

Synthetic tin-selenium cylindrite, with the empirical formula $\text{Sn}_{31.52}\text{Sb}_{6.23}\text{Fe}_{3.12}\text{S}_{59.12}$ based on electron-microprobe data, has a triclinic crystal structure composed of two alternating layer types, both with a pronounced one-dimensional modulation, and with a non-commensurate layer match in two dimensions. The pseudotetragonal (Q) layer is a two-atomic planes thick *MeSe* layer with lattice parameters $a = 5.969(2)$ Å, $b = 6.004(1)$ Å, and the layer-stacking vector $c = 12.238(1)$ Å, $\alpha = 87.98(4)^\circ$, $\beta = 83.14(3)^\circ$, and $\gamma = 90.01(4)^\circ$. The pseudohexagonal (H) layer is a single-octahedral *MeSe* layer with $a = 3.831(1)$ Å, $b = 6.580(3)$ Å, $c = 12.151(5)$ Å, $\alpha = 87.79(4)^\circ$, $\beta = 90.59(3)^\circ$, and $\gamma = 89.99(3)^\circ$; the *a* and *b* vectors of the two subsystems are parallel, the *c* vectors diverge. The transversal wave-like modulation has the wave-normal parallel to *b*, so that the modulation vector *q* is $0.0001 \mathbf{a}^* + 0.1921(4) \mathbf{b}^* - 0.0119(3) \mathbf{c}^*$ in terms of the pseudohexagonal subsystem. Superspace structure refinement in the superspace group *X*-1 where *X* stands for non-primitive centring vectors (1/2,1/2,0,0,0), (0,0,0,1/2), (1/2,1/2,0,0,1/2) in a five-dimensional superspace, and based on 2128 observed reflections, resulted in *R**I*=0.038 for all reflections. The cation-anion distances in the Q layer vary between 2.63 and 3.30 Å, indicating that the cations present are primarily Sn^{2+} (and Sb^{3+}) whereas those in the H layer lie between 2.67 and 2.72 Å and correspond to Sn^{4+} with admixture of Fe. The shortest cation-anion distance across the interlayer space is 3.24 Å. Relations between layer match and the modulation vector, divergence of layer stackings of the two components, and reasons for the modulation and for the pronounced disorder of the Q component will be illustrated and discussed in detail. In its structural principles, although not in numerical values, the Sn-Se cylindrite corresponds fully to the natural Pb-Sn-S cylindrite described previously by Makovicky, and Makovicky and Hyde.

Keywords: non-commensurate layer structure, layer-misfit structure, modulated structure

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Crystallization behaviour of sol-gel derived cordierite precursors

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Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) ceramics is technologically important material due to its low thermal expansion, small dielectric constant, and high chemical and thermal stability [1]. It occurs in two stable forms: in the high-temperature hexagonal alpha form, stable above 1450°C, [2] and in the orthorhombic beta form, stable below 1450°C [3]. Preparation routes of cordierite involve solid-state reactions, liquid phase sintering, glass-ceramic route or sol-gel synthesis. The interest in sol-gel synthesis lately increased because it enables excellent control of chemical composition and reduces the temperature of ceramic processing. Two sol-gel derived cordierite precursors were prepared using tetraethoxysilane, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Al-sec-butoxide (for precursor designated as BC) or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (for precursor designated as NC). Detailed studies of crystallization behaviour of those precursors were performed by DSC and in-situ high temperature XRD from RT up to 1165°C. The Rietveld method was performed for quantitative phase analysis of the crystallization products and for the refinement of their crystal structures.

Crystallization started at about 800°C for both precursors, but their crystallization sequences were rather different. For precursor BC crystallization involved the appearance of stuffed derivative of beta-quartz, alpha-cordierite, mullite and enstatite, while for precursor NC it involved the formation of stuffed derivative of beta-quartz, sapphirine, mullite, alpha-cordierite and beta-cristobalite.

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XRD study of sol-gel preparation of yttrium silicates

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Yttrium silicates phases (Y_2SiO_5 and $\text{Y}_2\text{Si}_2\text{O}_7$) are successfully used as materials for scintillation detectors. Their preparation by classical methods needs high temperatures what is unfavourable from the point of view of production costs. One of the possible solutions how to reduce these costs consists in the use of some low-temperature preparation. Mainly sol-gel methods are well-adapted for oxide-type materials. They reduce the temperature of preparation under 1000°C and one can obtain more homogeneous materials in comparison with classical ceramics methods. This method also makes the application of doping elements possible. One step synthetic procedure, consists of gelation, drying and heat treatment of TEOS (tetraethoxysilicate) added by formamide and yttrium nitrate, i.e. $\text{Y}(\text{NO}_3)_3$. The starting solutions contain the silicon and yttrium in the molar ratio of 1:2 and 1:1 corresponding to requested composition of Y_2SiO_5 and $\text{Y}_2\text{Si}_2\text{O}_7$, respectively. The samples, after the drying process at 40 deg C (air), were treated at different temperatures up to 1100°C. X-ray powder diffraction study reveals, that the crystallisation of the final phase in the case of Y_2SiO_5 starts at 600°C and is completed at 1000°C. No broad band at about 20° (2theta) was observed in XRD pattern indicating formation of amorphous phase. In the case of $\text{Y}_2\text{Si}_2\text{O}_7$, we have observed similar thermal behaviour and uni-phase material was observed at the treatment temperature of 1100°C. The XRD study of sol-gel preparation of yttrium silicates showed, that this method is well adapted for the preparation of these attractive materials. This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant KAN300100802).

Keywords: materials chemistry, sol-gel method, X-ray powder diffraction

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Study of guest ion site in Hollandite-type $\text{K}_{1.88}\text{Ga}_{1.88}\text{Sn}_{6.12}\text{O}_{16}$, from 293K to 93K

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