Synthetic tin-selenium cylindrite, with the empirical formula $Sn_{31.52}Sb_{6.23}Fe_{3.12}S_{59.12}$ 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, α = 87.98(4)º, β = 83.14(3) º, and γ = 90.01(4)º. The pseudohexagonal (H) layer is a single-octahedral MeSe2 layer with a = 3.831(1) Å, b = 6.580(3) Å, c = 12.151(5) Å, α = 87.79(4)º, β = 90.59(3)º, and γ = 89.99(3)º; 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 a^* + 0.1921(4) b^* - 0.0119(3) 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), (0,0,0,0,1/2), (1/2,1/2,0,0,1/2) in a five-dimensional superspace, and based on 2128 observed reflections, resulted in $R1$=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

P11.06.27

Crystallization behaviour of sol-gel derived cordierite precursors

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Cordierite ($Mg_2Al_4Si5O_{18}$) 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℃, [2] and in the orthorhombic beta form, stable below 1450℃ [3]. Preparation roots 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 tetraetoxysilane, $Mg(NO_3)_2 \cdot 6H_2O$ and Al-sec-butoxide (for precursor designated as BC) or $Al(NO_3)_3 \cdot 9H_2O$ (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℃. 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℃ 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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Keywords: cordierite, high temperature X-ray diffraction, Rietveld structure refinement

P11.10.28

XRD study of sol-gel preparation of yttrium silicates

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Yttrium silicates phases (Y_2SiO_5 and $Y_2Si_2O_7$) 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 this 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℃ 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 (tretraethoxysilicate) added by formamide and yttrium nitrate, i.e. $Y(NO_3)_3$. 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 $Y_2Si_2O_7$, respectively. The samples, after the drying process at 40 deg C (air), were treated at different temperatures up to 1100℃. X-ray powder diffraction study reveals, that the crystallisation of the final phase in the case of Y_2SiO_5 starts at 600℃ and is completed at 1000℃. No broad band at about 20º (2theta) was observed in XRD pattern indicating formation of amorphous phase. In the case of $Y_2Si_2O_7$, we have observed similar thermal behaviour and uni-phase material was observed at the treatment temperature of 1100℃. 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 $K_{1.88}Ga_{1.88}Sn_{6.12}O_{16}$, from 293K to 93K

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Hollandite-type compounds are showed with chemical formula as $A_xM_xM'_{8-x}O_{16}$. In A-site enter to alkali metal or an alkaline earth metal. In M-site enter to divalent or trivalent metal, and in M'-site enter to tetravalent metal ion. Metal-oxygen octahedron builds one-dimensional (1-D) tunnel taken along *c*-axis. The 1-D tunnel has cavity and bottle neck, and it is known that A-site will be settled in each cavity. In this study, the condition of guest ion sites of $K_{1.88}Ga_{1.88}Sn_{6.12}O_{16}$ was examined by single X-ray diffraction from 293K to 93K. And, the refinement used the following resiraint conditions; (a) full occupation at the metal site in a host structure, (b) charge neutrality in a whole crystal, (c) exist two K2-site (0, 0, z) shifted from cavity center <K1-site (0, 0, 0.5)> for one vacancy [1]. In refinement of $K_{1.88}Ga_{1.88}Sn_{6.12}O_{16}$ at 293K and 223K, the ADPs (Atomic Displacement Parameters) and the site occupation were optimized by using these restraint conditions. On the other hands, in refinement at 173K, 130K and 93K, the atomic coordinate of K1-site had to shift from cavity center for optimization. Furthermore, it was shown that the site occupation of K2-site increases from a theoretical value. Therefore, the newly following constraint conditions were introduced for optimizing refinement; (a') K2-site (0, 0, z) is the guest ion site which adjacent to vacancy, (b') the guest ion site next to K2-site is K3-site (0, 0, z'), and (c') other guest ion sites in cavity center are K1-site. By using these equations it was showed the degradation of ADPs and reliability factor of guest ion site. From these results, it was thought that two or more guest ion sites near vacancy would shift from cavity center.

Reference

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P11.07.30

New family of mixed nickel and group 13-14 metal tellurides with incommensurate structures

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Low-dimensional mixed nickel and main-group metal chalcogenides over the recent years have proven to be interesting both fundamentally and practically. Their structures, featuring extended systems of d-metal - p-metal bonds in a form of quasi-2D fragments separated by non-metallic ones, often provide unique physical properties (anisotropic conductivity, low-dimensional magnetism etc.). From a crystallographer's point of view, such compounds tend to present various problems associated with disorder and structural modulations. Here we present a new family of such compounds with the general formula $Ni_{3-x}MTe_2$ (M=Ga, In, Sn, Sb; x varies from 0 to 1, exact margins depend on M). All the compounds were obtained by a high-temperature (1023-1123K) synthesis from the elements and investigated by powder and single-crystal x-ray analysis, energy-dispersive x-ray spectroscopy and electronic microscopy. The structures of the compounds consist of the layers of heterometallic bonds, arranged according to the motif of the Ni_2In intermetallic structure, terminated by tellurium atoms that form the van der Waals gap. The key feature of the structures is the presence of two partially occupied Ni positions: one in the heterometallic layer and the other in the van der Waals gap. The ordering of occupancies makes the structures incommensurate along the c axis and requires the introduction of the modulation vector. For different crystals, the q-vector varies between 0.26 and 0.32, which roughly corresponds to the quadruple or triple original subcell. The presence of the domains with different ordering in the crystals is also confirmed by the electronic microscopy. *This work was supported by RFBR (grant No.06-03-32789a) and Presidential Programme of Russian Academy of Sciences.*

P11.07.31

Analysis of the misfit mixed-layer compound in the binary restacked nanosheet system MnO_2-$Ti_{0.91}O_2$

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A variety of layered compounds can be exfoliated into their unilameller crystallites, namely nanosheets. Restacking of the nanosheets may provide a route to the fabrication of novel materials. The two-component colloidal nanosheets in the MnO_2-$Ti_{0.91}O_2$ system with various compositions were restacked by flocculation with alkali ions. X-ray powder diffraction patterns of the products show remarkable broadening reflections. The structures are suggested to be mixed-layer type of MnO_2 and $Ti_{0.91}O_2$. The powder pattern simulation process, prepared for analysis of layered composite crystals with one-directional disorder, based on the matrix method (Hendrics & Teller, 1942) was used. We considered (1) stacking disorder in restacked MnO_2, (2) stacking disorder in restacked $Ti_{0.91}O_2$, and (3) sequence probabilities of MnO_2 and $Ti_{0.91}O_2$ nanosheets. Taking the chemical composition into consideration, three probability tables of (1), (2), (3) were unified into one large probability table. For 00zeta calculation, z coordinates of all atoms were used. As for hkzeta calculation except 00zeta, atom coordinates of MnO_2 were used on the trigonal MnO_2 cell and those of $Ti_{0.91}O_2$ were used on the orthorhombic $Ti_{0.91}O_2$ cell. Agreements in the total pattern fitting, between the experimental and calculated intensities, were satisfactory in all composition range. From the results, we can know the phase status, one-dimensional solid solution or one-dimensional phase separation, of the misfit mixed-layer material in the binary restacked nanosheet system of MnO_2-$Ti_{0.91}O_2$.

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Crystal structures and physical properties of donor type dithiolene complexes with cycloalkane rings

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