Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 689–692

MODIFIED PECHINI SYNTHESIS OF $Na_3Ce(PO_4)_2$ AND THERMOCHEMISTRY OF ITS PHASE TRANSITION

Aleksandra Matraszek[*] *and Irena Szczygieł*

Wrocław University of Economics, Department of Inorganic Chemistry, ul. Komandorska 118/120, 53-345 Wrocław, Poland

Effect of the synthesis conditions of Pechini technique on crystallinity and purity of $Na_3Ce(PO_4)_2$ compound was investigated. Nano-sized cerium–sodium phosphate obtained when EDTA was used as an additional chelating agent for Ln^{3+}. The total enthalpy change of $Na_3Ce(PO_4)_2$ phase transition was determined as 14.2 ±0.7 kJ mol^{-1} for sample synthesized by conventional solid–solid reaction. The phase transition process was confirmed to occur at 1060°C or in temperature range 920–1060°C depending on thermal treatment of powders.

Keywords: *binary phosphate, Pechini synthesis, phase transition*

Introduction

Several application fields of rare-earth phosphates caused an increasing interest in research on physical and chemical properties of compounds with the formula $M^I_3Ln(PO_4)_2$ (where M^I denotes an alkali metal) [1–5]. Their chemical nature and particle size of synthesized phosphates is highly dependent on the processing method. The compounds are usually obtained at relatively high temperatures by a solid state reaction [6] or by growing from a flux of molten phosphates [3]. The hydrothermal crystallization has been proposed by Xu [7], but there have been no up-to-date reports on synthesis of nanometric powders of binary phosphates. Actually, sol–gel methods are widely used to obtain nano-sized crystals. The conventional sol–gel process involves use of toxic and very expensive alkoxide precursors. An alternative approach is preparation of powders by the Pechini method [8], where inorganic salts are used as precursors and citric acid acts as chelating agent for metal-ion preventing phase separation before the expected crystallization occurs. These chelates can undergo polyesterification when heated in ethylene glycol to form a polymeric resin throughout which cations are uniformly distributed. Further annealing of dried gel to 800°C causes the forming of final product and removing of organic residues.

The self-combustion synthesis of powders by the auto-ignition process of citric acid is also known to produce fine powders with nanometric crystallites [9, 10]. The combustion process is an oxidation-reduction reaction in which NO_3^- ions act as oxidants for carboxyl groups (reductants).

In the presented paper we synthesized samples by the Pechini method supported by an auto-combustion process and investigated the influence of synthesis conditions on the phase purity and crystallinity of $Na_3Ce(PO_4)_2$ compound. Ethylenediamine tetraacetic acid (EDTA) as an additional chelating agent for Ce^{3+} has been proposed to decrease crystallite size. The phase purity of obtained powders was examined by means of XRD and FTIR methods. The IR spectroscopy was employed as complementary method to check XRD results.

Previous investigations on the system Na_3PO_4–$CePO_4$ showed, that parent phosphates at molar ratio 1:1 form a compound with the formula $Na_3Ce(PO_4)_2$ [6]. The low temperature β-$Na_3Ce(PO_4)_2$ phase was described to have orthorhombic structure [6, 7], that changes to glaserite-type when heated [11, 12]. It was mentioned that a polymorphic transition of the compound occurs at 1060°C or in temperature range of 920–1060°C, depending on the thermal treatment of the synthesized samples which was used. The investigated phosphate is stable up to 1550°C and at this point it melts incongruently depositing solid $CePO_4$ and a liquid Na_3PO_4-rich [6]. The data on the thermochemistry of structural transformations of binary phosphates is known only for potassium-lanthanide compounds with the formula $K_3Ln(PO_4)_2$ (*Ln*=Ce–Sc) [3]. In presented paper the enthalpy of structural change of $Na_3Ce(PO_4)_2$ compound was determined to complete the thermochemical data on double orthophosphates.

Experimental

Samples of $Na_3Ce(PO_4)_2$ composition were prepared using the stoichiometric amount of $Ce(NO_3)_3 \cdot 6H_2O$ (98.5%, POCh Gliwice), $Na_3PO_4 \cdot 12H_2O$ (98%, POCh

---

[*] Author for correspondence: aleksandra.matraszek@ue.wroc.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Gliwice) and $NH_4H_2PO_4$ (99.5%, POCh Gliwice). The molar ratios of citric acid (R_1), ethylene glycol (R_2) and nitric acid to the cerium precursor (R_3) used for obtaining the samples are listed in Table 1. The cerium(III) nitrate, citric acid (99.5%, Alfa Aesesar) and ethylene glycol (pure, POCh Gliwice) were dissolved in the concentrated nitric acid (65%, POCh Gliwice), distilled water (sample C) or 20 mL of saturated EDTA (99.0%, Fluka) solution (samples A and B) under stirring. Samples were heated at 70°C under mixing until a viscous gel obtained. Then $Na_3PO_4\cdot12H_2O$ and $NH_4H_2PO_4$ were added under stirring. The heating was continued until a white voluminous foam obtained, then temperature was raised up to 120°C to dry the samples for 20 h. The calcination of dried samples was performed in furnace preheated to 480°C for 20 h. During this step an auto-combustion process of samples at about 450°C was observed, which caused release of large volume of gases in a few minute period and obtaining the light gray foam-like gel. The as-obtained gels were ground in an agate mortar and heated for 20 h at 780°C to remove organic residues.

The thermal properties of $Na_3Ce(PO_4)_2$ were investigated on samples synthesized from $CePO_4$ by method described in [6] and $Na_3PO_4\cdot12H_2O$. The parent phosphates were mixed in molar ratios 1:1 and 1.5:1 in agate mortar. So obtained materials were pelletized and annealed at 1150°C for 20 h.

The synthesized light yellow powders were analyzed by XRD using CuK_α radiation (Siemens D5000) and by thermal analysis in a fully automated system of Setsys^{TM} (TG-DSC 1500; Setaram). From 15 to 20 mg of powdered samples placed in Pt crucible were heated to 1200°C and cooled to room temperature with heating/cooling rate 10°C min^{-1} using Ar as a purge gas. The temperature and sensitivity calibration were carried out using the phase transition and the melting points of K_2SO_4 (584 and 1069°C, respectively). A Fourier transform IR spectrometer (Perkin-Elmer System 2000 FTIR) was used to record IR spectra of the samples in KBr pressed pellets in the range of wavenumbers 400–4000 cm^{-1}. Crystallite size was estimated from XRD measurements by Scherrer's equation:

$$D=\frac{K\lambda}{B\cos\theta}$$

where D is the mean crystallite size in the direction perpendicular to the (hkl) plane of reflexes in nm, K is a Scherrer constant, $\lambda=0.154$ nm, B is the full-width at half-maximum (FWHM) of diffraction peak at angle θ. In presented paper the (332) and (324) peaks were chosen for calculations as the most suitable for crystallite size determination, because they didn't overlap with other reflexes. The $K=0.9$ was used in calculations as proposed by Klug *et al.* [13]. The precision of the crystallites size estimation (usually 10–20%) is dependent on particles geometry and size distribution, that could be evaluated by TEM.

Results and discussion

The XRD results of samples calcined at 780°C are shown in Fig. 1. They confirm the presence of crystalline $Na_3Ce(PO_4)_2$ phase, however secondary phases such as CeO_2 in the samples A, B and D, Na_3PO_4 phase in B–D samples and $Na_4P_2O_7$ in sample B have

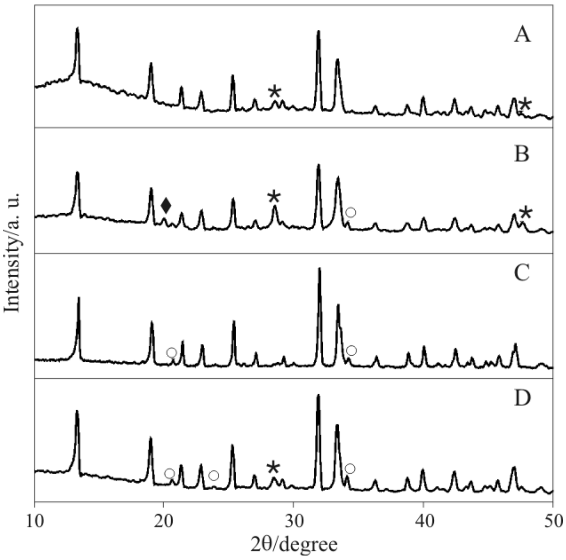

Fig. 1 X-ray diffractograms of samples A–D calcined at 780°C; ∗ – denotes CeO_2, ◆ – $Na_4P_2O_7$ and ○ – Na_3PO_4 secondary phases

Table 1 Initial composition of prepared samples, determined crystallite size of $Na_3Ce(PO_4)_2$ phase and the phase composition of samples after heating at 780°C

Sample	R_1	R_2	R_3	Crystallite size/nm	Phase composition
A	20	12	–	38	$Na_3Ce(PO_4)_2$, CeO_2
B	20	46	12	47	$Na_3Ce(PO_4)_2$, CeO_2, Na_3PO_4, $Na_4P_2O_7$
C	2	2	–	53	$Na_3Ce(PO_4)_2$, Na_3PO_4
D	4	18	280	50	$Na_3Ce(PO_4)_2$, CeO_2, Na_3PO_4, pyrophosphate*

*determined by FTIR; R_1=citric acid to Ce^{3+} molar ratio, R_2=ethylene glycol to Ce^{3+} molar ratio, R_3=HNO_3 to Ce^{3+} molar ratio been observed. No secondary phases were detected in samples heated for 1 h at 1100°C

Ceria was formed in gels containing high concentration of citric acid and ethylene glycol. The oxidation of Ce^{3+} to Ce^{4+} in the samples was possible under strongly oxidizing conditions of the self-combustion process, which was observed by heat treatment of gels. Lowering of the organic precursors content in the prepared sols has to prevent the Ce(III) oxidation, as was in sample C. Further calcining the samples up to 1100°C lowered the cerium dioxide and Na_3PO_4 content in samples, what indicated that samples calcined at 780°C were not finally reacted.

The phase composition of powders calcined at 780°C was checked also by FTIR spectra (Fig. 2). The main absorption bands were observed at 412–465, 547–601, 960 and 986–1118 cm^{-1}. The bands at 986–1118 cm^{-1} were due to the asymmetric stretching and the band at 960 cm^{-1} to the symmetric stretching of PO_4 group. The asymmetric and symmetric deformation modes of the PO_4 group can be observed at 547–601 and 412–465 cm^{-1}, respectively. The above mentioned absorption bands are in agreement with the literature data for IR spectra of $Na_3Ce(PO_4)_2$ compound [1]. In sample C additional peaks at 860, 1367 and 1470 cm^{-1} were attributed to Na_3PO_4 phase [14], which presence was first recognized by XRD. The strong absorption at 734 cm^{-1} in sample B was probably due to symmetric stretching the POP group observed for pyrophosphates [15]. Absorption at the same position, but much less intensive, was recognized for sample D, indicating the existence of pyrophosphate in the obtained powder. The XRD and FTIR results show that the pyrophosphates are built, when nitric acid is used (samples B and D). The phenomena of pyrophosphate formation on rare-earth orthophosphates synthesis was observed and explained in [16–18]. In acidic solutions, the HPO_4^{2-} for PO_4^{3-} substitution is possible. By further heating of the prepared material at temperatures higher than 500°C, the $P_2O_7^{4-}$ anions are formed from HPO_4^{2-} according to the reaction: $2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$.

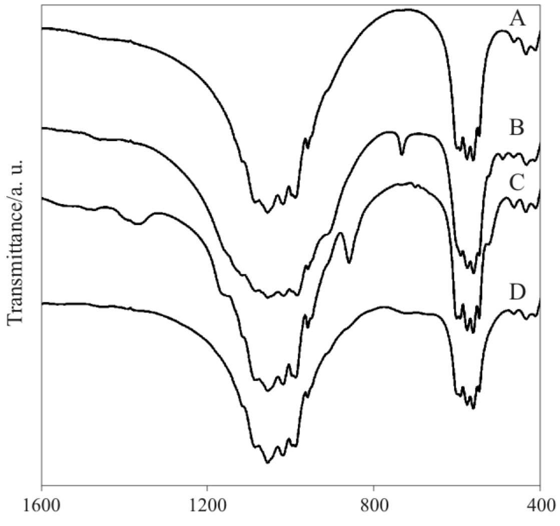

Fig. 2 FTIR spectra of samples A–D calcined at 780°C

The XRD results confirm that the pyrophosphate is present in sample B as the $Na_4P_2O_7$ phase. Nature of $P_2O_7^{4-}$ anion in sample D is non-crystalline and it could be not detected by XRD analysis. Karpowich *et al.* [18] reported that pyrophosphates could occur as a phosphate-rich amorphous phase at grain boundaries, even after heating up to 800°C, which could be also a good explanation of the amorphous state of $P_2O_7^{4-}$ in sample D.

The average crystallite size of $Na_3Ce(PO_4)_2$ phase calculated from the reflection broadening technique is found to be 47–53 nm (Table 1) for samples B–D. The estimated dimensions are very narrow, almost independent on the concentration of citric acid and ethylene glycol used in initial solutions. The smallest crystallites of 38 nm dimension in sample A were found, where EDTA without nitric acid addition was used during synthesis of this material. This could be explained by the fact, that stronger formation of cerium chelates could be achieved in sample A than in acidic conditions, as in sample B [19]. More efficient complexing in solution prevented faster crystallization of compounds.

The thermochemistry of phase transition of the $Na_3Ce(PO_4)_2$ compound was determined by the TG/DSC analysis. Szczygiel *et al.* [6] reported, that the polymorphic transition of the compound occurs at constant temperature (i.e. 1060°C) during cooling of molten samples and on heating of powders synthesized in temperatures up to 1150°C. Two effects (weak at 920 and strong at 1060°C) were observed otherwise. Unfortunately the temperature of the first one coincides with the point of β/δ’-transition of Na_3PO_4 (914°C). Since sodium orthophosphate could be present in the binary compound as a secondary phase or formed on its melting, we investigated firstly the thermal behavior of a sample containing 60 mol% of $CePO_4$ and 40 mol% of Na_3PO_4. The sample exhibited during cooling two exothermic effects in temperature range 920–1060°C. Since in this temperature interval monazite does not show any polymorphic transitions [17], then both effects are connected to α/β-phase transition of $Na_3Ce(PO_4)_2$.

The total enthalpy change of $Na_3Ce(PO_4)_2$ phase transition was determined on heating and cooling of sample containing 50 mol% of monazite and 50 mol% of sodium phosphate. One strong endothermic peak at 1060°C with the enthalpy change of 14.1±0.5 kJ mol^{-1} was observed (Fig. 3). During cool-

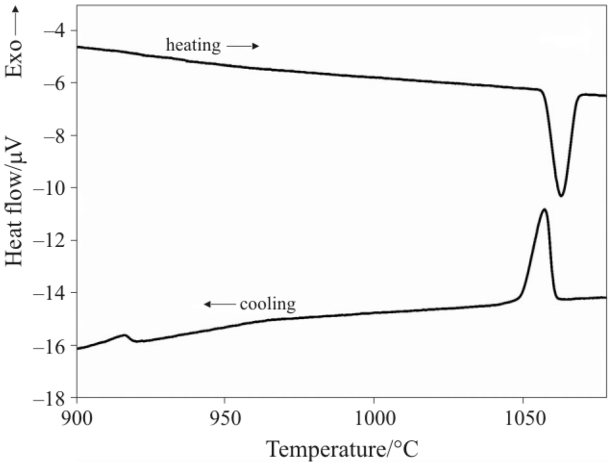

Fig. 3 DSC curve of $Na_3Ce(PO_4)_2$

ing of the sample, two effects on the DSC curve: at 1060 and 920°C were registered. The enthalpy change for the effects was 12.8±0.4 and 1.6±0.6 kJ mol^{-1}, respectively. The sum of these values agrees well with the enthalpy of phase transition during sample heating and it confirms that the phase transformation of the binary phosphate is also possible in temperature range as described in [6]. Under assumption that $\Delta G_{trans}=0$ for reversible reaction at onset point of phase transition, the value of entropy change $\Delta S_{trans}=11$ J mol^{-1} K^{-1} obtained.

Conclusions

Nanocrystalline $Na_3Ce(PO_4)_2$ phase was synthesized by the modified Pechini sol–gel method, where commercially available inorganic salts as precursors for the synthesis of sols were used. The non-acidic conditions are necessary for preparing powders with the lowest pyrophosphate content. The smallest crystallite size of double sodium cerium phosphate was found to be 38 nm, when EDTA was used to additionally chelate the Ce^{3+} ion. The lowering of preparation temperature is probably the way to achieve diameters smaller than 20 nm, expected for modern applications. Further optimization of Pechini process is needed to derive phase-pure powders of binary orthophosphates at temperatures lower than 800°C.

The enthalpy change of β-to-α transition of $Na_3Ce(PO_4)_2$ phase was determined to be 14.2±0.7 kJ mol^{-1}.

References

1 I. Szczygiel, L. Macalik, E. Radominska, T. Znamierowska, M. Maczka, P. Godlewska and J. Hanuza, Opt. Mater., 29 (2007) 1192.
2 L. Banarafa, L. Rghioui, R. Najjar, M. Saidi Idrissi, M. Knidiri, A. Lorriaux and F. Wallart, Spectrochim. Acta A, 61 (2005) 419.
3 S. Ushakov, A. Navrotsky, J. M. Farmer and L. A. Boatner, J. Mater. Res., 19 (2004) 2165.
4 S. Areva, J. Holsa, M. Kloss, M. Lahtinen, R. J. Lamminmaki, M. Lastusaari, L. Schwarz and J. Valkonen, Mater. Sci. Forum, 378-381 (2001) 644.
5 L. Schwarz, B. Finke, M. Kloss, A. Rohmann, U. Sasum and D. Haberland, J. Lumin., 72–74 (1997) 257.
6 I. Szczygiel and T. Znamierowska, J. Solid State Chem., 95 (1991) 260.
7 Y. Xu, S. Feng and W. Pang, Mater. Lett., 28 (1996) 313.
8 M. P. Pechini, US Patent 3330697, July 11, 1967.
9 J. Azadmanjiri and S. A. Seyyed Ebrahimi, Phys. Met. Metall., 102 (2006) 21.
10 R. D. Purohit, S. Saha and A. K. Tyagi, J. Nucl. Mater. 323 (2003) 36.
11 M. Mesnaoui, M. Maazaz, Z. J. Chao, C. Parent, R. Olazcuaga, G. Le Fem and P. Hagenmuller, Rev. Chim. Min., 24 (1987) 338.
12 T. A. Slivko, I. N. Smirnova, F. M. Spiridonov, G. V. Zimina and N. N. Chudinova, Zh. Neorg. Khim., 47 (2002) 202.
13 H. P. Klug and L. E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley & Sons, New York 1974.
14 NIST Standard Reference Database 69, June 2005, Release NIST Chemistry WebBook.
15 A. Lazarev, A. Mirgorodskii and I. Ignatiev, Vibrational Spectra of Complex Oxides, Nauka, Leningrad 1975, p. 225.
16 J. A. Diaz-Guillen, A. F. Fuentes, S. Gallini and M. T. Colomer, J. Alloys Compd., 427 (2007) 87.
17 R. Kijkowska, Thermochim. Acta, 404 (2003) 81.
18 L. Karpowich, S. Wilcke, R. Yu, G. Harley, J. A. Rreimer and L. C. De Jonhe, J. Solid State Chem., 180 (2007) 840.
19 C. N. Fredd and H. S. Fogler, J. Colloid Interface Sci., 204 (1998) 187.

DOI: 10.1007/s10973-008-9129-5