characterized with these methods.

Our recent study of crystalline materials under uniaxial stress will be illustrated by results on Si at high pressures. This study has revealed that there may be other interesting crystalline structures of Si to be found at high pressures in addition to those already well characterized.

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Keywords: prediction, pressure, first-principles

MS40.P07

The influence of the Jahn-Teller effect at Fe^{2+} on the structure of chromite at high pressure

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The crystal structure of chromite $FeCr_2O_4$ was investigated under high pressure with single-crystal x-ray diffraction techniques. A total of 7 datasets were collected up to 13.7 GPa at ambient temperature. The cubic unit-cell parameter decreases continuously from 8.3832 (5) Å to 8.2398 (11) Å up to 11.8 GPa. Fitting the P-V data to a Birch-Murnaghan equation of state (EoS) gives K_0 = 209 (13) GPa, K' = 4.0 (fixed), and V_0 = 588 (1) Å^3. The FeO_4 tetrahedra and CrO_6 octahedra are compressed isotropically with pressure, the Fe-O and Cr-O bond distances decreasing from 1.996 (6) to 1.949 (7) Å and from 1.997 (3) to 1.969 (7) Å respectively. From the structural refinements, the tetrahedral site occupied by the Fe^{2+} is more compressible (187%) than the octahedral site occupied by the Cr^{3+}. A discontinuous volume change is observed between 11.8 GPa and 12.6 GPa, consistent with a structural phase transition from cubic (space group $Fd\bar{3}m$) to tetragonal (space group $I4_1/amd$). At the phase transition boundary, the two Cr-O bonds parallel to the c-axis shorten from 1.969 (7) Å to 1.922 (17) Å and the other four Cr-O bonds parallel to the ab plane expand from 1.969 (7) Å to 1.987 (9) Å. The angular distortion in the octahedron decreases continuously up to 13.7 GPa, whereas the values of angular distortion in tetrahedron rise dramatically after the phase transition. This anisotropic deformation of the octahedra leads to a tetrahedral compression ($a > c$) along the c-axis. The Jahn-Teller effect at Fe^{2+} becomes observable at the phase transition pressure and gives rise to the tetrahedral angular distortion, which in turn results in the phase transition in $FeCr_2O_4$. With increasing pressure, the tetrahedral bond angles, referenced to the c-axis direction, decrease from 109.5° to 106.6 (7)°, resulting in a stretched tetrahedral geometry along the c-axis. A qualitative molecular orbital picture shows that, for the d^6 electronic configuration of Fe^{2+}, the metal-ligand antibonding orbitals of t_2 symmetry in the undistorted structure split into orbitals of e + b$_2$ symmetry as a result of the Jahn-Teller effect at Fe^{2+}. These two orbital sets behave differently in response to the shortening of the Fe-O bond in the tetrahedron with increasing pressure, and dictate the preferred distortion mode for the tetrahedral unit.

Keywords: chromite, Jahn-Teller effect, high pressure

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Anharmonic atomic vibration of $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxor under high pressure

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Lead-based relaxor ferroelectrics with complex perovskite structures exhibit a strong frequency-dispersive dielectric permittivity with the broad temperature dependence, superior piezoelectric properties [1,2]. Relaxors have huge electro- mechanical coupling and they are applied for ultrasonic transducer. X-ray and neutron experiments of lead relaxors show diffuse scattering around the Bragg peaks along <110> directions. We aim to clarify the microstructure origin of diffuse scattering features in the relaxor and paraelectric phases of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) which has a cubic perovskite structure with $Pm3m$. All atoms are located at the special positions and no variable positional parameters.

X-ray single-crystal diffraction studies of PMN were performed by four-circle diffractometer using synchrotron radiation (λ=20.0137 keV) at PF KEK with a diamond anvil cell at pressures up to12GPa. Average intensity data of reflections in the half-reciprocal space observed by omega scanning mode were used for structure refinement because of a large diffuse streak. The thermal vibration of atoms of PMN was investigated as a function of pressure at room temperature including anharmonic temperature factor in the least-squares refinement.

We study the influence of anharmonicity on the diffraction intensities. We adopt a multimodal distribution in the probability density function based on Gram-Charlier series expansion. The coefficients of anharmonic temperature factor T(H) is adopted up to fourth order as variable parameters. These tensors are constrained by the site symmetry. R-factor of the least-squares refinements at each pressure is extremely improved by appying the anharmonic tensor up to fourth order D_{ijkl} in comparison with the harmonic model second rank B_{ij}. Difference Fourier maps of the projection on to (100) at atoms of Pb and Nb(Mg) indicate the deformation of the electron density. Time and space average of dynamical phenomena or microdomain disorder is observed. Diffuse streaks found along <110> direction in the reciprocal lattice on (100) can be interpreted by the deformation mainly around Pb atom found in the difference Fourier maps. These deformations disappear at 7.2GPa and PMN becomes paraelectric crystal with the centric symmetry.

The present result is consistent with the first-principles MD simulations [3], which showed that a random field in the chemically disordered regions induces such ordered and disordered regions in polarization.

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