

Synthesis and Crystal Structure of the Strontium Beryllate $\text{Sr}_3\text{Be}_2\text{O}_5$

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Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of his 75th Birthday

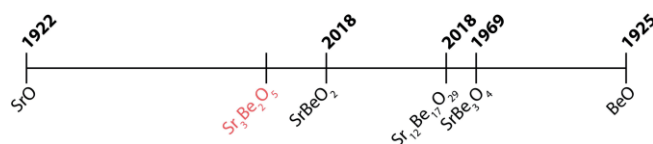
Abstract. Beryllates show an interesting and diverse structural chemistry, resembling that of well-investigated silicates. The coexistence of tetrahedral and trigonal coordination of Be by O atoms in oxoberyllates allows for an even broader variety of structural motives and implies a plurality of possible atomic ratios Be:O in ternary or higher compounds. We have now synthesized the novel strontium oxoberyllate $\text{Sr}_3\text{Be}_2\text{O}_5$ via a high-temperature high-pressure reaction and have

structurally characterized the ternary oxide by single-crystal and powder X-ray diffraction analysis. $\text{Sr}_3\text{Be}_2\text{O}_5$, a low condensed oxoberyllate, contains unprecedented $[\text{Be}_2\text{O}_5]^{6-}$ double triangles and Sr atoms in both double-capped trigonal-prismatic and octahedral coordination. These motifs show striking resemblance to α - SrBeO_2 and SrO , combining their structural properties. Lattice energy (MAPLE) calculations corroborate found parallels to the known phases SrO and α - SrBeO_2 .

Introduction

Albeit their structural diversity, matching well-investigated silicates, the chemistry of beryllates is widely unexplored.^[1–4] SrBe_3O_4 , published in 1969, was the only identified ternary phase in the system SrO - BeO until recently.^[5–7] This rarity of ternary phases is quite surprising due to the vast amount of structural possibilities and possible compositions allowed by a combination of an anionic $\text{Be}_x\text{O}_y^{z-}$ network with suitable counterions. As the Be coordination can either be tetrahedral, e.g. in $\text{Sr}_{12}\text{Be}_{17}\text{O}_{29}$, trigonal as in SrBe_3O_4 or 3+1 as in BeO , a broad variety of structural motifs is accessible by combination of the different Be–O polyhedra.^[8] This diversity is well known from borates, where a variety of ternary compounds with resembling structural motifs has been observed.^[9,10] New compounds are therefore expected to combine these known structural motifs to unrevealed structures (Scheme 1).

Herein, we report on the so far least condensed strontium beryllate, namely $\text{Sr}_3\text{Be}_2\text{O}_5$, exhibiting hitherto unknown $[\text{Be}_2\text{O}_5]^{6-}$ units. The crystal structure was solved and refined from single-crystal X-ray diffraction data and confirmed by Rietveld analysis of powder X-ray diffraction data.



Scheme 1. Hitherto known ternary strontium beryllates in the quasi binary system SrO - BeO with year of first publication.^[5–6,8]

Results and Discussion

$\text{Sr}_3\text{Be}_2\text{O}_5$ was synthesized under nitrogen pressure in a hot isostatic press (HIP) starting from SrO and BeO . The target phase could not be obtained by reaction of stoichiometric amounts of SrO and BeO at ambient pressure. Doping with 1 mol.-% (Eu) resulted in orange crystallites, showing no luminescence at ambient temperature. Non-doped $\text{Sr}_3\text{Be}_2\text{O}_5$ is colorless and transparent.

Rietveld refinement of powder X-ray diffraction data showed a product composition of ca. 80 wt.-% $\text{Sr}_3\text{Be}_2\text{O}_5$, ca. 20 wt.-% SrO and traces of α/β - SrBeO_2 , respectively (Figure 1). $\text{Sr}_3\text{Be}_2\text{O}_5$ crystallizes in space group $P2_1/c$ (no. 14).

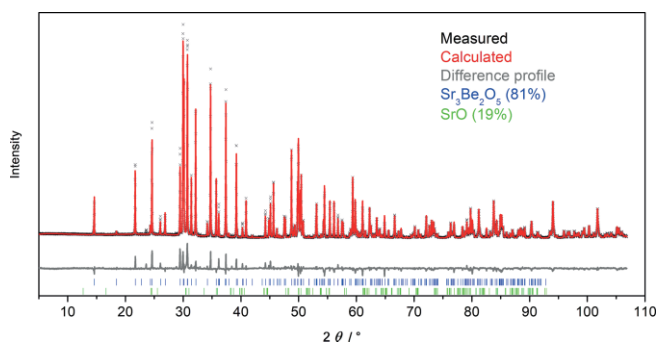


Figure 1. Result of the Rietveld refinement of $\text{Sr}_3\text{Be}_2\text{O}_5$. Powder X-ray diffraction diagram of $\text{Sr}_3\text{Be}_2\text{O}_5$ with the measured data (black crossmarks), pattern based on Rietveld refinement data (red line), difference curve (gray line) and position of allowed Bragg reflections (blue and green bars). Crystallographic data shown in supporting information.

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Single crystal structure determination resulted in a monoclinic cell with lattice parameters $a = 3.7000(7)$, $b = 9.600(2)$ and $c = 7.900(2)$ Å, $\beta = 99.00(3)^\circ$, $Z = 2$ and $V = 277.15(10)$ Å³. Rietveld refinement confirmed the metrics [$a = 3.70237(6)$, $b = 9.6069(2)$ and $c = 7.9004(1)$ Å, $\beta = 99.0076(4)^\circ$, $V = 277.539(8)$ Å³]. The structure is illustrated in Figure 2 and coordination polyhedra are depicted in Figure 3.

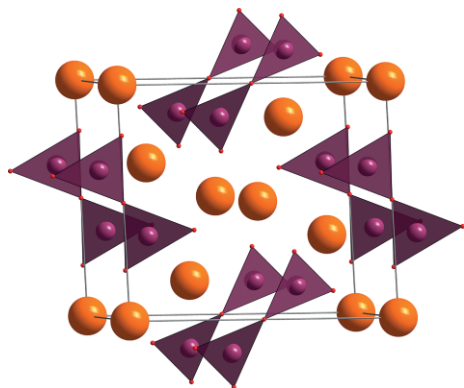


Figure 2. Crystal structure of $\text{Sr}_3\text{Be}_2\text{O}_5$. Sr (orange), Be (violet), O (red).

Two corner sharing BeO_3 triangles form a $[\text{Be}_2\text{O}_5]^{6-}$ unit with a torsion angle of 9.2° . Sr1 is coordinated by 6+2 O atoms forming a doubly capped trigonal prism. Sr2 is coordinated by six O atoms in a slightly distorted octahedron. The similarity of coordination of Sr1 and Be in $\text{Sr}_3\text{Be}_2\text{O}_5$ to the ones found in $\alpha\text{-SrBeO}_2$ and Sr2 in SrO become obvious in direct comparison (Figure 3). Isolated $[\text{Be}_2\text{O}_5]^{6-}$ units (a) can be seen as sections of the infinite *zweier* single chains of BeO_3 units (b). The Be–O distances of both species are identical within the limits of accuracy and vary between 1.545 and 1.549 Å. Furthermore, corresponding angles differ only slightly. For $\text{Sr}_3\text{Be}_2\text{O}_5$ the corresponding angles vary in the range $118\text{--}122^\circ$ and $113\text{--}123^\circ$ for $\alpha\text{-SrBeO}_2$. The 6+2 coordination of Sr1 as found in $\text{Sr}_3\text{Be}_2\text{O}_5$ (c) resembles the Sr coordination in $\alpha\text{-SrBeO}_2$ (d). The octahedral coordination of Sr2 by O (e) resembles the surrounding of Sr in SrO (f). While the Sr–O distances in Sr_3BeO_2 are 3–5 % smaller at 2.480–2.532 Å compared to 2.605 Å in SrO, the coordination octahedron is distorted. Bond angles are between 84 and 96° . Selected distances and angles are given in the Supporting Information.

Calculations of the Madelung part of lattice energy (MAPLE) of $\text{Sr}_3\text{Be}_2\text{O}_5$ yielded a value similar to the sum of lattice energies of twice $\alpha\text{-SrBeO}_2$ and SrO as detailed in Table 1.^[11–13]

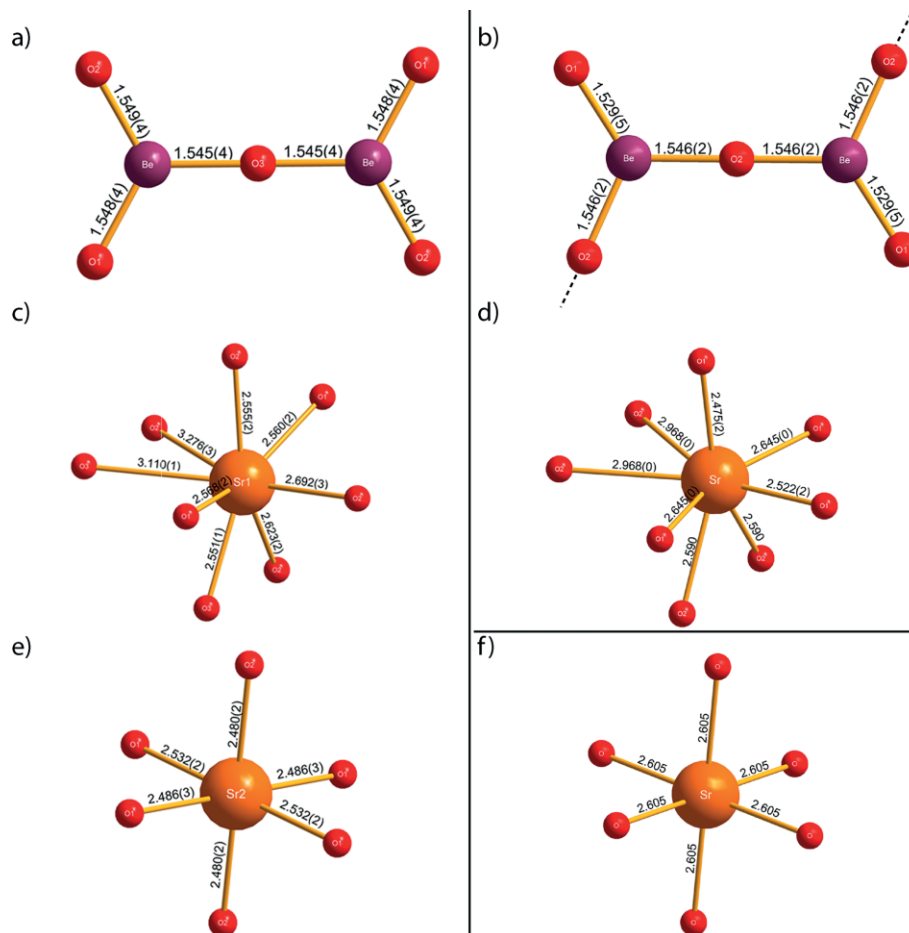


Figure 3. Comparison of cation coordination between $\text{Sr}_3\text{Be}_2\text{O}_5$ (a, c, e) and $\alpha\text{-SrBeO}_2$ (b, d)/SrO (f). Sr (orange), Be (violet), O (red). Distances are given in Å.

Conclusions

Single crystals of $\text{Sr}_3\text{Be}_2\text{O}_5$ were obtained by high-pressure high-temperature synthesis starting from the respective binary

Table 1. MAPLE data of selected Sr-Be-O phases in $\text{kJ}\cdot\text{mol}^{-1}$.

	$\text{Sr}_3\text{Be}_2\text{O}_5$	$\alpha\text{-SrBeO}_2$	SrO
Sr^{2+}	1776–1969	1818	1864
Be^{2+}	2936	2951	
O^{2-}	2155–2464	2160–2458	1864
Total	22495	9387	3727
$2 \alpha\text{-SrBeO}_2 + \text{SrO} = 22501 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta = 0.3 \%$			

oxides in a hot isostatic press. The crystal structure of strontium beryllate $\text{Sr}_3\text{Be}_2\text{O}_5$ contains unprecedented isolated $[\text{Be}_2\text{O}_5]^{6-}$ units. Surprisingly, oxoberyllates represent a largely unexplored substance class that could exhibit a broad spectrum of unexpected structural features and properties. Besides $[\text{BeO}_4]^{6-}$ tetrahedra, especially non-condensed trigonal planar $[\text{BeO}_3]^{4-}$ ions are expected to occur.

Experimental Section

Safety Precautions: Be is considered a highly hazardous element.^[14] Be containing dusts are known to cause CBD (chronic beryllium disease) and might be carcinogenic.^[15] To minimize the risk of exposure, all operations were performed in closed systems, like Schlenk-lines and gloveboxes.

Synthesis: All starting materials were handled in an argon atmosphere in a glovebox (Unilab, MBraun, Garching; $\text{O}_2 < 1 \text{ ppm}$, $\text{H}_2\text{O} < 1 \text{ ppm}$) due to their moisture sensitivity and the toxicity of Be and most Be containing compounds. The experiments were carried out in a rf-furnace attached to a Schlenk-type vacuum line (10^{-3} mbar) under dried Ar (Air Liquid, 5.0). The atmosphere was purified by passage through columns filled with KOH (Merck, $\geq 85 \%$), silica gel (Merck), molecular sieves (Fluka, 4 Å), P_4O_{10} (Roth, $\geq 99 \%$), and titanium sponge (Johnsen Matthey, 99.5%), heated to 730 °C. Crystals of $\text{Sr}_3\text{Be}_2\text{O}_5$ were obtained by reaction of SrO (Alfa Aesar, 46.6 mg, 0.45 mmol, 99.5%) and BeO (Alfa Aesar, 7.5 mg, 0.3 mmol, 99.95%) in a hot isostatic press (American Isostatic Presses) under 150 MPa of N_2 atmosphere at 1200 °C. After mixing the starting materials in a tungsten carbide mortar and transferring the mixture into W crucibles it was heated to 1200 °C in 4 h. This temperature was kept for 5 h and the crucible was cooled to room temperature in 6 h.

Single-crystal X-ray Diffraction: Single crystals of $\text{Sr}_3\text{Be}_2\text{O}_5$ were selected and fixed on a glass filament. X-ray diffraction data was collected on a Bruker D8 Venture rotary anode diffractometer with Goebel mirror optics for selection and focussing of Mo-K_α radiation [$\lambda = 0.71073 \text{ Å}$, $T = 297(2) \text{ K}$]. APEX3^[16] was used for integration and absorption correction. The crystal structures were solved by Direct Methods (SHELXS)^[17] and refined by full-matrix least-squares methods (SHELXL)^[18,19]

Powder X-ray Diffraction: The sample was ground and sealed in a glass capillary (Hilgenberg, $d = 0.3 \text{ mm}$) and mounted on a rotary head in a STOE STADI P diffractometer [Cu-K_α radiation, Ge(111) monochromator, Mythen 1k detector] with modified Debye–Scherrer setup. TOPAS 6 was used for Rietveld refinement.^[20]

Elemental Analysis: The elemental composition of $\text{Sr}_3\text{Be}_2\text{O}_5$ was determined by energy dispersive X-ray spectroscopy (EDS) on a Dual-beam Helios Nanolab G3 UC scanning electron microscope (SEM, FEI) with X-Max 80 SDD detector (Oxford Instruments). EDS data was obtained at an accelerating voltage of 20 kV from several particles.

Supporting Information (see footnote on the first page of this article): EDS data, experimental details about X-ray studies and crystallographic data

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Keywords: Beryllates; Oxides; Beryllium; Strontium; Solid-state structures

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