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Structure and morphology peculiarities of $Bi_{24}(Si,M)_2O_{40}$ (M = Mn, V) with sillenite structure

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Single crystals in the form of cubes, tetrahedra or combinations of cubes and tetrahedra with sillenite structure in the Bi_2O_3–SiO_2–MnO_2 system, as well as bulk crystals ($Bi_{24}Ge_2O_{40}$ used as a seed crystal) in the Bi_2O_3–SiO_2–V_2O_5 system, have been grown by the hydrothermal method. The results of the crystal chemical analysis by X-ray diffraction, together with the formal charges of the cations calculated by the bond-valence method, allowed establishing the formation of phases of the general compositions $Bi_{24}(Si,Mn)_2O_{40}$ and $Bi_{24}(Si,Bi,Mn)_2O_{40}$ with Bi^{3+}, Si^{4+}, and Mn^{4+} ions, and $Bi_{24}(Si,Bi,V)_2O_{40}$ with Bi^{3+}, Si^{4+}, V^{4+}, and V^{5+} ions. It was found that the phases of refined compositions $Bi_{24}(Si^{4+}{}_{0.9(1)}Mn^{4+}{}_{1.1})O_{40}$, $Bi_{24}(Si^{4+}{}_{0.04}Bi^{3+}{}_{0.60}Mn^{4+}{}_{1.36})(O_{39.70}\square_{0.30})$, $Bi_{24}(Si^{4+}{}_{0.17(1)}Bi^{3+}{}_{0.01}Mn^{4+}{}_{1.82})(O_{39.93(5)}\square_{0.07})$, $Bi_{24}(Si^{4+}{}_{1.160(6)}Bi^{3+}{}_{0.430}(V^{4+},V^{5+})_{0.410})(O_{39.970(20)}\square_{0.030})$, and $Bi_{24}(Si^{4+}{}_{1.150(6)}Bi^{3+}{}_{0.452}V^{5+}{}_{0.398})(O_{39.930(20)}\square_{0.070})$ crystallize in space group *P*23, in contrast to $Bi_{24}(Si^{4+}{}_{1.1}Bi^{3+}{}_{0.1}Mn^{4+}{}_{0.8})(O_{39.95}\square_{0.05})$ and $Bi_{24}(Si^{4+}{}_{0.58}Bi^{3+}{}_{0.02}Mn^{4+}{}_{1.4})(O_{39.99}\square_{0.01})$, which adopt space group *I*23. The lower symmetry can be explained by a kinetic phase transition of order-disorder type associated with peculiarities of the structure (different atoms in the same crystallographic site) and growth conditions. The crystals with a combination of cubes and tetrahedra (initial charge $Na_2SiO_3 \cdot 9H_2O : Mn(NO_3)_2 \cdot 6H_2O = 1:1$) have space group *I*23, whereas the crystals with cube ($Na_2SiO_3 \cdot 9H_2O : Mn(NO_3)_2 \cdot 6H_2O > 1$) or tetrahedron ($Na_2SiO_3 \cdot 9H_2O : Mn(NO_3)_2 \cdot 6H_2O < 1$) habit crystallize in space groups *I*23 and *P*23.

Sillenites / Composition / Crystal structure

Introduction

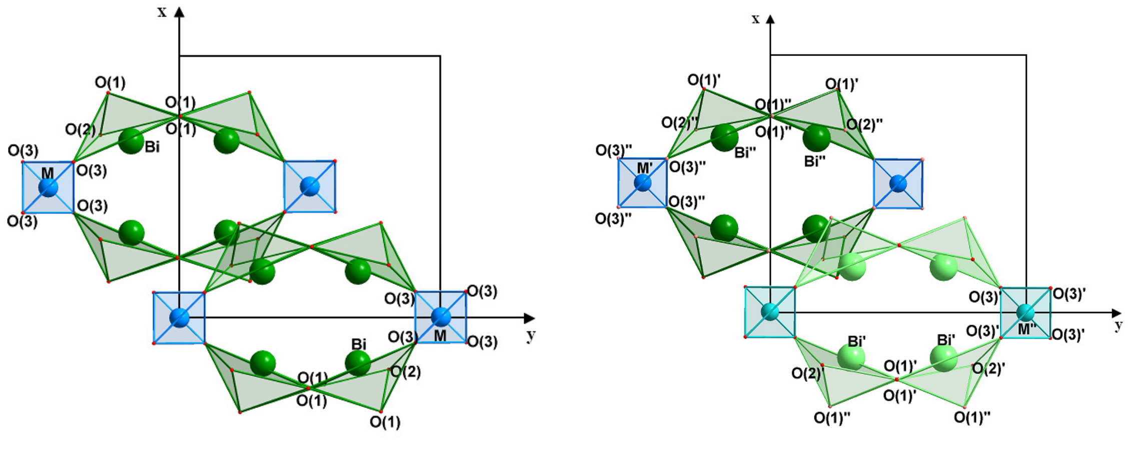
The members of the sillenite family, nowadays known as the phases $Bi_{24}M_2O_{40\pm\delta}$ and solid solutions $Bi_{24}(M'_xM''_{1-x})_2O_{40\pm\delta}$ (where M,M',M'' are cations with different formal charges in tetrahedral coordination), crystallize in space group *I*23 ($Z = 1$) [1,2] (Fig. 1a). These materials are of interest due to photoconductivity, piezo- and electrooptical effects and photorefractive properties. The physical properties depend on the cations in the tetrahedral site and their formal charge (FC).

The presence in tetrahedral sites of cations with different crystal chemical properties (dimension, electronegativity, cation FC) can lead to a kinetic phase transition of order-disorder type [3]. The ordering depends on structure peculiarities, properties of the components, and the method and conditions of preparation of the samples. There exists according to our knowledge no information about similar phenomena for sillenites.

The aim of this paper was to determine the composition and structure of sillenites in the Bi_2O_3–SiO_2–MnO_2 and Bi_2O_3–SiO_2–V_2O_5 systems. Structure refinements have been reported for some compositions in these systems: $Bi_{24}Si_{1.99}Mn_{0.01}O_{40}$ (a = 10.109(1) Å) [4], $Bi_{24}Si_2O_{40}$ (a = 10.10433(5) Å) [5], $Bi_{24}Mn_2O_{40}$ (a = 10.206(1) Å) [6], $Bi_{24}(V^{5+}{}_{1.78}Bi^{3+}{}_{0.06}\square_{0.16})O_{40.54}$ (a = 10.247(8) Å) [2], and $Bi^{3+}{}_{24}[(V^{5+}O_4)(Bi^{3+}O_4)]O_{32}$ (a = 10.222(4) Å) [7].

Experimental

All the crystals in the Bi_2O_3–SiO_2–MnO_2 and Bi_2O_3–SiO_2–V_2O_5 systems were grown by hydrothermal synthesis with initial charge compositions $NaBiO_3$ + $Na_2SiO_3 \cdot 9H_2O$ +



a b

Fig. 1 Arrangement of polyhedra in sillenites: space group $I23$ (a), space group $P23$ (b).

Table 1 Characterization of investigated crystals in the Bi_2O_3–SiO_2–M_xO_y (M = Mn, V) systems.

Sample	Refined composition, reliability factors R^a, D (%); $FC_{calc.}/FC_{exp}$	Space group	Morphology/ color	Cell parameter a (Å)
1	$Bi_{24}(Si^{4+}{}_{1.7(1)}Bi^{3+}{}_{0.1}Mn^{4+}{}_{0.2})(O_{39.95(2)}\square_{0.05})$ $R_1 = 11.04$, $wR_2 = 30.64$; $D = 3.9$; $FC_{calc.}/FC_{exp} = 3.3(6)/3.95$	$I23^b$	tetrahedron/ dark green	10.138(3)
2	$Bi_{24}(Si^{4+}{}_{1.1}Bi^{3+}{}_{0.1}Mn^{4+}{}_{0.8})(O_{39.95}\square_{0.05})$ $R_1 = 3.74$, $wR_2 = 3.95$; $D = 3.5$; $FC_{calc.}/FC_{exp.} = 3.5(3)/3.95$	$I23$	cube+ tetrahedron/ dark green	10.1456(1)
3	$Bi_{24}(Si^{4+}{}_{0.9(1)}Mn^{4+}{}_{1.1})O_{40}$ $R_1 = 4.13$, $wR_2 = 4.52$; $D = 3.6$; $FC_{calc.}/FC_{exp\ .} = 4.2(1)/4$	$P23$	cube/ dark green	10.1287(1)
4	$Bi_{24}(Si^{4+}{}_{0.04}Bi^{3+}{}_{0.60}Mn^{4+}{}_{1.36})(O_{39.70}\square_{0.30})$ $R_1 = 4.00$, $wR_2 = 4.55$; $D = 4.5$; $FC_{calc.}/FC_{exp} = 3.7(2)/3.7$	$P23$	tetrahedron/ dark green	10.1866(2)
5	$Bi_{24}(Si^{4+}{}_{0.58}Bi^{3+}{}_{0.02}Mn^{4+}{}_{1.4})(O_{39.99}\square_{0.01})$ $R_1 = 5.75$, $wR_2 = 5.27$; $D = 4.7$; $FC_{calc.}/FC_{exp.} = 4.0(4)/3.99$	$I23$	cube + tetrahedron/ dark green	10.1510(1)
6	$Bi_{24}(Si^{4+}{}_{0.17(1)}Bi^{3+}{}_{0.01}Mn^{4+}{}_{1.82})(O_{39.93(5)}\square_{0.07})$ $R_1 = 3.84$, $wR_2 = 4.13$; $D = 3.6$; $FC_{calc.}/FC_{exp.} = 4.2(2)/3.995$	$P23$	cube/ dark green	10.1504(1)
7	$Bi_{24}(Si^{4+}{}_{1.150(6)}Bi^{3+}{}_{0.452}V^{5+}{}_{0.398})(O_{39.930(20)}\square_{0.070})$ $R_1 = 7.73$, $wR_2 = 23.35$; $D = 5.2$; $FC_{calc.}/FC_{exp.} = 5.18/4.55$	$P23$	–/ orange	10.1504(2)
8	$Bi_{24}(Si^{4+}{}_{1.160(6)}Bi^{3+}{}_{0.430}(V^{4+},V^{5+})_{0.410})(O_{39.970(20)}\square_{0.030})$ $R_1 = 7.65$, $wR_2 = 21.98$; $D = 5.1$; $FC_{calc.}/FC_{exp.} = 5.12/4.57$	$P23$	–/ green	10.1429(2)

[a] The structure refinements were performed in space group $I23$.

[b] Space group not analyzed, space group $I23$ was used.

$Mn(NO_3)_2{\cdot}6H_2O$, and $NaBiO_3$ + $Na_2SiO_3{\cdot}9H_2O$ + V_2O_5, respectively (alkaline solvent NaOH, $T = 310°C$, $\Delta T = 40°C$, $p = 500$ kg/cm^2).

The crystals in the Bi_2O_3–SiO_2–MnO_2 system were grown as spontaneous single crystals (dark green color, cubes, tetrahedra and combinations of cube and tetrahedron crystal habits, dimensions ≤ 1 mm^3) (samples 1-6 in Table 1). The crystals in the Bi_2O_3–SiO_2–V_2O_5 system were grown as bulk crystals (green and orange color, $Bi_{24}Ge_2O_{40}$ seed crystal, dimensions ~3×3×3 mm) (samples 7, 8 in Table 1).

The morphology of the spontaneous single crystals in the Bi_2O_3–SiO_2–MnO_2 system depends on the initial charge composition: cubes for $Na_2SiO_3{\cdot}9H_2O : Mn(NO_3)_2{\cdot}6H_2O > 1$, tetrahedra for $Na_2SiO_3{\cdot}9H_2O : Mn(NO_3)_2{\cdot}6H_2O < 1$ and a combination of cube and tetrahedron habit for $Na_2SiO_3{\cdot}9H_2O : Mn(NO_3)_2{\cdot}6H_2O = 1{:}1$.

Structural analyses of the spontaneous single crystals (samples 1-6, Table 2) were carried out on Xcalibur and CAD-4 diffractometers at room temperature (Mo K_α radiation, graphite monochromator, ω scan mode). For preliminary data processing, we used the CrysAlis RED and WinGX packages, respectively. A neutron diffraction study of the samples prepared in the Bi_2O_3–SiO_2–V_2O_5 system (samples 7, 8, Table 2) was carried out on the Orphee 5C2 reactor (LLB, France; $\lambda = 0.828$ Å). Full-matrix least squares refinements, using the atomic coordinates of $Bi_{24}Si_2O_{40}$ [5] (space group $I23$) as starting parameters, were carried out with the SHELXL97 [8] and JANA2000 [9] program packages and included anisotropic displacement parameters for all the atoms. The individual occupancies of three different elements (Si, Mn, Bi and Si, V, Bi) on the tetrahedral site were assessed by the SHELXL97 program. The conditions for the data collection and refinement procedure were the same for all of the samples.

X-ray spectral microanalysis was carried out using an Oxford INCA Penta Fetx 3 instrument.

The formal charge (FC) of the tetrahedral site was controlled by the bond-valence method [10]. The electrostatic bond strength

$$S_{ij} = \exp[(R_{ij} - d_{ij}) / 0.37] \qquad (1)$$

where R_{ij} is the bond-valence parameter for a particular ion pair (tabulated data), and d_{ij} experimental values of the interatomic M-O or (M',M'')-O distances; $FC_{calc} = 4 \times S_{ij}$ (Table 1).

The value of the parameter D [11] was employed to test the validity of the crystal structures:

$$D = \frac{\sum|\Delta|}{\sum \upsilon_a}, \quad |\Delta| = \left|\sum \upsilon_{ij} - \upsilon_a\right| \qquad (2)$$

where $\upsilon_{ij} = k_j / r_i^n$ is the electrostatic bond strength from cations j to anions i, and

$$k_j = \upsilon_c / \left[\sum_i 1/r_i^n\right] \qquad (3)$$

is the constant of the cation polyhedra, υ_c is the cation valency, r_i is the cation-anion distance, υ_a is the anion valency. According to [11], the value of D must be less than 5 % (Table 1).

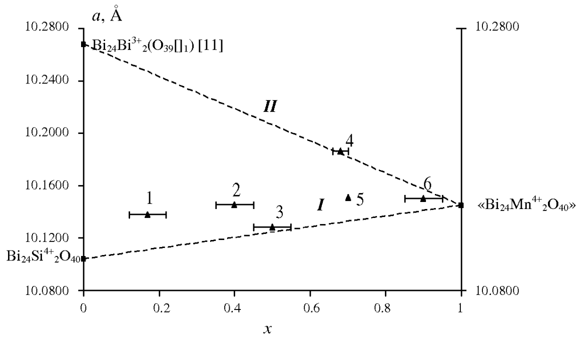


Fig. 2 Unit cell parameter a *vs.* x in the systems $(1\text{-}x)Bi^{3+}{}_{24}Si^{4+}{}_2O_{40}$–$x$"$Bi^{3+}{}_{24}Mn^{4+}{}_2O_{40}$" (*I*) and $(1\text{-}x)Bi^{3+}{}_{24}Bi^{3+}{}_2(O_{39}\square_1)$–$x$"$Bi^{3+}{}_{24}Mn^{4+}{}_2O_{40}$" (*II*).

Results and discussion

On the basis of the cell parameters of $Bi^{3+}{}_{24}Si^{4+}{}_2O_{40}$ (a = 10.104(1) Å) and $Bi^{3+}{}_{24}Ge^{4+}{}_2O_{40}$ (a = 10.153(4) Å [2]) and the corresponding ionic radii $r(Si^{4+})$ = 0.26 Å and $r(Ge^{4+})$ = 0.39 Å [12] we derived an expression for the cell parameters of all $Bi^{3+}{}_{24}M^{4+}{}_2O_{40}$ phases ($a = 0.3769r(M^{4+}) + 10.006$ Å) assuming the fulfillment of Vegard's law. Fig. 2 shows the dependence of the cell parameters of the sillenites in the $(1\text{-}x)Bi^{3+}{}_{24}Si^{4+}{}_2O_{40} - x$"$Bi^{3+}{}_{24}Mn^{4+}{}_2O_{40}$" (line I) and $(1\text{-}x)Bi^{3+}{}_{24}Bi^{3+}{}_2(O_{39}\square_1) - x$"$Bi^{3+}{}_{24}Mn^{4+}{}_2O_{40}$" (line II) systems on the composition (x value) using literature data for the $Bi^{3+}{}_{24}Si^{4+}{}_2O_{40}$ [5] and $Bi^{3+}{}_{24}Bi^{3+}{}_2(O_{39}\square_1)$ [13] phases and the calculated value $a \sim 10.15$ Å for the "$Bi^{3+}{}_{24}Mn^{4+}{}_2O_{40}$" phase ($r(Mn^{4+}) = r(Ge^{4+}) =$ 0.39 Å). These dependencies have been outlined by straight lines obeying Vegard's law.

The experimental points corresponding to $Bi_{24}(Si^{4+}{}_{0.9(1)}Mn^{4+}{}_{1.1})O_{40}$ (sample 3) and $Bi_{24}(Si^{4+}{}_{0.04}Bi^{3+}{}_{0.60}Mn^{4+}{}_{1.36})(O_{39.70}\square_{0.30})$ (sample 4) (□ – vacancy) fit well on the straight lines I and II, respectively. There is good agreement between the values of FC of the tetrahedral sites calculated by the bond-valence method and the experimental ones for samples 3 and 4 (Table 1). The positive deviation from the linear dependence I is ascribed to Bi^{3+} ions. The composition of sample 2 obtained using quantitative X-ray spectral microanalysis ($Bi_{24.2(1)}(Si_{0.7(1)}Mn_{1.1})O_{40}$) does not contradict the composition calculated from X-ray data (Table 1). This fact supports the presence of additional Bi^{3+} ions in samples 1, 5 and 6.

The crystal structures were refined in the I-centered space group $I23$; atomic coordinates, equivalent displacement parameters and occupancies of the tetrahedral cationic positions are listed in Table 2. The relatively low R discrepancy factors and the positive displacement parameters for all the atoms confirm the main features of the structure. However, the presence of a certain number of hkl reflections with $F > 3\sigma(F)$ (F is the structure factor) that are systematically absent in space group $I23$ (hkl with $h+k+l \neq 2n$, $0kl$ with $k+l \neq 2n$, hhl with $l \neq 2n$, $h00$ with $h \neq 2n$) for samples 3, 4, 6, 7 and 8 was a clear indication for lower symmetry. Data for sample 1 were collected for space group $I23$. The opportunity of changing to $P23$ symmetry was noticed in a later experiment for sample 3 and for samples 2-8 the space group was analyzed. All the crystallographic sites in the structure are split by the transition from space group $I23$ to space group $P23$ (Fig. 1). For example, the structure of sample 6 ($Bi_{24}(Si^{4+}{}_{0.17(1)}Bi^{3+}{}_{0.01}Mn^{4+}{}_{1.82})(O_{39.93(5)}\square_{0.07})$) refined in

Table 2 Atomic coordinates, equivalent isotropic thermal parameters $U_{eq}\times10^2$ (Å^2), site occupancies μ, and selected interatomic distances d (Å) determined on single crystals. Space group $I23$, Bi2,Si,M in Wyckoff position 2a (0 0 0), O2 and O3 in 8c (x x x).

Parameter		Sample							
		1	2	3	4	5	6	7	8
Bi1	x	0.82321(8)	0.17683(3)[a]	0.17664(4)[a]	0.17719(5)[a]	0.17729(5)[a]	0.31919(1)	0.17592(2)[a]	0.18167(3)[a]
	y	0.98153(8)	0.31960(4)	0.31919(5)	0.32060(6)	0.32027(6)	-0.01883(1)	0.31830(2)	0.32392(2)
	z	0.68064(8)	0.01915(4)	0.01872(5)	0.01774(5)	0.01964(6)	-0.17671(1)	0.01629(2)	0.48422(3)
	μ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$U_{eq}\times10^2$		1.037(15)	1.364(7)	0.724(8)	1.47(14)	1.3(1)	0.830(2)	1.753(4)	1.888(5)
Bi2	μ	0.05(7)	0.05(5)	-	0.30(4)	0.01(6)	0.006(2)	0.226(3)	0.215(3)
Si	μ	0.83(7)	0.55(5)	0.47(7)	0.02(4)	0.29(6)	0.084(2)	0.711(11)	0.750(12)
M	μ	0.1(7)	0.40(5)	0.53(7)	0.68(4)	0.70(6)	0.910(2)	0.575(3)	0.580(3)
$U_{eq}\times10^2$		0.9(3)	0.64(4)	0.7(2)	0.49(1)	0.90(6)	0.99(19)	0.199(3)	0.205(3)
O1	x	0.365(2)	0.1336(9)	0.135(1)	0.1352(12)	0.1379(11)	0.2553(3)	0.13488(3)	0.24922(4)
	y	0.009(2)	0.2492(8)	0.2511(9)	0.2493(11)	0.2520(10)	0.0102(3)	0.25113(3)	0.36543(4)
	z	0.247(2)	0.4890(9)	0.487(1)	0.4895(12)	0.4854(13)	-0.3694(3)	0.48620(3)	0.01439(4)
	μ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$U_{eq}\times10^2$		0.9(2)	1.7(2)	1.1(1)	1.8(3)	1.4(2)	2.13(7)	1.881(6)	2.024(8)
O2	x	0.803(2)	0.1975(9)	0.1988(9)	0.1898(13)	0.195(4)	0.1977(3)	0.19492(4)	0.30583(4)
	μ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$U_{eq}\times10^2$		1.0(4)	1.6(1)	0.8(2)	2.2(2)	1.6(2)	2.05(9)	1.859(8)	1.882(9)
O3	x	0.098(3)	0.9036(10)	0.905(1)	0.894(2)	0.902(4)	0.0915(3)	0.89984(3)	0.10011(4)
	μ	0.987(5)	0.75[b]	1.0	0.963[b]	0.998[b]	0.98(1)	0.983(5)	0.993(5)
$U_{eq}\times10^2$		2.3(9)	1.9(1)	1.6(3)	2.3(2)	2.2(2)	1.1(1)	2.208(10)	2.388(12)
Bi1	– 1×O1	2.07(2)	2.069(9)	2.06(1)	2.060(12)	2.044(11)	2.0805(28)	2.0684(4)	2.0673(4)
	– 1×O1	2.24(2)	2.200(9)	2.20(1)	2.220(12)	2.197(12)	2.1808(30)	2.2218(4)	2.2146(5)
	– 1×O1	2.59(2)	2.591(9)	2.61(1)	2.590(12)	2.650(12)	2.5545(30)	2.6221(4)	2.6181(5)
	– 1×O2	2.205(7)	2.203(9)	2.21(1)	2.205(13)	2.19(4)	2. 2036(11)	2.2120(3)	2.2121(3)
	– 1×O3	2.66(2)	2.677(10)	2.67(1)	2.62(2)	2.68(4)	2.7081(24)	2.6251(3)	2.6220(4)
$d(Bi1\text{-}O)_{av}$		2.35(2)	2.348(9)	2.35(1)	2.34(1)	2.35(2)	2.3455(25)	2.3499(4)	2.3468(4)
Bi2,Si,M	– 4×O3	1.73(5)	1.694(10)	1.67(1)	1.88(2)	1.72(4)	1.6071(53)	1.7609(6)	1.7587(7)

[a] Left form of the crystal

[b] Occupancy of the position was calculated on the base of neutrality of the system.

$I23$ symmetry contains a single lattice site 2a that is filled with ~14 % Si, ~8% Bi and ~78% Mn in random distribution, while for $P23$ symmetry two different crystallographic sites, 1a and 1b, exist (sites M'' and M' in Fig. 1b). Each of them can accommodate Si, Bi and Mn, but in general with different occupancy factors.

In this case we may deal with a kinetic phase transition of order-disorder type [3], *i.e.* a partially ordered phase with a P cubic unit cell forms in the stability area of the disordered phase with an I cubic unit cell under the influence of kinetic factors. The ordering will depend on the composition, structure peculiarities, and chemical properties of the components, as well as on the preparation conditions, in particular on the initial composition [14]. Based on preliminary results, the single crystals of cube and tetrahedron habits (different amounts of the starting materials $Na_2SiO_3{\cdot}9H_2O$ and $Mn(NO_3)_2{\cdot}6H_2O$) have space group $P23$, whereas the single crystals with a combination of cube and tetrahedron habit (equal amounts of the starting materials) crystallize in space group $I23$.

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