

Phase equilibria in the system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$

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Abstract The system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$ was investigated by thermoanalytical methods, X-ray powder diffraction, ICP, and FT-IR. On the basis of the obtained results its phase diagram was proposed. For this system with one intermediate compound, BaRbPO_4 , we found that this compound melts congruently at 1700 °C, exhibits a polymorphic transition at 1195 °C and is high-temperature unstable. Also, the intermediate compound was subject to gradual decomposes to $\text{Ba}_3(\text{PO}_4)_2$ (the solid phase) and vaporization (with conversion of phosphorus and rubidium oxides into vapor phase). We also found that Rb_3PO_4 melts congruently at 1450 °C and shows a polymorphic transition at 1040 °C. Regarding $\text{Ba}_3(\text{PO}_4)_2$, we have confirmed that it melts congruently at 1605 °C and exhibits a polymorphic transition at 1360 °C.

Keywords Rubidium and barium orthophosphates · BaRbPO_4 · Phase diagram · X-ray powder diffraction

Introduction

In the present article, the results of investigations pertaining to the equilibria which occur in the system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$ are described. Its phase diagram was not published previously. There is literature, however, concerning the initial orthophosphates Rb_3PO_4 , $\text{Ba}_3(\text{PO}_4)_2$ as well as the barium–rubidium orthophosphate BaRbPO_4 . The literature reports mainly concern on the methods of

obtaining, crystal structure, polymorphism, and the possibility of application. Elammari, Elouadi, and Müller-Vogt have noted [1] that some of the mixed orthophosphates of the formula $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{PO}_4$ (where A^{I} is a monovalent cation and B^{II} is a divalent cation) show ferroelectric properties; it can be mentioned that the BaRbPO_4 compound belongs to this group.

Orthophosphate Rb_3PO_4 has been found to be dimorphic. The low-temperature form is orthorhombic (s.g. Pnma; the lattice parameters are: $a = 1.17362(2)$, $b = 0.81046(1)$, $c = 0.615167(9)$ nm) [2]. The high-temperature form crystallizes in the cubic system (s.g. Fm 3; $a = 8.44$ Å) [3]. We found no reported data on the melting temperature of Rb_3PO_4 . The orthophosphate $\text{Ba}_3(\text{PO}_4)_2$ melts congruently at 1605 ± 2 °C [4] and >1620 °C [5]; it shows a polymorphic transition at 1360 ± 2 °C [4] and 1390 ± 15 °C [5]. The crystal structure of the low-temperature form of the $\text{Ba}_3(\text{PO}_4)_2$ has been reported in [6] (s.g. R 3 m; $a = 5.6038(7)$, $c = 21.000(5)$ Å). According to [7], diffraction pattern of $\text{Ba}_3(\text{PO}_4)_2$ corresponds to rhombohedral translation lattice (the unit cell dimensions are: $a = 7.696 \pm 0.002$ Å, $\alpha = 42^\circ 35' \pm 2'$). The orthophosphate BaRbPO_4 exhibits a reversible phase transition at 1060 °C [1]. According to [1, 8] this compound crystallizes in the orthorhombic system with Pnma space group ($a = 7.812(2)$, $b = 5.740(1)$, $c = 10.056(2)$ Å). We found no reported data on its melting point, too.

Studies of phase equilibria which occur in different systems, particularly for a wide temperature range, are of great importance in science and technology. Such new data can afford possibilities for identification of unknown phases with their physicochemical properties, and for offering different methods of obtaining. On the one hand they contribute to better knowledge and, on the other, help to search for new, suitable and low-cost materials with

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properties required in different technologies. Hence, the results of phase-equilibria studies can be applied to further specialized or interdisciplinary research work.

Experimental

In the present investigations of the system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$ the following commercial reagents (all analytical pure) were used: BaHPO_4 , BaCO_3 , Rb_2CO_3 , $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{Ba}(\text{NO}_3)_2$, citric acid monohydrate and ethylene glycol.

$\text{Ba}_3(\text{PO}_4)_2$, BaRbPO_4 , and Rb_3PO_4 compounds were prepared in our laboratory. Barium diphosphate $\text{Ba}_2\text{P}_2\text{O}_7$ was obtained from BaHPO_4 by heating at $900\text{ }^\circ\text{C}$ for 1 h. The barium orthophosphate $\text{Ba}_3(\text{PO}_4)_2$ was obtained from stoichiometric amounts of $\text{Ba}_2\text{P}_2\text{O}_7$ and BaCO_3 . The substrates, thoroughly mixed and rubbed, were sintered in a platinum crucible at $1300\text{ }^\circ\text{C}$ for 6 h. Rubidium orthophosphate Rb_3PO_4 was obtained from a stoichiometric mixture of dry Rb_2CO_3 (dried at $250\text{ }^\circ\text{C}$) and $(\text{NH}_4)_2\text{HPO}_4$. After mixing and rubbing, it was heated at $200\text{ }^\circ\text{C}$ for 4 h, then at $500\text{ }^\circ\text{C}$ for 4 h, thereafter rubbed and heated at $900\text{ }^\circ\text{C}$ for 10 h. After a new rubbing it was still heated at $1000\text{ }^\circ\text{C}$ for 20 h.

The phase equilibria in the system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$ were investigated using thermoanalytical methods, X-ray powder diffraction, ICP, and FT-IR technique. Samples for investigation were prepared from the parent substances mixed in the fixed amounts. In order to ensure their homogeneity, the mixtures were shaken in a weighing bottle and ground in an agate mortar, pelletized, placed in platinum crucibles, and then sintered. The conditions under which the samples were prepared (i.e., the sintering temperature and time) had been determined experimentally. The obtained sinters were crushed and finely ground.

The thermoanalytical investigations in the solid phase were carried out using a SETSYSTM (SETARAM) differential thermal analyzer (calorimeter) with a balance. The device enables one to perform simultaneous TGA-DTA or TGA-DSC measurements in the temperature range $20\text{--}1300\text{ }^\circ\text{C}$. Samples from 1 to 20 mg were placed in platinum crucibles and heated at a rate of $10\text{ }^\circ\text{C min}^{-1}$ in an atmosphere of argon. DTA, TG, analyses in the solid phase were also carried out in the air, up to $1400\text{ }^\circ\text{C}$, by using a derivatograph type 3427 (MOM, Hungary) with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$, platinum crucibles, sample weight $0.3\text{--}0.6\text{ g}$. Temperature was measured by means of a Pt/PtRh10 thermocouple which was calibrated against the melting points of NaCl , K_2SO_4 , $\text{Ca}_2\text{P}_2\text{O}_7$, and the transition point of K_2SO_4 . In order to determine the temperature for the thermal effect, the peak parameter on the DTA-heating curve was taken into account. The high-temperature

thermal investigations (above $1400\text{ }^\circ\text{C}$) were carried out under argon in a horizontal, resistance furnace with a molybdenum winding. Presynthesized samples were pressed into pellets of $1\text{--}2\text{ g}$ weight and loaded in boats of a PtRh30 alloy. The temperature point at which a sample was diffusing and got blurred in the field of observation to finally disappear was read by means of an optical pyrometer calibrated against the melting points of Na_3PO_4 and $\text{Ca}_3(\text{PO}_4)_2$. For the samples that were melted in a temperature range, the points determined were approximate. After melting, the samples were cooled down to room temperature. The quenching-in-ice technique (both for the sinters and for the melted samples) was also employed; a high-temperature vertical-tubular furnace ($20\text{--}1750\text{ }^\circ\text{C}$; Nabertherm RHTV 120-300/18) was used.

The phase purity of the commercial and the self-prepared parent phosphates, and the phase composition of both the sintered and the melted samples of the investigated system, were controlled by X-ray powder diffraction at room temperature. A SIEMENS D 5000 diffractometer with CuK_α radiation and a Ni filter was used. The quantitative analysis was performed using an emission spectrometer with argon plasma excitation (ICP Model ARL 3410). The vaporization of the orthophosphates Rb_3PO_4 and BaRbPO_4 has been studied by using the thermal analysis (Netzsch 409C) combined with mass spectrometry (Balzers Instruments ThermoStar). FT-IR spectra were measured over the range $1400\text{--}400\text{ cm}^{-1}$ (with KBr as diluent; Perkin-Elmer System 2000 FT-IR).

Results and discussion

Finding the phase equilibria existing in the $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$ system was preceded by investigation of thermal stability, polymorphism and other properties of the orthophosphates $\text{Ba}_3(\text{PO}_4)_2$, Rb_3PO_4 , and BaRbPO_4 . This was aimed at confirmation or verification or complementing the literature data. It is well known that the character of phase equilibria which arise in binary systems essentially depends on the properties of parent components.

Regarding Rb_3PO_4 , we have found that the compound melts congruently at about $1450\text{ }^\circ\text{C}$ and shows two polymorphic modifications with the transformation point at $1040\text{ }^\circ\text{C}$. The orthophosphate is strongly hygroscopic; for a presynthesized sample of Rb_3PO_4 , TG/DTA-heating curves indicated water losing in a few stages in the temperature range $100\text{--}430\text{ }^\circ\text{C}$. Also, a slow gradual loss of mass was observed on TG/DTA-heating curves (as shown in Fig. 1) during continued heating, from a temperature of $\sim 1150\text{ }^\circ\text{C}$. The loss noted was $\sim 5.5\text{ wt}\%$ as a result of melting up the Rb_3PO_4 sample. In order to explain the deficit, applied was thermal analysis combined with

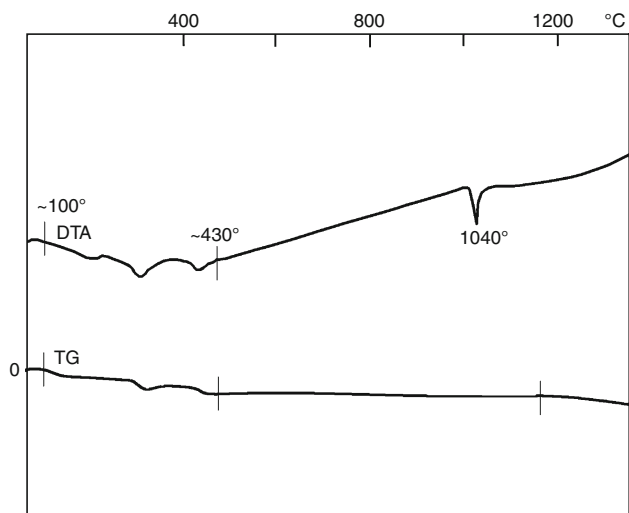


Fig. 1 TG and DTA curves of presynthesized Rb_3PO_4 , in air atmosphere

mass-spectrometric analysis. Presynthesized Rb_3PO_4 was heated from 20 to 1400 °C at a rate of 10 °C min^{-1} . The mass-spectrometric analysis of the gaseous phase revealed the presence of the ions PO^+ , PO_2^+ , $\text{P}_4\text{O}_{10}^+$, RbO^+ , RbO_2^+ , Rb_2O_2^+ . The FT-IR spectra both for the presynthesized Rb_3PO_4 and for the melted sample, were taken, too. It appeared that their infrared spectra were the same (see Fig. 2). Those results indicated that the stoichiometric composition of the condensed phase did not change.

It was confirmed, in accord with the results of [4], that the orthophosphate $\text{Ba}_3(\text{PO}_4)_2$ melts congruently at 1605 °C and occurred in two polymorphic modifications;

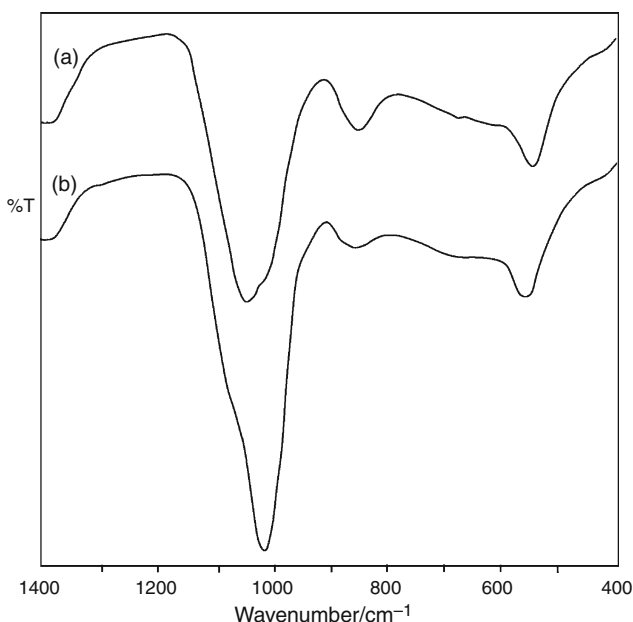
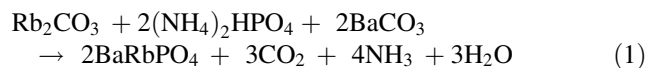


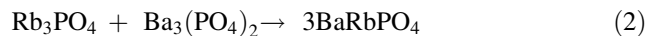
Fig. 2 FT-IR spectra of Rb_3PO_4 ; **a** melted, **b** presynthesized

the transition point being 1360 °C. Our thermal investigations confirmed the stability of $\text{Ba}_3(\text{PO}_4)_2$ compound. No weight loss in TG curves was noted in the temperature range 20–1400 °C during the DTA-heating of the orthophosphate samples of both the presynthesized and the melted ones. No difference was found in powder X-ray diffractograms for $\text{Ba}_3(\text{PO}_4)_2$ between the presynthesized samples and the melted ones via slow crystallization (at a rate of 3 °C min^{-1}). It was noted that the melted $\text{Ba}_3(\text{PO}_4)_2$ had a tendency to appear partially in the glassy form. An amorphous form appeared for a sample of $\text{Ba}_3(\text{PO}_4)_2$, which was crystallized fast (~ 15 °C min^{-1}) after melting. This was observed using reflected light microscopy of polished sections.

BaRbPO_4 orthophosphate was obtained by the standard method of solid-phase reaction according to the following reaction networks.



The conditions under which the above reaction was made were those given in paper [1]. It appeared, however, that additional roasting at 900 °C for 10 h was necessary to attain the BaRbPO_4 of phase purity.



In the method (2) the parent orthophosphates were thoroughly mixed (by shaking in a weighing bottle), rubbed in an agate mortar, pressed into pellets, and heated at 1000 °C for 2.5 h. The conditions (i.e., temperature and time) of both reactions were experimentally found.

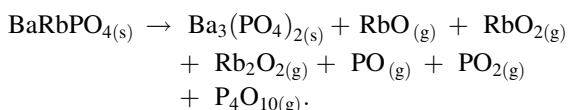
X-ray powder diffraction of the sinters obtained by reactions (1) and (2) showed the phase-pure BaRbPO_4 structure in agreement with [1, 8]. We found that the orthophosphate melts congruently at about 1700 °C. Next, its thermal stability and polymorphism were investigated. During the DTA/DSC-heating of the presynthesized BaRbPO_4 a slight, gradually proceeding loss of mass (noticeable in the TG curve) was observed from ~ 1230 °C. Figure 3 shows the TG/DTA-heating curves for the presynthesized BaRbPO_4 . It was also noted that the BaRbPO_4 sample lost ~ 10 wt% of its original mass as a result of melting. Its phase composition was verified by X-ray powder analysis. The diffractogram revealed reflections typical of $\text{Ba}_3(\text{PO}_4)_2$, apart from BaRbPO_4 diffraction lines. This evidenced that the orthophosphate BaRbPO_4 is high-temperature unstable and subjected to a gradual decomposition and vaporization. To verify the conclusion:

- A quantitative determination of rubidium, barium and phosphorus content was made for the samples of both the presynthesized compound and the melted one. The

quantitative analysis was performed using an emission spectrometer with argon plasma excitation. It appeared that the presynthesized and the melted samples differed in rubidium, barium and phosphorus content. Rubidium and phosphorus content decreased by ~ 5 and 0.6 wt%, respectively, for the melted sample and that of barium increased by ~ 4.7 wt% (with respect to the stoichiometric composition of the compound).

- The thermal analysis combined with mass spectrometry was performed. A sample of presynthesized BaRbPO_4 was heated from 20 to 1600 °C at a rate of 10 °C min^{-1} . The mass spectrometry of the gaseous phase showed the presence of the ions: PO^+ , PO_2^+ , $\text{P}_4\text{O}_{10}^+$, RbO^+ , RbO_2^+ , Rb_2O_2^+ .

In view of all the results of this study the decomposition and vaporization of orthophosphate BaRbPO_4 occur according to the reaction:



The appearance of the BaRbPO_4 in two modifications was confirmed in our thermoanalytical investigations. However, a disagreement was concerning the temperature of the transition. The differential thermal analysis of heating was performed for both presynthesized and melted BaRbPO_4 . The DTA/DSC-heating curve of sinter in the temperature range 20 – 1350 °C revealed an endothermic effect to which a temperature of 1195 °C corresponded (see Fig. 3). Accordingly, a melted sample of BaRbPO_4 was investigated by using DTA/DSC-heating (being aware that stoichiometry of the melted sample and BaRbPO_4 are different). This time

the DTA/DSC-heating curves showed a single endothermic effect, too, but at a corresponding temperature of ~ 1090 °C (see Fig. 4). As was subsequently found, the effect was present on the DTA/DSC-heating curves for all the presynthesized samples with composition ranging between 65 and 99 wt% $\text{Ba}_3(\text{PO}_4)_2$. In view of all results of the present study we ascribe a temperature point of 1195 °C to the polymorphic transformation of BaRbPO_4 .

The previously unknown phase equilibria in the Rb_3PO_4 – $\text{Ba}_3(\text{PO}_4)_2$ system were investigated in the entire composition range up to a temperature of 1800 °C. BaRbPO_4 appeared as an intermediate compound in the system. Due to the synthesis conditions of the orthophosphate, the thermal instability of the phosphates Rb_3PO_4 and BaRbPO_4 at high temperatures, the hygroscopicity of Rb_3PO_4 , and also to meet the requirement of equilibrium composition, the following two series of samples were used.

- Heteromolar mixtures of $(\text{NH}_4)_2\text{HPO}_4$, dry Rb_2CO_3 , and BaRbPO_4 —to determine the phase equilibria within the composition range 0 – 60 wt% $\text{Ba}_3(\text{PO}_4)_2$. Those mixtures, after mixing and grinding, were heated at 200 °C for 4 h, at 500 °C for 4 h, at 900 °C for 10 h and at 1000 °C for 20 h with intermediate grindings to ensure a total reaction.
- Heteromolar mixtures of BaRbPO_4 and $\text{Ba}_3(\text{PO}_4)_2$ orthophosphates—to determine the phase equilibria within the composition range 65 – 100 wt% $\text{Ba}_3(\text{PO}_4)_2$. Those mixtures were presynthesized via the solid-phase reaction by heating at 950 °C for 2 h.

The sinters obtained by the above methods were cooled down to room temperature and homogenized by rubbing, then were subjected to thermal analyzing. The

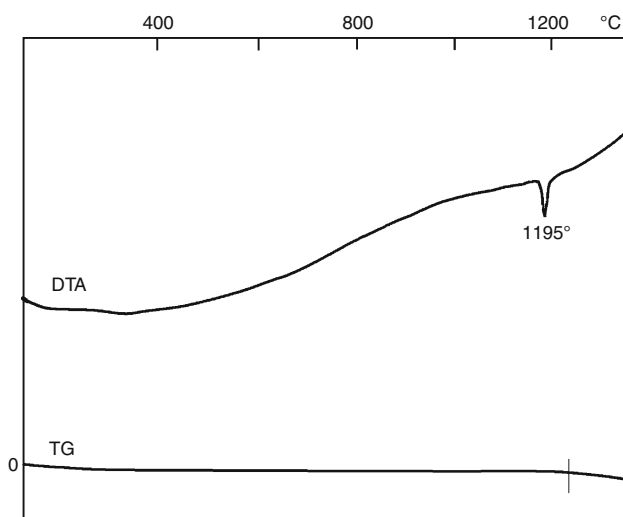


Fig. 3 TG and DTA curves of presynthesized BaRbPO_4 , in air atmosphere

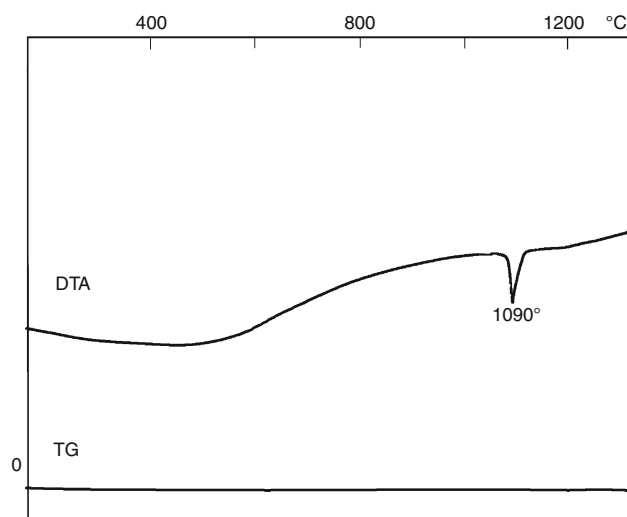


Fig. 4 TG and DTA curves of the melted BaRbPO_4 , in air atmosphere

phase composition of the sinters was identified by X-ray powder diffraction at room-temperature. Testing procedure showed that all samples of the system of interest melted in excess of 1400 °C. Accordingly, to draw the liquidus curves the samples after pressing into pellets were placed in PtRh30 boats and heated under argon in the horizontal furnace. The temperature of the pellets' diffusion was read by means of optical pyrometer. The outline of both the liquidus and the solidus curves, therefore, is approximate as shown by dashed lines.

The liquidus curve of the system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$, at ~30 wt%, had a maximum at ~1560 °C (Fig. 5, point B of the phase diagram). This indicated, for such a composition, the possibility of formation of another intermediate compound which would congruently melt. The compound's formation seemed likely since either the molar ratio $\text{Rb}_3\text{PO}_4\text{:Ba}_3(\text{PO}_4)_2$ equal to 4:1 or the molar ratio $\text{Rb}_3\text{PO}_4\text{:BaRbPO}_4 = 1\text{:}1$ (i.e., theoretical formula of the compound $\text{BaRb}_4(\text{PO}_4)_2$) correspond to the percentage composition in question (30 wt% $\text{Ba}_3(\text{PO}_4)_2$ and 70 wt% Rb_3PO_4). Compounds of the type $\text{M}_4^{\text{I}}\text{M}^{\text{II}}(\text{PO}_4)_2$ (where $\text{M}^{\text{I}} = \text{Na, K}$; $\text{M}^{\text{II}} = \text{Mg, Ca}$) are known in the literature [9–12].

In order to verify the hypothesis the following was done.

- An heteromolar mixture of Rb_3PO_4 and BaRbPO_4 (after a thorough homogenization) was sintered at 1150 °C for 2 h and quenched.
- A mixture of 4 mol Rb_3PO_4 and 1 mol $\text{Ba}_3(\text{PO}_4)_2$ (after a thorough homogenization) was sintered at 1100 °C for 5 h and for 1 h at 1150 °C, then quenched.

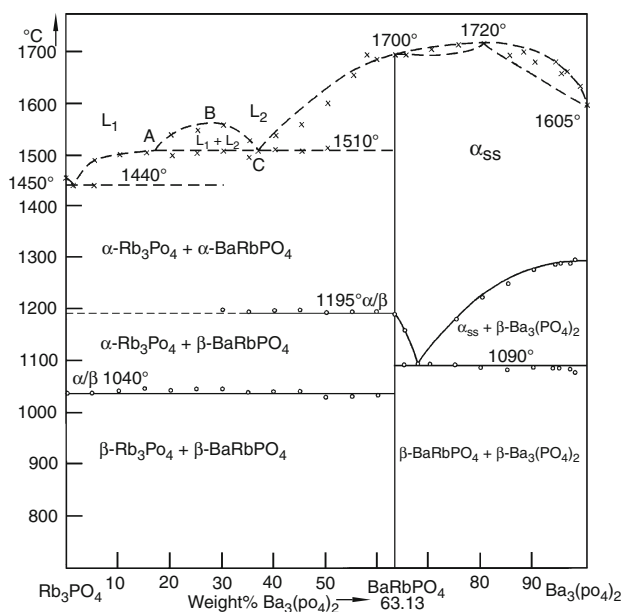


Fig. 5 Phase diagram of the system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$

- A modified Pechini method was employed; stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$, Rb_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in a small portion of distilled water, then citric acid and ethylene glycol were added as the complexing agent. The mixture was dried at 120 °C for 24 h, then heated at 450 °C for 24 h, rubbed, heated at 1150 °C for 2 h and quenched.

Phase composition of reaction products from the above processes was verified by X-ray powder diffraction. Diffractograms revealed only reflections from Rb_3PO_4 and BaRbPO_4 phosphates. Consequently, the maximum present on the liquidus curve (at ~30 wt% $\text{Ba}_3(\text{PO}_4)_2$) can account for division of the liquid phase into the two liquid solutions L_1 and L_2 . Hence, the ABC area (in the composition range 17–36 wt% $\text{Ba}_3(\text{PO}_4)_2$) represents a mixture of liquid solutions $L_1 + L_2$. A transformation at a constant temperature of ~1510 °C can be ascribed to point C, according to the reaction network: $L_{2C} \rightarrow L_{1A} + \text{BaRbPO}_4$ (where L_{2C} denotes the liquid L_2 with a composition of point C, and L_{1A} – liquid L_1 with a composition of point A). An eutectic occurs in the Rb_3PO_4 -rich part of the system of interest at ~1.0 wt% $\text{Ba}_3(\text{PO}_4)_2$, which melts at ~1440 °C. In the $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$ system, within the composition range 63.14–100 wt% $\text{Ba}_3(\text{PO}_4)_2$; high-temperature, continuous solid solutions α exhibit their maximum melting point at ~1720 °C.

In order to find the phase equilibria for the system $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$, the DTA/DSC-heating of solid-phase presynthesized samples was performed in the subsolidus area. Thermal instability of Rb_3PO_4 and BaRbPO_4 phosphates hindered dealing with melted samples because of changes in original composition. The elaborated phase diagram of the $\text{Rb}_3\text{PO}_4\text{--Ba}_3(\text{PO}_4)_2$ system is shown in Fig. 5.

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