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An IR and Calorimetric Investigation of the Structural, Crystal-Chemical and Thermodynamic Properties of Hydrogrossular

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The garnet class of phases is extremely broad in terms of composition and structural properties. Garnet is found in nature and various synthetic garnet phases have a number of important technical applications. There exist the rock-forming silicate garnets that are so widespread geologically. An additional class is given by the so-called "hydrogarnets" in which the tetrahedral site (Wyckoff position 24d) is empty. At relatively low temperatures there is complete solid solution between $Ca_3Al_2Si_3O_{12}$ and $Ca_3Al_2H_{12}O_{12}$, for example. The substitution mechanism can be written as $O_4H_4 \Leftrightarrow SiO_4$. The latter, pure OH-containing end-member, which has not been found in nature, is termed katoite/hydrogrossular. Its structure has been investigated by various workers by X-ray and neutron diffraction and by proton NMR, IR and Raman spectroscopic methods. At ambient conditions the structure has the "standard" garnet cubic symmetry of Ia-3d. At high pressures, and possibly at low temperatures, a different structure may occur.

We measured the low temperature IR spectra and heat capacity of katoite in order to understand its structural, crystal-chemical and thermophysical properties. A sample of $Ca_3Al_2H_{12}O_{12}$ was synthesized hydrothermally in Au capsules at 250 °C and 3 kb water pressure. X-ray powder measurements show that about 98-99% katoite was obtained. Powder IR spectra were recorded between 298 K and 10 K. The measured spectra are considerably different in the high wavenumber region, where O-H stretching modes occur, between 298 K and 10 K. At room temperature the IR-active O-H band located around 3662 cm^{-1} is broad and it narrows and shifts to higher wavenumbers and also develops structure below about 80 K. Concomitantly, additional weak intensity O-H bands located around 3600 cm^{-1} begin to appear and they become sharper and increase in intensity with further decreases in temperature down to 10 K. The spectra indicate that the vibrational behavior of individual OH groups and their collective interactions measurably affect the lattice dynamic (i.e. thermodynamic) behavior.

The low temperature heat capacity behavior was investigated with a commercially designed relaxation calorimeter between 5 and 300 K on a mg-sized sample. The heat capacity data are well behaved at $T < 300$ K and show a monotonic decrease in magnitude with decreasing temperature. A standard third-law entropy value of $S^o = 421.7 \pm 1.6$ J/mol·K was calculated. Using this new calorimetric-based S^o value and published standard enthalpy of formation data for katoite, a calorimetric-based Gibbs free energy of formation at 298 K can be obtained as $\Delta G°f = -5021.2$ kJ/mol. The Cp data show no evidence for any phase transition as possibly expected by the change in OH-mode behavior with decreasing temperature. We have no explanation for the appearance of the additional modes. It is worth noting that the katoite crystal structure in terms of lattice dynamic or thermodynamic behavior should be thought of having OH groups and not O_4H_4 clusters or polyhedral units as is often written in the literature. The single crystallographic OH group in katoite shows very weak, if any, hydrogen bonding and the H atoms have large amplitudes of vibration. The weak H bonding controls the nature of low energy OH-related vibrations and this leads to its large S^o value.