INTRODUCTION

Tisinalite, a new mineral of the lovozerite group, was described by Yu.L. Kapustin et al. [1] in 1980. This mineral was discovered in the hyperagpaitic pegmatites from the Khibiny alkaline massif (the Kola Peninsula). The formula \( \text{Na}_3\text{H}_3(\text{Mn,Ca,Fe})\text{TiSi}_6(\text{O,OH})_{18} \cdot \text{H}_2\text{O} \) attributed to this mineral is still indicated in the mineralogical nomenclature [2]. It has been established that this mineral belongs to the trigonal system, but its crystal structure and space group remain unknown. Tisinalite was also found in the Lovozero alkaline massif adjacent to the Khibiny massif. Initially, the latter specimen was characterized under the conditional name hydrokazakovite [3]. In the Khibiny massif, tisinalite occurs very rarely, whereas in the Lovozero massif, it is often observed as an accessory mineral of weakly altered hyperagpaitic rocks and pegmatites. According to A.P. Khomyakov [3], tisinalite cannot crystallize alone; it is generated as a product of the transformation of kazakovite \( \text{Na}_6(\text{Mn,Ca})\text{TiSi}_6\text{O}_{18} \) when the alkalinity of the medium decreases. No facts that contradict this hypothesis are presently known. This transformation may lead to a substantial change in the symmetry because of the different arrangement of large cations, water molecules, and vacancies in the structures of the parent phases and newly formed minerals [5].

The tisinalite sample used for X-ray diffraction study was found in hyperagpaitic pegmatoid naujaites (poikilitic nepheline–sodalite syenites) from the Alluaiv mountain in the Lovozero massif. The tisinalite that replaces kazakovite forms mustard-yellow grains up to 1 cm in diameter. In cavities, tisinalite was found as cuboidal crystals up to 2 mm in diameter. This mineral occurs in association with aegirine, eudyalite, lamprophyllite, serandite, parakeldyshite, lomonsovite, etc. Tisinalite is substantially enriched with Zr and Nb. Its cation composition determined by electron probe microanalysis is as follows: Na, 10.07; CaO, 1.07; MnO, 5.86; FeO, 1.99; CeO, 0.17; SiO, 59.37; TiO, 6.38; ZrO, 3.06; NbO, 3.48; and the sum is 91.45 wt %. The empirical formula calculated for Si\(_6\)(O,OH)\(_{18}\) is \( (\text{Na}_{1.97}\text{Ce}_{0.01})\Sigma_{1.98}(\text{Mn}_{0.50}\text{Ca}_{0.12})\Sigma_{0.62}(\text{Ti}_{0.49}\text{Nb}_{0.15}\text{Zr}_{0.15} \).
Fe$_{0.15}^{3+}$Si$_6$O$_{18}$[O$_{13.05}$(OH)$_{1.95}$]$_{18}$. According to IR spectroscopy data, this mineral contains a considerable amount of OH groups in the absence of water molecules and free H$_2^+$ ions [6].

A great diversity of mineral species in the lovozerite group is associated with the fact that all the cation positions (except for the positions of the Si$^{4+}$ cations tetrahedrally coordinated with O atoms) can be occupied differently or remain vacant. This fact accounts for both variations in the symmetry of the crystal structures of lovozerite-like compounds and the difference in their unit-cell parameters. The lovozerite structure type is based on pseudocubic blocks (with each one containing one lovozerite-type [Si$_6$O$_{18}$] ring) with the parameter $a = 7.5$ Å and the general formula $A_1B_1C_3M[Si_6O_{18}]$. In this structure type, cations occupy the following strictly particular positions. The $M$ positions in the vertices of the pseudocubic parent unit cell are occupied by Zr, Ti, and Fe$^{3+}$; the $A$ and $B$ positions in the midpoints of the edges and centers of the faces of the parent unit cell are occupied by Na and H$_2$O, respectively; and Mn, Ca, and Na are located in the C positions corresponding to the centers of two octants devoid of the Si$^{4+}$ cations and located on a single threefold axis of the parent unit cell (Fig. 1).

**EXPERIMENTAL. SOLUTION AND REFINEMENT OF STRUCTURE**

The parameters and symmetry of the trigonal unit cell ($a = 10.036$ Å, $c = 12.876$ Å) were refined on an automated single-crystal SYNTEX $P\overline{1}$ diffractometer. The X-ray diffraction data were collected on the same diffractometer. The principal details of X-ray data collection are given in Table 1. The nonequivalent intensities of pairs of the $hkl$ and $khl$ reflections and the presence of a small number of weak (but more intense than $3\sigma(I)$) reflections not satisfying the rule of systematic extinction $-h + k + l = 3n$ indicate two possible space groups, $P3$ and $P\overline{3}$. All the computations were made with the use of the SHELX97 program package [7].

At the first stage, we used the atomic coordinates of lovozerite proceeding from the similarity in composition, symmetry, and unit-cell parameters and considering the presence of the $R$ pseudotranslation. These coordinates were refined within the centrosymmetric space group $R3$ to the final reliability factor $R_{hkl} = 0.1147$ (anisotropic refinement) [5] and then were used as the starting model for the structure determination. Taking into account the high $R_{hkl}$ factor and a substantial scatter in the Si–O distances in the tetrahedra, we rejected the above space group and performed further computations within the primitive trigonal unit cell (sp. gr. $P3$). The atomic coordinates modified to sp. gr. $P3$ were refined anisotropically by the least-squares method to $R_{hkl} = 0.0523$.

Analysis of the resulting model of the tisinalite structure revealed the presence of a center of inversion, which was obeyed by all the atoms including those in the $C$ position. By contrast, the latter position is the only position that violates the centrosymmetricity of the lovozerite structure. The anisotropic refinement of the tisinalite structure within the centrosymmetric space group $P\overline{3}$ converged to the reliability factor $R_{hkl} = 0.0565$ and gave reliable structural parameters. The final coordinates of the basis atoms are given in Table 2. The extended and simplified crystallochemical formulas of tisinalite are as follows ($Z = 3$, $\rho_{\text{calc.}} = 2.62$ g/cm$^3$): (Na$_{2.1}^{2+}$Ca$_{0.1}^{2+}$)[Mn$_{0.2}^{2+}$Fe$_{0.15}^{3+}$]$_2$(Ti$_{0.5}$Zr$_{0.15}$Nb$_{0.15}$]$\cdot$(Na$_{2}^{+}$Ca$_{0.1}^{+}$OH)$_{1.95}$.

**Table 1. Characteristics of X-ray diffraction study of tisinalite**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Sp. gr.</td>
<td>$P\overline{3}$</td>
</tr>
<tr>
<td>Unit-cell parameters, Å</td>
<td>$a = 10.036(5)$, $c = 12.876(9)$, $V = 1123(1)$ (Å$^3$)</td>
</tr>
<tr>
<td>Number of formula units (Z)</td>
<td>3</td>
</tr>
<tr>
<td>$\rho_{\text{calc.}}$, g/cm$^3$</td>
<td>2.62</td>
</tr>
<tr>
<td>Linear crystal dimensions</td>
<td>0.300 × 0.250 × 0.200 mm</td>
</tr>
<tr>
<td>Automated single-crystal diffractometer</td>
<td>SYNTAX $P\overline{1}$</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoK$_\alpha$</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Graphite</td>
</tr>
<tr>
<td>Scanning technique</td>
<td>$29 : \theta$</td>
</tr>
<tr>
<td>Minimum and maximum $\sin \theta/\lambda$</td>
<td>0.039, 1.064</td>
</tr>
<tr>
<td>Scan rate</td>
<td>4–24 deg/min</td>
</tr>
<tr>
<td>Scan ranges</td>
<td>$0 \leq h \leq 17$, $-19 \leq k \leq 16$, $0 \leq l \leq 24$</td>
</tr>
<tr>
<td>Total number of measured reflections</td>
<td>1616</td>
</tr>
<tr>
<td>Number of independent reflections with $I &gt; 2\sigma(I)$</td>
<td>951</td>
</tr>
<tr>
<td>$R_{\text{int}}$</td>
<td>0.0983</td>
</tr>
<tr>
<td>Program used in computations</td>
<td>SHELX97</td>
</tr>
<tr>
<td>Reliability factor:</td>
<td>$R_{hkl}$ (anisotropic refinement)</td>
</tr>
<tr>
<td>$wR(F^2)$</td>
<td>0.1525</td>
</tr>
<tr>
<td>Weighting scheme in least-squares refinement</td>
<td>$w = 1/[\theta^2(F^2) + (0.0645P)^2 + $</td>
</tr>
<tr>
<td>$\Delta \rho_{\text{max}}$, e/Å$^{-3}$</td>
<td>0.64</td>
</tr>
<tr>
<td>$\Delta \rho_{\text{min}}$, e/Å$^{-3}$</td>
<td>-0.47</td>
</tr>
</tbody>
</table>

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