

has a six-pointed starlike shape like ones of hexagonal crystals. We recently examined the structures of the titanium species in the starting solutions and the starlike aggregates. The starting solutions were transparent aqueous ones of crystalline titanate colloids having a layered lepidocrocite-type structure. The starlike aggregates consisted of acicular anatase crystals elongated along the *c*-axis. The acicular crystals were assembled by oriented attachment and twinning on the {112} planes, to form an arm of the aggregates. The fact that the angle between (112) and (11-2) is about 60° contributes to the six-fold symmetry of the starlike aggregates. In this study, the influence of the type of the tetraalkylammonium hydroxide on the formation of the starlike aggregates was examined in order to elucidate the formation mechanism of the aggregates. TMAOH, N(C₂H₅)₄OH (TEAOH), N(C₃H₇)₄OH (TPAOH) and N(C₄H₉)₄OH (TBAOH) were used as the alkylammonium hydroxide. The use of TMAOH and TEAOH led to the formation of a large number of starlike aggregates. On the other hand, the use of TPAOH and TBAOH decreased the number of the starlike aggregates. It is known that the intercalation of TPA⁺ and TBA⁺ ions into the interlayer of the lepidocrocite-type titanate leads to exfoliation of the titanate layers. Thus, it is inferred that the layered structure of the colloids in the starting solutions plays an important role in the formation of the six-pointed starlike anatase aggregates.

Keywords: titanium oxide compounds, hydrothermal synthesis, aggregates

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A systematic study of the crystal structures of monomethine cyanine dyes

Peter N Horton, Martin C Grossel, Georgina L Hallworth
University of Southampton, School of Chemistry, Highfield, Southampton, Hampshire, SO17 1BJ, UK, E-mail: pnh@soton.ac.uk

Cyanines are an important class of dyes which are known for their spectral sensitisation properties and various technical applications. Many of their spectral properties arise from their ability to form aggregates in both solution and on surfaces for which a large number of studies have been made. However there is little information concerning their solid crystalline forms; indeed relatively few examples of their structures are known. For example, in the current version of the CSD there is only one monomethine dye with a simple counterion (Br⁻). We have made a systematic study of a series of monomethine crystal structures and present here a survey of their similarities, trends and differences.

Keywords: crystal systematic, dyes, packing analysis

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Growth and characterization of new nonlinear optical crystals L-valine and L-valine hydrobromide

Sweta Moitra, Tanusree Kar
Indian Association for the Cultivation of Science, Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata - 700032, India., Kolkata, West Bengal, 700032, India, E-mail: sweta_moitra@yahoo.com

The growth of a new nonlinear optical material L-valine and its inorganic complex L-valine hydrobromide (VHBr) are reported

here. The grown crystals were characterized by FTIR, single crystal XRD, DTA-TGA, DSC, optical transmission and second harmonic generation (SHG) efficiency measurement. Bulk single crystals of L-valine and VHBr were grown from their aqueous solution by solvent evaporation method at constant temperature 28°C and 35°C respectively. Single crystal XRD of L-valine and VHBr reveals the lattice parameters to be $a = 9.701(3)\text{Å}$, $b = 5.261(2)\text{Å}$, $c = 11.953(2)\text{Å}$ and $\beta = 90.66^\circ(1)$ for L-valine and $a = 10.154(2)\text{Å}$, $b = 7.415(2)\text{Å}$, $c = 5.333(2)\text{Å}$, and $\beta = 91.22^\circ(2)$ for VHBr. The result of DTA-TGA study indicates that there is no water of crystallization present in either of the samples. DSC study shows the possibility of phase transition in VHBr. Both the crystals of L-valine and VHBr are optically transparent in the UV-Vis-NIR region with 80% transmission for L-valine and 100% transmission for VHBr. Lower percentage of transmission for crystals of L-valine may be due to poor crystal quality in comparison to VHBr. The second harmonic efficiency of L-valine is 0.82 times that of KDP where as that of VHBr is found comparable to Urea. The above discussion reveals that both L-valine and its derivative VHBr can be used effectively as a new nonlinear optical materials, but the SHG efficiency of VHBr is much higher than that of L-valine. Though L-valine is thermally more stable than VHBr but VHBr is optically more transparent than L-valine as the crystals are superior. The crystals of VHBr are more readily obtained than that of L-valine. Lastly, a probability of phase transition made VHBr a very interesting new NLO material.

Keywords: nonlinear optical materials, crystal growth from solution, characterization

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Powder X-ray diffraction of stacking fault containing β -FeSi₂

Hisanori Yamane, Takahiro Yamada
Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan, E-mail: yamane@tagen.tohoku.ac.jp

β -FeSi₂ has been studied as thermoelectric materials and optoelectric semiconductor materials. We noticed that the intensities of some specific diffraction peaks were smaller than those calculated with the structure parameters determined by single crystal XRD. We prepared β -FeSi₂ from a mixture of Fe and Si at 873-1173 K by using a Na. The powder XRD patterns of the samples were compared with the patterns calculated with DIFFaX for the crystals containing stacking faults. The small diffraction intensities were caused by stacking faults.

Keywords: powder X-ray diffraction, thermoelectric materials, stacking faults in inorganic structures

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The doubly non-commensurate structure of synthetic tin-selenium cylindrite

Emil Makovicky⁴, V. Petricek², M. Dusek², D. Topa³
¹University of Copenhagen, Geography and Geology, Oestervoldgade 10, Copenhagen, Sjaelland, DK1350, Denmark, ²Institute of Physics, Czech Academy of Sciences, ³Department of Material Research, University of Salzburg, ⁴Department of Gology and Geography, University of Copenhagen, E-mail: emilm@geol.ku.dk

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 $a = 5.969(2) \text{ \AA}$, $b = 6.004(1) \text{ \AA}$, and the layer-stacking vector $c = 12.238(1) \text{ \AA}$, $\alpha = 87.98(4)^\circ$, $\beta = 83.14(3)^\circ$, and $\gamma = 90.01(4)^\circ$. The pseudohexagonal (H) layer is a single-octahedral *MeSe* layer with $a = 3.831(1) \text{ \AA}$, $b = 6.580(3) \text{ \AA}$, $c = 12.151(5) \text{ \AA}$, $\alpha = 87.79(4)^\circ$, $\beta = 90.59(3)^\circ$, 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

Emilija Tkalcec¹, Jasminka Popovic², Biserka Grzeta², Hrvoje Ivankovic¹

¹Faculty of Chemical Engineering and Technology, University of Zagreb, Marulicev trg 20, Zagreb, HR-10000, Croatia (Hrvatska), ²Division of Materials Physics, Rudjer Boskovic Institute, Bijenicka cesta 54, P.O. Box 180, Zagreb, HR-10002, Croatia (Hrvatska), E-mail: etkalcec@pierre.fkit.hr

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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Keywords: cordierite, high temperature X-ray diffraction, Rietveld structure refinement

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XRD study of sol-gel preparation of yttrium silicates

Ivan Nemeč, Jakub Ruzicka, Daniel Niznansky

Charles University in Prague, Faculty of Science, Department of Inorganic Chemistry, Hlavova 8, Prague 2, Bohemia, 128 40, Czech Republic, E-mail: agnemeč@natur.cuni.cz

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

Kenjiro Fujimoto^{1,2}, Emmanuel Wenger², Massimo Nespolo², Claude Lecomte²

¹Tokyo University of Science, Department of Pure and Applied Chemistry, 2641, Noda, Chiba, 278-8510, Japan, ²LCM3B, UMR - CNRS 7036,