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Towards a revisitation of vesuvianite-group nomenclature: the crystal structure of Ti-rich vesuvianite from Alchuri, Shigar Valley, Pakistan

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Vesuvianite containing 5.85 wt% TiO_2 from an Alpine-cleft-type assemblage outcropped near Alchuri, Shigar Valley, Northern Areas, Pakistan, has been investigated by means of electron microprobe analyses, gas-chromatographic analysis of H_2O, X-ray powder diffraction, single-crystal X-ray structure refinement, ^{27}Al NMR, ^{57}Fe Mössbauer spectroscopy, IR spectroscopy and optical measurements. Tetragonal unit-cell parameters are: a = 15.5326 (2), c = 11.8040 (2) Å, space group $P4/nnc$. The structure was refined to final R_1 = 0.031, wR_2 = 0.057 for 11247 $I > 2\sigma(I)$. A general crystal-chemical formula of studied sample can be written as follows (Z = 2): $^{[8-9]}(Ca_{17.1}Na_{0.9})$ $^{[8]}Ca_{1.0}$ $^{[5]}(Fe^{2+}_{0.44}Fe^{3+}_{0.34}Mg_{0.22})$ $^{[6]}(Al_{3.59}Mg_{0.41})$ $^{[6]}(Al_{4.03}Ti_{2.20}Fe^{3+}_{1.37}Fe^{2+}_{0.40})$ $(Si_{18}O_{68})$ $[(OH)_{5.84}O_{2.83}F_{1.33}]$. The octahedral site $Y2$ is Al-dominant and does not contain transition elements. Another octahedral site $Y3$ is also Al-dominant and contains Fe^{2+}, Fe^{3+} and Ti. The site $Y1$ is split into $Y1a$ and $Y1b$ predominantly occupied by Fe^{2+} and Fe^{3+}, respectively. The role of the $Y1$ site in the diversity of vesuvianite-group minerals is discussed.

1. Introduction

Vesuvianite-group minerals are important components of different contact metamorphic rocks associated with limestones, different regionally metamorphosed rocks, Fe-, Sn- and complex ores related to skarns, as well as rodingites (Deer *et al.*, 1982; Meinert *et al.*, 2005; Rice, 1983). These minerals and their synthetic counterparts are of geological and technological interest because of their specific chemical and physical properties. They are characterized by rather high chemical and thermal stability (Plyusnina & Likhoidov, 1993; Żabiński *et al.*, 1996; Tribaudino & Prencipe, 1999, 2001; Ogorodova *et al.*, 2011; Lai *et al.*, 2013). Owing to a high surface activity (Elmi *et al.*, 2011) these compounds are able to accumulate trace elements from fluids (Fukuyama *et al.*, 2012). Vesuvianite-group minerals are of interest for U–Pb dating of rocks (Romer, 1992), while their synthetic analogues can be considered as potential components of silicate materials for the immobilization of dangerous waste products including toxic and radioactive metals (Li *et al.*, 2009; Malczewski &

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