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Refinement of the Mangan-neptunite Crystal Structure

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Abstract—The crystal structure of mangan-neptunite, a manganese analogue of neptunite, has been refined in two space groups (*Cc* and *C2/c*). The mineral is monoclinic, with the correct space group *Cc*; the unit-cell dimensions are: a = 16.4821(6), b = 12.5195(4), c = 10.0292(3) Å, β = 115.474(1)°, and V = 1868.31 Å^3. The crystal structure has been refined to R_1 = 0.0307 (wR_2 = 0.0901) on the basis of 4892 observed reflections with $|F_{hkl}| \geq 4\sigma|F_{hkl}|$. The most plausible acentric model is caused by the Ti- and (Fe, Mn, Mg)-ordering in the structure. Ti-octahedrons are strongly distorted and consist of short bond Ti–O (1.7 Å), one long bond (2.2 Å), and four equal bonds (2.0 Å). Fe-octahedrons are regularly shaped, with all Fe–O bonds being approximately identical.

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The first publications on the structure of neptunite were published in the mid-1960s (Borisov et al., 1965; Canniloe et al., 1966). The first structural investigations were carried out using the photomethod and the visual estimation of the maximum reflection intensity. Neptunite was determined as a centrosymmetrical mineral, with the space group *C2/c* [R = 11% (Cannilo et al., 1966)]. During these studies, neptunite crystals revealed a piezoelectric effect that is probable for acentric structures only. Therefore, it was concluded that additional studies of the neptunite structure were necessary to provide insight into the probable absence of the center of symmetry (space group *Cc*) originating from the ordering in the octahedral chains.

More detailed and comprehensive investigations and the refinement of the neptunite structure were carried out with temperature-dependent neutron- and X-ray single-crystal structural methods and Mössbauer spectroscopy (Kunz et al., 1991). These structural studies established that the mineral is actually acentric and attributed to space group *Cc* owing to the ordering of Ti and (Fe,Mn,Mg) in octahedral sites. In this paper, we present the data obtained from the structural investigations of mangan-neptunite, a manganese analogue of neptunite. The studied samples of mangan-neptunite were taken from a hydrothermal vein exposed at Mt. Kaskasnyuncharr, the Khibiny alkaline pluton (Yakovenchuk et al., 2005). The selected single crystal was mounted in a SMART APEX diffractometer equipped with a CCD flat detector. The unit-cell dimensions were determined and refined using the least-squares method. The mineral is monoclinic, and the space group is *Cc*; the unit-cell dimensions are a = 16.4821(6), b = 12.5195(4), c = 10.0292(3) Å, β = 115.474(1)°, and V = 1868.31 Å^3. A correction for the absorption was introduced taking into account the crystal habit. Determination of the structure has been carried out with a Wingx32 program package. The structure has been solved using direct methods and refined to R_1 = 0.0307 (wR_2 = 0.0901) on the basis of 4892 observed reflections with $|F_{hkl}| \geq 4\sigma|F_{hkl}|$. The final model included the coordinates and an equivalent atomic displacement for all atoms (Table 1). Interatomic distances are given in Table 2. In addition to the refinement of the mangan-neptunite structure in space group *Cc*, for comparison, we refined this structure in space group *C2/c* to R_1 = 0.0710 (wR_2 = 0.3164) on the basis of 3647 observed reflections with $|F_{hkl}| \geq 4\sigma|F_{hkl}|$. The comparison clearly indicates that the acentric model deduced from Ti- and (Fe, Mn, Mg)-ordering is more appropriate for both mangan-neptunite and neptunite structure (Kunz et al., 1991). The crystallochemical formula of the mineral is $KNa_2Li(Fe,Mn)_2Ti_2(Si_8O_{24})$.

A three-dimensional Si–O framework consisting of vertice-sharing SiO_4-tetrahedrons running along the [110] and $[\bar{1}10]$ directions and bonded to each other along [001] is the basis of the structure. Such a three-dimensional Si–O framework is bound in mangan-neptunite with a similar framework consisting of chains of edge-sharing octahedrons TiO_6 and $(Fe,Mn,Mg)O_6$ also running along [110] and $[\bar{1}10]$ and bonded to each other along [001] (Fig. 1). The ordering of cation sites Ti and (Fe, Mn, Mg) in both neptunite and mangan-neptunite is worth noting. Two octahedral Ti sites and two octahedral (Fe,Mn,Mg) sites, which alternate within chain as shown in Fig. 1, are recognized in the

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Table 1. Atomic coordinates and equivalent atomic displacement in the structure of mangan-neptunite

Atom	x	y	z	$U_{eq} \times 100$, Å^2
Si1	0.14640(6)	0.40807(7)	0.0626(1)	0.61(2)
Si2	0.85522(6)	0.59502(7)	−0.0595(1)	0.65(2)
Si3	0.52338(6)	0.22472(7)	0.0836(1)	0.70(2)
Si4	0.47738(6)	0.77184(7)	−0.0855(1)	0.62(2)
Si5	0.76903(6)	0.47365(7)	0.1105(1)	0.65(2)
Si6	0.22894(6)	0.52406(7)	0.8915(1)	0.65(2)
Si7	0.89388(6)	0.15208(7)	0.0790(1)	0.69(2)
Si8	0.10519(6)	0.85221(7)	−0.0834(1)	0.64(2)
Ti1	0.34233(3)	0.3264(5)	0.10313(6)	0.62(2)
Ti2	0.08716(4)	0.05326(4)	0.11462(6)	0.64(1)
Fe1*	0.66082(3)	0.68390(5)	−0.09788(5)	1.18(1)
Fe2*	−0.08942(3)	−0.06065(4)	0.88539(6)	1.22(1)
Na1	0.2654(1)	0.1974(1)	0.3127(2)	2.10(4)
Na2	0.7368(1)	0.8012(1)	0.6971(2)	1.70(3)
K1	−0.00131(8)	0.42070(6)	0.2497(1)	2.34(1)
Li1	0.5007(6)	0.4349(4)	0.249(1)	1.50(9)
O1	0.9580(2)	0.0530(2)	0.0768(3)	0.74(4)
O2	0.0502(2)	−0.0437(2)	−0.0702(3)	0.78(4)
O3	0.4558(2)	0.3229(2)	0.0729(3)	0.76(4)
O4	0.5418(2)	0.6704(2)	−0.0658(3)	0.90(4)
O5	0.1086(2)	0.1672(2)	0.2606(3)	0.95(4)
O6	0.8878(2)	0.8261(2)	0.7290(3)	1.24(5)
O7	0.3705(2)	0.4295(2)	0.2227(3)	1.05(4)
O8	0.6216(2)	0.5498(2)	0.7383(3)	1.15(4)
O9	0.2052(2)	0.0727(2)	0.0992(3)	0.87(4)
O10	0.7901(2)	−0.0801(2)	−0.0894(3)	0.87(4)
O11	0.7116(2)	0.3650(2)	0.0386(3)	0.97(4)
O12	0.2900(2)	0.6307(2)	0.0500(3)	1.03(4)
O13	0.2141(2)	0.3104(2)	0.0800(3)	0.77(4)
O14	0.7961(2)	0.6972(2)	0.0649(3)	0.86(4)
O15	0.8319(2)	0.4954(2)	0.0236(3)	0.94(4)
O16	0.1672(2)	0.5105(2)	−0.0187(3)	0.93(4)
O17	0.1586(2)	0.4513(2)	0.2237(3)	0.99(4)
O18	0.8385(2)	0.5513(2)	0.7784(3)	1.02(4)
O19	0.3968(2)	0.2114(2)	0.2511(3)	1.02(4)
O20	0.6042(2)	0.7944(2)	0.7408(3)	1.18(5)
O21	0.4628(2)	0.1158(2)	0.0223(3)	0.92(4)
O22	0.5403(2)	0.8791(2)	−0.0266(3)	0.87(4)
O23	0.9252(2)	0.2609(2)	0.0225(3)	0.92(4)
O24	0.0684(2)	0.7458(2)	−0.0341(3)	1.04(4)

* Fe sites are occupied by Fe, Mn, and Mg.

structure. Ti-octahedrons are strongly distorted: the length of one Ti–O bond is about 1.7 Å, the second, about 2.2 Å; the four other bonds are about 2.0 Å long (Fig. 2). In contrast, Fe octahedrons are regularly shaped with approximately equal Fe–O bonds. This facilitates distinguishing Ti and (Fe,Mn,Mg) sites and

Table 2. Interatomic distances Å in the structure of mangan-neptunite

Si1–O13	1.613(3)	Si8–O5	1.609(3)	Li1–O7	2.048(9)
Si1–O22	1.626(3)	Si8–O2	1.624(2)	Li1–O8	2.051(9)
Si1–O17	1.632(3)	Si8–O24	1.627(3)	Li1–O2	2.128(9)
Si1–O16	1.634(2)	SiS–O11	1.662(3)	Li1–O4	2.135(9)
⟨Si1–O⟩	1.626	⟨Si8–O⟩	1.630	Li1–O3	2.125(9)
				Li1–O1	2.151(9)
Si2–O14	1.595(2)	Ti1–O7	1.712(2)	⟨Li1–O⟩	2.106
Si2–O21	1.622(3)	Ti1–O19	1.958(3)		
Si2–O18	1.622(3)	Ti1–O3	2.018(3)	Na1–O5	2.437(3)
Si2–O15	1.635(2)	Ti1–O13	2.032(3)	Na1–O9	2.485(3)
⟨Si2–O⟩	1.618	Ti1–O10	2.120(2)	Na1–O12	2.493(3)
		Ti1–O14	2.195(2)	Na1–O19	2.500(3)
Si3–O20	1.585(3)	⟨Ti1–O⟩	2.006	Na1–O13	2.542(3)
Si3–O3	1.631(2)			Na1–O23	2.621(3)
Si3–O21	1.645(2)	Ti2–O8	1.709(2)	Na1–O11	2.874(3)
Si3–O24	1.663(3)	Ti2–O5	1.964(2)	⟨Na1–O⟩	2.565
⟨Si3–O⟩	1.631	Ti2–O1	1.996(3)		
		Ti2–O9	2.032(3)	Na2–O6	2.389(3)
Si4–O4	1.612(3)	Ti2–O2	2.076(2)	Na2–O20	2.409(3)
Si4–O19	1.620(3)	Ti2–O4	2.195(3)	Na2–O10	2.439(3)
Si4–O22	1.643(2)	⟨Ti2–O⟩	1.995	Na2–O14	2.518(3)
Si4–O23	1.653(3)			Na2–O11	2.541(3)
⟨Si4–O⟩	1.632	Fe1–O20	2.026(3)	Na2–O24	2.810(3)
		Fe1–O14	2.115(3)	⟨Na1–O⟩	2.518
Si5–O9	1.599(3)	Fe1–O4	2.127(3)		
Si5–O18	1.609(3)	Fe1–O8	2.241(2)	K1–O17	2.783(3)
Si5–O11	1.636(2)	Fe1–O13	2.261(2)	K1–O18	2.798(3)
Si5–O15	1.638(3)	Fe1–O9	2.266(2)	K1–O24	2.868(3)
⟨Si5–O⟩	1.620	⟨Fe1–O⟩	2.173	K1–O15	2.866(3)
				K1–O23	2.878(3)
Si6–O10	1.608(3)	Fe2–O6	2.027(3)	K1–O16	2.882(3)
Si6–O17	1.611(3)	Fe2–O10	2.120(3)	K1–O21	3.071(3)
Si6–O12	1.621(3)	Fe2–O2	2.158(3)	K1–O22	3.171(3)
Si6–O16	1.631(3)	Fe2–O7	2.206(2)	K1–O21	3.218(2)
⟨Si6–O⟩	1.618	Fe2–O3	2.239(2)	K1–O22	3.235(2)
		Fe2–O1	2.243(2)	⟨K1–O⟩	2.977
Si7–O6	1.574(3)	⟨Fe2–O⟩	2.166		
Si7–O1	1.636(3)				
Si7–O23	1.642(2)				
Si7–O12	1.663(3)				
⟨Si7–O⟩	1.629				

indicates their ordering in the structure (Table 2). The distorted Ti-octahedrons are also recognized in Ti-bearing minerals, e.g., in titanite (Speer and Gibbs, 1976), tetragonal $BaTiO_3$ (Harada et al., 1970), and brookite (Meagher and Lager, 1979). Occasionally, such irregular distribution of Ti–O bond lengths leads to the fivefold coordination of titanium as, for instance, in fresnoite (Moore and Louisnathan, 1969).

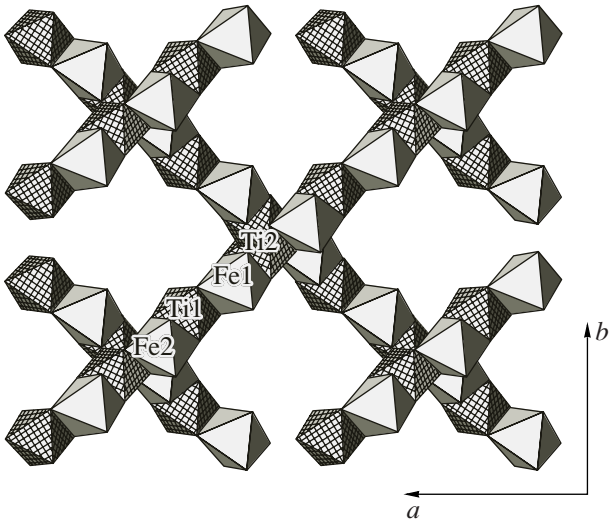

Fig. 1. Octahedral TiO_6–(Fe,Mn,Mg)O_6 chains running along the [110] and [$\bar{1}$10] directions.

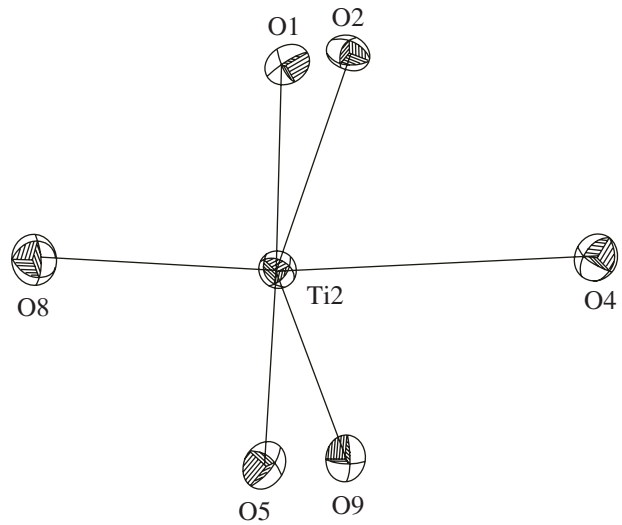

Fig. 2. Image of the Ti2 distorted octahedron: short bond Ti2–O8 (1.7 Å), long bond Ti2–O4 (2.2 Å), and four equal bonds Ti2–O1, Ti2–O2, Ti2–O5, and Ti2–O9 (2.0 Å).

The out-of-framework cations (Li1), (Na1, Na2), and (K1) are present in the structure in addition to the above-described framework atoms.

Thus, the refinement of the mangan-neptunite structure showed that the ordering of octahedral Ti and (Fe,Mn,Mg) sites resulted in the absence of the center of symmetry in the mineral that is described in space group *Cc*.

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