

Two new members of the rhodesite mero-plesiotype series close to delhayelite and hydrodelhayelite: synthesis and crystal structure

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Abstract: Two new members of the mero-plesiotype rhodesite series ($\text{KCa}_2\text{Na}[\text{Si}_8\text{O}_{19}]\cdot 5\text{H}_2\text{O}$, abbreviated as TR03; a 6.5850, b 23.776, c 7.0250 Å; $Pn2_1m$; and $\text{KNa}_3\text{Sr}[\text{Si}_8\text{O}_{19}]\cdot 4.3\text{H}_2\text{O}$, TR04; a 6.5699, b 23.7225, c 7.0225 Å, β 91.81°; $P2_1/m$) have been hydrothermally synthesized in Teflon-lined autoclaves at 200–230 °C and structurally characterized using X-ray diffraction single-crystal data (Bruker-AXS Smart Apex diffractometer equipped with a CCD area detector, $\text{MoK}\alpha$ radiation). The crystal structures were solved by direct methods and refined to $R = 0.090$ [TR03; 2634 reflections with $I_o > 2\sigma(I_o)$; {010} twinning by merohedry] and $R = 0.062$ [TR04; 4535 reflections with $I_o > 2\sigma(I_o)$]. Both structures are based on a rhodesite-type porous heteropolyhedral framework, where two types of channels (effective width about 3.5 Å in the widest channel) cross the double silicate layer. They show specific “octahedral” O layers that are discussed with particular reference to delhayelite and hydrodelhayelite. TR03 can be considered a Na-bearing hydrodelhayelite; this extra cation resides in the O layer and connects two edge-sharing rows of Ca-octahedra that, instead, are isolated in hydrodelhayelite. A further increase of the number of cations pfu leads to a fully occupied O layer, as found in delhayelite and TR04. The H_2O molecules are hosted both in the channels and in the O layer; bond lengths and Raman spectra show that they are loosely hydrogen bonded. The structural features that support the wide range of chemical compositions found in the rhodesite series are discussed.

Key-words: hydrothermal synthesis, crystal structure, rhodesite series, delhayelite, hydrodelhayelite, twinning by merohedry, layered microporous silicate.

1. Introduction

Minerals and synthetic phases belonging to the rhodesite ($\text{KCa}_2[\text{Si}_8\text{O}_{18}(\text{OH})]\cdot 6\text{H}_2\text{O}$, a 23.416, b 6.555, c 7.050 Å, $Pm\bar{m}$; Hesse *et al.*, 1992) mero-plesiotype series (Ferraris & Gula, 2005) are well-known modular (Ferraris *et al.*, 2008) microporous silicate phases based on a heteropolyhedral framework (Ferraris & Merlino, 2005). The crystal structures of this series (Table 1) are based on a double silicate layer that is formed via corner sharing of two apophyllite-like tetrahedral sheets (Fig. 1). The layer is crossed by eight-membered channels along two different directions that have an effective width (McCusker *et al.*, 2003) of about 3 Å (Fig. 2). The silicate module alternates with different types of “octahedral” (O) layer (Fig. 3). According to the categorization proposed by Makovicky (1997), the rhodesite series is merotypic because the common silicate module alternates with a variable O layer; at the same time, the series is plesiotypic because the ratio between the number of up- and down-pointing

tetrahedra in the apophyllite-like sheets may vary between members of the series and, also, Al can substitute Si (Fig. 1; Ferraris & Gula, 2005).

The rhodesite-type microporous structure shows at the same time layered and heteropolyhedral-framework features. The former aspect allows synthesizing chemically different compounds while keeping constant a module of the structure. Contrary to the porous materials whose framework is based only on tetrahedra (*e.g.*, zeolites), which can be occupied by a limited number of cations, the heteropolyhedral frameworks allow a wider chemical variability, because the higher coordination polyhedra (*e.g.*, octahedra) can host a large variety of cations. The heteropolyhedral porous structures are well represented in the mineral realm (Ferraris & Merlino, 2005) and often were the incentive for the synthesis of new compounds suitable for technological applications [*e.g.*, ion exchange and luminescence due to the presence of rare earth elements (REE) in the framework]. Several synthetic members of the rhodesite series have been described (Rocha & Lin, 2005;