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$_4$]$_6$O$_{3-0.5\delta}$, 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 formed between the three end-members of apatite-type alkaline earth element-yttrium-silicate oxybritholites with the hexagonal structure (P6$_3$/m). The stoichiometric composition of these compounds corresponds to the formula AEE$_\delta$Y$_{10-\delta}$(SiO$_4$)$_6$O$_{3-0.5\delta}$, where AEE=Ca, Sr and Ba and parameter $\delta \rightarrow 2$. 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$_2$Y$_8$[SiO$_4$]$_6$O$_2$ and Sr$_2$Y$_8$[SiO$_4$]$_6$O$_2$, 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 the ternary system. All attempts for the preparation of pure Ba$_2$Y$_8$[SiO$_4$]$_6$O$_2$ 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**$_4$)$_6$**X**$_2$. The "*single form*" is the formula written as **M**$_5$(**TO**$_4$)$_3$**X** [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 $O^{2-}+2$ (F^-, Cl^- or 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 O^{2-} (oxy-apatite [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 H_2O 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, 29,34–38]) 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 ellestadite [19,48–50] groups. Although the kind of original apatite "*sensu lato*" is uncertain the most important minerals of the apatite group are fluorapatite ($Ca_{10}(PO_4)_6F_2$, often abbreviated as FAP [51]), chlorapatite ($Ca_{10}(PO_4)_6Cl_2$, ClAP [52]) and hydroxylapatite ($Ca_{10}(PO_4)_6OH_2$, 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 **P6₃/m**) and contains the species-defining cation in two crystallographic sites: **M**(1) and **M** (2) with the Wyckoff position of **4f** and **6h**, 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 [19,59,60]: ^{IX}**M**(1)$_2$^{VII}**M** (2)$_3$(^{IV}**T**O_4)$_3$**X** (**Z**=2). The left superscript introduces an ideal

coordination number [19]. The monoclinic (P2₁/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 (P2₁ [63], Fig. 1(b)) and hexagonal (P6₃) dimorphs of britholite are similar to the atomic arrangement of apatite (a). The first structural investigation concluded a hexagonal apatite substructure (P6₃) [64]. Noe et al. [63] solved the crystal structure of monoclinic dimorph 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 P6₃/m apatite symmetry yielding to monoclinic P2₁ 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 of apatites [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 $SrY_4(SiO_4)_3O$ (or by "double formula" the $Sr_2Y_8(SiO_4)_6O_2$) oxyapatite 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 ($AEE_\delta Y_{10-\delta}(SiO_4)_6O_{3-0.5\delta}$, where AEE=Ca, Sr and Ba and the value of $\delta \rightarrow 2$). The course of synthesis was
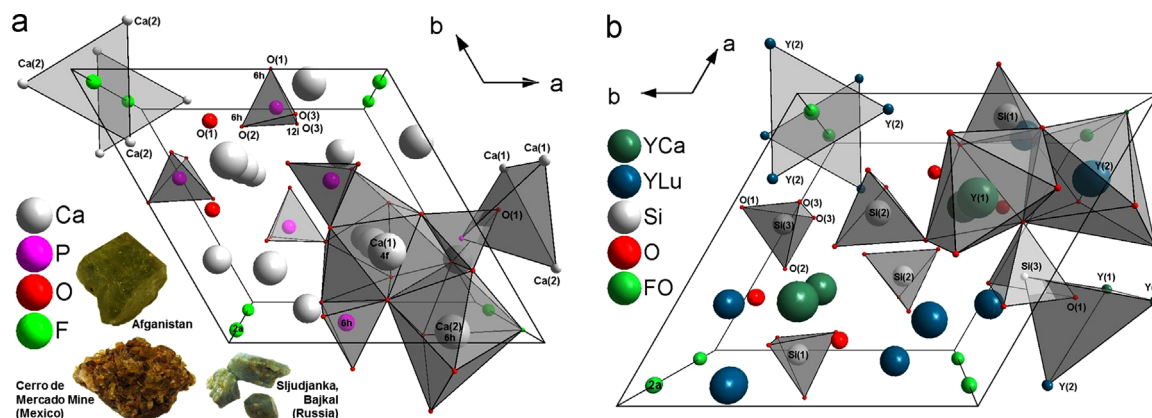

Fig. 1. The structure of fluorapatite (a, perspective view along the *c*-axis, i.e. from [001]) according to Hughes et al. [58] displayed with the examples of Ca(1), Ca (2), F and O(1) polyhedra. The structure of monoclinic britholite-(Y) (b, perspective) solved by Noe et al. [63].