Keywords: thin films, titanium dioxide, crystallization

MS05.P13

Structural behavior of anhydrous wadsleyite and forsterite

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Forsterite and wadsleyite are the major minerals in the Earth’s upper mantle and transition zone. The forsterite-wadsleyite phase transition is thought to produce a seismic discontinuity at 410 km depth. In order to calculate stability fields of mantle minerals, a useful approach is to refine thermodynamic parameters using high-pressure (HP) experimental phase relations. Such calculations benefit if parameters used in calculations, such as thermal expansivity and bulk modulus, can be accurately determined independently. However, significant divergences occur between results of previous thermal expansion studies of wadsleyite. Therefore, the high-temperature (HT) expansivities of the anhydrous wadsleyite and, for comparative purposes, forsterite were reinvestigated. An analysis of HT structural variations in wadsleyite was also undertaken.

Samples were synthesized at HP HT conditions at the BGI–multianvil facility (wadsleyite sample numbers z626, z627). In situ structural studies on wadsleyite were performed at the synchrotron facility HASYLAB/DESY (Hamburg, Germany) with the powder diffractometer at beam-line B2 up to 1083 K. The thermal expansion of forsterite was measured using a furnace mounted on the Philips Xpert powder diffractometer up to 1313 K.

The HT thermal expansion of wadsleyite and forsterite was parameterized on the basis of the 1st order Grüneisen approximation using a Debye function for the internal energy. The values for hypothetical volume at T=0 K, Debye temperature and Grüneisen parameter of forsterite equal 288.80(2) Å$^3$, 771(9) K, 1.26(2), respectively, with a fixed to 125 GPa bulk modulus. The extrapolation of $V/T/V_p$ values to melting of forsterite at ~2150 K agrees with experimental $V/T/V'_p$ [1]. This demonstrates the main advantage of using of 1st order Grüneisen approximation for forsterite and confirms validity of such model for expansivity parameterization. The values for hypothetical volume at T=0 K, Debye temperature, Grüneisen parameter for wadsleyite equal 536.86(14) Å$^3$, 900(55) K, 1.28(2) and 537.00(13) Å$^3$, 887(50) K, 1.26(1) for z626 and z627, respectively, with a fixed to 161 GPa bulk modulus. The best agreement of the expansivity is observed with results of references [2, 3].

Larger compressibility of the c-axis of wadsleyite was attributed to the pseudo-lowering features with Mg-O layers within the a-b plane and its cross linking by Si$_4$O$_8$ dimers along c-axis [4]. By the analogy, the same structural features might explain the large expansivity along the c-axis. However, Mg-O bonds response in different ways to temperature than to the pressure increase. The temperature-induced changes in interpolyhedral angles correlate well with significantly larger expansivity along the c-axis of wadsleyite and in contrast to anisotropic compression, can not be neglected in their contribution to the anisotropic thermal expansion.

Support from the ERC advanced grant no. 227893 “DEEP” funded through the EC 7th Framework Programme. The measurements with synchrotron radiation were carried out during beamtime allocated to Project I-20090287 at HASYLAB/DESY.

Key words: silicate, thermal expansion, powder diffraction

MS05.P14

Ordering effects in BiFeO$_3$-based solid solutions
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The research was supported by RFFI(grant № 10-03-00189-a).

In solid solutions of BiFeO$_3$ and KNbO$_3$ the order parameter transitions should occur: magnetic, ferro-(antiferro)electric, and of ferroelastic nature.

X-ray diffraction study in 20°C<30°C temperature range of (1-x)BiFeO$_3$-(x)KNbO$_3$(BFKNO) and (1-x)BiFeO$_3$-(x)NaNbO$_3$(BFNNO) solid solutions systems’ samples has allowed to make the (x,T) phase diagrams of the systems. It was established that in BFKNO system the R3c, Pbnm, Pm3m phases’ boundaries of pure BiFeO$_3$ with KNbO$_3$ are decreased in transition temperature with the increase of X. The transition temperatures between Amm2, Pmmn and Pm3m phases of pure KNbO$_3$ are also decreased with the decrease of X.

The comparison of BFKNO and BFNNO phase boundaries shows that in these systems the ferroelectric phase transitions’ temperatures of BiFeO$_3$, KNbO$_3$, and NaNbO$_3$ decrease with the increase of secondary component’s content. This is also proved by preliminary results of permittivity-temperature dependencies investigations.

Key words: ferroic, ferroelectricity, X-ray

MS05.P15

Structural study of SrPrMRuO$_3$ double perovskites by symmetry-mode analysis
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The natural way to study the phase-transitions is the use of the symmetry-mode analysis, to understand in a proper way the microporous mechanisms responsible for the phase-transitions. For that propose we have used the Bilbao Crystallographic Server [1][2][3] together with FullProf Suit [4].

The SrPrMRuO$_3$ (M=Zn,Co,Mg,Ni) materials have been elaborated by the conventional Solid Sate Reaction Method. Rietveld analysis of laboratory X-ray Powder Diffraction (XRPD), Synchrotron Radiation Powder Diffraction (SRXPD) and Neutron Powder Diffraction (NPD) shows that these materials are double perovskites with a primitive space group: P2$_1$/n (No. 14, non conventional setting). In the four compounds Sr$^{2+}$ and Pr$^{3+}$ are totally disorderes in A- and A’-sites; whereas M$^{2+}$ and Ru$^{4+}$ are completely ordered, in B- and B’-sites, respectively. For the refinements we have used AMPLIMODES for FullProf [3][5-6]. AMPLIMODES carries out a symmetry-mode analysis of a displacive phase-transition. Starting from the experimental structures of the parent-phase (virtual or real, Fm-3m, No. 225 conventional setting) and knowing the metric of the low-symmetry phase (P2$_1$/n), the program determines the symmetry modes compatible with the symmetry break. In the NPD data analysis two modes have been identified as active: the ones responsible to yield the P2$_1$/n space group: GM$_1$ and X$_{-}$.

The high-temperature (HT) laboratory XRPD analysis has revealed the following temperature phase-transition sequence [7]: P2$_1$/n-R-3m-Fm-3m. HT neutron diffraction data of SrPrMgRuO$_3$, material has been used to study the phase-transition by the symmetry-mode analysis. According to the theory, the two order parameters actuating in the monoclinic phase are expected to thermally stabilize and become zero at higher temperature. Taking into account that the amplitudes are different, it can be expected that one of them will become zero before the other and, thus, an intermediate phase will appear, before the cubic one. A first order phase-transition has been observed between P2$_1$/n and R-3 (No. 148 conventional setting). None of the amplitudes of the active modes will reach the zero value at the transition temperature. In the symmetry breaking from the prototype cubic phase into the trigonal intermediate (HT) phase a unique active mode has been identified: GM$_1$, which generates a rotation of the octahedra around the hexagonal c axis.

Key words: transition-metal perovskites, phase-transitions, symmetry-mode analysis

MS05.P16

High-pressure behavior of high silica ferrierite
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Ferrierite (FER framework topology) is a well-known aluminosilicate zeolite mineral. An understanding of the structure and properties of FER remains important because of its role as a catalyst in commercial reactions. For example, it is important in the petrochemical industry, where it has been used as a shape selective catalyst for the production of isobutene. The thermal behavior of this phase (in its high silica form) was recently studied by Bull et al [1], while its compressibility has never been investigated before.

The high pressure (HP) behavior of synthetic high silica zeolite ferrierite (FER) was investigated by means of in-situ synchrotron X-ray powder diffraction, with the aim to understand the P-induced deformation mechanism. The microporous material was synthesized starting from pure silica and pyridine and propyl-amine as structure directing agents. Here we report the preliminary results on the compressibility of the as synthesized phase. The study of the compressibility of the calcined one will be carried out in the following steps of the project.

Key words: transition-metal perovskites, phase-transitions, symmetry-mode analysis