氏　　名	汪　日平
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学位授与番号	博甲第４８４８号
学位授与の日付	平成２５年　９月３０日
学位授与の要件	自然科学研究科　地球物質科学専攻 （学位規則第５条第１項該当）
学位論文の題目	First-principles study on high-pressure phases of $AlPO_4$ compound: compression mechanism, dielectric properties, lattice dynamics, thermodynamics properties, and phase diagram （$AlPO_4$ 高圧相の第一原理法による研究 : 圧縮機構、誘電性、格子力学、熱力学的性質と相図）
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学位論文内容の要旨

This study employed first-principles approach to investigate the high-pressure phases of $AlPO_4$ compound. The investigated phases are berlinite, moganite-like, $AlVO_4$, the $P2_1/c$, $CrVO_4$ stishovite-like, and m-$CaCl_2$. Among them, moganite-like, $AlVO_4$ the $P2_1/c$, $CrVO_4$ phases are for the first-time theoretically investigated here, after having been synthesized in recent quench experiments, and stishovite-like phase is a newly predicted in this study, as to be a stable at high pressure and high temperature. For each phase, this study investigated its compression mechanism, dielectric properties, lattice dynamics, thermodynamics properties, and stability field. The accomplished phase diagram for this $AlPO_4$ compound covers pressure up to 100 GPa and temperature up to 2000 K.

The phase stability at 0 K and the compression behavior along pressure were analyzed based on results of density functional theory (DFT) calculations. These calculations optimizes the structure by minimizing the ground-state energy. The transition sequence at 0 K is berlinite, moganite-like, $AlVO_4$ and $P2_1/c$, $CrVO_4$, stishovite-like, and m-$CaCl_2$, with transition pressure 4.1, 5.0, 7.0, 31.5, and 45.3 GPa, when the phases of $AlVO_4$ and $P2_1/c$ treated as a group because of their fairly closeness in energy. The structural evolution along pressure are closely analyzed, regarding bond length, angles, and distortion within polyhedra. They tell the compression mechanism, which differs from phase to phase. For instance, moganite-like phase is compressed with two-stage model, stishovite-like is dominated by normal compression mechanism where as m-$CaCl_2$ phase by shear compression.

The dielectric properties, lattice dynamics, and phonon spectra were calculated using density functional perturbation theory (DFPT). This method incorporates the linear response theory to the framework of DFT, so that the response of crystals on the perturbation of electric field and atomic displacements could be disclosed. Since this $AlPO_4$ compound as polar material, there exist long-range dipole-dipole interactions, and then dielectric properties are couple with lattice dynamics in constructing phonon spectra. Perturbation on both electric field and atomic displacements were performed, and such calculation gave dielectric tensor, Born effective charge, and interatomic force constants. The combination of these parameters generates Hessian matrix, by diagonalizing which the full spectra of phonon dispersion were calculated. The resulted phonon spectra show LO-TO splitting because of the well treatment on dipole-dipole interaction.

The thermodynamics properties and phase diagram were calculated using quasiharmonic approximation (QHA). QHA formulate the free energy at finite temperatures by combining the static energy obtained from DFT and the phonon density of state obtained from DFPT. With these free energies, a full set of equilibrium thermodynamic properties could be derived with well-established thermodynamic relationships, and the most basic ones were analyzed in details, including thermal expansivity, thermal bulk modulus, heat capacity. Most of them are for the first-time provided and without experimental data for comparison, except that thermal expansivity shows good agreement with experiments available at ambient pressure. Since stable phase has the lowest Gibbs free energy among all the competing phases, the comparison of Gibbs free energies gave phase diagram. The phase relations are very similar to that gained at 0 K, but this QHA calculations found that $AlVO_4$ phase is stable only at temperatures below 600 K where as $P2_1/c$ phase is stable only above. The accomplished phase diagram compares well with previous experiments, which are yet available only at limited pressure-temperature conditions.

論文審査結果の要旨

本論文では，所属研究室で急冷実験から発見された$AlPO_4$ の３つの高圧相およびその他の相について，第一原理法を使って，それらの物性と相関係を研究した。その結果，それら３相が全て高温高圧下で安定相であることを示した。また，新たにstishovite構造を持つ相が安定であることを見つけて，その相が強弾性転移することを示した。

主な結果を要約すると次の通りである。
（１）密度汎関数法，密度汎関数摂動法と準調和近似を使って，様々な$AlPO_4$ 相の圧縮挙動，格子力学，熱力学的性質を計算し，それらを基に相平衡図を求めた。
（２）所属研究室で急冷実験から発見された３つの高圧相が真に安定相であることが分かった。計算された相平衡図は急冷実験結果と定性的に一致したが，定量的には圧力を 2-3 GPa過剰評価してることが分かった。また，１つの相境界については転移温度を約 1000 K過小評価しており，その理由が構造の類似性から自由エネルギーが異常に近いことによると示した。
（３）新たにstishovite構造を持つ相が安定であることを発見し，この相の高圧相との関係が強弾性転移であることを結晶構造と格子力学計算から明らかにした。
（４）上記以外に個々の相の誘電性および圧縮挙動とその結晶化学的な意味についても調べた。

同氏の成果は，国際英文誌へ掲載論文が１編（第一著者１編）である。

以上の様に本論文は表記研究題目に関して，系統的な計算を行い，理論的な考察を行い，学術的に意義のある結果を得ている。よって，本論文は博士（理学）の学位論文として値するものとして認める。