

Crystal structure and low-temperature behavior of “disordered” thomsonite

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ABSTRACT

The crystal structure, crystal chemistry, and low-temperature structural evolution of natural thomsonite from Terzigno, Somma-Vesuvius volcanic complex, Naples Province, Italy, have been investigated by means of in situ single-crystal X-ray diffraction, electron microprobe analysis in the wavelength dispersive mode, and Raman spectroscopy. Six structure refinements have been obtained at different temperatures: 295.5, 248.0, 198.0, 148.0, 98.0, and 296.0 K (after the low- T experiments). The reflection conditions and the structure refinements prove that the crystal of thomsonite here investigated is orthorhombic with $a = 13.0809(3)$, $b = 13.0597(3)$, $c = 6.6051(1)$ Å, $V = 1128.37(14)$ Å³, and space group $Pbmn$, which differs from thomsonite from different localities reported in previous studies (with $a \sim 13.1$, $b \sim 13.06$, $c \sim 13.2$ Å, and space group $Pncn$). The refined bond distances suggest that the Si/Al-distribution in the tetrahedral framework is fully “disordered,” giving rise to the halving of the c axis relative to that found in “ordered” thomsonites. The extra-framework population consists of: (1) one site about 50% occupied by Ca (labeled as “Ca”); (2) one site occupied by Na (~70%) and Ca (~30%) (labeled as “Na”); and (3) three water molecule sites (“W1,” “W2,” “W3”). The structure refinements allowed the location of all the proton sites, and the hydrogen-bonding scheme in the structure is provided. The low-temperature refinements show no significant change in the structure within the T -range investigated. The evolution of the unit-cell volume with T exhibits a continuous and linear trend, without any evident thermo-elastic anomaly, with thermal expansion coefficients $\alpha_v = V^{-1} \cdot \partial V / \partial T = 20(2) \cdot 10^{-6}$ K⁻¹ (between 98.0 and 295.5 K). A list with the principal Raman active modes is provided and a comparison with the vibrational modes previously found for “ordered” thomsonite is carried out.

Keywords: Zeolite, thomsonite, Somma-Vesuvius, crystal chemistry, low temperature, single-crystal X-ray diffraction, single-crystal Raman spectroscopy