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Some thermodynamic properties of larnite (β-Ca_2SiO_4) constrained by high *T*/*P* experiment and/or theoretical simulation

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Abstract

Pure larnite (β-Ca_2SiO_4; Lrn) was synthesized at 6 GPa and 1473 K for 6 h by using a cubic press, its thermal expansivity was investigated up to 923 K by using an X-ray powder diffraction technique (ambient *P*), and its compressibility was investigated up to ~16 GPa by using a diamond-anvil cell coupled with synchrotron X-ray radiation (ambient *T*). Its volumetric thermal expansion coefficient (α_V) and isothermal bulk modulus (K_T) were constrained as $\alpha_V = 4.24(4)\times10^{-5}$ K^{-1} and $K_T = 103(2)$ GPa [the first pressure derivative K_T' obtained as 5.4(4)], respectively. Its compressibility was further studied with the CASTEP code using density functional theory and planewave pseudopotential technique. We obtained the K_T values as 123(3) GPa (LDA; high boundary) and 92(2) GPa (GGA; low boundary), with the values of the K_T' as 4.4(9) and 4.9(5), respectively. The phonon dispersions and vibrational density of states (VDoS) of Lrn were simulated using density functional perturbation theory, and the VDoS was combined with a quasi-harmonic approximation to compute the isobaric heat capacity (C_P) and standard vibrational entropy (S^0_{298}), yielding $C_P = 212.1(1) - 9.69(5)\times10^2T^{-0.5} - 4.1(3)\times10^6T^{-2} + 5.20(7)\times10^8T^{-3}$ J/(mol·K) for the *T* range of ~298–1000 K and $S^0_{298} = 129.8(13)$ J/(mol·K). The microscopic and macroscopic thermal Grüneisen parameters of Lrn at 298 K were calculated to be 0.75(6) and 1.80(4), respectively.

Keywords: β-Ca_2SiO_4, compressibility, entropy, heat capacity, larnite, thermal expansivity, thermal Grüneisen parameter, thermodynamic property