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# HIGH TEMPERATURE INVESTIGATIONS OF LANTHANUM-NICKEL OXYPHOSPHATE

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Thermal analysis X-ray powder diffraction, IR spectroscopy were carried out for the structural studies of lanthanum-nickel oxyphosphate $La_3(PO_4)O_3.Ni_{1-x}O$. The lanthanum-nickel phase crystallizes in the monoclinic system with the following lattice parameters $a = 11.57(2)$Å; $b = 12.22(3)$Å; $c = 6.73(2)$Å; $\gamma = 111.36(4)$; $V = 886.87(1)$Å$^3$.

The first data about oxyphosphates were found in papers by Tananaev [1], with the formula $9LnPO_4.Ln(OH)_3.xH_2O$, which decompose at high temperatures. Serra *et al.* synthesized lanthanum oxyphosphate $La_3PO_7$ by reaction between lanthana and ammonium hydrogen phosphate in air at 880° to 1200° [2]. Serra *et al.* reported about the new oxyphosphates $La_3PO_7$ and $La_7P_3O_{18}$ which were obtained in 1978 [3]. Serra *et al.* reported that the structures of both $La_3PO_7$ and $La_7P_3O_{18}$ are monoclinic and $La_7P_3O_{18}$ exists in low - and high - temperature forms, transforming reversibly at 1650° [4]. Kizillyalli and Welch prepared $La_3PO_7$ by the solid state reaction of $LaPO_4$ with $Na_2CO_3$ at 700° to 900° [5]. Park and Kreidler found by quenching studies that $La_3PO_7$ has a sluggish inversion at 935° [6]. The lanthanum oxyphosphates $La_5(PO_4)(O_3)_2$ and $La_3(PO_4)O_3$ were found by Kropiwnicka [7, 9] by solid state reactions. The lanthanum oxyphosphate $La_3(PO_4)O_3$ melts incongruently as a result of the following peritectic reaction $C + \alpha\text{-}La_5(PO_4)(O_3)_2 = La_3(PO_4)O_3$ at the 1590° [7, 8, 10]. The low - temperature phase of $\epsilon\text{-}La_5(PO_4)(O_3)_2$ occurs in the monoclinic system the lattice parameters being $a = 13.11$ Å; $b = 13.58$ Å; $c = 8.08$ Å; $\gamma = 113.90$; $V = 1315.40$ Å$^3$ [7, 8, 10]. Powder diffraction studies for the homogeneous phase $La_3(PO_4)O_3$ are reported in [8, 10]. The lattice parameters for the monoclinic oxyphosphates $Na_4La_2(PO_3)_4O_3$ - $Na_8La_2(PO_3)_8O_3$ were

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worked out for the first time by Kropiwnicka *et al.* [7, 11, 12] over the temperature range from 25° to 1500°, by thermal analysis, X-ray, IR and microscopic methods.

Willer and Daire found that the solid solution of NiO in $La_2O_3$ stabilizes the *B* - type structure. Hexagonal (*A* - type lanthana) is the only phase expected to appear in this study [13]. There are many references concerned with nickel oxides of the NaCl halit - structure [14, 15]. The full structure of the non - stoichiometric compounds was reported by Azaroff [14]. Studies on the oxidation of the nickel at high temperatures were carried out, taking into consideration practical points of view [15]. Because of the thermodynamic stability of NiO we deal with the model binary phase (Ni-O) [16]. Several authors reported about the temperature dependence of the interaction coefficients of oxide and sulphur for rare earth elements, the standard free energy of solution, in liquid nickel [18]. The metallic nickel with formula $ABO_{3-x}$(A-Ba, B-Co, Ni, Fe) with oxide deficiency [19] forms with alkali metals hexagonal non - stoichiometric phases. Literature reports that Ni, Co, Cu, and Pd, form with PtP amorphous binary alloys quenched rapidly from the melt and the stability and structural change of the amorphous phases [20, 21].

## Experimental

Structural studies, thermal analysis (DTA, TG), X-ray powder diffraction, IR spectroscopy, and chemical analysis of lanthanum oxyphosphate $La_3(PO_4)O_3$ with the metallic nickel have been carried out. The lanthanum oxyphosphate was synthesized in a solid state reaction from $NH_4H_2PO_4$ (Anal.grade) $La_2O_3$ 99.9% (USSR) by the following reaction

$$2\,NH_4H_2PO_4 + 3\,La_2O_3 = 2\,La_3PO_7 + 2NH_3 + 3\,H_2O$$

The reaction proceeds in two stages:

1. at 400° temperature for 6 hours
2. at 1440° temperature for 8 hours

in a platinum crucible, and as a second method, from - oxyphosphate $La_5(PO_4)(O_3)_2$ and $NH_4H_2PO_4$ (Anal. grade POCH). Synthesis were carried out in the solid phase by sintering the materials taken in a specific weight ratio at 390° for 2 h and then at 1300° for 18 h. The purity of the phosphate was checked by X-ray (camera Guinera) and IR spectroscopic methods.

*Methods*

A MOM derivatograph was used in the thermal studies, with photographic recording over the temperature range from 25° to 1300°. Operating conditions were as follows - sensitivity TG - 500 mg; heating rate 10 deg/min. $Al_2O_3$ was used as reference material. High - temperature X-ray GPWT - 1500 attachment installed in a GUR - 5 goniometer of a DRON - 2.0 diffractometer. (Department of Inorganic Chemistry, Academy of Economics Wroclaw). The temperature range in air was 25° to 1200°. The temperature was measured by means of a Pt/PtRh 10 thermocouple accurate to ±5°, CuK$\alpha$ radiation was applied; goniometer travel rate 1/4°, 2$\theta$/min. IR spectra have been obtained by Specord IR - 75 (University of Wroclaw). Infrared spectra were taken in Nujol and KBr pellets.

## Results and discussions

Lanthanum oxyphosphate $La_3(PO_4)O_3$ melts incongruently as a result of peritectic reaction at 1590° [7, 8, 10] and is formed from a liquid phase C and a high temperature phase of the oxyphosphate $\alpha$-$La_5(PO_4)(O_3)_2$. The low - temperature phase of $\varepsilon$-$La_5PO_{10}$ crystallizes in the monoclinic system and the lattice parameters are as follows: $a = 13.11$ Å; $b = 13.58$ Å; $c = 8.08$ Å; $\gamma = 113.90$; $V = 1315.40$ Å$^3$. Powder diffraction data for the homogeneous phase $La_3(PO_4)O_3$ are presented in Table 1.

**Table 1** Lattice parameters for the oxyphosphate $La_3(PO_4)O_3$

| Homogeneous phase $La_3(PO_4)O_3$ | |
|---|---|
| $a$ = 11.20 Å | |
| $b$ = 11.94 Å | = 93.79 |
| $c$ = 7.01 Å | $V$ = 936.97Å$^3$ |
| monoclinic system | |

There are no data concerning the pure oxyphosphate defined as compounds with oxygen atoms non - connected by chemical bonding with the phosphorus atom, but of terminal or bridges character. Figure 1 shows the IR spectrum of $La_3(PO_4)O_3$ in the range 400-1400 cm$^{-1}$ taken of KBr pellets. Table 2 contains the $\nu$ - frequences of lanthanum oxyphosphate.

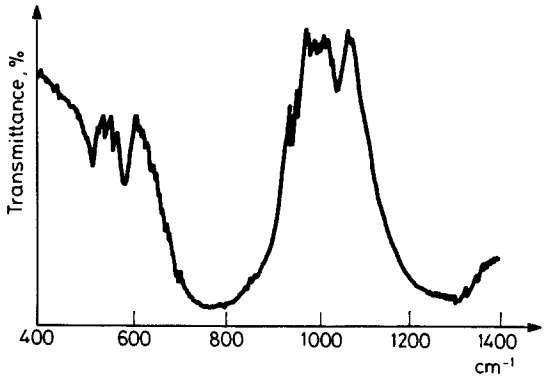


**Fig. 1** IR spectroscopy for the $La_3(PO_4)O_3$

**Table 2** IR spectroscopy data for the $La_3(PO_4)O_3$

| Compound | $\nu$ (PO) $cm^{-1}$ | $\delta$(OPO) $cm^{-1}$ | $\nu$ (OLa O La) $cm^{-1}$ |
|---|---|---|---|
| $La_3(PO_4)O_3$ | 925 w. | 547 s. | 610 v.s. |
| | 930 w. | 552 s. | |
| | 948 s. | 555 s. | |
| | 960 s. | | |
| | 980 w. | | |
| | 1010 w. | | |
| | 1025 w. | | |
| | 1040 w. | | |
| | 1080 v.s. | | |

Samples of the metallic nickel were heated with $La_3(PO_4)O_3$ at 900°, 1000° and above 1100° temperatures under neutral gas. Samples were uenched to room temperature at a rate of 10 deg/min. In this case we deal with an intercrystalline corrosion as a result of a high temperature intercristalline oxidation and formation of nickel oxides $Ni_{1-x}O$. High temperature diffraction data indicate the corrosion process. On the basis of X-ray powder studies it was found that nickel oxides $Ni_{1-x}O$ occur in samples of the $La_3(PO_4)O_3$ (16.8 weight % Ni(II)). The samples $La_3(PO_4)O_3$ - $Ni_{1-x}O$ (with 6.4 weight % Ni(II)) above 1370° decompose to give lanthanum oxide $La_2O_3$. In this case the peak (101) characteristic of $La_2O_3$ was separated from a set of reflections given for $La_3(PO_4)O_3.Ni_{1-x}O$. Differential thermal analysis of the sample $La_3(PO_4)O_3.Ni_{1-x}O$ (16.8 weight % Ni(II)) under nitrogen indicates two exothermic effects at 270° and 500°. The one exothermic effect at 450° and the endothermic one at 760° occurs for the sample

$La_3(PO_4)O_3.Ni_{1-x}O$ (6.4 weight % Ni(II)). The thermogravimetric studies do not indicate any decrease in mass. Probably a new lanthanum - nickel phase is formed in a solid state reaction above 1000°. An examination of the non - stoichiometric $La_3(PO_4)O_3.Ni_{1-x}O$ phase shows that it crystallizes in the monoclinic system. Lattice parameters are given in Table 3.

**Table 3** Lattice parameters for nickel - lanthanum oxyphosphate phase

| $d$ exp.x $10^{-1}$ μm | $d$ cal.x $10^{-1}$ μm | hkl |
|---|---|---|
| 6.752 | 6.732 | 001 |
| - | 6.702 | 110 |
| 5.791 | 5.794 | 011 |
| 5.673 | 5.691 | 020 |
| 5.539 | 5.551 | $1\bar{1}1$ |
| 4.384 | 4.371 | $2\bar{1}1$ |
| 3.838 | 3.852 | $3\bar{1}0$ |
| - | 3.827 | $2\bar{3}0$ |
| 3.270 | 3.270 | $3\bar{3}0$ |
| 3.253 | 3.248 | 321 |
| 2.876 | 2.874 | $4\bar{2}0$ |
| 2.850 | 2.855 | 202 |
| - | 2.846 | 040 |
| 2.676 | 2.676 | 122 |
| 2.675 | 2.677 | 230 |
| 2.638 | 2.635 | 320 |
| - | 2.643 | $4\bar{1}1$ |
| - | 2.567 | $3\bar{4}1$ |
| 2.431 | 2.456 | $4\bar{2}1$ |
| 1.996 | 2.454 | 302 |
| - | 2.453 | 321 |
| 1.965 | 2.430 | $4\bar{4}0$ |
| - | 2.000 | 123 |
| 1.951 | 1.997 | $1\bar{6}0$ |
| 1.895 | 1.965 | $1\bar{3}3$ |
| - | 1.962 | $5\bar{5}0$ |
| 1.790 | 1.949 | $2\bar{6}1$ |
| - | 1.895 | 430 |
| - | 1.897 | 060 |
| 1.787 | 1.787 | $6\bar{4}1$ |

monoclinic system $a$ = 11.57 [2] Å, $b$ = 12.22 [3] Å, $c$ = 6.73 [2] Å, $\gamma$ = 111.36 [4], $V$ = 886.87 [1] $Å^3$

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**Zusammenfassung** — Zur Strukturuntersuchung von Lanthan-nickel-oxyphosphat $La_3(PO_4)O_3Ni_{1-x}O$ wurden Thermoanalyse, Pulverdiffraktionsaufnahmen und IR-Spektroskopie herangezogen. Die Verbindung kristallisiert in einem monoklinen System mit den Gitterparametern: $a$ = 11.57(2) Å; $b$ = 12.22(3) Å; $c$ = 6.73(2) Å; $\gamma$ = 111.36(4); $V$ = 886.87(1) Å$^3$.