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CRYSTAL STRUCTURE AND OPTICAL PROPERTIES OF POLLUCITE

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Pollucite, the principal source of the element cesium, is found among the granitic pegmatites of New England. Gem quality specimens were recently collected by Henry Barbour of Fryeburg, Maine. The euhedral single crystals are colorless and transparent, ranging in size up to 15 mm. Some of the physical properties and crystal structure of this material are described in this paper.

An approximate chemical formula was established by thermogravimetric measurements and x-ray fluorescence analysis. X-ray emission spectra were detected for four alkali metals with the following weight percentages: Cs (32%), Na (2%), K ($<\frac{1}{2}\%$), Rb ($<\frac{1}{2}\%$). Similar tests for alkaline earth and transition metal elements gave negative results. The water content was estimated by weight-loss measurements; heating a powdered specimen to 720°C for five hours gave a weight reduction of 1.8 percent. Assuming this is caused by trapped water, the approximate composition is expressed by

$$Cs_{1-x}Na_xAlSi_2O_6 \cdot xH_2O, \qquad x \sim 0.3.$$

The Na and H_2O concentrations are nearly equal, as suggested by Nel (1944). The proposed formula is also consistent with the observed density, since it yields a calculated specific gravity of 2.94. Gravimetric measurements on large single crystals gave $\rho = 2.936 \pm 0.001$ g/cc.

A refractive index of $n = 1.520 \pm 0.002$ at 25°C was obtained by immersion methods. Capacitance bridge measurements on single crystal pollucite gave a dielectric constant $K = 6.4 \pm 0.1$ which is independent of frequency in the range 0.1Kc to 10Mc. K is considerably larger than n^2, perhaps indicative of microwave relaxation phenomena associated with the rotational motion of H_2O.

The trapped water vibrational spectrum shown in Figure 1 was obtained with a Beckman DK-2A spectrophotometer. Nearly identical results were obtained with three pollucite crystals (thickness 0.9 to 2.5 mm). Similar absorption bands have been reported for cordierite (Farrell and Newnham, 1967). The interpretation of spectra becomes obvious when compared to the water vapor spectrum (Herzberg, 1945). Water molecules in these minerals are only weakly bonded to the silicate network and behave as nearly free H_2O. The pollucite spectrum is dominated by intense absorption near 2.7μ caused by the O-H stretching fundamentals. Most of the smaller peaks occurring at shorter wavelengths can be identified as combination bands involving the symmetric (ν_1) and antisymmetric (ν_3) stretching modes and the bending mode (ν_2). Tentative vibrational quantum number assignments (ν_1, ν_2, ν_3) for the various excited states are listed in Figure 1.

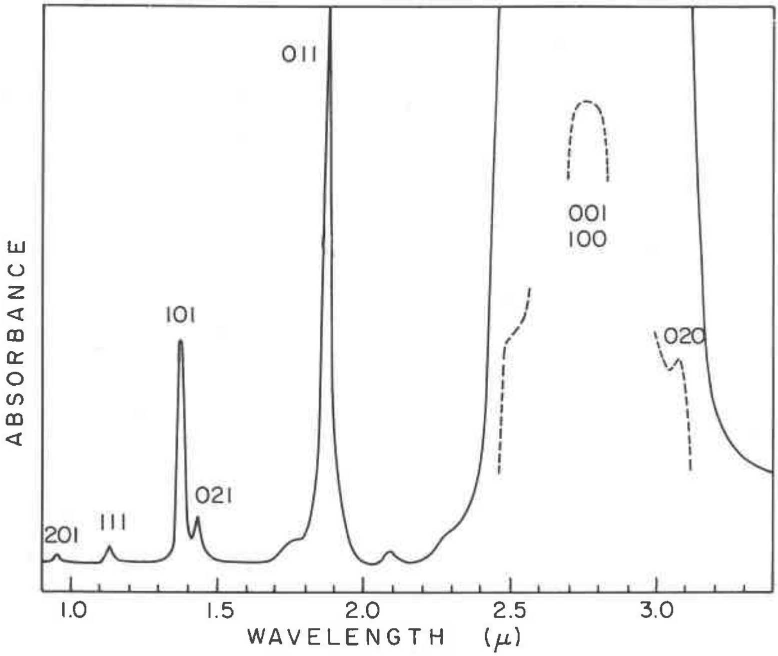

FIG. 1. The near infrared absorption spectrum of pollucite.

The crystal structure of pollucite proposed by Naray-Szabo (1938) was confirmed by X-ray analysis. No deviation from the cubic space group *Ia3d* was observed either optically or by x-rays; symmetry-related reflections were carefully examined and found to be identical within experimental error. Graphical extrapolation of high-angle diffractometer data gave a cell dimension of $a = 13.682 \pm 0.003$ Å. Three-dimensional intensities were collected about [001] using a Weissenberg camera and filtered CuKα radiation. Some 191 independent intensities were estimated visually from multiple films for the zero- and first four upper layers. Of these, 43 were below the observable limit, and five intense reflections suffered badly from extinction. The remaining 143 were used in refining the four positional coordinates and three temperature factors of the pollucite structure. Ten least-squares cycles calculated with the

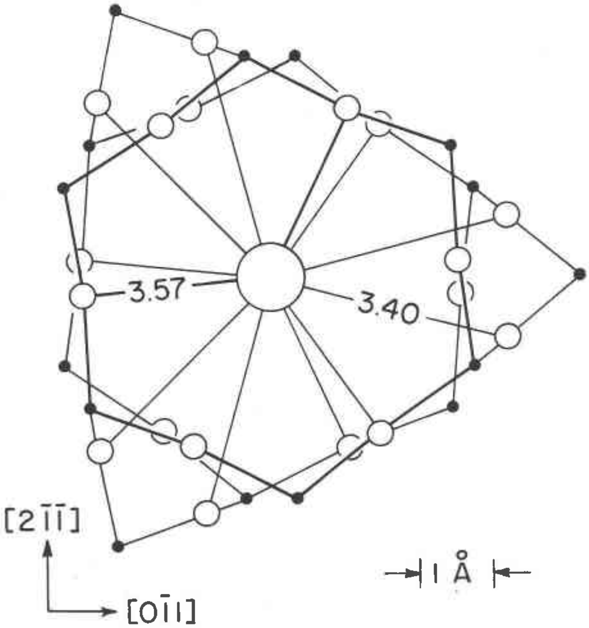

FIG. 2. Crystal structure of pollucite viewed long [111]. Cesium, silicon and oxygen positions are represented by a large open circle, solid circles and small open circles, respectively.

Busing-Levy ORFLS program led to the following results

Cs in $16b$ $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$, $B = 1.7 \pm 0.2$.

Al, Si) in $48g$ $(\frac{1}{8}, u, \frac{1}{4} - u)$, $u = 0.6631 \pm 0.0009$, $B = 0.3 \pm 0.2$.

0 in $96h$ (x, y, z), $x = 0.1036 \pm 0.0012$, $y = 0.1333 \pm 0.0014$,

$z = 0.7216 \pm 0.0013$, $B = 1.8 \pm 0.4$.

The last recorded changes in the seven variables were ten times smaller than the standard error, indicating complete refinement. None of the correlation coefficients involving positional coordinates exceeded 0.2 but those between scale and temperature factors were sizeable, ranging between 0.3 and 0.8. The observed and calculated structure factors, which are available on request, gave an agreement index of $R = 0.13$.

A question concerning the disposition of Na^+ ions and H_2O molecules arose during the foregoing analysis. Do both substitute for cesium in the large cavity or, as in analcite (Taylor, 1938), does water take the 16b positions while Na is randomly distributed over $24c$ $(\frac{1}{8}, 0, \frac{1}{4})$? The calculations described in the previous paragraph are based on the former possibility, but a refinement of the analcite arrangement was also attempted. The Na temperature factor rapidly diverged to a value of 22 during three least-squares cycles, indicating little or no electron density near ($\frac{1}{8}$, 0, $\frac{1}{4}$). A complete analcite-pollucite solid solution series also seems unlikely on crystallochemical grounds, based on the following argument. Each 24*c* equipoint is only 2.42 Å away from two cesium/sites, which are in turn surrounded by three of the potential sodium positions. Impossibly short Cs-Na distances would result during substitution. It is therefore concluded that the large cages are jointly occupied by Na and H_2O; both are probably displaced from the center of the cavity, contributing to the large temperature factor of Cs.

Pollucite is a network aluminosilicate with interconnected rings of four and six tetrahedra. The mean (Si,Al)-0 distance calculated from the refined coordinates is 1.64, two at 1.60 and two at 1.68 Å. A value of 1.65 Å is predicted from the Smith-Bailey (1963) calibration. The six shortest oxygen-oxygen distances are 2.56(1), 2.65(1), 2.70(2) and 2.71 Å(2). Cesium is coordinated to a distorted close-packed arrangement of twelve oxygens (Fig. 2), six at 3.40 and six at 3.57 Å. The Cs cages form channels along the non-intersecting three-fold symmetry axes and are joined together by even larger holes in the ⟨110⟩ directions.

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