Si, Al ordering in the double-ring silicate armenite, BaCa$_2$Al$_6$Si$_9$O$_{30}$·2H$_2$O: A single-crystal X-ray and ²⁹Si MAS NMR study

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ABSTRACT

The ²⁹Si MAS NMR spectrum of armenite from Wasenalp (Valais, Switzerland) indicates complete Si, Al ordering. The same chemical shifts (82.3, 95.0, and 101.8 ppm) were also measured for armenite from Rémiigny (Quebec, Canada), however, the intensity ratios of the NMR bands for the latter sample differed. A full sphere of X-ray single-crystal data on an optically homogeneous domain of armenite from Rémiigny was collected on a three-circle diffractometer equipped with a CCD area-detector. The crystal structure was refined in the acentric space group $Pnc\overline{2}$ [$a = 18.660(2)$, $b = 10.697(1)$ $c = 13.874(2)$ Å] to R1 = 3.6% based on 4275 reflections. These results confirm complete Si, Al ordering. Mean Si-O distances range between 1.615 and 1.629 Å; mean Al-O distances between 1.734 and 1.742 Å. Calcium is sevenfold coordinated by six framework O atoms and one H$_2$O molecule. Barium is 12-fold coordinated by framework O atoms. Polarized IR spectra in the region of OH absorptions (between 5700 and 1300 cm$^{-1}$) were recorded on polished slabs of Wasenalp armenite and structurally related milarite from Val Giuf. In general, milarite and armenite show similar anisotropy of H$_2$O related absorptions.

INTRODUCTION

Armenite, BaCa$_2$Al$_6$Si$_9$O$_{30}$·2H$_2$O, named after its first description from the Armen mine, Kongsberg, Norway (Neumann 1941), is a rather rare silicate mineral found in Ba-rich hydrothermal veins or fissures (e.g., Pouliot et al. 1984; Mason 1987; Semenenko et al. 1987; Zak and Obst 1989; Balassone et al. 1989; Senn 1990; Fortey et al. 1991). In hitherto described occurrences armenite displays a complicated twinning pattern and has essentially end-member composition with a constant Si/Al ratio of 9/6.

Armenite possesses six-membered double-rings of tetrahedra and is a member of the milarite-group of minerals (Hawthorne et al. 1991). Among this group, armenite has the most pronounced Al ↔ Si substitution, which may be responsible for a deviation from hexagonal symmetry (Armbruster and Czank 1992) observed for most other members of this group. Previous single-crystal X-ray and TEM studies (Armbruster and Czank 1992; Ferraris et al. 1991) indicated that various armenite modifications with variable degrees of Si, Al ordering give rise to different super-structures. Recently, Winter et al. (1995) studied the hexagonal structure of the high-temperature synthetic double-ring silicate BaMg$_2$Al$_6$Si$_9$O$_{30}$, which has the same Al/Si ratio as armenite but Ca is replaced by Mg and the synthetic compound is anhydrous.

Milarite, a fissure mineral with the simplified formula KNa$_{2-x}$Ca$_x$(Be$_{3-x}$Al)$_4$Si$_{12}$O$_{30}$·nH$_2$O, shows similar anomalous optical properties as armenite (e.g., Černý et al. 1980; Janeczek 1986), which were interpreted to be caused by long range H$_2$O ordering (Armbruster et al. 1989).

Two topologically distinct types of tetrahedra exist in the milarite group of minerals: tetrahedra building the double-ring units (12 T1 pfu) and the ring-connecting tetrahedra (3 T2 pfu), which alternate with edge-sharing CaO$_6$ octahedra to form twelve-membered rings (Fig. 1). In milarite T1 tetrahedra are occupied by Si only, whereas in armenite Si and Al share T1 sites (Armbruster and Czank 1992). The T2 tetrahedra in milarite show a mixed Al, Be occupation (e.g., Černý et al. 1980; Armbruster et al. 1989) and in armenite a mixed Si, Al occupation. O$_2$ connects T1 to six-membered rings, O$_1$ connects the six-membered rings to double-ring units, and O$_3$ connects the double-ring units to T2 tetrahedra thus a tetrahedral framework is formed. Above and below the double-ring units the structural channels are plugged by Ba (armenite) or K (milarite). In armenite (Armbruster and Czank 1992) and milarite (Armbruster et al. 1989) H$_2$O occupies structural interstices (B* sites) close to Ca and increases the Ca coordination from six to seven. Armenite is completely hydrated and has 2 H$_2$O pfu. Milarite has non-stoichiometric H$_2$O K$_2$ pfu and additional Na, K, and Ca may enter the ninefold-coordinated B site, which is 0.7 Å apart from B*.

The cordierite, Mg$_2$Al$_4$Si$_5$O$_{18}$, and beryl, Al$_2$Be$_3$Si$_6$O$_{18}$, structures are closely related to double-ring silicates (e.g., Armbruster et al. 1995). Six-membered single-rings in cordierite and beryl are also connected by additional T sites to form a framework. Unfortunately, a different no-