

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

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ABSTRACT

$(\text{Al}_{1-x}\text{Cr}_x)^{3+}\text{Nb}^{5+}\text{O}_4$ (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 ϵ 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: Alumiobite, X-ray powder diffraction, electronic absorption spectroscopy, structural relaxation, cation ordering