The field of solid solutions in ternary system of synthetic apatite-type alkaline earth element-yttrium-silicate oxybritholite phases of the composition: \( AEE_\delta Y_{10-\delta}[SiO_4]_6O_3-0.5\delta \), where \( AEE=Ca, Sr \) and \( Ba \)

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Abstract

This contribution deals with the synthesis, properties and investigation of the field of solid solutions between the three end-members of apatite-type alkaline earth element-yttrium-silicate oxybritholites with the hexagonal structure (P\(6_3/m\)). The stoichiometric composition of these compounds corresponds to the formula \( AEE_\delta Y_{10-\delta}[SiO_4]_6O_3-0.5\delta \), where \( AEE=Ca, Sr \) and \( Ba \) and parameter \( \delta \to 2 \). These compounds and their solid solutions crystallize from non-equilibrium high temperature flux as the main product of sinter-crystallization process. Increasing ionic radius of \( AEE \) cations has significant effect to the lattice parameters, properties and miscibility of apatite phases. While there is non-limited miscibility of solid solutions formed between \( Ca_2Y_8[SiO_4]_6O_2 \) and \( Sr_2Y_8[SiO_4]_6O_2 \), the highest content of barium in the binary solution with these species is limited to 28% and 38%, respectively. The connecting line of these points marks out the borderline for the field of solid solutions in ternary system. All attempts for the preparation of pure \( Ba_2Y_8[SiO_4]_6O_2 \) end-member via the ceramic method were not successful.

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1. Introduction

Apatite is the most abundant phosphate mineral, which accounts for more than 95% of total phosphorus (P is the tenth most abundant element on Earth) in the Earth’s crust [1]. Sedimentary (80% of total world production) and igneous phosphate rocks are an important mineral commodity used in the chemical industry (manufacturing of phosphorus, phosphoric acid, etc.) and food production (production of phosphate fertilizers) [2]. Furthermore, apatites and their synthetic analogs represent a major class of ionic compounds [3] of interest to many disciplines including medical and biomaterials sciences [4–10], geology [11], cosmology [3], environmental [12] and nuclear sciences [3], preparation of apatite phosphors [13], pigments [14] catalysts in organic synthesis [15] and magneto-optical materials [16].

Apatite is the generic name which was first introduced by German geologist A.G. Werner [17] to describe calcium phosphates of composition given by simplified “double form” \( (Z=2) \) formula \( M_{10}(TO_4)_6X_2 \). The “single form” is the formula written as \( M_2(TO_4)_3X \) [18] where the letters \( M \) and \( X \) represent a cation with charge +1, +2 or 3 + (\( Ca^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Na^+, Ce^{3+}, La^{3+}, Y^{3+}, Bi^{3+} \) [8]) and monovalent anion (\( F^-, Cl^- \) and \( OH^- \)), respectively. Cations with charges +4, +5 and +6 (\( P^{5+}, As^{5+}, V^{5+}, Si^{4+}, S^{6+}, B^{3+} \) etc.) can occupy the \( T \) site in the structure of apatite. This

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composition corresponds to 50 negative charges per unit cell (i.e. 24 $\text{O}^{2-} + 2 (\text{F}^-, \text{Cl}^- \text{or } \text{OH}^-)$) [3,19–22] and enables partial or complete substitution for cationic (M) as well as anionic (T and X) sites [23,24]. In synthetic compounds with apatite structure, the X-site can be occupied by $\text{O}^{2-}$ (oxyapatite [25,26]) or (CN)$_2^{2-}$ (nitrogen-containing apatite [27]) ions which increase the above-mentioned negative charges per unit cell. On the contrary, the vacancies [28,29] or $\text{H}_2\text{O}$ molecule [19] on the X-site can decrease the total negative charge depending on the substitutions within the M-site (Cd [30], Co [31], K [32,33] and almost all REE [28, 29,34]) and T-site (Be [19], Cr [39,40], Ge [26,41] and Mn$^{5+}$ [19,37]).

The apatite group of minerals is one of five groups categorized in the apatite supergroup of minerals. The other members are hedyphane [42], belovite [43,44], britholite [19,45–47] and ellesstadite [19,48–50] groups. Although the kind of original apatite *"sensu lato"* is uncertain the most important minerals of the apatite group are fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, often abbreviated as FAP [51]), chlorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$, C glAP [52]) and hydroxylapatite (Ca$_{10}(\text{PO}_4)_6\text{OH}_2$, HAP [53]). These minerals were later renamed as apatite-(CaF), apatite-(CaCl) and apatite-(CaOH) [19,54], respectively. Currently the mineral names are changed back to fluorapatite, chlorapatite and hydroxylapatite [19]. The nomenclature and the classification (approved by the IMA Commission on New Minerals) of the apatite supergroup minerals is described by Pasero et al. [19].

The crystal structure of apatite ("sensu stricto" fluorapatite) was first independently solved in 1930 by Mehmel [55] and Náray-Szabó [56]. The archetype of crystalline structure is hexagonal (space group P6$_3$/m) and contains the species-defining cation in two crystallographic sites: M(1) and M(2) with the Wyckoff position of 4$f$ and 6$h$, respectively. M(1) site is nine-fold coordinated (6 + 3) and forms a polyhedron which is often referred to as the metaprism [19,40,57–59] and described as distorted pentagonal bipyramid [19,21]. M(2) site shows seven-fold (6 + 1) coordination. The unit-cell parameters are $a = 9.3–9.6$ Å and $c = 6.7–6.9$ Å [19]. With respect to the structure of apatite-type compounds (Fig. 1(a)), the generic formula can be written as $\text{M}_{(1)}\text{M}_{(2)}\text{X}^{10}$ [19,59,60]: $\text{IX}$$^{10}$M$_{(1)}$[M$_{(2)}$X$_{(2)}$(YTO$_4$)$_{2}$]X (Z = 2). The left superscript introduces an ideal coordination number [19]. The monoclinic (P$2_1$/b) variant (it is not considered for distinct species [3,18] from the hexagonal variant) of hydroxylapatite (clinohydroxylapatite [61]) and chlorapatite was formerly named as apatite-(CaOH)-M and apatite-(CaCl)-M [54], respectively. Latterly they were renamed as hydroxylapatite-M and chlorapatite-M [19,54,62].

Britholite (first described by Winther [45]) is one of more common and economically important rare earth element (REE) bearing minerals. The structures of monoclinic (P$2_1$ [63], Fig. 1(b) and hexagonal (P$6_3$) dimorphs of britholite are similar to the atomic arrangement of apatite (a). The first structural investigation concluded a hexagonal apatite substructure (P$6_3$) [64]. Noe et al. [63] solved the crystal structure of monoclinic britholite with similar atomic arrangement to apatite and explained the biaxial optical characteristics of britholite by the reduction of symmetry (removing the 3/m element from hexagonal P$6_3$/m apatite symmetry yielding to monoclinic P$2_1$ symmetry). Monoclinic and hexagonal dimorphs of natural phase exist as a result of differing arrangements of long and short equivalents of the apatite Ca(1)-O(3) bonds [63].

The preparation of numerous compounds with the apatite-type structure including synthetic analogs ofapatites [65], britholites [21,22,66,67], belovites [68], etc., and their solid solutions [69] was described in the literature. Usually applied methods involve the high-temperature solid-state synthesis [4,21,22,66], the sol–gel process [4,16], the precipitation method [4,70], the hydrothermal [69–71] or mechanochemical hydrothermal synthesis [9], the citrate gel pyrolysis method [10], the combustion method [65], the microwave processing [4] and the emulsion methods [4,72], etc. The preparation techniques based on aqueous precipitation at moderate temperatures often lead to non-stoichiometric apatites [3].

In the previous work [34], the synthesis, properties and the role of non-equilibrium flux formed during the sinter-crystallization process of Sr$_2$Y$_{6}$(SiO$_4$)$_3$O (or by "double formula" the Sr$_2$Y$_{6}$(SiO$_4$)$_3$O$_2$) oxypatite phase was described. This contribution deals with the preparation, properties and examination of the field of solid solutions miscibility between three end-members of alkaline earth element-yttrium-silicate phases (AEE$_2$Y$_{10–δ}$(SiO$_4$)$_3$O$_{3–0.5δ}$, where AEE=Ca, Sr and Ba and the value of $δ \rightarrow 2$). The course of synthesis was
investigated by the methods of thermal analysis, X-ray diffraction analysis, infrared spectroscopy and electron microscopy. These results were used for the definition of range of miscibility region of ternary solid solutions and for the investigation of effect of AEE\(^{2+}\) cation on the system stoichiometry, i.e. the variation of parameter \(\delta\) in the formula of apatite unit and the lattice parameters.

2. Experimental

2.1. Synthesis of samples

Raw meals for the syntheses of apatite phases were prepared via ceramic route by mixing calcium (CaCO\(_3\)) strontium (SrCO\(_3\)) and barium carbonate (BaCO\(_3\)), yttrium oxide (Y\(_2\)O\(_3\)) and silica (SiO\(_2\)) in the molar ratio (1:2:3) which corresponds to the ideal stoichiometry of reaction [34,73]:

\[
\text{AEECO}_3 + 2\text{Y}_2\text{O}_3 + 3\text{SiO}_2 \rightarrow \text{AEEY}_4\text{SiO}_4 \ (\text{g})
\]

where AEE denotes alkaline earth element (Ca, Sr and Ba, where \(x + y + z = 1\)). All chemicals were of analytical purity grade and used without further purification or treatment. The composition and numeric notation of prepared samples (S1–S18, e.g. S1 is pure end-member of Ca\(_2\)Y\(_8\)(SiO\(_4\))\(_6\)O\(_2\)) are introduced in Fig. 2(a).

Mixing and short milling (2 min) in laboratory ball mill was applied for initial homogenization of raw meal. The flowchart in Fig. 2(b) explains the preparation of raw meal and introduces the conditions of pressing and thermal treatment.

2.2. Investigation of the course of synthesis and properties of prepared samples

The course of synthesis of AEE apatite-type yttrium silicate phases during thermal treatment was investigated by TG–DTA and EGA (SDT Q600, Thermal Instruments connected with the measuring cell (FTIR-TGA interface) of infrared spectrometer iS10, Thermo Scientific via steel capillary). 30 mg of sample was inserted into alumina cup heated in air (100 cm\(^3\) min\(^{-1}\) free of CO\(_2\) and water vapor) with the rate of 10 °C min\(^{-1}\). The process of sinter-crystallization of apatite phase was investigated by heating microscopy (EM 201, Leitz) using cylindrical specimen with the diameter and the height of 3 mm, which was pressed out from raw meal under the pressure of 1 MPa. The changes in the phase composition during thermal treatment were evaluated by high temperature X-ray analysis (XRD, X’Pert Empyrean, PANanalytical with Cu(K\(_\alpha\)) radiation at 40 kV and the current of 30 mA applying high temperature chamber HTK 16, Anton Paar). Scanning electron microscopy with EDX (SEM, Zeiss EVO LS10 with W-cathode) was used for the analysis of sample after the thermal treatment.

The average of linear expansion coefficient (\(\alpha_L(25–1500 \degree C)\)) was determined from the results of heating microscopy of sintered specimen. The thermal conductivity (\(\lambda\)) was measured by C-ThermTci analyzer at the temperature of 25 °C using Silicone 120 (Wakefield) as thermal joint compound. HSC v.7.1 software was used for the estimation of thermodynamic (TD) data including standard formation enthalpy (\(\Delta H_f\)) and Gibbs free energy (\(\Delta G_f\)), entropy (\(S_f\)) and molar heat capacity (\(c_{p,m}\)) at the temperature of 298 K and the pressure of 1 bar.

3. Results and discussion

3.1. The end-member phases

The end-member phases in the investigated ternary diagram of alkaline earth element-yttrium-silicate oxybritholite system (Fig. 2(a), samples S1, S2 and S3) have stoichiometric composition given by the formula AEE\(_\delta\)Y\(_{10–\delta}\)(SiO\(_4\))\(_6\)O\(_3\)–0.5, where AEE=Ca, Sr and Ba and \(\delta \rightarrow 2\). That leads to three compounds with the composition:

1) Ca\(_2\)Y\(_8\)(SiO\(_4\))\(_6\)O\(_2\) (dicalcium octayttrium(III) (hexakis) silicate dioxide, S1);

2) Sr\(_2\)Y\(_8\)(SiO\(_4\))\(_6\)O\(_2\) [34,73] (distrontium octayttrium(III) (hexakis)silicate dioxide, S2);

3) Ba\(_2\)Y\(_8\)(SiO\(_4\))\(_6\)O\(_2\) (bisdibarium octayttrium(III) (hexakis) silicate dioxide, S3);
3) Ba$_2$Y$_8$(SiO$_4$)$_6$O$_2$ (dibarium octayttrium(III) (hexakis)silicate dioxide, S3).

The values of parameter $\delta$ resulting from elemental analysis of phases S1 and S2 (please refer to Table 2) are 2.02 $\pm$ 0.07 and 1.90 $\pm$ 0.04, respectively. That means that the composition of these samples is almost stoichiometric. The compound S3 cannot be prepared for the reasons discussed below, there is an option to prepare binary and ternary solutions of this phase, which is discussed in Sections 3.2 and 3.3.

Fig. 3(a) shows the results of TG–DTA and EGA of raw meal. The endothermic peak at the temperature of 573 °C results from reversible athermal (displacive) transformation between low quartz (trigonal $\alpha$-SiO$_2$) and high quartz (hexagonal $\beta$-SiO$_2$) polymorphs of SiO$_2$ [74]. This process is followed by endothermic peak of thermal decomposition of AEECO$_3$:

$$\text{AEECO}_3 \xrightarrow{T} \text{AEEO} + \text{CO}_2(g), \quad \text{AEE} = \text{Ca}, \text{Sr} \text{and} \text{Ba} \quad (2)$$

While the peak temperature increases with increasing thermal stability of carbonate [75], the measured weight loss decreases with increasing molecular weight of carbonate (please consult with Fig. 3(a)).

The thermal decomposition of calcium, strontium and barium carbonates shows endothermic peaks at the temperatures of 747 (S1), 963 (S2) and 1000 °C (S3), respectively. The transformation to high-temperature polymorphs takes place during the thermal decomposition of SrCO$_3$ and BaCO$_3$. Orthorhombic polymorph of $\alpha$-SrCO$_3$ (Pmcn) transforms to hexagonal form of $\beta$-SrCO$_3$. The process shows sharp endothermic peak at the temperature of 931 °C [75,76]. Polymorphic transformation of orthorhombic $\alpha$-BaCO$_3$ (Pmcn) into hexagonal $\beta$-BaCO$_3$ (R3m) [77,78] and next to cubic $\gamma$-BaCO$_3$ phase [79] takes place at the temperature of 828 and 960 °C, respectively.

Thermal decomposition of carbonates increases the intensity of CO$_2$ bands on EGA plot (Fig. 3(a)). The strong central bands of antisymmetric stretching mode ($\nu_3$) and degenerated bending mode ($\nu_2$) are located within the wavenumber intervals from 2400 to 2220 cm$^{-1}$ and from 760 to 575 cm$^{-1}$, respectively. The small peaks within the wavenumber intervals from 3770 to 3655 cm$^{-1}$ and from 3656 to 3535 cm$^{-1}$ are the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination bands, respectively [76].

The formation of intermediate phases appearing within the temperature interval which is limited by the temperature of thermal decomposition of carbonate and sinter-crystallization of apatite phase (S1 and S2) or yttrium oxyorthosilicate (S3) was investigated by HT-XRD. The results for phases S1 and S3 are shown in Fig. 4 (the behavior of sample S2 during thermal treatment is described in previous work [34]).

Thermal decomposition of carbonates (Eq. (2)) leads to the formation of oxide species, which means that the diffraction...
lines of CaO ($T \geq 600^\circ C$) and BaO ($T \geq 675^\circ C$) appear. The features of CaCO$_3$ and BaCO$_3$ gradually disappear by the temperature of 750 and 1050 $^\circ C$, respectively. CaO (S1, $T \geq 900^\circ C$) and BaO (S3, $T \geq 800^\circ C$) oxides react with SiO$_2$ to form alkaline earth orthosilicates (AEE$_2$SiO$_4$):

$$2\text{AEE}_2\text{O}_3 + \text{SiO}_2 \rightarrow \text{AEE}_2\text{SiO}_4$$  (3)

While the reaction of Ca$_2$SiO$_4$ with Y$_2$O$_3$ in sample S1 leads to the formation of hexagonal ternary calcium yttrium silicate oxide phase of 4CaO·3Y$_2$O$_3$·6SiO$_2$ (P6$_3$/m), orthosilicate Ba$_2$SiO$_4$ in sample S3 reacts with SiO$_2$ to form orthorhombic metasilicate BaSiO$_3$:

$$2\text{Ca}_2\text{SiO}_4 + 3\text{Y}_2\text{O}_3 + 2\text{SiO}_2 \stackrel{T \geq 1000^\circ C}{\rightarrow} \text{Ca}_4\text{Y}_6\text{O}(\text{SiO}_4)_6$$  (4)

$$\text{Ba}_2\text{SiO}_4 + \text{SiO}_2 \rightarrow 2\text{BaSiO}_3$$  (5)

The results of heating microscopy (Fig. 3(b)) show that the formation of these compounds significantly increases the specimen height for samples S2 and S3, while the changes measured for S1 are negligible. The sintering temperature decreases in the order S1, S2, and S3. Large amount of formed melt phase leads to the deformation of S3 specimen at the temperature of 1480 $^\circ C$ and to the highest measured value of firing shrinkage.

The formation of high-temperature flux and sinter-crystallization of apatite phase (samples S1 and S2 [34]) or yttrium oxyorthosilicate (Y$_2$O$_3$·SiO$_2$, YSO [80,81]) in sample S3 starts by endothermic effect (melting), which transforms to exothermic peak (crystallization) at the temperature of 1385, 1383 and 1296 $^\circ C$ (Fig. 3(a)), respectively. The process of sinter-crystallization is connected with shrinkage, which increases in the order from S1 to S3.

The SEM analysis of samples S1 and S2 (Fig. 5) revealed hexagonal prisms terminated by basal pinacoids (pyramid forms are not present) of Ca$_2$Y$_8$(SiO$_4$)$_6$O$_2$ and Sr$_2$Y$_8$(SiO$_4$)$_6$O$_2$ crystals, respectively. These crystals are surrounded by solidified glass-like phase and often fill the space of ceramic body as clusters, where the hexagonal prisms are arranged to the hexagonal prismatic honeycomb.

The decreasing value of Y$_2$O$_3$ to SiO$_2$ (Y/S) ratio and/or the presence of additives [34] improve the morphology of apatite crystals (please compare Fig. 5 and Fig. 6 where Y/S=0.67 and 0.50, respectively). Some Ca$_2$Y$_8$(SiO$_4$)$_6$O$_2$ prisms in Fig. 6, terminated by pyramid Sample S3 (Fig. 5) show the formation of crystals of yttrium oxyorthosilicate (1) surrounded by glassy phase with high content of barium (2).

Standard formation energies, entropies and molar heat capacities estimated for pure end-members are listed in Table 1. The value of $\Delta G_f^\circ$ shows decreasing stability in the order S1 ($r^{2+}_{Ca}=99$ pm, $X=1.1$) > S2 ($r^{2+}_{Sr}=112$ pm, $X=0.95$) > S3 ($r^{2+}_{Ba}=138$ pm, $X=0.89$), so the TD stability decreases with increasing AEE$^{2+}$ ionic radius ($R^2=0.993$) and increasing ionic character of AEE–O bond ($R^2=0.952$) estimated from Pauling’s approximation ($100\cdot(1-e^{-1.54\Delta X})$), where $\Delta X$ is the difference in Pauling’s electronegativity of AEE and O$^{2-}$ (3.44). This behavior is in agreement with the effect of $\Delta X$ between M$^{2+}$ and X$^-$ as well as with general AEE stability tendency of apatite minerals (Ca $>$ Sr $>$ Ba) described by Drouet [3].

3.2. Binary systems

The sides of ternary diagram (Fig. 2) constitute of three binary systems of AEE$_4$Y$_{10–δ}$(SiO$_4$)$_6$O$_3–0.5\delta$ oxybritholite phases, where AEE=Ca–Sr (samples S4–S6), Ca–Ba (S7–S9) and Sr–Ba (S10–S12). The results of TG–DTA and EGA analysis (a) and heating microscopy (b) for these samples are shown in Fig. 7. Whereas the temperature intervals of thermal

Fig. 5. Scanning electron microscopy of samples S1, S2 and S3 treated to the temperature of 1600 $^\circ C$. 

P. Ptáček et al. / Ceramics International 42 (2016) 6154–6167
decomposition of SrCO₃ and BaCO₃ are overlap each other, the temperature of thermal decomposition of CaCO₃ is significantly lower (please consult with the detail of Fig. 3).

For that reason, two endothermic effects can be recognized on DTA in samples from the Ca–Sr and Ca–Ba series. Also the results of TG and EGA show two separate effects in the order of increasing content and thermal stability of carbonate.

The temperature of sinter-crystallization is reduced with increasing content of Ca₂Y₈(SiO₄)₆O₃ in Ca–Sr series. Since total composition of samples S8, S9, S11 and S12 is located out of the field of solid solutions (Fig. 12(a)), the highest intensity of sinter-crystallization effect in the Ca–Ba and Sr–Ba series can be observed in samples S7 and S10. This behavior, as results from the comparison of results of SEM analysis (Fig. 8) with the end-member apatite species (Fig. 5), indicates that barium partially acts as sintering additive [34] which improves the morphology of formed AEEₓY₁₀₋ₓSiO₄O₃₋₀.₅₆ crystals.

The values of parameter δ determined from the compositions of pure and binary phases (Fig. 8) are listed in Table 2. The results (δ ≈ 2) indicate that the compositions of prepared specimens are close to stoichiometric ones. Fig. 12(a) shows that there is unlimited Ca²⁺ ↔ Sr²⁺ substitution in the binary system of (Ca–Sr)ₓY₁₀₋ₓSiO₄O₃₋₀.₅₆. On the contrary, the BaₓY₁₀₋ₓSiO₄O₃₋₀.₅₆ analog (S3) of S1 and S2 apatite-type phase cannot be prepared via applied ceramic route, as the extend of Ca²⁺ ↔ Ba²⁺ and Sr²⁺ ↔ Ba²⁺ substitutions is limited to 28 ± 4 and 38 ± 4 mol%, respectively.

Higher content of Ba in binary series III can be explained by the selectivity of REE for Ca-bearing minerals and by progressive change of REE preference for M(2) site (Fig. 1(a)) through the 4f–4f transition series. It decreases from La to Er and the behavior of Y (please see Fig. 1(b)) is here similar to that of Ho [84]. Another strong evidence that the changes in site preference (whether 4f or 6h) of REE may influence the stability of Ca-bearing phases (minerals) are the syntheses of BaₓLa₈₋ₓ(SiO₄)₆O₂₋₆ and CaₓCeₓ(SiO₄)₆O₂ oxypaties described by Takeda et al. [85] and Skakle et al. [86], respectively.

### 3.3. Ternary systems

The results of TG–DTA and EGA analyses of ternary systems S13–S18 are shown in Fig. 9(a). The low (α) to high (β) transformation of quartz shows small endothermic peak at the temperature of 573 °C. With increasing temperate, the features related to the thermal decomposition of alkaline earth carbonates appear according to increasing thermal stability. Depending on the sample composition, two or three peaks of CO₂ appear on EGA. The results of TG and EGA analyses of ternary systems S13–S18 are shown in Fig. 9(a).

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>M [g mol⁻¹]</th>
<th>ΔH° [J mol⁻¹]</th>
<th>S [J mol⁻¹ K⁻¹]</th>
<th>ΔG° [J mol⁻¹]</th>
<th>cP,m [J mol⁻¹ K⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>CaₓY₈(SiO₄)₆O₂</td>
<td>1470.98</td>
<td>−14,645.9</td>
<td>760.2</td>
<td>−14,860.6</td>
</tr>
<tr>
<td>S2</td>
<td>SrₓY₈(SiO₄)₆O₂</td>
<td>1750.40</td>
<td>−14,597.3</td>
<td>736.5</td>
<td>−816.8</td>
</tr>
<tr>
<td>S3</td>
<td>BaₓY₈(SiO₄)₆O₂</td>
<td>1570.40</td>
<td>−14,699.9</td>
<td>691.1</td>
<td>−14,875.8</td>
</tr>
</tbody>
</table>

*Value estimated by the Latimer method [82,83].
formation of larger amount of smaller crystals indicates enhanced nucleation ability in the melt of this composition. The values of parameter $\delta$ for the crystals of $\text{AEE}\delta\text{Y}_{10}\text{SiO}_4\text{O}_3\text{SiO}_2/\text{C}_0$ formed in the ternary region listed in Table 3 do not show any significant differences from the system stoichiometry.

The highest determined content of barium in the apatite-type AEE–yttrium orthosilicate oxybritholites crystals enables to evaluate the borders of field of solid solutions for samples located out of the field of solid solutions (Fig. 11). These data were used for the construction of ternary diagram in Fig. 12(a).

Since the composition of $\text{AEE}_2\text{Y}_8\text{SiO}_4\text{O}_2$ phase can be derived from $\text{Y}_{10}\text{SiO}_4\text{O}_2$ [87] or more precisely from $\text{Y}_{9.333}\text{SiO}_4\text{O}_2$ (please check both formulas for the average oxidation state of Si atom) via the substitution of 1.333 yttrium atoms by two AEE ($\text{AEE}_2^+\text{Ba}^2+$) and the solid solution of $\text{AEE}_\delta\text{Y}_{10}\text{SiO}_4\text{O}_3/\text{C}_0^{0.5}$ is in the equilibrium with $\text{Y}_2\text{O}_3/\text{C}_1\text{SiO}_2$, the relationship of investigated field of solid solutions with related phase equilibrium system is shown in detail (b). The results in detail (c) reveal that samples with $\text{r}_{\text{AEE}}/\text{r}_{\text{Si}}$ ionic radius ratio $\geq 2.96$ are located out of the field of solid solutions. Therefore $\text{r}_{\text{AEE}}/\text{r}_{\text{Si}}^+$ ratio is an important

![Fig. 7. Thermal analysis of binary systems S1, S2 and S3 (Fig. 2): (Ca–Sr)$_\delta\text{Y}_{10}\text{SiO}_4\text{O}_3/\text{C}_0^{0.5}$ (a), (Ca–Ba)$_\delta\text{Y}_{10}\text{SiO}_4\text{O}_3/\text{C}_0^{0.5}$ (b) and (Sr–Ba)$_\delta\text{Y}_{10}\text{SiO}_4\text{O}_3/\text{C}_0^{0.5}$ (c).](image-url)
parameter for the prediction of stability of AEE–yttrium orthosilicate oxybritholites.

Since the composition of prepared samples does not show any significant difference from the system stoichiometry (δ = 2), all these samples lie on the same plane (Fig. 12(b)). Based on the existence of $\text{Ca}_4\text{Y}_6[\text{SiO}_4]_6\text{O}_2$ apatite-type phase[88,89] ($\delta = 4$), at least one other plane with its own field of solid solutions can be expected beyond this plane.

Standard formation energies ($\Delta H^f_1$, $S^0$ and $\Delta G^f_1$, a) and molar heat capacities (b) at 25 °C and 1 bar predicted over investigated field of solid solutions are introduced by Table 4. The effect of AEE can be expressed by the order: Ca, Sr and Ba, where increasing content of left element increases the thermodynamic stability of AEE as well as decreases its molar heat capacity. The values of $c_{p,m}$ calculated from the contribution of cation and anion (Latimer [82,83]) are in good agreement with these results.

The change of lattice parameters ($a$, $c$, $a/c$ and $V$) with the composition of prepared solid solutions (Fig. 13(a)) was determined from XRD pattern (b). Since the trivalent REE cations show strong preference for the M(2) position in synthetic apatites and oxyapatites[84,90], the structure of prepared AEE$_2$$\text{Y}_8[\text{SiO}_4]_6\text{O}_2$ samples is more similar to NaY$_9(-\text{SiO}_4)_6\text{O}_2$ [90] than to Ca$_2$Ce$_8$(SiO$_4$)$_6\text{O}_2$ oxyapatite [86]. The volume of elemental unit cell increases with increasing content of cation with higher atomic number, i.e. in the order: Ca, Sr and Ba. The highest value ($V = 531.90 \text{ Å}^3$) is then located on the cross solid solution area borderline with Sr–Ba side (binary series III.) of ternary diagram.

The results of infrared spectroscopy (Fig. 14) show the same pattern for all prepared samples. The spectrum consists of five bands with the most characteristic vibration mode at the wave-number 940.1 cm$^{-1}$. Other four bands are located at 562.6 cm$^{-1}$, 511.8 cm$^{-1}$, 477.6 cm$^{-1}$ and 435.7 cm$^{-1}$. These bands show the average intensity ratio of 1:0.77:0.74:0.61:0.59 (± 0.03). Based on our previous investigation [34], on literature [91,92] and with the consideration of composition of prepared oxybritholites, where only the features of Si tetrahedra and Y polyhedrons can be expected over investigated range of IR region, the most expressive band is recognized as triply-degenerated $\nu_3(F_2)$ as symmetric stretching mode of Si–O bond in SiO$_4$ tetrahedra. The band shows composed structure (Fig. 14(b)) which results from overlapping of modes of different symmetry ($\delta$ = 3). The weak bands at

![Fig. 8. Scanning electron microscopy and WDX analysis of samples S5 (Ca–Sr series), S8 (Ca–Ba series) and S11 (Sr–Ba series).](image)

<table>
<thead>
<tr>
<th>System</th>
<th>Sample</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure phases</td>
<td>S1</td>
<td>2.02 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>1.90 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>2.05 ± 0.09</td>
</tr>
<tr>
<td>(AEE)$<em>3$$\text{Y}</em>{10-\delta}[\text{SiO}_4]_3\text{O}_3-0.5\delta$, AEE = Ca and Sr (binary series I, Fig. 2(a))</td>
<td>S4</td>
<td>2.06 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>1.90 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>S6</td>
<td>1.90 ± 0.06</td>
</tr>
<tr>
<td>(AEE)$<em>2$$\text{Y}</em>{10-\delta}[\text{SiO}_4]_3\text{O}_3-0.5\delta$, AEE = Ca and Ba (binary series II)</td>
<td>S7</td>
<td>1.98 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>S8</td>
<td>1.99 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>S9</td>
<td>2.04 ± 0.34</td>
</tr>
<tr>
<td>(AEE)$<em>2$$\text{Y}</em>{10-\delta}[\text{SiO}_4]_3\text{O}_3-0.5\delta$, AEE = Sr and Ba (binary series III)</td>
<td>S10</td>
<td>1.84 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>S11</td>
<td>1.95 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>S12</td>
<td>2.02 ± 0.05</td>
</tr>
</tbody>
</table>
1091 and 797 cm\(^{-1}\) are assigned to \(\nu_3(F_2)\) asymmetrical stretching in glassy-like phase (\(G\), please refere to the discussion of Fig. 5) and to symmetrical stretching vibration (\(\nu_1(A_1)\)) of Si–O bond, respectively. Other four bands in infrared spectrum were assigned as shown in Fig. 14(a).

While the position of \(\nu_3(F_2)\) band is affected by the composition of sample, other peaks are not changed significantly. The highest wavenumber of this mode can be observed for sample S1 (949.3 cm\(^{-1}\)) and the lowest one for sample S11 (929.0 cm\(^{-1}\)). This behavior could be explained by geometrical distortion in apatite-type lattice caused by increasing repulsive interaction between Si\(^{4+}\) and AEE\(^{2+}\) ion(s). Removing of degeneracy of \(\nu_3(F_2)\) mode leads to increased intensity of complexity of this band. This explanation is in agreement with the effect of increasing ionic radius from Ca to Ba as well as with the effect of \(r_{AEE}^{2+}/r_{Si}^{4+}\) ratio on the stability of solid solution (Fig. 12(c)). On the other hand the behavior is also affected by the distribution of yttrium and then also AEE\(^{2+}\) ions between M(1) and M(2) positions as was disused above.

The theoretical density of oxybritholites samples (Fig. 2) was calculated \(\rho_t = \frac{M}{Z/V \cdot N_A}\), where \(Z = 2\) and \(N_A = 6.022 \cdot 10^{23}\) mol\(^{-1}\) from the data of molar mass (Fig. 12(a)) and volume of
Fig. 11. Samples with the composition out of the border of miscibility region.

Table 3
Variation of parameter δ in the AEE$_{2}$Y$_{10-δ}$SiO$_{4}$O$_{3-0.5δ}$ ternary system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S13</th>
<th>S14</th>
<th>S15</th>
<th>S16</th>
<th>S17</th>
<th>S17</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>1.95 ± 0.05</td>
<td>1.94 ± 0.08</td>
<td>1.92 ± 0.07</td>
<td>1.81 ± 0.05</td>
<td>1.87 ± 0.05</td>
<td>2.02 ± 0.06</td>
</tr>
</tbody>
</table>

Fig. 12. Field of solid solutions (a) in the ternary apatite-type system of AEE$_{2}$Y$_{10-δ}$SiO$_{4}$O$_{3-0.5δ}$ (AEE=Ca, Sr and Ba and δ→2). Details (b) and (c) show the sketch (not in scale) of location of these compounds in more general phase equilibrium system, and the values of $r_{AEE}^{+}/r_{Si}^{4+}$ ionic radius ratio, respectively.
elemental unit cell (Fig. 13(a)). It is introduced in Fig. 15 (a) together with other determined properties, i.e. thermal conductivity ($\lambda$) and average linear expansion coefficient $\alpha_L(25-1500 \, ^\circ\text{C})$ of prepared apatite specimens. Measured values of $\lambda$ and $\alpha_L$ as well as high thermal stability (please consult with the results of heating microscopy) predestine the utilization of these oxybritholites (primarily Ca$_2$Y$_8$(SiO$_4$)$_6$O$_2$) as ceramics with low expansion coefficient, i.e. the materials with good thermal shock resistance. Depending on their composition and mechanical treatment the samples show green, orange or dark blue luminescence (Fig. 15(b)).

### 4. Conclusion

Alkaline earth element-yttrium-silicate oxybritholites with the structure of apatite form the field of solid solutions of $(\text{Ca}_{x}\text{Sr}_{y}\text{Ba}_z)\text{Y}_{10-x}x(\text{SiO}_4)_{6}x\text{O}_2$ where $x+y+z=\delta$ where the limiting value of parameter $z$ was determined to be 28%.
and 38% for Ca$_2$Y$_8$[SiO$_4$]$_6$O$_2$ and Sr$_2$Y$_8$[SiO$_4$]$_6$O$_2$ end-member, respectively. Since all attempts for the synthesis of Ba$_2$Y$_8$[SiO$_4$]$_6$O$_2$ phase via the ceramic route were unsuccessful, it may be prepared only in a solid solution where $r_{AEE}^{+}/r_{Sr}^{+}$ ionic radius ratio is $\geq 2.96$. The stability of solid solution then decreases with increasing value of ionic radius ratio as the consequence of geometrical distortion caused by increasing repulsive interactions between Si$^{4+}$ and AEE$^{2+}$ ion(s).

The selectivity of Ca-bearing minerals for REE and low preference of Y for M(2) site [84] decrease the limiting content of barium in binary Ba–Ca and ternary solid solutions compared to the system of Sr–Ba. The miscibility between Ca$_2$Y$_8$[SiO$_4$]$_6$O$_2$ and Sr$_2$Y$_8$[SiO$_4$]$_6$O$_2$ constituents is not limited. The composition of all prepared specimens of alkaline earth element-yttrium-silicate oxybritholites is close to stoichiometric one ($\delta \approx 2$).

Within the field of solid solutions composition, AEE$_2$Y$_4$[SiO$_4$]$_6$O$_2$ crystallizes in the form of hexagonal prisms terminated by basal pinacoid. The variation of lattice parameters shows that the volume of elemental cell increases with increasing content of alkaline earth element of higher atomic number. Good thermal stability of sintered specimens, together with their other determined properties including the average linear expansion coefficient and the thermal conductivity enable the utilization in preparation of refractory ceramics with low expansion coefficient.

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References


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