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On the crystal structure and crystal chemistry of pollucite, $(Cs,Na)_{16}Al_{16}Si_{32}O_{96}\cdot nH_2O$: A natural microporous material of interest in nuclear technology

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Abstract

The crystal structure and crystal chemistry of two natural pollucite samples, from Buckfield, Oxford County, Maine (sample M3), and from Kanzit Mawaie, Laghman, Nooristan, Afghanistan (sample N5), have been investigated by means of wavelength-dispersive X-ray microanalysis, thermogravimetric analysis, single-crystal X-ray and neutron diffraction, and single-crystal Fourier-transform infrared spectroscopy. The X-ray and neutron diffraction patterns of the two pollucite crystals show a metrically cubic unit cell [with $a_{M3} = 13.6914(6)$ Å and $a_{N5} = 13.6808(6)$ Å by neutron diffraction data; the deviation from isometry is $<1.5\sigma(l_i)$, where l_i is the unrestrained unit-cell length] and the reflection conditions are consistent with the space group $Ia\bar{3}d$. Anisotropic neutron structural refinements gave final agreement indices: $R_1 = 0.0543$ for 32 refined parameters and 372 unique reflections with $F_o > 4\sigma(F_o)$ for M3 and $R_1 = 0.0693$ for 31 refined parameters and 331 unique reflections with $F_o > 4\sigma(F_o)$ for N5. The structure refinements show a disordered Si/Al-distribution in the tetrahedral framework. The analysis of the difference-Fourier maps of the nuclear density confirms the presence of extra-framework water molecules with oxygen sharing the Cs site (at 1/8, 1/8, 1/8, Wyckoff-16*b* position). However, the minima, ascribable to the proton sites, are very weak in density. Two possible proton positions, leading to a reasonable H_2O configuration, are given, and the possible hydrogen bonding is described. Sodium is located at 1/4, 1/8, 0 (Wyckoff-24*c* position). The main IR absorption bands in the regions typical of H_2O are assigned, and the presence of hydroxyls in the studied samples is ruled out. Neutron diffraction and FTIR data agree with the presence of very weak hydrogen bonds in the structure. The detailed description of the crystal structure and crystal chemistry of pollucite (e.g., Si/Al-distribution, configuration of the extra-framework content, possible hydrogen bonding scheme) reported in this study is the key to understand the high thermo-elastic stability of pollucite, the immobility of Cs at non-ambient conditions, and the extremely low leaching rate of Cs, which make this open-framework silicate a promising material with potential use for fixation and deposition of Cs radioisotopes.

Keywords: Pollucite, zeolite, crystal chemistry, single-crystal X-ray diffraction, single-crystal neutron diffraction, single-crystal FTIR