

Ca, S and O have been refined from these data, following calibration of the sample to image plate distance with silicon powder.

Keywords: synchrotron X-ray diffraction, high-pressure X-ray diffraction, monochromator

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High Pressure Synthesis of $\text{EuGa}_{2-x}\text{Si}_{4+x}$ [$x = 1.3(1)$]

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The title compound was prepared using a pressure of 8 GPa and a temperature of 1000 °C followed by slow cooling under pressure. After releasing pressure the sample was examined by x-ray powder diffraction, metallographical and EDX analysis. In the sample after the preparation, the compound $\text{EuGa}_{2-x}\text{Si}_{4+x}$ is found to coexist with $\text{EuGa}_{4-x}\text{Si}_x$ (EuGa_4 type) and Si.

$\text{EuGa}_{2-x}\text{Si}_{4+x}$ is the second representative of the EuGa_2Ge_4 structure type [1] and crystallizes in space group *Cmcm* with $a = 4.348(1)$ Å, $b = 10.457(1)$ Å and $c = 11.938(2)$ Å ($V = 542.8$ Å³). Gallium and germanium build up a three-dimensional network of four-bonded atoms with europium located in large voids. By replacing germanium with silicon the volume decreases by about 12 %. This change in volume is pronouncedly anisotropic; the length of the a axis increases by 4.6 % whereas the b and c axis shorten by 7.2 % and 9.3 %, respectively.

Due to a partial replacement of gallium by silicon, the electron balance can be written as $\text{Eu}^{2+}[\text{Ga}(3b)]^{1-0.7}[\text{Si}(4b)]^{0.5,3} \cdot 1.3e^-$. Thus, we expect metal-type conductivity. Magnetic susceptibility, electrical resistance and thermoelectric properties of the silicon compound are currently under investigation.

[1] Carrilo-Cabrera W., Paschen S., Grin Yu., *J. Alloys Comp.*, 2002, 333, 4.

Keywords: high-pressure synthesis, high-pressure crystal structure, physical properties

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The Phase Transition of Hydrogen-bonded Ferroelectric PbHPO_4 under High Pressure

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PbHPO_4 (LHP), undergoes a phase transition from Phase I to Phase II at $T_c = 310$ K under ambient pressure. The lower-temperature ferroelectric phase (Phase II) with pseudo-one dimensional hydrogen bonded structure has a space group of *Pc*. The paraelectric phase (Phase I) has been assumed to have *P2/c*. The T_c is gradually lowered with increasing pressure and then T_c goes down to room temperature. The transition pressure has been determined to be 0.15 GPa [1]. But the phase transition was no more found over 3 GPa. In this present work, x-ray powder diffraction study of LHP was carried out using synchrotron radiation with diamond anvil pressure cell under hydrostatic conditions at room temperature on BL-18C (KEK), Tsukuba. We could not detect any differences in the diffraction patterns of Phase II and Phase I with increasing pressure up to 5 GPa. By further compression a new pressure-induced phase (Phase III) appears at about 6.5 GPa. We have determined that the structure of Phase III has a possible space group of *Pmmm*, which is stable up to 17 GPa. During decompression cycle, phase III is covered back to the original phase I at 0.7 GPa.

[1] Mylov V. P., et al., *Sov. Phys. - Crystallogr.*, 1979, 24, 738.

Keywords: ferroelectrics, high pressure, phase transition

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High Pressure Structures and Compressibilities of YF_3 and LaF_3

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Many studies have been devoted to the study of laser-hosting *Ln* (*Ln* = REE, Y, Sc) fluorides; particularly ALnF_4 phases crystallizing in the scheelite structure. Yet, for many *Ln* chemistries the scheelite form is unknown and, in the case of those known compositions, e.g. LiGdF_4 , decomposition, to $\text{LiF} + \text{LnF}_3$, occurs at high- p [1]. We have investigated how the LnF_3 structure controls both the synthesis and the decomposition of the binary fluoride phase at high p conditions.

YF_3 crystallizes in the $\beta\text{-YF}_3$ -type structure at ambient p . It has been proposed [2], though not observed, that the high- p , RT structure is the same as that of LaF_3 , tysonite-type. This conjecture we can confirm, in addition to obtaining compressibilities of high- and low- p forms. These data allow calculation of molar volumes at high- p , e.g. LiYF_4 cf. $\text{LiF} + \text{YF}_3$ and judge the effect of increase in REE-coordination at phase transitions on phase stability.

LaF_3 has no known binary fluoride scheelite forms and undergoes a phase transition at $p > 12$ GPa to a structure previously described in *Cmma* and *I4/mmm* symmetries (subgroups of CaF_2 structure) [3,4]. We will present our determination of the high- p structure of this phase that extends the currently known transition sequence for LnF_3 , thus:

$\delta\text{-UO}_3$ (ReO_3) to dist-ReO_3 to $\alpha\text{-UO}_3$ to $\beta\text{-YF}_3$ to LaF_3 to *Pmmm*.

[1] Grzechnik, et al., *J. Phys.: Cond. Matt.*, 2004, 16, 7779. [2] Atavaeva E.Y., Bendeliani N.A., *Inorganic Materials*, 1979, 15, 1487. [3] Dyuzheva, et al., *J. Alloys Comps.*, 2002, 335, 59. [4] Winkler, et al., *J. Alloys Comps.*, 2003, 349, 111.

Keywords: high-pressure structures, transformation, fluorides

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Isosymmetric Reversible Phase Transition in Sodium Oxalate

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Oxalate ions are widely used in the design of supramolecular structures. Anhydrous metal oxalates (like sodium oxalate) are interesting because they have not H-bonds and their structures are determined by the interactions in the system "oxalate-anions - metal cations" only.

At 3.8 GPa an isosymmetric phase transition was observed, preserving the *P21/c* space group despite a jumpwise change in cell parameters and volume. The orientation of oxalate-ions and the coordination of sodium-cations by oxygen atoms change jumpwise at the transition point. The packing of the centroids of oxalate-anions remains preserved to a large extent. It distorts anisotropically with increasing pressure.

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Keywords: phase transitions, pressure, powder method

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Isostructural Transformation and Polymorphism of Thiourea Dioxide at High Pressure

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