Structural stability, cation ordering, and local relaxation along the AlNbO$_4$-$\text{Al}_{0.5}\text{Cr}_{0.5}\text{NbO}_4$ join

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ABSTRACT

($\text{Al}_i\text{.},\text{Cr}_i$)$_3^+$Nb$^{5+}$O$_4$ (with $0 \leq x \leq 0.5$) compounds have been investigated through the combination of X-ray powder diffraction (XRPD) and electronic absorption spectroscopy (EAS). In spite of the natural occurrence of AlTaO$_4$, the lack of a mineral with composition AlNbO$_4$ contrasts with the strong geochemical affinity between Nb and Ta elements. Rietveld refinements of XRPD data showed that the effective coordination numbers of the two non-equivalent octahedral sites ($M1$ and $M2$) in the AlNbO$_4$ structure are much lower than expected, especially the one mainly occupied by Nb. This is in agreement with the very low crystal field strength values ($10Dq$) found by EAS for Cr$^{3+}$ replacing Al at site $M2$. These findings imply that an unfavorable bonding situation occurs for Nb, Al, and Cr ions in the AlNbO$_4$ structure, which can be regarded as substantially strained compared to AlTaO$_4$, thus explaining the lack of a natural AlNbO$_4$ isomorph. The observed long local Cr–O distances (low $10Dq$) reveal that the AlNbO$_4$ lattice is not relaxed as a consequence of the Cr–Al substitution (the relaxation coefficient $\epsilon$ is close to zero) and the AlNbO$_4$ structure appears to follow the Vegard’s law. This is due to the fact that the Cr$^{3+}$ for Al$^{3+}$ substitution, for the limited range of solid solution (up to 0.2 apfu at site $M2$), does not induce any additional octahedral strain in a lattice already significantly strained.

Keywords: Alumoniobite, X-ray powder diffraction, electronic absorption spectroscopy, structural relaxation, cation ordering

INTRODUCTION

The niobium and tantalum elements mainly occur in nature within accessory minerals in granitic pegmatites. On account of their close chemical affinity, these two elements typically give rise to isomorphous series of oxides. The most widespread and abundant family is that of columbite–tantalite minerals ($AB_2O_6$, with $A = \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+}$ and $B = \text{Nb}^{5+}, \text{Ta}^{5+}$), but many other niobium- and tantalum-bearing groups exist, such as pyrochlores, fergusonites, euxenites, asechinylites, and others. On the other hand, contrary to the natural occurrence of the orthorhombic alumoniobite, AlTaO$_4$ (Voloshin et al. 1981; Ercit et al. 1992), only synthetic materials are reported for niobium compounds with the same stoichiometry, therefore a niobium isomorph of AlTaO$_4$ does not occur in nature, to the best of our knowledge.

Ternary oxides with general formula $M^+\text{Nb}^{5+}O_4$ (where $M = \text{Al, Cr, Fe, and Ga}$) are octahedral structures characterized by a large variety of polymorphs based upon sequences of closest-packed oxygen atoms. Isostructural AlNbO$_4$ and GaNbO$_4$ crystallize in the monoclinic $C2/m$ space group. Their crystal structure, originated from the ReO$_4$-type structure by means of crystallographic shear operations, is made by sub-units of four distorted edge-sharing MO$_6$ octahedra (see Fig. 1). These sub-units are connected to each other by sharing edges along the $a$ and $b$ directions and corners parallel to the $c$ axis, forming a three-dimensional network (Pedersen 1962; Morosini 1965). The structure was initially described with a fully ordered distribution of Al and Nb over two non-equivalent octahedra, $M1$ and $M2$, respectively (Pedersen 1962). Later, the structure of AlNbO$_4$ was refined revealing a partially disordered occupation of the metal sites (Efremov et al. 1981; Greis et al. 1996) with about 20% of inversion degree between the two octahedra (i.e., Al$_{0.3}$Nb$_{0.7}$O$_6$ and Al$_{0.5}$Nb$_{0.5}$O$_6$ for $M1$ and $M2$ sites, respectively).

At variance with AlNbO$_4$, albeit having the same stoichiometry, CrNbO$_4$ has been reported as crystallizing with a rutile-type structure (space group $P4/mmm$) with a disordered distribution of Cr and Nb over the edge-sharing octahedral chains parallel to the $c$ axis and corner connected in the (001) plane (Christensen et al. 1976; Petersen and Müller-Buschbaum 1992). This model has been recently questioned by Smirnov and Zvereva (2003) who suggested that a cation ordering, with non-equivalent octahedral chains connected to each other by corner-sharing as in the AIWO$_4$-type structure (space group $C2/m$), occurs in CrNbO$_4$. Such an octahedral arrangement would ensure the maximal distance between the same and equally charged cations, limiting the probability of charged cluster formation in the crystal. An even more complex situation is delineated for the FeNbO$_4$ compound, which crystallizes with the monoclinic wolframite-type structure (space group $P2_1/c$) stable up to 1385 K. At higher temperatures, it evolves through three structural modifications with increasing temperature. Between 1385 and 1653 K, the wolframite-type structure, based on zigzag chains of edge-sharing octahedra, is modified into an orthorhombic $\alpha$-PbO$_2$-type phase, in which the separate chains of the former polymorph become identical. At higher temperature, the structure undergoes a further change to a rutile-type polymorph, taking the polyhedral arrangement of the CrNbO$_4$ compound, and finally to the monoclinic AlNbO$_4$-type structure (Tabero 2007 and literature therein).