

Combined neutron and X-ray diffraction determination of disorder in doped zirconolite-2M

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ABSTRACT

Zirconolites based on the replacement of Ti^{4+} with equimolar amounts of Nb^{5+} and Fe^{3+} , $\text{CaZrTi}_{2-2x}\text{Nb}_x\text{Fe}_x\text{O}_7$, have been jointly refined using high-resolution neutron powder diffraction and resonant X-ray powder diffraction data, with extra information provided from ^{57}Fe Mössbauer spectroscopy, to determine cation disorder. The results indicate that the $\text{CaZrTi}_{2-2x}\text{Nb}_x\text{Fe}_x\text{O}_7$ series adopts the zirconolite-2M polytype across the range, with the replacement of Ti^{4+} by Fe^{3+} and Nb^{5+} located within the hexagonal tungsten bronze (HTB) layers. Mössbauer spectroscopy shows that Fe^{3+} preferentially fills the Ti split (C2) site, with secondary filling of the C1 site and no observable occupancy of the C3 site. This has been confirmed by neutron and resonant X-ray diffraction. Niobium has been found to occupy both the C1 and C3 sites with no evidence for occupancy of the C2 site.

Keywords: Zirconolite, resonant X-ray diffraction, neutron diffraction, Mössbauer