

FA2-MS17-T01

High-pressure melting of silicon. Innokenty Kantor^{a,b}, Vitaly Prakapenka^a. ^aGSECARS, *Advanced Photon Source, Argonne, USA.* ^bESRF, *Grenoble, France.*
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Silicon is one of the most intensively used chemical elements in the modern technology. The vast majority of semiconductive electronics, CCD chips, solar batteries, etc. is based on pure or doped silicon. Silicon is also considered as a possible light element in the Earth's core, and therefore its high-pressure and temperature properties are also important for geosciences.

There are seven known silicon phases at high pressure [1,2]. Accurate measurements of Si phase diagram including melting curve were performed at a large-volume multianvil press, and are limited to pressures of about 15 GPa [3].

There are two main experimental challenges of doing laser heating melting experiments in a diamond anvil cell. First is the detection of melting: Si is a relatively weak X-ray scatterer and it is difficult to observe diffraction from a melt liquid. Second difficulty is the accurate temperature determination. At low pressures Si melts at temperatures around 1000 K, which is below the limit of conventional spectrographic temperature measurements.

With the advanced laser-heating facility at 13IDD and a high brightness monochromatic X-ray beam with fast CCD area detector it was possible to map Si phase diagram and to determine melting curve of silicon even at lowest pressures.

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Keywords: high-pressure diffraction, melting, silicon

FA2-MS17-T02

Single crystal diffraction at Earth's mantle conditions. Marco Merlini. *Università degli Studi di Milano, Dipartimento di Scienze della Terra, Milano, Italy.*

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Recent improvements at synchrotron beamlines and on Diamond Anvil Cells techniques allow single crystal diffraction experiments at non ambient conditions on very small crystals, one order of magnitude smaller compared to samples routinely investigated on conventional laboratory sources. Three examples concerning high pressure single crystal diffractions at Earth's Mantle conditions will be illustrated and discussed: structural determination of CaFe₂O₄ and CaCO₃ across electron Fe³⁺ and Fe²⁺ spin transition (around 50 GPa) and elasticity and phase transitions of CaFeO_{2.5} defective brownmillerite/perovskite at lower mantle conditions.

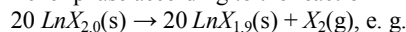
Keywords: single crystal, high pressure Earth's lower mantle

FA2-MS17-T03

High-Pressure Synthesis of Rare Earth Metal Polychalcogenides. Thomas Doert^a, Carola J. Müller^{a,b}, Ulrich Schwarz^b, Peer Schmidt^a. ^a*Department of Chemistry and Food Chemistry, TU Dresden, Germany.* ^b*Max Planck Institute of Chemical Physics of Solids, Dresden, Germany.*

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The structural chemistry of the polychalcogenides of the trivalent rare earth metals LnX_{2-δ} (Ln = Y, La – Nd, Sm, Gd – Lu, Lu; X = S, Se, Te; 0 ≤ δ < 0.3) is characterized by a multiplicity of compounds which exhibit closely related crystal structures with slightly different compositions: LnX_{2.0} LnX_{1.9} LnX_{1.875}, and LnX_{1.85}. Structurally, all compounds can be regarded as superstructures of the ZrSSi type containing puckered [LnX]⁺ double sheets and planar [X_{1-δ}]⁻ layers. Depending on δ, the anionic layers contain X₂²⁻ dimers, X²⁻ anions and vacancies. Thermoanalytical and tensimetric studies reveal that polysulfides and polyselenides LnX_{2-δ} generally decompose at elevated temperatures by a stepwise release of molecular chalcogen X₂ to form the adjacent metal richer phase according to the reaction



The decomposition process stops as soon as the sesquichalcogenide Ln₂X₃ is finally reached. Polychalcogenides of the smaller rare-earth metals are known to have higher decomposition pressures. For this reason all attempts to synthesize stoichiometric disulfides or diselenides of those metals under ambient pressure conditions failed up to now.

In a series of experiments we synthesised rare earth metal polychalcogenides under high pressure conditions to directly counteract the decomposition pressure. Single phase powder samples of several LnX_{2.0} and LnX_{1.9} phases were prepared at pressures up to $p = 8$ GPa and temperatures up to $T = 1450^\circ \text{C}$ [1, 2]. Under optimised reaction conditions it was also possible to obtain twinned crystals of GdS₂, TbS₂, ErS₂ und TmS_{1.9} suitable for X-ray structure determination. The disulfides adopt the monoclinic α -LnS₂ structure [3] (space group $P2_1/a$), TmS_{1.9} crystallises in the CeSe_{1.9} type [4] in space group $P4_2/n$. All investigated LnX_{2-δ} phases are semiconductors and contain Ln³⁺. The compounds obtained from high pressure syntheses exhibit much smaller band gaps (approximately 0.4 vs. 2 eV) than phases prepared under ambient pressure conditions. Going from lanthanum to thulium, the lattice parameters in the series LnX_{2.0} and LnX_{1.9} shrink about 4 % although the lanthanide radii decrease by approximately 14 %. As the covalent bond distance within the X₂²⁻ dimers do not change within the experimental error, the distance between the anions in the planar [X_{1-δ}]⁻ layers decline. As a result, the antibonding interactions between these anions grow and destabilise the structure.

[1] Müller, C. J., *Diploma thesis*, TU Dresden 2009; [2] Müller, C. J., Schwarz, U., Schmidt, P., Schnelle, W., Doert, Th., *Z. Anorg. Allg. Chem.*, 2010, in press (doi: 10.1002/zaac.2010.00015); [3] Marcon, J. P., Pascard, R., *C. R. Acad. Sci. Paris*. 1968, C266, 270; [4] Plambeck-Fischer, P., Abriel, W., Urland, W., *J. Solid State Chem.* 1989, 78, 164.

Keywords: Polychalcogenides, rare earth, high pressure