated RbH_2PO_4.

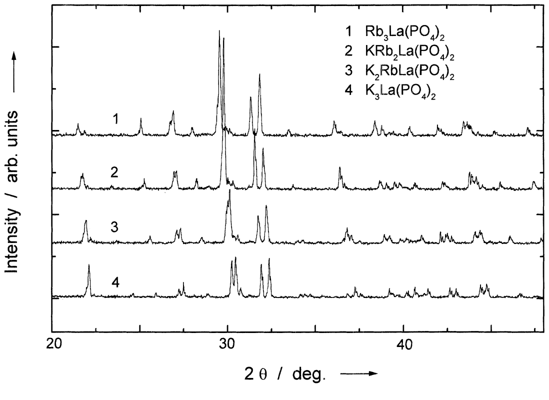

Fig. 5. X-ray diffraction pattern of $(K_{1-x}Rb_x)La(PO_4)_2$ powders.

Acknowledgements

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