

with quenching pressure. Our studies also yields the evidences of the size reduction and the ordering of intermediate range structure with increasing pressure, in which the first sharp diffraction peak (FSDP) in the diffraction pattern shifts toward higher momentum transfer and becomes sharp by compression.

Keywords: silicate melt, aluminium coordination number, melt structure

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The *ab initio* high pressure solid solution behaviour of the Al_2O_3 - MgSiO_3 system

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With the assumption that the lower mantle is pyrolytic, $(\text{Mg,Fe})\text{SiO}_3$ perovskite (70 vol%) is thought to be the most abundant phase in the Earths lower mantle, followed by magnesiowüstite $(\text{Mg,Fe})\text{O}$ with (20 vol%) and CaSiO_3 perovskite, which comprises between 6 and 12 vol%. The Al_2O_3 content of fertile mantle compositions amounts to about 4-6 mol% and is supposed to dissolve mainly into MgSiO_3 perovskite. Experimental and theoretical studies have shown that a fair amount of Al_2O_3 can be dissolved in MgSiO_3 and that at pressures above 27 GPa MgSiO_3 perovskite and Al_2O_3 corundum form coexisting solid solutions. No further aluminous phase has been observed up to the pressure of the Al_2O_3 phase transformation to the $\text{Rh}_2\text{O}_3(\text{II})$ structure at 80-100 GPa. To what extent the recently discovered high pressure phases of MgSiO_3 and Al_2O_3 will change reciprocal solubilities of the phases in the MgSiO_3 - Al_2O_3 system is still unknown. Using static *ab initio* point defect calculations and simple thermodynamic models, qualitatively correct solid solution behavior of the MgSiO_3 - Al_2O_3 system was predicted. The solubility of Al in MgSiO_3 is large throughout the mantle and increases with pressure and temperature. Even though the high pressure phase transitions reduce the reciprocal solubilities, these are always large enough to completely assimilate the Al of the pyrolytic mantle. Information on the solubility of Al in MgSiO_3 might elucidate mineralogically more complex systems in the lower mantle of the Earth. Incorporation of other impurities present in significant quantities in the Earths mantle (Fe^{2+} , Fe^{3+} , and to a lesser extent Cr), into the MgSiO_3 host might influence the Al-solubility, and thus change the now well established behaviour in the MgO - AlO - SiO system.

Keywords: *ab-initio* calculations, solid solutions, high-pressure minerals

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Oxygen partitioning between magnesiowüstite and Fe-liquid: Implication to the earth's core

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Oxygen is potentially an important light element in the Earth's outer core (e.g., Ringwood 1977). In order to constrain the oxygen content of the core, the dependence of the oxygen concentration in liquid iron on pressure, temperature and oxygen fugacity needs to be clarified up to the relevant P-T conditions. We have conducted partitioning experiments of FeO between magnesiowüstite and liquid iron at conditions up to 70 GPa and 3500 K with laser heated diamond anvil cell. Focused ion beam (milling) was used to prepare thin foil from run products for transmission electron microscopy. The technique has the advantage of site-specificity at the submicron meter scale and homogeneous thinning of the samples having multi-layers of different phases or the two-phase interface. The compositions of coexisting quenched iron and magnesiowüstite were measured using a transmission electron microscope equipped with energy dispersive X-ray spectrometer and electron energy-loss spectrometer. Applying a thermodynamic model to describe the partitioning of oxygen, $\Delta H^0 - T \Delta S^0 + \int_{V_0}^V \Delta V dP + RT \ln K_d = 0$, we obtained thermodynamic parameters, $\Delta H^0 = 170000$ (J/mol), $\Delta S^0 = 56$ (J/K/mol), and the hypothetical equation of state of the Fe-O metallic liquid component ($K = 74$ GPa, $K' = 6.7$, $V_0 = 13.2$ cm³/mol). In case of core-mantle equilibrium, the results show that the outer core must be undersaturated in oxygen, which causes a layer at the very base of the mantle to be depleted in FeO. However, such an MgO-rich layer might be very thin because Fe-Mg diffusion, at least in silicate perovskite, is extremely slow at core-mantle boundary conditions (Holzapfel et al. 2005).

Keywords: high pressure, electron energy loss spectroscopy, thermodynamics

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Phase transitions and incommensurate structures in the brownmillerite system $\text{Ca}_2(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_5$

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The solid solution series is reported to exist from $x=0$ up to $x=0.69$ (e.g. [1] and references therein) at ordinary pressures. A phase boundary between structures adopting space group *Pnma* and *I2mb* was found close to $x=0.28$ [2]. Crystals with higher Al-contents can be synthesised using high pressure [3, 4]. HT phase transitions are known for the iron end-member and the structures crystallising in *Pnma* [2]. The HT phases were considered to conform to *I2mb* or *Imma* space group symmetry. Recent single crystal diffraction studies have found that $\text{Ca}_2\text{Fe}_2\text{O}_5$ transforms to a modulated structure in the range of 960-980K. This incommensurate phase can be described in superspace group *Imma(00 γ)s00* [5]. The modulated structure exhibits an aperiodic sequence of tetrahedral (FeO_4) chains. The temperature range of the transition is characterised by phase-coexistence, which can be observed by *in situ* HT single crystal X-ray diffraction experiments. Diffraction data collected in this region

can be used to perform a two-phase refinement using Jana2006 [6]. Furthermore, domains of the two phases were observed by HT high-resolution transmission electron microscopy (TEM) and dark field TEM. The aluminium end-member $\text{Ca}_2\text{Al}_2\text{O}_5$ shows an isotypic incommensurate structure above 1075(10)K.

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Keywords: incommensurate phases, high-temperature structures, TEM

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T, 2T and 4T wollastonites derived by the Ge substitution

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Four kinds of structures of wollastonite whose compositions were CaGeO_3 , $\text{Ca}(\text{Ge}_{0.65}\text{Si}_{0.35})\text{O}_3$, $\text{Ca}(\text{Ge}_{0.50}\text{Si}_{0.50})\text{O}_3$ and $\text{Ca}(\text{Ge}_{0.15}\text{Si}_{0.85})\text{O}_3$ were studied. They are called 100Wo, 65Wo, 50Wo and 15Wo, respectively. The lattice constants of 100Wo, 65Wo, 50Wo and 15Wo are: (angstrom, degree) $a=8.125(2)$, $2X8.038(4)$, $2X7.995(2)$, $4X7.949(5)$, $b=7.554(1)$, $7.451(1)$, $7.400(1)$, $7.352(1)$, $c=7.292(2)$, $7.194(2)$, $7.148(2)$, $7.093(1)$, $\alpha=90.11(3)$, $89.93(2)$, $90.05(2)$, $90.06(2)$, $\beta=94.40(3)$, $94.85(2)$, $94.97(2)$, $95.11(1)$, $\gamma=103.48(1)$, $103.34(2)$, $103.43(1)$, $103.39(1)$, respectively. 100Wo shows the basic-wollastonite. 65Wo consists of the neighbouring two units of the basic-wollastonite along the a-axis. The X-ray diffraction pattern showed a pseudo-C lattice. Therefore, the stacking sequence of 65Wo can be represented as AB, where A is the unit cell of the basic-wollastonite and B is the unit cell of the basic-wollastonite with $b/2$ displacement. 50Wo consists of the neighbouring two units of the basic-wollastonite along the a-axis, too. However, the X-ray diffraction pattern was different from 65Wo. Judging from the X-ray diffraction, the stacking sequence of 50Wo is represented as AA. 15Wo consists of the four units of the basic-wollastonite along the a-axis. There were four possible stacking sequences: AAAA, ABAB, AABB and AAAB. The structure having the sequence AAAA will show the strong intensity on the $h=4n$ diffraction. The structure ABAB will show the strong intensity on the $h=2n$ diffraction. The structure AABB will show the extinction rule of the pseudo-C lattice. The last structure AAAB will not show any characteristic rules. As the result of the observation of the X-ray diffraction of 15Wo, it was clear that the stacking sequence AAAA was most reasonable.

Keywords: germanates, crystal structure determination, superstructures

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Description of modular minerals within the superspace approach

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Modular structures are frequently observed in the mineral world. These structures are built of modules, approximately described by simpler structures. The Pb-Bi-Ag sulphosalts of the lillianite homologous series are examples of modular minerals based on PbS-like structure. The fact that the structure of these minerals can be described with the help of a simple average structure in combination with additional small distortions moved us to explore the potential of the so-called superspace approach for their description. The superspace formalism was originally developed for the study of modulated structures and is by now a well established tool for the treatment of incommensurately modulated structures, composite crystals or quasicrystals. But superspace is also a powerful and efficient tool for dealing with the structural properties of commensurate systems with large unit cells. A necessary condition is that the structures have approximate much smaller subperiodicities, which is the case for modular structures. The superspace formalism allows a unified description of whole homologous series, with the number of structural parameters smaller than in a conventional approach, and predicts the observed three dimensional space groups of individual members. With the introduction of some new concepts we have successfully applied the superspace method to the analysis and refinement of the lillianite homologues. The structures are best described as modulated structures, but with unusually large displacive modulations of a linear "zig-zag" type. An efficient treatment required the modification of the refinement program JANA2006 in order to introduce this type of functions as alternative basic modulations.

Keywords: modular structures, superspace approach, lillianite homologous series

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Polytypism in cronstedtite

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Cronstedtite is a trioctahedral 1:1 phyllosilicate, with iron and silicon as major cations. It occurs in low- and medium- tempered hydrothermal deposits and in some kinds of meteorites. Its structure is composed of the octahedral (Oc) and tetrahedral (Tet) sheets forming the 1:1 layer by sharing apical oxygen atoms. All octahedral positions are fully occupied by Fe^{2+} and Fe^{3+} ; the Si atoms in tetrahedra are partially replaced by Fe^{3+} . The layers are linked together mainly by hydrogen bonds. The polytypes of cronstedtite are divided into