

Jahnsite-(CaMnMn), a new member of the whiteite group from Mangualde, Beira, Portugal

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ABSTRACT

Jahnsite-(CaMnMn), a new mineral species from Mangualde, Beira, Portugal, occurs as equant, brownish yellow crystals to 0.5 mm, associated with phosphosiderite, zodacite, varulite, and microcline. The mineral is transparent and has a vitreous luster. It is brittle with a poor parting on {001} and has a hardness of approximately 4 (Mohs). $D_{\text{obs}} = 2.78(8)$ and $D_{\text{calc}} = 2.798 \text{ g/cm}^3$. Optically it is biaxial negative, $\alpha = 1.643(1)$, $\beta = 1.659(1)$, $\gamma = 1.671(1)$, $2V_{\text{meas}} = 80(2)^\circ$, $2V_{\text{calc}} = 81^\circ$. It is monoclinic with possible space groups $P2/a$ or Pa , $a = 14.887(8)$, $b = 7.152(7)$, $c = 9.966(6) \text{ \AA}$, $\beta = 109.77(5)^\circ$, and $Z = 2$. The strongest X-ray powder diffraction lines are [$d(\text{\AA})$, I , hkl] 9.40 (10) (001), 5.74 (2) (111, 011), 5.02 (2) (210), 4.971 (2) (102), 4.704 (3) (202, 002), 3.532 (2) (312), 3.463 (2) (120), 2.986 (213, 113), 2.870 (8) (313), and 2.608 (2) (510). Electron microprobe and TGA analyses gave Al_2O_3 0.7, Fe_2O_3 21.5, MgO 0.5, CaO 5.8, MnO 20.2, P_2O_5 34.3, H_2O 18.5, total 101.5 wt%, which yields the formula $\text{Ca}_{0.86}\text{Mn}_{0.80}(\text{Mn}_{1.56}\text{Fe}_{0.34}\text{Mg}_{0.10})_{22}(\text{Fe}_{1.89}\text{Al}_{0.11})_{22}(\text{PO}_4)_4(\text{OH})_{1.66} \cdot 7.67\text{H}_2\text{O}$ or ideally $\text{CaMnMn}_2\text{Fe}_2^+(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, based on 4 P atoms.

INTRODUCTION

During the investigation of the new mineral species whiteite-(CaMnMg) (Grice et al., 1989) other specimens of the whiteite group were routinely checked for variations in chemical composition. As a result the new species jahnsite-(CaMnMn) was discovered.

Moore and Ito (1978) proposed that the whiteite group, which has the general formula $\text{XM}(1)\text{M}(2)_2\text{M}(3)_{2+}(\text{PO}_4)_4(\text{OH})_2 \cdot \text{H}_2\text{O}$, is considered to consist of two series, with the M(3) site dominantly Al^{3+} for the whiteite series and Fe^{3+} for the jahnsite series. At present there are seven species within the group: whiteite-(CaFeMg), whiteite-(MnFeMg), rittmannite (Marzoni Fecia Di Cossato et al., 1989) (whiteite series), jahnsite-(CaMnMg), keckite (jahnsite series) (Mücke, 1979), and jahnsite-(CaMnMn) (this study). Both the new mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names. The name jahnsite-(CaMnMn) is in keeping with the nomenclature proposed by Moore and Ito (1978), which incorporates the series name suffixed by chemical descriptors. This nomenclature is referred to as the "extended Levinson system" (Bayliss and Levinson, 1988), which has also been used in part for the pumpellyite group. Although this system has a certain amount of appeal in mineral systematics, it may lead to confusion, since several distinct species will have very similar names and the order of assigning the chemical suffixes is critical for species differentiation.

The holotype specimen is in the collection of the Smithsonian Institution, catalogue no. NMNH 149953, and a portion of this holotype is preserved in the National Museum of Natural Sciences, Ottawa, catalogue no. NMNS 53784.

PHYSICAL AND OPTICAL PROPERTIES

Jahnsite-(CaMnMn) occurs with phosphosiderite, zodacite, varulite, and microcline as equant, subhedral to euhedral, brownish yellow crystals up to 0.5 mm in size (Fig. 1). Crystals are transparent with a vitreous luster, and they do not fluoresce. The mineral has a Mohs' hardness of approximately 4 and is brittle. The fracture is splintery. There is no apparent cleavage, and there is a poor parting on {001}. The average measured density, as determined by flotation in a bromoform-butyl-alcohol solution, is $2.78(8) \text{ g/cm}^3$, which agrees well with the calculated density of 2.798 g/cm^3 .

The optical properties of jahnsite-(CaMnMn) were measured in Na light ($\lambda = 589 \text{ nm}$). It is biaxial negative, with indices of refraction $\alpha = 1.643(1)$, $\beta = 1.659(1)$, and $\gamma = 2.671(1)$; $2V_{\text{meas}} = 80(2)^\circ$ and $2V_{\text{calc}} = 81^\circ$. The optical orientation is $Z \parallel b$, $X \wedge c = +20^\circ$ (in β obtuse). Dispersion was not noted, but there is a slight pleochroism with X pale yellow-green, Y brown-green, and Z yellow-green, which gives the absorption formula $Y > Z > X$. These optical properties are very similar to those of jahnsite-(CaMnMg).

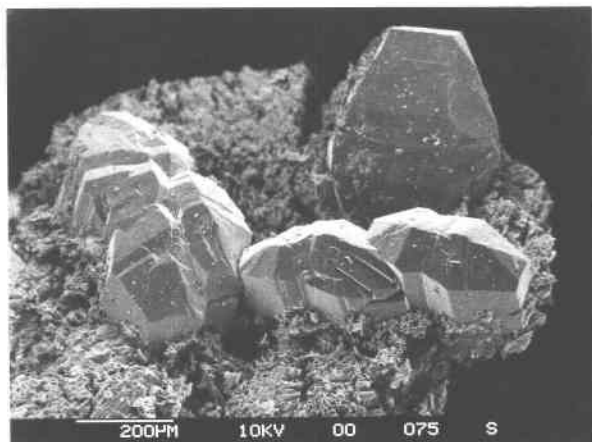


Fig. 1. Jahnsite-(CaMnMn) crystals flattened on {001}.

CHEMICAL COMPOSITION

Jahnsite-(CaMnMn) was chemically analyzed for elements with atomic numbers greater than nine using an ARL-SEM-Q electron microprobe with an operating voltage of 15 kV and a sample current of 0.025 μ A, measured on brass. Homogeneity was established using a small beam spot, but a broader beam was used during analysis to minimize boil-off of H₂O. The standards used were montgomeryite (Ca, Al, P, Mg), maricite (Fe), and manganite (Mn). The data were corrected using a modified version of the MAGIC-4 program.

Water was determined by TG-EGA on a 1.6-mg sample with a heating rate of 10 °C/min in vacuum. Approximately 1.7 wt% was initially lost under vacuum prior to heating, and this was assumed to be adsorbed and very loosely bonded water. A further 16.8 wt% was lost between 50 and 550 °C, for a total H₂O content of 18.5 \pm 0.5 wt%. The complexity of this loss is illustrated by the H₂O partial-pressure curve (Fig. 2). Major pressure maxima occur at 125, 310, and 415 °C, with corresponding losses of approximately 5.3, 0.9, and 2.3 H₂O per formula unit. After cooling from 800 °C, the product gave an alaudite-like X-ray diffraction pattern.

The chemical analysis yielded Al₂O₃ 0.7, Fe₂O₃ 21.5, MgO 0.5, CaO 5.8, MnO 20.2, P₂O₅ 34.3, and H₂O 18.5, total 101.5 wt%. The empirical formula calculated on the basis of 4 P atoms is Ca_{0.86}Mn_{0.80}(Mn_{1.56}Fe_{0.34}Mg_{0.10})_{22.00}-(Fe_{1.39}Al_{0.11})_{22.00}(PO₄)₄(OH)_{1.66} · 7.67H₂O, which corresponds to the ideal end-member formula CaMnMn₂Fe₂(PO₄)(OH)₂ · 8H₂O with Z = 2.

X-RAY CRYSTALLOGRAPHY

X-ray precession photographs show jahnsite-(CaMnMn) to be monoclinic, with P2/a or Pa as possible space groups. Single-crystal diffraction spots are diffuse. The unit-cell dimensions were refined from X-ray powder diffraction data obtained using a 114.6-mm-diameter Gandolfi camera with Mn-filtered FeK α radiation (Table

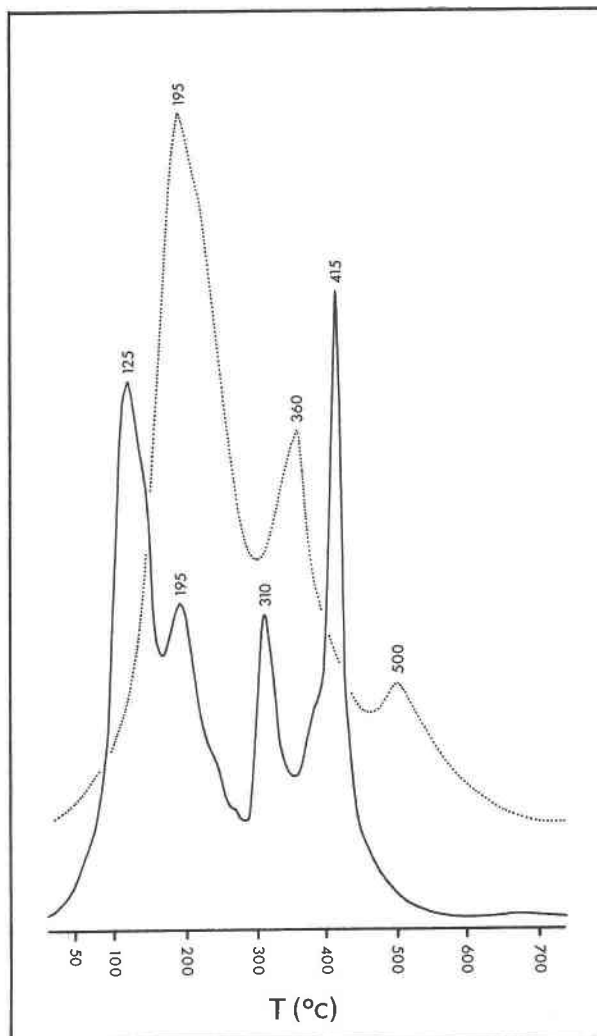


Fig. 2. The H₂O partial-pressure curves for jahnsite-(CaMnMn) (solid line) and whiteite-(CaMnMg) (dotted line). Ordinate is ion peak-height for $m/e = 18$; scale and baseline are adjusted for ease of comparison.

1). The refined cell parameters are $a = 14.877(8)$, $b = 7.152(7)$, $c = 9.966(6)$ Å, $\beta = 109.77(5)^\circ$, and $V = 997(1)$ Å³ with $Z = 2$.

DISCUSSION

To date only the jahnsite-(CaMnMg) crystal structure has been solved (Moore and Araki, 1974) among all the members of the whiteite group. This situation is likely due to the poor crystallinity of these minerals. Invariably crystals are twinned on {001}, and X-ray diffraction maxima are uniformly diffuse. Twinning is probably due to growth reversals of tetrahedral-octahedral layers within the [CaMnFe₃⁺(OH)₂[PO₄]₄]⁴⁻ slabs described by Moore and Araki (1974). The twinning is expressed in the lattice by a pseudo-orthogonal cell with a and b the same for both cells, and with c of the twin cell equal to $2c \cos(\beta -$

TABLE 1. X-ray powder diffraction data for jahnsite-(CaMnMn)

| <i>hkl</i> | <i>d</i> _{calc} [*] | <i>d</i> _{obs} | <i>I</i> _{est} | <i>hkl</i> | <i>d</i> _{calc} [*] | <i>d</i> _{obs} | <i>I</i> _{est} |
|------------|---------------------------------------|-------------------------|-------------------------|------------|---------------------------------------|-------------------------|-------------------------|
| 001 | 9.38 | 9.40 | 10 | 602 | 2.445 | 2.449 | <1 |
| 110 | 6.37 | 6.43 | <1 | 030 | 2.384 | 2.374 | <1 |
| 111 | 5.69 | 5.74 | 2 | 130 | 2.350 | 2.349 | <1 |
| 011 | 5.68 | | | 404 | 2.350 | | |
| 210 | 5.00 | 5.02 | 2 | 604 | 2.033 | 2.032 | <1 |
| 102 | 4.983 | 4.704 | 3 | 621 | 2.031 | | |
| 202 | 4.699 | | | 205 | 2.988 | 1.985 | <1 |
| 002 | 4.689 | 4.124 | <1 | 430 | 1.970 | 1.977 | 1 |
| 112 | 4.088 | | | 415 | 1.882 | 1.884 | 2 |
| 302 | 4.066 | 4.075 | <1 | 803 | 1.810 | 1.810 | <1 |
| 212 | 3.928 | 3.955 | 1 | 140 | 1.774 | 1.770 | <1 |
| 401 | 3.717 | 3.766 | <1 | 624 | 1.767 | | |
| 020 | 3.576 | 3.578 | 1 | 240 | 1.732 | 1.731 | <1 |
| 312 | 3.535 | 3.532 | 2 | 241 | 1.730 | | |
| 120 | 3.464 | 3.463 | 2 | 141 | 1.729 | 1.700 | <1 |
| 202 | 3.400 | 3.399 | <1 | 404 | 1.700 | | |
| 203 | 3.300 | 3.300 | 1 | 810 | 1.700 | 1.689 | <1 |
| 411 | 3.298 | | | 142 | 1.683 | | |
| 220 | 3.185 | 3.187 | <1 | 525 | 1.664 | 1.663 | <1 |
| 412 | 3.080 | 3.083 | <1 | 712 | 1.607 | 1.607 | <1 |
| 213 | 2.997 | 2.986 | 2 | 913 | 1.589 | 1.589 | 1 |
| 113 | 2.984 | | | 116 | 1.575 | 1.575 | <1 |
| 122 | 2.905 | 2.905 | <1 | | | 1.564 | <1 |
| 313 | 2.870 | 2.870 | 8 | | | 1.550 | <1 |
| 510 | 2.607 | 2.608 | 2 | | | 1.539 | <1 |
| 203 | 2.551 | 2.521 | <1 | | | 1.515 | <1 |
| 420 | 2.501 | | | | | | |

* Calculated from the cell parameters refined from the powder diffraction data: $a = 14.877(8)$, $b = 7.152(7)$, $c = 9.966(6)$ Å, $\beta = 109.77(5)^\circ$.

90°) of jahnsite and β approximately 90°. The mosaic spread of the X-ray diffraction maxima for whiteite group minerals might be attributed to cation disorder within the four octahedral sites of the structure, namely, X, M(1), M(2), and M(3). This disorder would result in stacking faults within the lattice causing diffuse diffractions.

Differentiation of the species within the whiteite group can only be made with a good chemical analysis. Even then there can be uncertainty as to the assignment of cations to the octahedral sites. Table 2 summarizes the unit-cell parameters and optical data for the whiteite group.

TABLE 2. Cell parameters and optical data for the whiteite group

| Species | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | | 2 <i>V</i> (°) | Sign | Color | Ref.* | | | |
|------------------------|--------------|--------------|--------------|-------|----------------|-------|-------|-------|---|--------|---|
| Whiteite series | | | | | | | | | | | |
| Whiteite-(CaFeMg) | 14.90 | 6.98 | 10.13 | 113.1 | 1.580 | 1.585 | 1.590 | 40–50 | + | tan | 1 |
| Whiteite-(MnFeMg) | 14.99 | 6.96 | 10.14 | 113.3 | 1.575 | 1.585 | 1.595 | 80–90 | – | brown | 1 |
| Whiteite-(CaMnMg) | 14.84 | 6.98 | 10.11 | 112.6 | 1.580 | 1.584 | 1.591 | 81 | + | yellow | 2 |
| Rittmannite | 15.01 | 6.89 | 10.16 | 112.8 | 1.622 | 1.626 | 1.654 | 43 | + | yellow | 3 |
| Jahnsite series | | | | | | | | | | | |
| Jahnsite-(CaMnMg) | 14.94 | 7.14 | 9.93 | 110.2 | 1.640 | 1.658 | 1.670 | large | – | brown | 4 |
| Jahnsite-(CaMnMn) | 14.88 | 7.15 | 9.97 | 109.8 | 1.643 | 1.659 | 1.671 | 80 | – | amber | 5 |
| Keckite | 15.02 | 7.23 | 2 × 9.87 | 110.5 | | 1.692 | 1.699 | | – | brown | 6 |

* References: (1) Moore and Ito (1978). (2) Grice et al. (1989). (3) Marzoni Fecia Di Cossato et al. (1989). (4) Moore (1974). (5) This study. (6) Mücke (1979).

From these data it can be seen that the two series jahnsite and whiteite may be readily distinguished. The Fe³⁺ in the M(3) cation sites of the jahnsite series results in significantly higher refractive indices than does the Al³⁺ in the whiteite series. Also the Fe³⁺ cation, which is larger than the Al³⁺ cation (ionic radius of 0.64 vs. 0.50 Å), causes an increase in the *b* cell dimension of jahnsite relative to that of whiteite, since the M(3) cations form chains parallel to the *b*-axis (Moore and Araki, 1974).

The complexity of water losses for whiteite-(CaMnMg) and jahnsite-(CaMnMn) (Fig. 2) may indicate that the structures can readily be reorganized at lower hydration levels and/or a complexity of H₂O sites in the initial structures. The whiteite-(CaMnMg) thermal data are consistent with the successive formation from the initial hydroxide trihydrate of a hydroxide octahydrate (temperature interval to 300 °C), a hydroxide (300 to 450 °C), and finally an anhydride (450–700 °C).

The H₂O loss for jahnsite-(CaMnMn) is more complex, and there is a general shift to temperatures lower than those observed for whiteite-(CaMnMg). The loss associated with the highest temperature peak (415 °C) cannot be interpreted as solely dehydroxylation, if the general structural formula is valid. Either dehydration is occurring as well, or considerably more OH⁻ is present than the structural formula permits. Alternatively, if the loss associated with the 310 °C peak is taken to represent dehydroxylation (a weight loss consistent with the general structural formula), then breakup of the OH-bearing phosphate sheets of the jahnsite structure (Moore and Araki, 1974) must occur prior to full dehydration.

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