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Hydrothermal synthesis of mixed phosphates of neodymium and alkaline metals ($Me_2O \cdot Nd_2O_3 \cdot 4P_2O_5$)

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The phase formation in the system $Me_2O–Nd_2O_3–P_2O_5–H_2O$ (where Me = Li, Na, K, Rb and Cs) has been studied under hydrothermal conditions in the temperature and pressure range 300 to 700° C and 0.5 to 600 atm, respectively, using vitreous carbon glass liners. A composition diagram showing the possible fields of crystallization of different phases under equilibrium conditions is given. AB-diagrams of fields of crystallization of different phases in the system investigated are given. These diagrams are in correspondence with the theoretical composition diagram. The advantages and disadvantages of different methods employed in the growth of MeNd-phosphates are discussed. The crystals obtained were characterized by various methods.

1. Introduction

Interest in mixed phosphates of neodymium and alkaline metals $MeNdP_4O_{12}$, where Me = Li, Na, K, Rb and Cs, is connected with the possibility of their applications in optoelectronics [1, 2]. At present, laser beams are being obtained from $LiNdP_4O_{12}$ [3] and $KNdP_4O_{12}$ [4] monocrystals. The size of the laser crystals has been reduced by up to tens of microns. The $LiNdP_4O_{12}$ crystals were obtained by the flux method [5] and $KNdP_4O_{12}$ crystals were obtained from aqueous solutions [6] by earlier workers. The main attention is given to the quality and habitus of the crystals while working out the technology of the growth of monocrystals for miniature lasers. Because the crystals used in miniature laser technology are too small, it is extremely difficult to polish the crystals. Therefore, it is desirable to obtain mirror surfaces in these crystals during the growth process itself. With this point in mind, amongst the existing growth methods for rare-earth phosphates, growth from aqueous solutions, particularly from high-temperature aqueous solutions (hydrothermal synthesis), is found to be highly suitable. There is no doubt that the growth from such solutions leads to the existence of a distinct amount of $(OH)^{-1}$ molecules, which greatly reduces the laser quality of the crystals. However, a high temperature of crystallization (500 to 600° C) often reduces the concentration of $(OH)^{-1}$ molecules to an admissable extent.

In order to determine the possibility of growing $MeNdP_4O_{12}$ crystals suitable for miniature lasers, we have studied the phase formation and crystallization in the system $Me_2O–Nd_2O_3–P_2O_5–H_2O$, where Me = Li, Na, K, Rb, Cs under hydrothermal conditions.

2. Experimental methods

In the system investigated the composition of the solvents can be considered as the mixture of P_2O_5 and Me_2O. The concentration of P_2O_5 and Me_2O varies from 50.0% to 90.0% and 1% to 45%, respectively. The starting solutions are prepared either by dissolving P_2O_5 in water, followed by the addition of the respective carbonate of alkaline metals, or by the introduction of the carbonate of alkaline metals to the phosphoric acid in various proportions (maximum filling 86 wt%). After complete evolution of CO_2 from the starting solution, it was transfered into a special ampoule, into which Nd_2O_3 was later added. Two types of ampoules were used in our experiments: (i) germitized ampoules; the pressure inside such

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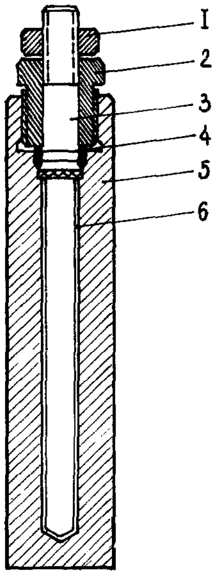


Figure 1 Autoclave: (1) lock nut, (2) main nut, (3) plunger, (4) sealing unit, (5) main body of the autoclave, (6) ampoule.

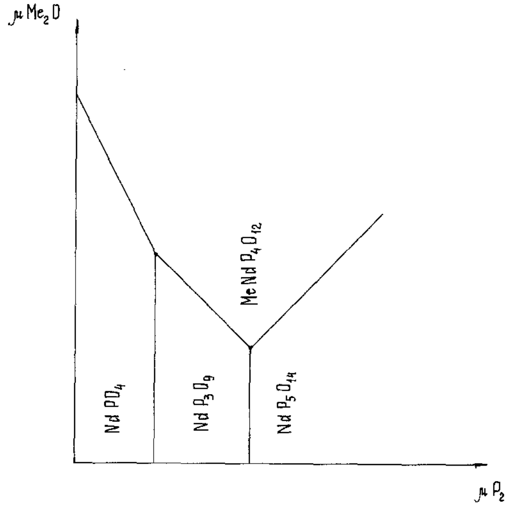


Figure 2 Composition diagram for the system $Me_2O-Nd_2O_3-P_2O_5-H_2O$.

ampoules is counter balanced as a result of the expansion or contraction of the walls, (ii) ampoules with a special lock; the pressure in such ampoules is counter balanced as a result of the changes in the volume of the liquid. In a series of experiments, we have used autoclaves containing teflon, vitreous carbon and platinum liners. Experiments were carried out in the temperature range 300 to 700° C and pressure range 0.5 to 600 atm in the autoclaves shown in Fig. 1.

3. Phase formation

The X-ray analysis shows that the products of crystallization in the investigated system are orthophosphate $NdPO_4$, metaphosphate $Nd(PO_3)_3$, ultraphosphate NdP_5O_{14} and mixed phosphates $MeNdP_4O_{12}$. The system is a four component one, with temperature and pressure as constants, according to the Gibb's phase rule in the invariant equilibrium only four phases can exist in such a system, out of which one liquid phase and three crystalline phases are produced. It is convenient to represent the relationship between the different phases as a composition diagram Fig. 2. The variation in the concentration of phosphorus and alkaline metal oxides determines the fields of crystallization of different phases in the composition diagram. The following reactions are used in the construction of such a composition diagram:

$$NdPO_4 + P_2O_5 + G_1 \rightleftarrows Nd(PO_3)_3 + G_2$$

$$2NdPO_4 + Me_2O + P_2O_5 + G_3$$
$$\rightleftarrows 2MeNdP_4O_{12} + G_4$$

$$Nd(PO_3)_3 + P_2O_5 + G_5 \rightleftarrows NdP_5O_{14} + G_6$$

$$2Nd(PO_3)_3 + Me_2O + P_2O_5 + G_7$$
$$\rightleftarrows 2MeNdP_4O_{12} + G_8$$

$$2NdP_5O_{14} + Me_2O + G_9$$
$$\rightleftarrows 2MeNdP_4O_{12} + P_2O_5 + G_{10}$$

where G is a liquid phase having transitional composition. The presence of a divariant field of stability of $MeNdP_4O_{12}$ (Fig. 2) indicates the possibility of growing these crystals from solutions with variable concentrations of phosphorous and alkaline metals. However, this theoretical composition diagram does not give the exact size of the divariant field of crystallization. For practical applications, the relevant empirical AB-diagrams of fields of crystallization have been considered in our studies ($A = Me_2O/Nd_2O_3$; $B = P_2O_5/Me_2O + Nd_2O_3$). The AB-diagrams of fields of crystallization for systems containing Cs, K and Rb are given in Fig. 3 [7, 8]. Let us consider how the changes in temperature and pressure influence the equilibrium state of the system. The dependence of the changes in chemical potential and PT conditions of the system is

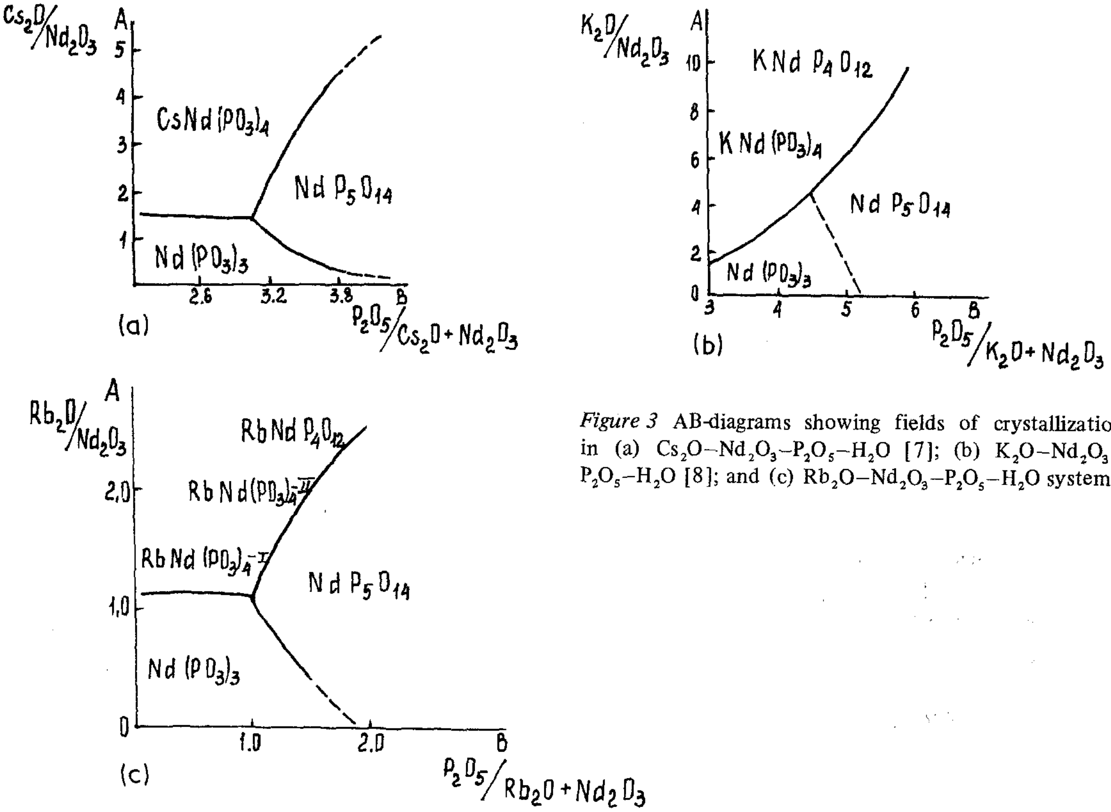


Figure 3 AB-diagrams showing fields of crystallization in (a) $Cs_2O–Nd_2O_3–P_2O_5–H_2O$ [7]; (b) $K_2O–Nd_2O_3–P_2O_5–H_2O$ [8]; and (c) $Rb_2O–Nd_2O_3–P_2O_5–H_2O$ systems.

shown in Figs. 4 and 5. The increase in temperature is proportional to the decrease in concentration of alkaline elements and phosphorus in the system, such that, depending upon the initial conditions of crystallization we obtain the fields of crystallization of either $Nd(PO_3)_3$ or $NdPO_4$. The rise in temperature and the variation in the concentration of the initial components within the field of crystallization of $MeNdP_4O_{12}$ give different polymorphic modifications. For example, in the system $Cs_2O–Nd_2O_3–P_2O_5–H_2O$ below 500° C mixed cyclic phosphate $CsNdP_4O_{12}$ containing four-membered rings of phosphoro-oxygen anions in its structure are crystallized, but above 500° C mixed polyphosphates containing infinite chains of phosphoro-oxygen anions in their structures crystallize. In hydrothermal systems, the pressure measured corresponds to the pressure of the aqeuous solutions. Therefore, the influence of pressure is quite important. At constant temperature, it increases with reference to the molar fraction of the water. To determine in advance the behaviour of the system with reference to the changes in the water pressure is rather difficult since, none of the crystallized phase has a distinct amount of water content in its composition.

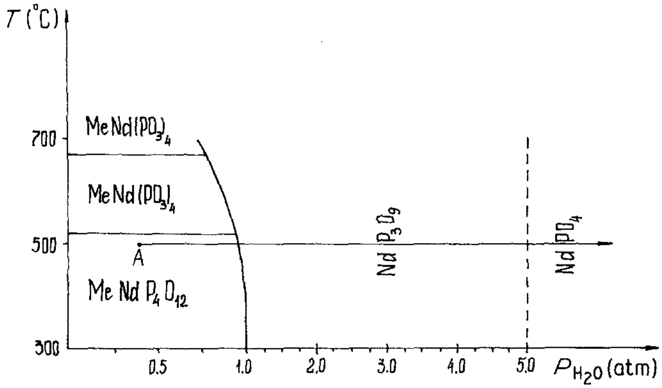


Figure 4 Phase transformation with reference to the changes in PT conditions.

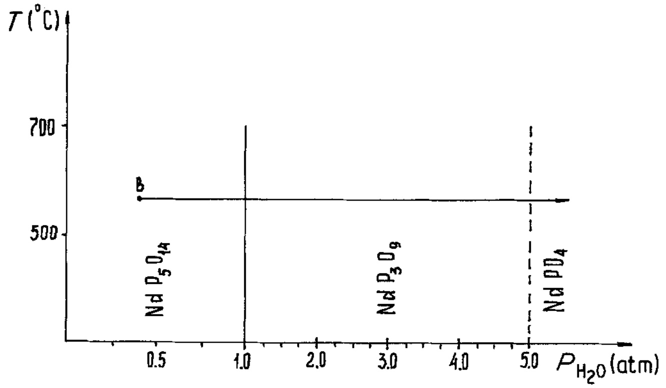


Figure 5 Phase transformation with reference to the changes in PT conditions (while moving away from point B).

In the pressure range 1 to 600 atm, the boundaries of phase formation (in the experiments carried out in closed ampoules) do not change. In this case the changes in phase formation takes place only during changes in the concentration of water in the ampoule. With an increase in the molar fraction of water, the following phase transformations take place:

$MeNdP_4O_{12} \rightarrow NdP_3O_9 \rightarrow NdPO_4$ (point A, Fig. 4)

$NdP_5O_{14} \rightarrow NdP_3O_9 \rightarrow NdPO_4$ (point B, Fig. 4).

In the experiments, where the pressure is controlled by the concentration and volume of the solution, the analagous results were obtained, i.e. with an increase in molar fraction of water, the formation of simple phosphates takes place irrespective of the water pressure in the system. In this case depolymerization of the phosphorooxygen anions accompanied by the reverse reactions takes place.

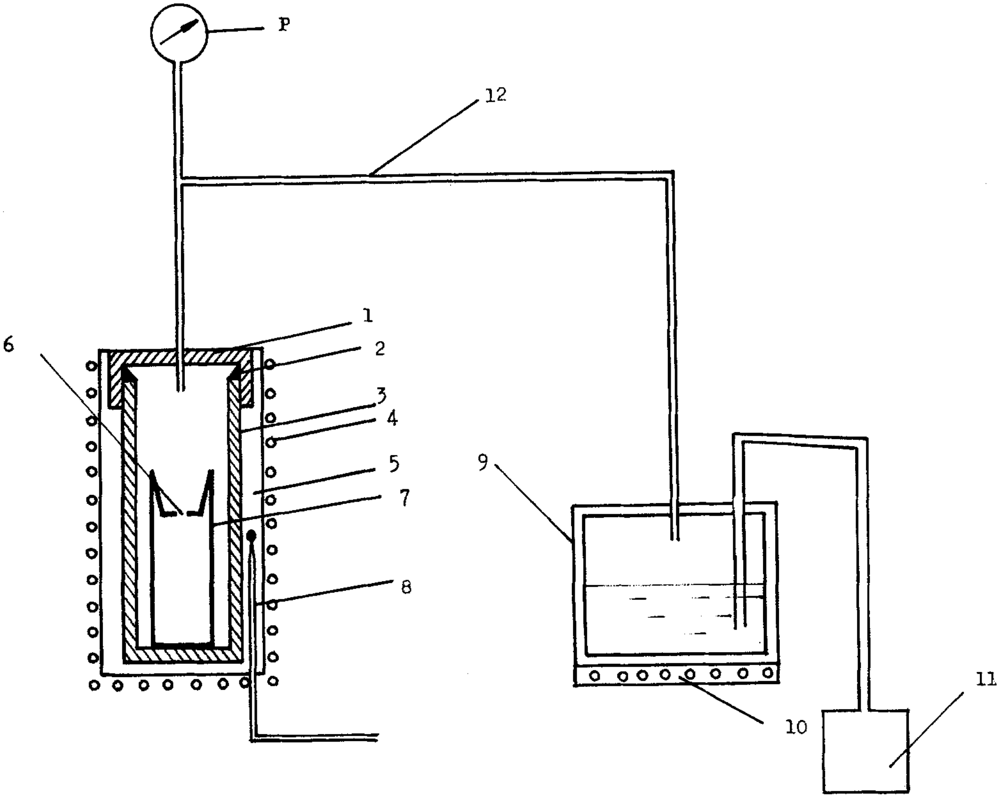
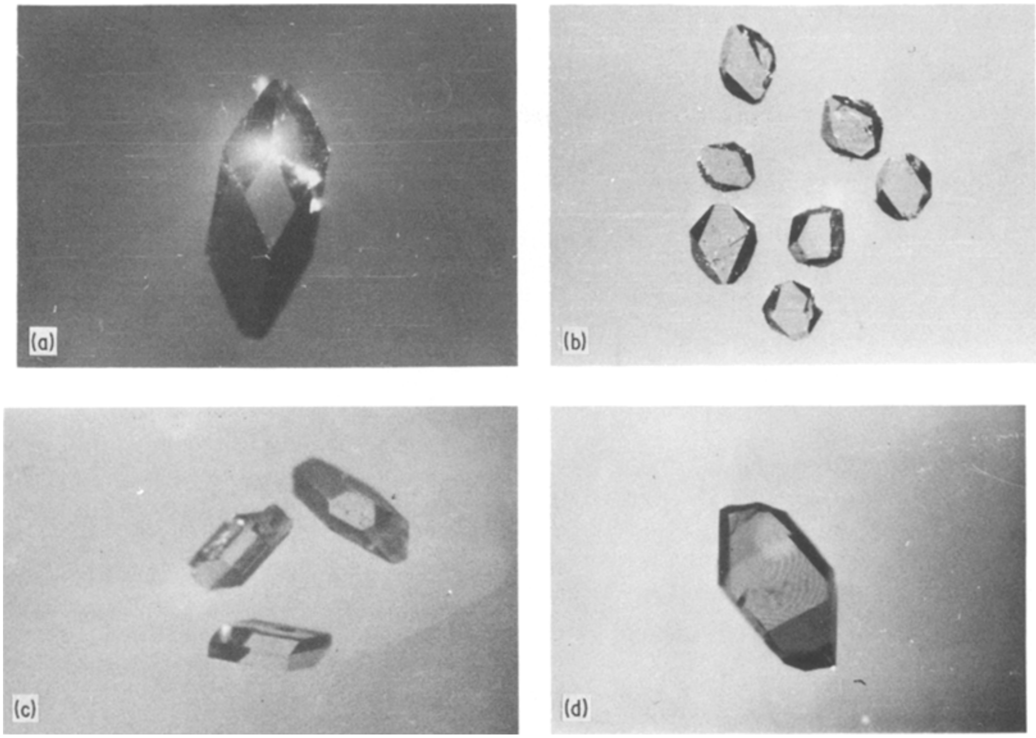


Figure 6 Crystallization apparatus for the growth of MeNd-phosphate monocrystals: (1) thick metallic cap; (2) copper seal rings; (3) thick stainless-steel vessel (autoclave); (4) heater; (5) main body (outer body of the autoclave); (6) opening in the vitreous carbon glass cylinder to control the evaporation; (7) vitreous carbon glass cylinder; (8) thermocouple; (9) evaporator; (10) heater; (11) air compressor; (12) water vapour inlet. P – pressure barometer.



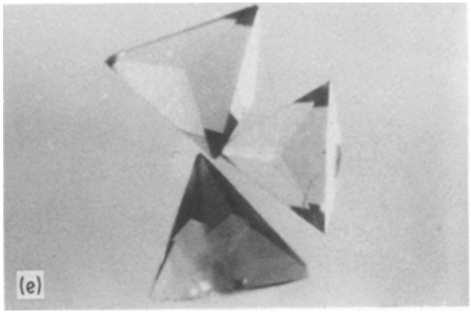


Figure 7 Representative photographs of $MeNdP_4O_{12}$ crystals: (a) $LiNdP_4O_{12}$, 15×; (b) $NaNdP_4O_{12}$, 10×; (c) $KNdP_4O_{12}$, 10×; (d) $RbNdP_4O_{12}$, 15×; (e) $CsNdP_4O_{12}$, 10×.

After determining the conditions of crystallization within the AB-diagrams of crystallization, the problem of selecting the growth method arises. There are three popular methods of growing rare-earth phosphates: (i) evaporation of the solutions, (ii) chemical reactions and (iii) slow heating. The use of the latter method is connected with the negative temperature coefficient of solubility. A sufficiently high dependence of solubility and temperature gives the hope of growing rare-earth phosphates with a temperature gradient as for quartz. The trail runs in teflon liners showing that the phosphates recrystallize in the hotter zones from the cooler zones.

The negative temperature coefficient of the solubility of phosphates acts as a direct clue to the growth of these crystals from solutions. The growth of mixed rare-earth phosphates was carried out in a special apparatus, which works in the pressure range 0.1 to 10 atm and up to a temperature limit of 800° C (Fig. 6). The rate of evaporation is controlled by temperature, pressure and the diameter of the opening in the cylinder. Growth takes place in the following way. The solution containing Me_2O, P_2O_5 and H_2O was placed in a vitreous carbon glass cylinder. Later Nd_2O_3 (usually 5 to 7 times less than the weight of P_2O_5) was added to this mixture. The temperature of the furnace was raised to 250° C and held for 1 day until the desired equilibrium was established and the homogenization of the solution in the cylinder had taken place. The partial pressure of the water was controlled separately by the help of a compressor. Later, the temperature of the furnace was raised to that required and held for 7 to 8 days. The monocrystals of mixed rare-earth phosphates were obtained in this way under constant temperature and pressure conditions.

The synthesis of crystals by chemical reactions was carried out in germitized ampoules. In this case, supersaturation takes place as a result of the interaction of the starting components. A serious set back to this method is the smaller size of crystals obtained (< 1.0 mm). However, the short runs (2 to 3 days) permitted the growth of mixed rare-earth phosphates with an almost 100% output in the form of crystallized powder, which can be used as a chemical reagent for other purposes. The volume of the resultant product is limited only by the size of the autoclave.

The negative temperature coefficient of solubility of rare-earth phosphates leads to their growth in the form of monocrystals by slow heating. By this method, monocrystals up to 6 mm in size can be grown and it is found to be most suitable for growing rare-earth phosphates. It is necessary to carry out growth at lower temperatures ($< 350°$ C) than at higher temperatures. With an increase in the growth temperature the concentration of $(OH)^{-1}$ molecules decreases considerably.

The monocrystals obtained were characterized by various methods. Representative photographs of $MeNdP_4O_{12}$ crystals are given in Fig. 7.

4. Conclusions

(1) The study of phases and crystallization in the $Me_2O-Nd_2O_3-P_2O_5-H_2O$ system under hydrothermal conditions shows that four phases can crystallize in the system investigated: $NdPO_4$, $Nd(PO_3)_3$, NdP_5O_{14} and $MeNdP_4O_{12}$.

(2) Using an AB-diagram of fields of crystallization, monocrystals of $MeNdP_4O_{12}$ can be grown successfully under hydrothermal conditions.

(3) The polymerization of the phosphoric acid decreases with an increase in the concentration of H_2O and Me_2O in the system.

(4) Beyond 5 atm partial pressure of water in the system leads to the crystallization of orthophosphates only.

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