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Dedicated to the memory of
Luciano Ungaretti

A new occurrence of katoite and re-examination of the hydrogrossular group

ORAZIO FERRO[1], ERMANNO GALLI[1], GÁBOR PAPP[2], SIMONA QUARTIERI[3], SÁNDOR SZAKÁLL[4] and GIOVANNA VEZZALINI[1,*]

[1] Dipartimento di Scienze della Terra, via S. Eufemia 19, I-41100 Modena, Italy
* Corresponding author, e-mail: giovanna@unimo.it
[2] Dept. of Mineralogy and Petrology, Hungarian Natural History Museum, Ludovika tér 2, H-1083 Budapest, Hungary
[3] Dipartimento di Scienze della Terra, Salita Sperone 31, I-98166 Messina S. Agata, Italy
[4] Dept. of Mineralogy, Herman Ottó Museum, Kossuth u. 13, H-3525 Miskolc, Hungary

Abstract: A new occurrence of katoite ($Ca_{2.95}Fe_{0.03}Al_{2.03}(SiO_4)_{1.12}(OH)_{7.51}$; a = 12.286) found near Dunabogdány (Hungary), along with its structural refinement is reported here. The crystal-chemical data, the physical properties, and the structure refinement of this new member of the $Ca_3Al_2(SiO_4)_3$–$Ca_3Al_2(O_4H_4)_3$ series indicate the presence of about 37% grossular. The positional disorder of the oxygen atom, a peculiar feature of the hydrogarnet structure, is described here in terms of both anisotropy along the *d*-O vector, and presence of two distinct oxygen sites (unsplit- and split-O models, respectively). The hydrogen atom was localised for both models in the difference Fourier map. The structural features of the katoite from Dunabogdány are compared with those of other hydrogrossulars and with the two end-members "anhydrous" grossular, and Si-free katoite. The results of the unsplit-O model refinement confirm the increase of the tetrahedron volume with the substitution of Si by $4H^+$. The geometry of the coordination polyhedra in the two configurations resulting from the split-O model are also discussed. This second model better describes from the crystallochemical point of view the substitution of Si^{4+} with $4H^+$ in the tetrahedra. However, the tetrahedra of the two dimensions are randomly distributed in the unit cell and hence domains of the two end-member configurations are not expected in katoite structure. This conclusion is also strengthened by the TEM study of katoite from Dunabogdany.**

Key-words: katoite, hydrogrossular, garnet, crystal structure, chemical analysis.

Introduction

The hydrogrossular group can be described as a solid solution between grossular, (Gr) $Ca_3Al_2(SiO_4)_3$ (s.g. Ia-3d, a = 11.845(1)Å; Novak & Gibbs, 1971) and Si-free hydrogrossular $Ca_3Al_2(O_4H_4)_3$ (a = 12.5695(1) Å; Lager *et al*., 1987a). Following the nomenclature proposed by Passaglia & Rinaldi (1984), the minerals of this series with a Gr component ≥ 50% are called hibschites, whereas those with Gr < 50% are called katoites. The same authors state that the distinctive properties of the katoite members are: refractive index n < 1.67, unit cell edge larger than 12.21 Å, presence of the (220) line in the X-ray powder pattern. Structural and crystal-chemical data on natural and synthetic hydrated members of this series are available for: hibschites (Basso *et al.*, 1983; Lager *et al*., 1987b; Armbruster & Lager, 1989), katoite (Passaglia & Rinaldi, 1984; Sacerdoti & Passaglia, 1985; Armbruster & Lager, 1989) and synthetic Si-free hydrogrossular (Cohen-Addad *et al*., 1967; Lager *et al*., 1987a). Minor OH^- substitution is also reported for garnets in the grossular-andradite-almandine-spessartine system (Hsu, 1980; Basso *et al*., 1981; Basso *et al*., 1984a, b; Lager *et al.*, 1989; Armbruster, 1995).

In the hydrogrossular where H substitutes for silicon (in *d* position, site symmetry –4) each oxygen around the tetrahedral void is bonded to one H. As a consequence the *d*-O distance lengthens from 1.641 Å in grossular (Novak & Gibbs, 1971) to 1.950 Å in the silicon-free member (Lager *et al*., 1987a). Because of the random arrangement of SiO_4 and (O_4H_4) tetrahedra in the structure, the space group symmetry is unaffected by the substitution of Si^{4+} with $4H^+$. Moreover this substitution increases the tetrahedron size, but does not change its shape and orientation. As a result, katoite-type oxygens are displaced, relative to grossular-type oxygens, in a direction away from the position *d* along the *d*-O vector. The existence of two O sites separated by about 0.30 Å in garnet-hydrogarnet solid solutions and of an associated high positional disorder were discussed in detail by Armbruster & Lager (1989). These authors, on the basis of a re-examination of the structure of a number of hydrogarnets, evaluated the difference displacement parameters ΔU = U(O)-U(Si) along the tetrahedral *d*-O vector as a func-

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