Sol-gel synthesis of $CaBPO_5$: phase composition and thermal properties

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A citrate-assisted sol–gel route was investigated for the preparation of crystalline calcium borophosphate ($CaBPO_5$). To the best of our knowledge, this is the first report of crystalline $CaBPO_5$ obtained by this route. The phase compositions of products prepared with different H_3BO_3 excesses and precursor-concentration procedures were compared. Concentration under heating produced multiphase products containing $CaBPO_5$ and calcium phosphate secondary phases; increasing the H_3BO_3 content did not eliminate these impurities. Under optimized conditions, involving 20 mol.% excess H_3BO_3, a reduced precursor-solution volume, and gel formation at room temperature, crystalline $CaBPO_5$ without secondary phases detectable by powder X-ray diffraction was obtained after thermal treatment. Rietveld refinement confirmed the formation of trigonal stillwellite-type $CaBPO_5$ in the $P3_121$ space group, with unit-cell parameters close to reported values. The Crystallographic Information File (CIF) for the synthesized $CaBPO_5$ sample is available in the Cambridge Structural Database under the registration number CSD 2596463. Differential thermal analysis revealed a high-temperature endothermic event with an onset temperature of 1037.1°C, assigned to the onset of incongruent melting. The study demonstrates the feasibility of citrate-assisted sol–gel synthesis of crystalline $CaBPO_5$ and identifies a combination of precursor-preparation conditions yielding a product without PXRD-detectable secondary crystalline phases.

Keywords: $CaBPO_5$; calcium borophosphate; citrate-assisted sol–gel synthesis; phase formation; powder X-ray diffraction; thermal analysis.

$CaBPO_5$-ті золь-гель әдісімен синтездеу: фазалық құрамы және термиялық қасиеттері

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Кристалды кальций борофосфатын ($CaBPO_5$) алудың цитратты золь–гель тәсілі зерттелді. Бізге белгілі мәліметтер бойынша, бұл — кристалды $CaBPO_5$-ті осы тәсілмен алу туралы алғашқы жұмыс. H_3BO_3-тің әртүрлі артық мөлшерлері мен прекурсорлар ерітіндісін қоюландырудың әртүрлі режимдері қолданылған кезде алынған өнімдердің фазалық құрамы салыстырылды. Қыздыру арқылы қоюландыру құрамында $CaBPO_5$ және кальций фосфаттарының қосалқы фазалары бар көпфазалы өнімдердің түзілуіне әкелді; H_3BO_3 мөлшерін арттыру бұл қоспаларды жоюға мүмкіндік бермеді. H_3BO_3-тің 20 мол.% артық мөлшерін, прекурсорлар ерітіндісінің азайтылған көлемін және бөлме температурасында гель түзуді қамтитын оңтайландырылған жағдайларда термиялық өңдеуден кейін ұнтақтық рентгендік дифракция әдісімен анықталатын қосалқы фазаларсыз кристалды $CaBPO_5$ алынды. Құрылымды Ритвельд әдісімен нақтылау стиллвеллит типті құрылымы және $P3_121$ кеңістік тобы бар тригоналды $CaBPO_5$ түзілгенін растады; элементар ұяшық параметрлері әдебиетте келтірілген мәндерге жақын болды. Синтезделген $CaBPO_5$ үлгісінің кристаллографиялық ақпараттық файлы (CIF) Cambridge Structural Database дерекқорында CSD 2596463 тіркеу нөмірімен қолжетімді. Дифференциалдық термиялық талдау басталу температурасы 1037,1°C болатын жоғары температуралық эндотермиялық әсерді анықтады; бұл әсер инконгруэнтті балқудың басталуымен байланыстырылды. Жұмыс кристалды $CaBPO_5$-ті цитратты золь–гель әдісімен алу мүмкіндігін көрсетеді және ұнтақтық рентгендік дифракция әдісімен анықталатын қосалқы кристалды фазаларсыз өнім алуды қамтамасыз ететін прекурсорды дайындау жағдайларының үйлесімін айқындайды.

Түйін сөздер: $CaBPO_5$; кальций борофосфаты; лимон қышқылының қатысуымен золь-гель синтезі; фазалардың түзілуі; ұнтақтық рентгендік дифракция; термиялық талдау.

Золь-гель синтез $CaBPO_5$: фазовый состав и термические свойства

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Исследован цитратный золь–гель маршрут получения кристаллического борофосфата кальция ($CaBPO_5$). Насколько нам известно, это первое сообщение о получении кристаллического $CaBPO_5$ данным методом. Сопоставлен фазовый состав продуктов, полученных при различных избытках H_3BO_3 и режимах концентрирования раствора прекурсоров. Концентрирование при нагревании приводило к образованию многофазных продуктов, содержащих $CaBPO_5$ и вторичные фазы фосфатов кальция; увеличение содержания H_3BO_3 не обеспечивало устранения этих примесей. В оптимизированных условиях, включающих 20 мол.% избытка H_3BO_3, уменьшенный объём раствора прекурсоров и гелеобразование при комнатной температуре, после термообработки получен кристаллический $CaBPO_5$ без вторичных фаз, обнаруживаемых методом порошковой рентгеновской дифракции. Уточнение структуры методом Ритвельда подтвердило образование тригонального $CaBPO_5$ со структурой типа стиллвеллита и пространственной группой $P3_121$, с параметрами элементарной ячейки, близкими к литературным значениям. Кристаллографический информационный файл (CIF) синтезированного образца $CaBPO_5$ доступен в Cambridge Structural Database под регистрационным номером CSD 2596463. Дифференциальный термический анализ выявил высокотемпературный эндотермический эффект с температурой начала 1037,1°C, соответствующий началу инконгруэнтного плавления. Работа демонстрирует возможность получения кристаллического $CaBPO_5$ цитратным золь–гель методом и позволяет определить сочетание условий приготовления прекурсора, обеспечивающее получение продукта без вторичных кристаллических фаз, обнаруживаемых методом порошковой рентгеновской дифракции.

Ключевые слова: $CaBPO_5$; борофосфат кальция; золь-гель синтез с использованием лимонной кислоты; фазообразование; порошковая рентгеновская дифракция; термический анализ.

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Article

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1. Introduction

Borophosphates constitute a broad class of complex oxyanion compounds exhibiting considerable structural diversity. The presence of BO_3 triangles alongside BO_4 and PO_4 tetrahedra allows diverse combinations and connectivity patterns, providing multiple possibilities for anionic polymerization. The resulting chain-like, layered, and framework architectures make borophosphates of interest in solid-state chemistry and the development of functional materials [1].

Calcium borophosphate ($CaBPO_5$) is a representative member of the anhydrous alkaline-earth metal borophosphates. Its crystal structure belongs to the stillwellite structure type and consists of corner-sharing BO_4 and PO_4 tetrahedra. $CaBPO_5$ has been investigated in both its undoped form and as a host material activated with rare-earth ions. Owing to the possibility of incorporating rare-earth ions into its cationic sublattice, $CaBPO_5$ is considered a promising host matrix for luminescent, scintillation, and radiophotoluminescent materials [2–4].

Solid-state synthesis is the most commonly employed method for preparing $CaBPO_5$ and related doped materials. This approach is widely used for phosphor production owing to its technological simplicity [2,5–10]. However, product formation relies on the diffusion of reactants across interphase boundaries, typically requiring high reaction temperatures, prolonged heat treatments, and repeated grinding to achieve complete reaction. In doped materials, an additional limitation is the potentially nonuniform distribution of activator ions within the crystalline host lattice, which may affect energy-transfer efficiency and luminescence properties.

Alternative approaches to the synthesis of doped $CaBPO_5$ have also been reported. In particular, $CaBPO_5$: Eu^{3+} has been prepared by coprecipitation followed by thermal treatment of the precursor [3]. Also, a hydrothermal method was reported for the synthesis of Eu^{3+}- and Tb^{3+}-activated $CaBPO_5$ phosphors [11].

These findings demonstrate the potential of solution-based precursor preparation for obtaining materials of this composition. Nevertheless, coprecipitation requires careful control over precipitation conditions and the composition of the resulting precipitate, whereas hydrothermal synthesis generally involves sealed reaction vessels and prolonged treatment under elevated temperature and pressure.

The sol–gel method is a promising approach for the synthesis of multicomponent oxide materials. It involves mixing the starting components in a liquid medium, followed by gel formation, drying, and subsequent thermal treatment. Compared with conventional mechanical mixing of solid reactants, this approach offers the potential for a more homogeneous distribution of the constituent elements and dopants within the precursor. Subsequent calcination in air facilitates the removal of volatile and organic components, promotes solid-state reactions, and leads to the formation of the crystalline phase [12].

Although sol–gel approaches have been applied to other borophosphate materials [13,14], to the best of our knowledge, the preparation of crystalline $CaBPO_5$ by a citrate-assisted sol–gel route has not previously been reported.

The aim of the present study was to investigate the feasibility of synthesizing crystalline $CaBPO_5$ via the sol–gel method followed by calcination of the precursor in air. The

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developed approach may subsequently be applied to the synthesis of doped $CaBPO_5$-based materials and to investigations of the effects of activator type and concentration on their structural and luminescence properties.

2. Experiment

2.1 Sol–Gel Synthesis of $CaBPO_5$

Calcium borophosphate ($CaBPO_5$) was synthesized using $CaCO_3$ (>99.0%, Guandong Guanghua Chemical factory), H_3BO_3 (99.8%, Laborpharma), $(NH_4)_2HPO_4$ (>99.0%, Laborpharma), anhydrous citric acid ($C_6H_8O_7$, >99.5%, Sigma Aldrich), and HNO_3 (≥65 wt%, puriss. p.a., Honeywell Fluka) as starting reagents. All reagents were used as received without further purification. For the stoichiometric batch, corresponding to a theoretical $CaBPO_5$ yield of approximately 1.000 g, 0.618 g of $CaCO_3$, 0.816 g of $(NH_4)_2HPO_4$, 0.382 g of H_3BO_3, and 0.833 g of anhydrous citric acid were used. These amounts correspond to a nominal Ca : B : P molar ratio of 1 : 1 : 1 and a citric acid : Ca molar ratio of approximately 0.70 : 1. For the boron-excess batches, the H_3BO_3 amount was increased by 5, 10, or 20 mol.% relative to the stoichiometric requirement, while the amounts of the other reagents were kept constant.

The calculated amounts of $C_6H_8O_7$ and H_3BO_3 were mixed with deionized water under magnetic stirring. The calcium precursor solution was obtained by dissolving $CaCO_3$ in an aqueous HNO_3 solution, prepared by diluting 1 mL of concentrated HNO_3 (65 wt.%) with deionized water. Equal volumes of deionized water were used to prepare the $C_6H_8O_7$–H_3BO_3 mixture and the calcium precursor solution. Once a calcium-containing solution was obtained, it was added to the $C_6H_8O_7$–H_3BO_3 solution. Subsequently, $(NH_4)_2HPO_4$ was introduced under continuous stirring.

The total volume of deionized water was approximately 50 mL in the initial experiments and 10 mL in the final synthesis. The reagent amounts and the volume of concentrated HNO_3 were kept unchanged.

Two different procedures were employed to concentrate the precursor solution. In the first procedure, the solution was heated under vigorous magnetic stirring on a hotplate with a surface temperature set to 250 °C until a dry gel was obtained. In the second procedure, the solution was continuously stirred at room temperature for 48 h until gel formation occurred, followed by drying at 60 °C for 12 h. In both cases, the dried precursors were ground in an agate mortar.

The resulting precursors were placed in alumina crucibles and introduced into a furnace preheated to 500 °C, where they were held for 1 h. After further grinding, the powders were introduced into a furnace preheated to 950 °C, where they were calcined in air for 12 h. The crucibles were subsequently removed from the hot furnace and allowed to cool to room temperature.

2.2 Powder X-ray Diffraction Analysis

The phase composition of the synthesized samples was investigated by powder X-ray diffraction (PXRD) using a TD-3700 diffractometer (Tongda, China) in Bragg-Brentano geometry with Cu Kα radiation at room temperature. The X-ray tube was operated at 30 kV and 20 mA. Diffraction data were collected over the 2θ range of 10.01-60.00° with a step size of 0.0188°. Phase identification was performed using XRD Phase Finder [15] by comparison of the experimental diffraction patterns with reference diffraction data for $CaBPO_5$ (COD No. 96-151-1467), $Ca_2P_2O_7$ (PDF-2 No. 01-071-2123), BPO_4 (PDF-2 No. 01-074-1169) and $Ca_3(PO_4)_2$ (PDF-2 No. 00-009-0169).

The crystal structure of the sample without secondary phases detectable by PXRD was refined by the Rietveld method using the GSAS-II software package [16]. The previously reported stillwellite-type structural model of $CaBPO_5$ [17] in the trigonal space group $P3_121$ was used as the starting model. The refinement was performed in several stages to minimize parameter correlations. First, the scale factor, background, zero shift, peak-profile parameters, and unit-cell parameters were refined while the atomic model was kept fixed. Atomic coordinates of Ca, P, and O were subsequently refined, whereas the coordinates of B were kept fixed because of its weak contribution to laboratory X-ray diffraction intensities.

To stabilize refinement of the light-atom positions, eight soft bond-distance restraints were applied to the BO_4 and PO_4 tetrahedra. The restrained distances were P-O2 = 1.5089 Å and P-O1 = 1.5625 Å with an estimated standard deviation of 0.02 Å, and B-O3 = 1.4386 Å and B-O1 = 1.5682 Å with an estimated standard deviation of 0.03 Å. A restraint weight factor of 10 was used. In the final stage, the atomic coordinates were fixed and the isotropic atomic displacement parameters were refined separately. The isotropic displacement parameters of the three crystallographically distinct O sites were constrained to a common value, while those of Ca and P were refined independently. The isotropic displacement parameter of B was fixed because it could not be determined reliably from the laboratory PXRD data.

The experimental and refinement details and the final crystallographic parameters are summarized in Table 1. Atomic coordinates and selected interatomic distances are given in Tables S1 and S2, respectively. The observed and calculated profiles, background, difference curve, and Bragg reflection positions are shown in Figure 3. The final refined structural model was reconstructed and analyzed using CRAFT [18], including evaluation of coordination environments, interatomic distances, and polyhedral connectivity.

2.3 Thermal Analysis

The thermal behavior of the synthesized $CaBPO_5$ sample was investigated by thermogravimetric analysis (TG) and differential thermal analysis (DTA) using a NETZSCH STA 449 F3 Jupiter thermal analyzer. Measurements were performed on a 50 mg sample in an Al_2O_3 crucible under a nitrogen flow of 50 mL/min. The sample was heated from 30 to 1200 °C at a heating rate of 20 °C/min.

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3. Results and Discussion

Initially, $CaBPO_5$ was synthesized using a stoichiometric molar ratio of Ca : B : P = 1 : 1 : 1. The reaction mixture was concentrated under vigorous stirring on a hotplate set to 250 °C until a gel-like precursor was formed. Following preliminary heat treatment at 500 °C for 1 h and subsequent calcination at 950 °C for 12 h, the X-ray diffraction pattern of the resulting product exhibited additional reflections attributed to $Ca_2P_2O_7$ [19] and BPO_4 alongside those of the target $CaBPO_5$ phase (Figure 1).

The formation of $Ca_2P_2O_7$ and BPO_4 as secondary phases may indicate local deviations from the stoichiometry required for phase-pure $CaBPO_5$ formation within the precursor. Since boric acid and other boron-containing compounds can be partially transferred from aqueous solutions into the vapor phase during evaporation, the formation of the calcium phosphate impurity may be associated with a reduction in the actual boron content during gel formation [20–22]. To examine this hypothesis, additional samples were synthesized with 5, 10 and 20 mol.% excess H_3BO_3 relative to the stoichiometric amount.

As shown in Figure 1, increasing the H_3BO_3 content in the initial reaction mixture did not eliminate the secondary crystalline phases. The sample prepared with 5 mol.% excess H_3BO_3 contained both $Ca_2P_2O_7$ and BPO_4. No reflections attributable to BPO_4 were observed in the samples prepared with 10 and 20 mol.% excess H_3BO_3. Even with 20 mol.% excess H_3BO_3, a single-phase $CaBPO_5$ product was not obtained when the precursor solution was concentrated under heating: $Ca_2P_2O_7$ remained detectable, and additional reflections attributed to $Ca_3(PO_4)_2$ were observed.

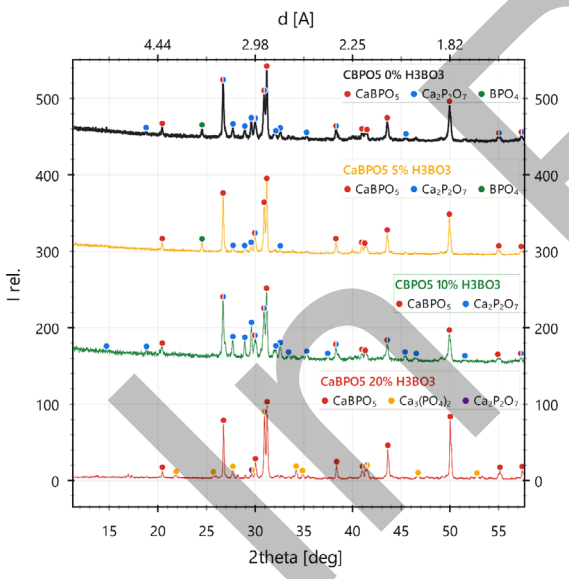


Figure 1 – Powder X-ray diffraction patterns of $CaBPO_5$ samples synthesized with 0, 5, 10 and 20 mol.% excess H_3BO_3 after calcination at 950 °C for 12 h, together with reference diffraction patterns of $CaBPO_5$ and secondary phases

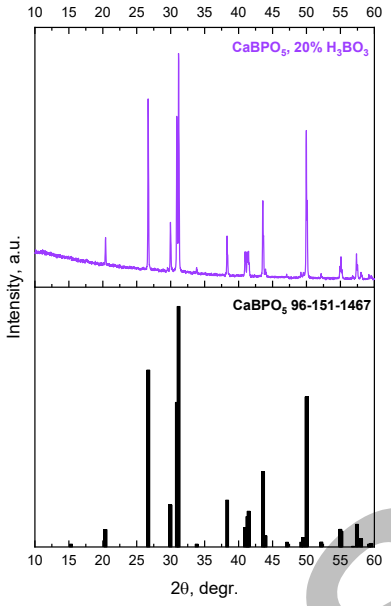


Figure 2 – Powder X-ray diffraction pattern of $CaBPO_5$ synthesized with 20 mol.% excess H_3BO_3 using the room-temperature gel formation procedure, followed by calcination at 950 °C for 12 h, compared with the reference diffraction pattern of $CaBPO_5$

The persistence of secondary phases despite increasing the H_3BO_3 excess suggests that their formation is not governed solely by the nominal reactant composition. Concentration of the solution under heating may have resulted in nonuniform solvent removal, redistribution of the components within the forming gel, and potentially uncontrolled losses of boron-containing species. Consequently, the actual elemental ratios in the dried precursors may have varied between synthesis runs, even when the same nominal composition was used.

Since increasing the nominal H_3BO_3 content did not eliminate secondary phases, further optimization of the synthesis procedure focused on modifying the conditions of sol–gel precursor formation. It was hypothesized that eliminating external heating during solvent evaporation could minimize deviations of the actual B/P ratio from its nominal value while improving the chemical homogeneity of the precursor during gel formation.

To this end, the reaction mixture was concentrated without external heating. In addition, the total amount of added water was reduced from 50 to 10 mL to shorten the solvent-removal stage. A 20 mol.% excess of H_3BO_3 was used to compensate for potential changes in the boron content during precursor formation. The resulting solution was maintained at room temperature under continuous stirring for 48 h until gel formation occurred. The resulting gel was subsequently dried in an oven at 60 °C for 12 h and ground in an agate mortar. The dried precursor was initially calcined in air at 500 °C for 1 h, followed by further grinding and calcination at 950 °C for 12 h.

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The X-ray diffraction pattern of the product obtained by concentrating the precursor solution at room temperature is presented in Figure 2. In contrast to the samples synthesized by evaporation on a hotplate, only reflections corresponding to the crystalline $CaBPO_5$ phase were observed. No additional reflections characteristic of $Ca_2P_2O_7$, BPO_4 or $Ca_3(PO_4)_2$ were detected within the detection limits of powder X-ray diffraction. However, the individual effects of solution volume and gel formation conditions could not be isolated, as both were varied simultaneously.

The optimized citrate-assisted sol-gel procedure yielded crystalline $CaBPO_5$ without secondary phases detectable by PXRD. Rietveld refinement in $P3_121$ converged with R_p = 3.48%, R_{wp} = 4.61%, R_{exp} = 3.35%, and GOF = 1.38 (Figure 3). The refined unit-cell parameters are a = 6.68253(21) Å, c = 6.60852(11) Å, and V = 255.574(12) Å^3. These values agree closely with the literature values for $CaBPO_5$ [17] (a = 6.6799(2) Å, c = 6.6111(3) Å, $V \approx$ 255.47 Å^3), supporting formation of the expected trigonal stillwellite-type phase (Table 1).

The refined structure is shown in Figure 4. It consists of BO_4 and PO_4 tetrahedra together with distorted ten-coordinate CaO_{10} polyhedra. The BO_4 tetrahedra contain two shorter B-O3 bonds of 1.442(3) Å and two longer B-O1 bonds of 1.568(4) Å, whereas the PO_4 tetrahedra contain two shorter P-O2 bonds of 1.495(8) Å and two longer P-O1 bonds of 1.568(9) Å. Ca is coordinated by ten oxygen atoms with Ca-O distances of 2.275(6)-2.854(4) Å. The resulting coordination geometry is consistent with the known crystal chemistry of stillwellite-type $CaBPO_5$.

Final atomic coordinates and displacement parameters are available in Table S1 and as CIFs in the Cambridge Structure Database, deposition numbers: CSD 2596463. Selected interatomic bond distances are listed in Table S2.

Table 1 – Crystal, experimental, and refinement data for $CaBPO_5$

Parameter	Value
Chemical formula	$CaBPO_5$
Space group	$P3_121$
Crystal system	Trigonal
Z	3
Temperature	Room temperature (~300 K)
a, Å	6.6825(2)
b, Å	6.6825(2)
c, Å	6.6085(1)
α, °	90
β, °	90
γ, °	120
V, Å^3	255.574(12)
Instrument model	Tongda TD3700
Collection method	Powder X-ray diffraction; Bragg-Brentano geometry
Radiation	Cu Kα1,2
Wavelength, Å	1.5405; 1.5443
Calculated density, Mg m^{-3}	3.1549
2θ minimum, °	10.0084
2θ maximum, °	59.9976
2θ step, °	0.0188
R_p, %	3.483
R_{wp}, %	4.614
R_{exp}, %	3.347
GOF	1.38
Reflections used in refinement	38
Restraints	8
Maximum shift / standard uncertainty	0.00002

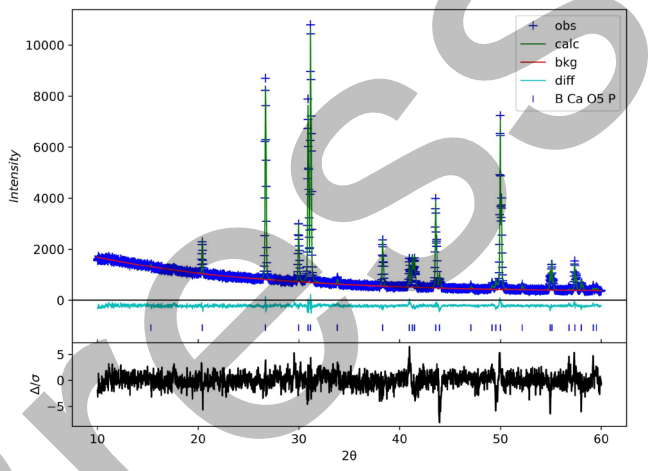


Figure 3 – Rietveld refinement of the PXRD pattern of $CaBPO_5$ obtained by the optimized citrate-assisted sol-gel route. Blue crosses: observed data; green line: calculated pattern; red line: background; cyan line: difference profile; vertical tick marks: Bragg reflection positions of $CaBPO_5$

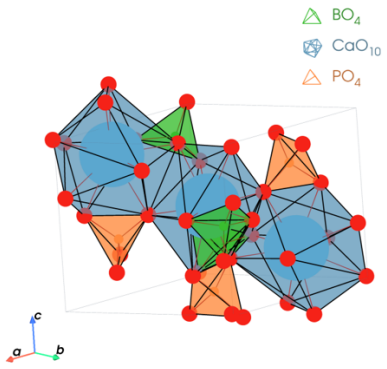


Figure 4 – Polyhedral representation of the refined $CaBPO_5$ structure generated in CRAFT. BO_4 and PO_4 tetrahedra are shown together with CaO_{10} coordination polyhedra

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Because the B coordinates and displacement parameter are only weakly constrained by laboratory X-ray data, the B position was not refined freely in the final model. Nevertheless, the close agreement between the observed and calculated diffraction profiles, the agreement of the unit-cell parameters with the literature data, and the chemically reasonable BO_4/PO_4 geometry together confirm formation of structurally well-defined $CaBPO_5$. Thus, the selected citrate precursor formation conditions yielded crystalline $CaBPO_5$ with the expected stillwellite-type structure, without secondary crystalline phases detectable by PXRD.

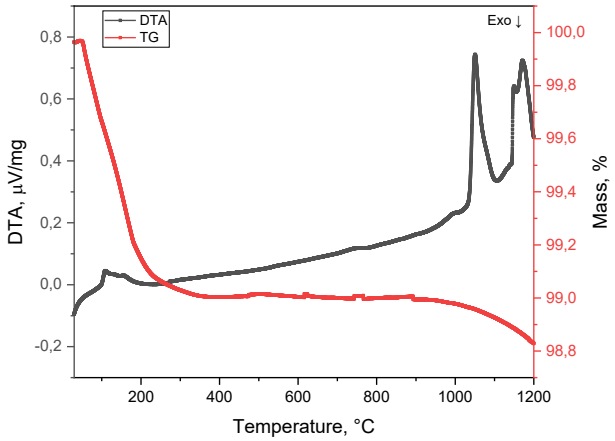


Figure 5 – TG and DTA curves of the synthesized $CaBPO_5$ recorded upon heating under a nitrogen atmosphere

Figure 5 presents the results of thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the synthesized $CaBPO_5$. The mass change of the sample over the investigated temperature range was relatively small, with a total mass loss of approximately 1.17% upon heating to 1200 °C. The main mass loss occurred in the low-temperature region, after which the sample mass remained nearly constant up to elevated temperatures. The DTA curve exhibited a pronounced endothermic event at high temperatures, with an onset temperature of 1037.1 °C, consistent with literature reports of the incongruent melting of $CaBPO_5$ [17]. The second effect at approximately 1170 °C may be associated with further melting or phase transformations following the initial high-temperature event. Multiphase regions and liquid–solid coexistence have been reported in the $CaO–P_2O_5–B_2O_3$ system at 1200 °C [23].

4. Conclusion

To the best of our knowledge, in this work, crystalline calcium borophosphate, $CaBPO_5$, was synthesized for the first time by a citrate-assisted sol–gel method. The results show that the phase composition of the calcined products is strongly affected by the conditions used for formation of the citrate-gel precursor. Concentration under heating using 50 mL of added water resulted in multiphase products. Increasing the initial H_3BO_3 content by 5, 10, or 20 mol.% did not eliminate secondary phases under these conditions.

A single-phase product within the detection limits of XRD was obtained using 10 mL of added water with 20 mol.% excess H_3BO_3, followed by gel formation under stirring at room temperature for 48 h and drying at 60 °C. Subsequent thermal treatment at 500 °C for 1 h and calcination at 950 °C for 12 h yielded crystalline $CaBPO_5$ without detectable $Ca_2P_2O_7$, BPO_4 or $Ca_3(PO_4)_2$ reflections. Rietveld refinement confirmed formation of the trigonal stillwellite-type $CaBPO_5$ structure ($P3_121$); the refined unit-cell parameters agreed closely with reported literature values. The synthesized $CaBPO_5$ exhibited a small total mass loss of approximately 1.17% upon heating to 1200 °C. The high-temperature endothermic event beginning at 1037.1 °C is consistent with the reported onset of incongruent melting of $CaBPO_5$. Thus, the developed citrate-assisted sol–gel route enables the preparation of crystalline $CaBPO_5$ and can serve as a basis for the further synthesis of doped $CaBPO_5$-based functional materials.

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CRediT authorship contribution statement

Ye. Zholdas: Methodology, Investigation, Data curation, Writing – original draft. Zh. Amanbayeva: Investigation. K. Saliyeva: Investigation. A. Bakhadur: Conceptualization, Investigation, Methodology, Visualization, Data curation, Writing – original draft. A. Kuznetsov: Conceptualization, Methodology, Investigation. A. Mukanov: Methodology, Investigation, Data curation. K. Kokh: Supervision, Conceptualization, Resources, Writing – review and editing.

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