New zinc and potassium chlorides from fumaroles of the Tolbachik volcano, Kamchatka, Russia: mineral data and crystal chemistry. I. Mellizinkalite, K₃Zn₂Cl₇

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Abstract: The new mineral mellizinkalite, K₃Zn₂Cl₇, is found in the Glavnaya Tenoritovaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia, Associated minerals are belloite, avdoninite, eriochalcite, sylvite, halite, carnallite, mitscherlichite, sanguite, chrysothallite, romanorlovite, gypsum, chlorothionite, kainite and earlier hematite, tenorite and chalcocyanite. Mellizinkalite occurs as irregularly shaped grains up to 0.5 mm across or crude elongated crystals up to 0.25×1.3 mm, their clusters and crysts up to 2×2 mm in area and up to 0.5 mm thick. The mineral is yellow-brown to reddish brown, transparent, with vitreous lustre. It is moderately brittle, slightly plastic. The Mohs' hardness is *ca.* 2. Cleavage is not observed, the fracture is uneven. $D_{\text{meas}} = 2.46(2)$ and $D_{\text{calc}} = 2.49 \text{ g cm}^{-3}$. Mellizinkalite is optically biaxial (-), $\alpha = 1.556(5)$, $\beta = 1.612(5)$, $\gamma = 1.663(5)$ and $2V_{\text{meas}} = 85(5)^{\circ}$. The Raman spectrum is reported. The chemical composition (wt.%, electron-microprobe data) is: K 23.5, Rb 0.52, Mg 0.47, Cu 1.77, Zn 24.4, Cl 50.0, total 100.7. The empirical formula calculated on the basis of 12 atoms pfu is: $(K_{2.95}Rb_{0.03})_{\Sigma_{2.98}}(Zn_{1.84}Cu_{0.14}Mg_{0.09})_{\Sigma_{2.07}}Cl_{6.95}$. Mellizinkalite is triclinic, $P\bar{1}$, a = 6.7737(4), b = 10.5715(13), c = 11.0730(9) Å, $\alpha = 117.930(10), \beta = 106.909(5), \gamma = 90.389(8)^{\circ}, V = 660.61(10)$ Å³ and Z = 2. The strongest reflections of the X-ray powder pattern [d,Å (I) (hkl)] are: 9.20(69)(001, 010, 0-11), 6.40(100)(100), 5.712(47)(-110, -1-11), 4.608(92)(002, 020), 3.499(55)(012), 3.473(73)(0-13, 0-31, 0-23), 3.393(66)(-201) and 3.075(49)(003). The crystal structure, solved from single-crystal X-ray diffraction data (R = 0.065), is unique. It consists of alternating layers of different ZnCl₄ polyhedra. The Zn(1) cations are located in flat squares which are connected to each other via common Cl-Cl edges to form Zn_2Cl_6 dimers, whereas Zn(2) cations occupy isolated tetrahedra. Potassium cations occupy sites between the layers of Zn-centred polyhedra. The mineral (IMA2014-010) is named from three Latin words, mellis - honey, zincum and kalium, alluding to its colour and species-defining cations, zinc and potassium.

Key-words: mellizinkalite; new mineral; potassium zinc chloride; crystal structure; fumarole; Tolbachik volcano; Kamchatka.

Introduction

Active fumarole fields related to the Tolbachik volcano at Kamchatka, Russia, produce unique, diverse and sporadically very rich mineralization. More than two hundreds minerals of fumarolic origin, including almost seventy new species, were found there during the period following the Great Tolbachik Fissure Eruption (GTFE) of 1975–1976. In the diversity of fumarolic minerals Tolbachik is the record-holder among all volcanoes in the world. One of the brightest mineralogical features of the Tolbachik fumaroles is the extremely high concentration and great diversity of the "ore" minerals represented by oxysalts, oxides and chlorides with Cu, Fe, As, V, Pb and Se. Minerals with species-defining Tl, Zn, Cd, Sn, Au, Bi, Te and Mo also occur here. Copper mineralization in the Tolbachik fumaroles is outstanding in terms of both diversity (about 75 minerals with species-defining Cu^{2+} including 31 new species) and richness (Vergasova & Filatov, 2012; our data). The occurrences of tenorite and Cu

sulphates at the Second scoria cone of the Northern Breakthrough of the GTFE were even evaluated in 1980s as a potentially interesting target for copper mining (Naboko & Glavatskikh, 1983; Vergasova & Filatov, 1993). Zinc mineralization in the Tolbachik fumaroles is relatively poor, in comparison with the diversity and the abundance of copper minerals, and reported in few publications: until recently, only two minerals with speciesdefining zinc were described here, both selenite chlorides: sofiite, Zn₂(SeO₃)Cl₂ (Vergasova et al., 1989), and extre- $KPb_{1.5}Cu_{6}Zn(SeO_{3})_{2}O_{2}Cl_{10}$ prewittite, melv rare (Shuvalov *et al.*, 2013). The scattering of Zn^{2+} in abundant and numerous oxysalts and halides of Cu^{2+} seems an important cause of the relative scarcity of zinc mineralization at Tolbachik. The admixture of 0.1–1 wt.% Zn is here typical for copper sulphates, arsenates and chlorides while some vanadates and selenites contain up to 5-8 wt.% Zn substituting Cu (Vergasova et al., 1999, 2014; Zelenski et al., 2011; Pekov et al., 2013, 2014).

The work we carried out in 2012–2014 on active fumarole fields located at the First and the Second scoria cones of the Northern Breakthrough of the GTFE significantly extended the knowledge on the mineralogy of zinc at Tolbachik. We have found in the fumarolic sublimates four oxides with species-defining Zn, namely zincite ZnO and three spinel-group members represented by unusual Cuvarieties: gahnite $(Zn,Cu)Al_2O_4,$ franklinite rich (Zn,Cu)(Fe,Al)₂O₄, and zincochromite (Zn,Mg,Cu)(Cr,Al)₂ O₄. Besides, we discovered six new zinc minerals belonging to four chemical classes; all were approved by the IMA Commission on New Minerals, Nomenclature and Classification in 2014. There are the selenite zincomenite. ZnSeO₃ (IMA No. 2014–014), the arsenate pharmazincite, KZnAsO₄ (IMA2014–015), the borate chubarovite, KZn₂(BO₃)Cl₂ (IMA2014–018), and three chlorides: flinteite, K₂ZnCl₄ (IMA2014–009), mellizinkalite, K₃Zn₂Cl₇ (IMA2014–010) and cryobostryxite, KZnCl₃·2H₂O (IMA2014-058). These three new chloride minerals have the same species-defining cations but are quite different in terms of stoichiometry and crystal structure. This is a reason to give for them a series of three coupled papers. Note that chlorides of Zn and K were unknown in nature before.

In the present article we describe mellizinkalite (Cyrillic: меллицинкалит) named from three Latin words, *mellis* – honey, *zin*cum and *kal*ium, alluding to its colour and species-defining cations, zinc and potassium. The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 94375.

Occurrence and general appearance

Specimens with the new mineral were collected in July 2013 from the Glavnaya Tenoritovaya ("Major Tenorite") fumarole at the apical part of the Second scoria cone of the Northern Breakthrough of the GTFE. This scoria cone, a

monogenetic volcano about 300 m high and approximately 0.1 km³ in volume, formed in 1975, is situated 18 km SSW of the active volcano Ploskiy Tolbachik (Fedotov & Markhinin, 1983).

The Glavnaya Tenoritovaya fumarole is located in the western wall of a big contraction fracture cross-cutting the top of the scoria cone in the near-meridional direction. Gas vents belonging to this fumarole occupy an area of 1.7×4.2 m. The main part of this area is at temperatures of 350-360°C, as measured by us at about 20 cm depth (using chromel-alumel thermocouple in July 2013); major minerals formed in this zone are sulphates (euchlorine, dolerophanite, chalcocyanite, anglesite, krasheninnikovite and anhydrite), hematite and tenorite. The rich chloride mineralization was observed only in an outer, moderately hot (110°C, from our measurements) zone in the northern flank of the fumarole. The area in which chlorides are concentrated is a lenticular body about 1.5 m long and up to 0.2 m thick. These minerals are represented by belloite, avdoninite, eriochalcite, sylvite, halite. carnallite, mitscherlichite, sanguite KCuCl₃ (IMA2013-002), chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4 \cdot H_2O$ (IMA2013-008). romanorlovite $K_8Cu_6Cl_{17}(OH)_3$ (IMA2014-011), mellizinkalite, flinteite and an incompletely studied K-Pb-Cu hydroxychloride. Other minerals are gypsum, chlorothionite, kainite and earlier hematite, tenorite and chalcocyanite. Unlike the hottest oxide-sulphate zone (350–360°C) in which only anhydrous minerals are present, in this sulphate-chloride zone OH- and H2O-bearing minerals are abundant.

Mellizinkalite is one of the last minerals to form in the assemblage. It was found in small amounts only in cavities of the chloride and sulphate-chloride incrustations. Mellizinkalite mainly occurs as equant, elongated or flattened, irregularly shaped grains up to 0.5 mm across, their clusters, groups (Fig. 1a) or granular crusts (Fig. 1b) up to 2×2 mm in area and up to 0.5 mm thick. Individual crystals of the mineral typically have smooth contours (Fig. 2). Crude acicular crystals and anthodites of mellizinkalite up to 1.3 mm long and up to 0.25 mm thick, sometimes strongly twisted or curled, were also observed.

Physical properties and optical characteristics

Mellizinkalite is yellow-brown to reddish brown, typically honey- or cognac-coloured. Its streak is yellow. The mineral is transparent, with vitreous lustre. Mellizinkalite is moderately brittle, slightly plastic. The Mohs' hardness is *ca*. 2. Cleavage or parting were not observed. The fracture is uneven. Density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.46(2) g cm⁻³. The density calculated using the empirical formula is 2.49 g cm⁻³.

Optical properties were determined in orthoscopic and conoscopic illumination. Cargille immersion liquids used for the refractive index measurements were checked with refractometer before and after the measurements. The data



Fig. 1. Aggregates formed by grains (crude crystals) of mellizinkalite (1): a – with kainite (2) on crust consisting of belloite and sylvite; b – with sanguite KCuCl₃ (2), avdoninite (3) and chlorothionite (4) on white crust consisting of carnallite and sylvite. Photo: I.V. Pekov & A.V. Kasatkin.

were obtained at 22(2)°C using yellow filter, $\lambda = 589$ nm. Mellizinkalite is optically biaxial (–), $\alpha = 1.556(5)$, $\beta = 1.612(5)$, $\gamma = 1.663(5)$ (589 nm), $2V_{\text{meas}} = 85(5)^{\circ}$ and



Fig. 2. Typical crude crystals of mellizinkalite, with smooth contours, on fine-grained carnallite aggregate. Scanning electron microscope image (secondary electrons).

 $2V_{\text{calc}} = 85^{\circ}$. Dispersion of optical axes is distinct, r < v. Pleochroism is strong, the absorption scheme is: *Z* (brown or, in thick grains, reddish brown) >> Y (swamp green) > X (pale swamp green to almost colourless).

Raman spectroscopy

The Raman spectrum of mellizinkalite (Fig. 3) was obtained from a polycrystalline sample using an EnSpectr R532 spectrometer with a green laser (532 nm) at room temperature. The power of the laser beam on the sample was about 3–3.5 mW. The spectrum was processed using the EnSpectr expert mode program in the range 100–4000 cm⁻¹ with the use of a holographic diffraction grating with 1800 lines cm⁻¹ and a spectral resolution of 6 cm⁻¹. The diameter of the focal spot on the sample was about 10 μ m.

All absorption bands in the Raman spectrum have maxima below 330 cm⁻¹. According to the data reported by Moyer *et al.* (1966) for ZnCl₂ and K-Zn chlorides, bands in the region 210–400 cm⁻¹ (at 310, 274 and 264 cm⁻¹ in the spectrum of mellizinkalite) are assigned as Zn–Cl stretching vibrations and bands with frequencies below 200 cm⁻¹ (at 188 and 128 cm⁻¹ in the spectrum of mellizinkalite) correspond to lattice modes involving Zn–Cl bending and K–Cl stretching vibrations. An absence of absorption bands in the region higher than 600 cm⁻¹ indicates the absence of groups with O–H, C–H, C–O, N–H, N–O, B–O, Be–O and Li–O bonds in mellizinkalite.

Chemical data

Chemical data for mellizinkalite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University), an acceleration voltage of 20 kV, a beam current of 20 nA, and a 5 μ m beam diameter. The following standards were used:



Fig. 3. Raman spectrum of mellizinkalite. The insert shows an enlargement of the low-frequency region.

microcline (K), Rb₂Nb₄O₁₁ (Rb), diopside (Mg), CuFeS₂ Table 1. X-ray powder diffraction data for mellizinkalite. (Cu), ZnSe (Zn), and NaCl (Cl).

The average (4 spot analyses) chemical composition of mellizinkalite (wt%, ranges are in parentheses) is: K 23.48 (22.87–24.07), Rb 0.52 (0.00–1.01), Mg 0.47 (0.26–0.85), Cu 1.77 (1.13-3.08), Zn 24.44 (23.11-25.72), Cl 50.02 (49.31–50.47), total 100.70. Contents of other elements with atomic numbers higher than carbon are below detection limits.

The empirical formula of mellizinkalite calculated on the basis of 12 atoms per formula unit (pfu) is: $(K_{2,95}Rb_{0,03})$ $\Sigma_{2.98}(Zn_{1.84}Cu_{0.14}Mg_{0.09})$ $\Sigma_{2.07}Cl_{6.95}$. The idealized formula K₃Zn₂Cl₇ requires K 23.64, Zn 26.35, Cl 50.01, total 100.00 wt%.

Mellizinkalite dissolves easily, after several seconds in H₂O at room temperature. The mineral is unstable in a humid atmosphere, is hygroscopic and moistens under ordinary room conditions.

X-ray crystallography and crystal structure

The X-ray powder diffraction study of mellizinkalite was carried out on a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image-plate detector using Debye-Sherrer geometry (d = 127.4 mm; CoK α -radiation). X-ray powder diffraction data for the new mineral are given in Table 1. The triclinic unit-cell parameters refined from the powder data are: a = 6.78(1), b = 10.57(2), c = 11.06(2) Å, $\alpha = 117.74(6), \beta =$ 106.92(5), $\gamma = 90.52(6)^{\circ}$ and $V = 661.8(8) \text{ Å}^3$.

Single-crystal X-ray studies were carried out using an Xcalibur S CCD diffractometer. More than a hemisphere of three-dimensional data was collected. Crystal data, datacollection information and structure refinement details are given in Table 2. Data reduction was performed using CrysAlisPro Version 1.171.35.21 (Agilent, 2012). The data were corrected for Lorentz and polarization effects. Numerical absorption correction is based on gaussian integration over a multifaceted crystal model. The structure was solved by direct methods and refined with the use of SHELX software package (Sheldrick, 2008) on the basis of 2001 independent reflections with $I > 2\sigma(I)$.

Mellizinkalite could be considered as triclinic pseudoorthorhombic, a = 6.79, b = 10.58, c = 18.48 Å, $\alpha =$ 90.55, $\beta = 90.83$ and $\gamma = 90.45^{\circ}$ (however, all three angles are significantly different from 90°). Merging statistics R_{int} (data obtained using CrysAlis software: Oxford Diffraction, 2010) for *mmm* symmetry was 0.415. All attempts to choose a monoclinic unit cell were unsuccessful: R_{int} was not less than 0.23 and the deviations of two angles from 90° were significant. Merging in Laue class $\overline{1}$ yielded $R_{\text{int}} = 0.052$. This indicates that the structure is really triclinic. The structure of mellizinkalite was solved and refined in space group $P\bar{1}, a = 6.7737(4), b = 10.5715(13), c = 11.0730(9)$ Å, $\alpha =$ $117.930(10), \beta = 106.909(5), \gamma = 90.389(8)^{\circ}$. This unit cell can be transformed to the abovementioned pseudoorthorhombic cell using the matrix -1 0 0/0-1 0/1

Iobs	$d_{\rm obs}$	I_{calc}^*	$d_{\rm calc}^{**}$	h k l
69	9.20	20, 30, 25	9.256, 9.205, 9.139	001, 010, 0-11
100	6.40	100	6.387	100
47	5.712	32, 33	5.721, 5.685	-110, -1-11
3	5.289	1, 1	5.297, 5.285	0-12, 0-21
6	4.852	8	4.846	-111
7	4.808	10	4.805	-1-12
92	4.608	23, 65	4.613, 4.603	002, 020
27	4.074	11, 3, 14	4.079, 4.076, 4.065	1-21, -120, -1-21
16	3.624	12	3.611	111
27	3.592	29	3.578	-112
13	3.551	12	3.554	-1-13
55	3.499	50	3.493	012
13	3.473	28, 30, 31	3.475, 3.466, 3.461	0-13, 0-31, 0-23
66	3.393	91	3.386	-201
36	3.262	51	3.260	102
21	3.196	20	3.194	200
27	3.170	33 50	3.105	-202
49	3.075	50	3.075	005
33	3.004	27	3.008	0.32
10	2 0 4 0	20	2.040	1 33
8	2.940	20	2.241	-1-55 -2, 13
22	2.850	11 15	2.035	1 23 - 122
20	2.707	27 21	2.770, 2.704	201 - 1 - 24
47	2.747	36 14	2.740, 2.730	112 1 - 13
21	2.685	8 1 13	2,700, 2,686, 2,668	-113 - 1 - 14 022
27	2.644	15. 32	2.648, 2.643	0-24, 0-42
9	2.603	6	2.600	130
22	2.558	17.19	2.559, 2.553	031, 0–14
18	2.535	11, 17	2.538, 2.535	0-34, 0-43
48	2.433	2, 28, 67	2.431, 2.430, 2.427	-1-43, 2-31, -230
36	2.415	48, 37	2.417, 2.407	-2-32, -2-33
11	2.307	23	2.306	004
7	2.280	2, 3, 3	2.285, 2.280, 2.275	0-44, 2-32, -2-31
5	2.245	2, 3, 4	2.250, 2.245, 2.241	-2-34, -301, 122
3	2.232	1	2.232	1–24
4	2.202	1, 1, 8	2.205, 2.205, 2.196	-3-12, 131, -132
5	2.169	7	2.174	-1-35
5	2.151	5	2.150	113
7	2.119	11	2.119	032
8	2.096	8, 3, 2	2.102, 2.098, 2.090	0-35, 0-53, 2-41
10	2.069	13, 3	2.070, 2.066	-2-25, -321
8	2.045	5, 5, 5	2.045, 2.040, 2.038	2-33, 2-42, -240
14	2.017	13, 4, 10	2.019, 2.017, 2.016	-2-44, -2-35, 014
0	1.991	5	1.994	0-34
ð	1.979	0, 3, 4, 2	1.984, 1.977, 1.977,	-515, 5-21, -5-14,
4	1 0/1	7	1.977	1-31 301
4 8	1.941	5 6	1.958	_330 2 /3
5	1.907	5,0	1.907, 1.900	-330, 2-43 2 45 331
14	1.870	0346	1.865, 1.865	-2-43, -331 -3, 34, 123, 005, 1, 25
14	1.040	2, 3, 4, 0,	1.842, 1.842	-1-36
7	1.826	3, 5, 3	1.828, 1.827, 1.821	0-55, -1-26, 3-22
18	1.806	5, 5, 6, 9,	1.809, 1.806, 1.805,	141, 3–12, –323, 311,
		3, 15, 2	1.805, 1.804, 1.802, 1.802	-142, 231, 2-24
20	1.798	2, 14, 6,	1.799, 1.799, 1.794,	1-45, 2-34, -3-25,
		17, 4	1.791, 1.791	-233, 2-52
10	1.773	16	1.774	-2-36
14	1.765	6, 6, 7, 24	1.767, 1.766, 1.763,	3-32, 0-36, -3-31,
			1.762	0–63
5	1.732	6	1.733	0-62

Table 1. Continued

$d_{\rm obs}$	I_{calc}^*	$d_{\rm calc}^{**}$	h k l
1.697	2, 7, 3, 3, 18	1.701, 1.700, 1.697, 1.694, 1.693	-3-44, 1-63, -1-63, 150, -402
1.668	7	1.670	-401
1.658	4, 1, 1, 3, 2	1.661, 1.656, 1.656, 1.655, 1.655	-403, -341, 051, -3-42, 0-16
1.642	1, 1, 5	1.642, 1.641, 1.641	321, 3-23, 0-65
1.619	2, 2	1.618, 1.617	-2-51, 2-54
1.609	1, 2, 4	1.610, 1.609, 1.606	-413, -4-23, 312
1.600	4, 2	1.602, 1.600	-3-36, -2-56
1.586	2, 2	1.591, 1.584	-134, 142
1.570	2	1.567	2-62
1.554	2, 2, 3, 4	1.559, 1.558, 1.558,	-2-64, 1-26, -342,
		1.553	-1-61
1.532	1, 1	1.533, 1.530	-2-65,410
1.516	2	1.518	1–56
1.504	3	1.504	0–74
1.493	6, 3	1.492, 1.490	401, 115
1.485	7,3	1.482, 1.482	-116, -432
1.476	2, 6, 4	1.476, 1.475, 1.474	1-73, 3-34, -405
1.449	2,4	1.452, 1.446	-3-56, 340
1.428	3	1.430	1–66
1.407	3, 3	1.406, 1.405	061, -415
1.393	2, 2	1.394, 1.391	0–76, 233
1.386	3, 3, 4	1.387, 1.387, 1.385	2-36, 134, 3-54
1.372	2,5	1.373, 1.371	-2-74, -2-38
1.358	1, 1, 4	1.360, 1.359, 1.356	3-63, 2-26, -406
1.344	2	1.345	1–27
	$\begin{array}{c} d_{\rm obs} \\ \hline 1.697 \\ 1.668 \\ 1.658 \\ 1.658 \\ 1.642 \\ 1.619 \\ 1.609 \\ 1.609 \\ 1.500 \\ 1.554 \\ 1.570 \\ 1.554 \\ 1.570 \\ 1.554 \\ 1.516 \\ 1.504 \\ 1.493 \\ 1.485 \\ 1.476 \\ 1.493 \\ 1.485 \\ 1.476 \\ 1.493 \\ 1.428 \\ 1.407 \\ 1.393 \\ 1.386 \\ 1.372 \\ 1.358 \\ 1.344 \end{array}$	$\begin{array}{c cccc} d_{\rm obs} & I_{\rm calc} * \\ \hline 1.697 & 2, 7, 3, 3, \\ 18 \\ \hline 1.668 & 7 \\ \hline 1.658 & 4, 1, 1, 3, \\ 2 \\ \hline 1.658 & 4, 1, 1, 5 \\ \hline 1.619 & 2, 2 \\ \hline 1.600 & 1, 2, 4 \\ \hline 1.600 & 4, 2 \\ \hline 1.586 & 2, 2 \\ \hline 1.570 & 2 \\ \hline 1.554 & 2, 2, 3, 4 \\ \hline 1.532 & 1, 1 \\ \hline 1.516 & 2 \\ \hline 1.504 & 3 \\ \hline 1.493 & 6, 3 \\ \hline 1.493 & 6, 3 \\ \hline 1.449 & 2, 4 \\ \hline 1.428 & 3 \\ \hline 1.407 & 3, 3 \\ \hline 1.393 & 2, 2 \\ \hline 1.386 & 3, 3, 4 \\ \hline 1.372 & 2, 5 \\ \hline 1.358 & 1, 1, 4 \\ \hline 1.344 & 2 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

*Only reflections with intensities ≥ 1 are given.

**For unit-cell parameters calculated from single-crystal data.

1 2. In initial stages, the crystal structure was refined anisotropically to R = 0.0981 and it was found that the studied crystal is microtwinned. The twin law $-1 \ 0 \ 0/0$ 1 0/0-1-1, which corresponds to two-fold rotation

about b of the pseudo-orthorhombic cell, gave the final R = 0.0653. The refined twin ratio is 84:16.

Atom coordinates and displacement parameters for mellizinkalite are given in Table 3, selected interatomic distances in Table 4 and bond-valence calculations in Table 5. Measured and calculated powder X-ray diffraction patterns are in good agreement one with another (Table 1).

The crystal structure of mellizinkalite (Fig. 4) is unique. It consists of alternating layers of different $ZnCl_4$ polyhedra coplanar to *ab*. Zinc cations occupy two crystallographically independent positions. Zn(1) cations are located in flat Zn(1)Cl₄ squares which are connected with each other *via* common Cl-Cl edges to form Zn₂Cl₆ dimers elongated along the *b* axis, whereas Zn(2) cations occupy three crystallographically independent sites located between the layers of Zn-centred polyhedra.

Discussion

No mineral or synthetic compound close to mellizinkalite in terms of structure is known. The phase $K_3Zn_2Cl_7$ was synthesized and studied, in the thermodynamic aspect, as one of the solids in the system KCl–ZnCl₂ (Nikonova *et al.*, 1941; Kruglov *et al.*, 1986; Baxter & Heikinheimo, 2005) but we found no crystal data for this compound in the literature and databases. Other known synthetic chlorides with the stoichiometry $A^+_3M^{2+}_2Cl_7$, namely the isostructural tetragonal $K_3Mn_2Cl_7$, Rb₃Zn₂Cl₇ (Seifert & Koknat, 1965) and Cs₃Mg₂Cl₇ (Al-Aql *et al.*, 1981) are quite different from mellizinkalite in structure.

Table 2. Crystal data, data-collection information and structure-refinement details for mellizinkalite.

Formula weight	496.19		
Crystal system, space group	Triclinic, $P\overline{1}$		
Unit-cell dimensions	$a = 6.7737(4) \text{ Å}$ $\alpha = 117.930(10)^{\circ}$		
	$b = 10.5715(13)$ Å $\beta = 106.909(6)^{\circ}$		
	$c = 11.0730(9) \text{ Å} \qquad \gamma = 90.389(8)^{\circ}$		
Volume; Z	$660.61(10) \text{ Å}^3; 2$		
μ	5.939 mm^{-1}		
F(000)	472		
Crystal size	$0.08 imes 0.10 imes 0.12~\mathrm{mm}$		
Data collection	XcaliburS CCD		
Temperature	293(2) K		
Radiation, wavelength	MoK α ; $\lambda = 0.71073$ Å		
θ range for data collection	3.19 to 26.37°		
Reflections collected	4879		
Unique reflections	2699		
Unique reflections with $I > 2\sigma(I)$	2001		
Structure solution	direct methods		
Refinement method	full-matrix least-squares on F^2		
Number of refined parameters	110		
Weighting scheme	$1/[\sigma^2(F_0^2) + (0.0390P)^2 + 2.2088P],$		
	$P = [max(F_o)^2 + 2(F_c)^2]/3$		
$R_F/wR(F^2)$ $(I \ge 2\sigma(I))$	0.065/0.121		
GoF	1.034		
$\Delta \rho_{\rm mx} / \Delta \rho_{\rm min}$	0.959/-0.867 e/Å ³		

Atom	X	у	z	$U_{ m eq}$
K(1)	0.3886(4)	0.9051(3)	0.7798(3)	0.0429(6)
K(2)	0.9033(4)	0.1883(3)	-0.2240(3)	0.0475(7)
K(3)	0.1332(4)	0.4129(3)	0.2860(3)	0.0514(8)
Zn(1)	0.5070(2)	0.34275(14)	0.01227(18)	0.0386(4)
Zn(2)	0.64580(18)	0.73248(14)	0.44018(14)	0.0333(3)
Cl(1)	0.6745(5)	0.8392(3)	0.3103(4)	0.0465(8)
Cl(2)	0.6950(5)	0.4985(3)	0.3492(4)	0.0502(8)
Cl(3)	0.2785(4)	0.1995(3)	0.0271(3)	0.0328(6)
Cl(4)	0.2754(4)	0.5033(3)	0.0105(3)	0.0402(7)
Cl(5)	0.7453(4)	0.1971(3)	0.0155(3)	0.0338(6)
Cl(6)	0.3141(4)	0.7327(3)	0.4523(3)	0.0394(6)
Cl(7)	0.8630(5)	0.8586(3)	0.6733(3)	0.0493(8)

Table 3. Atom coordinates and isotropic displacement parameters (\AA^2) for mellizinkalite.

Table 4. Selected interatomic distances (Å) in the structure of mellizinkalite.

$\begin{array}{l} K(1)-polyhedron\\ K(1) - Cl(6) 3.076(4)\\ - Cl(3) 3.213(4)\\ - Cl(5) 3.257(4)\\ - Cl(1) 3.284(4)\\ - Cl(5) 3.296(4)\\ - Cl(3) 3.313(4)\\ - Cl(7) 3.362(4)\\ - Cl(7) 3.362(4)\\ - Cl(7) 3.693(4)\\ - Cl(2) 3.788(4)\\ < K(1) - Cl 3.365>\\ K(2)-polyhedron\\ K(2) - Cl(6) 3.014(4)\\ - Cl(5) 3.099(4)\\ - Cl(7) 3.100(4)\\ - Cl(3) 3.127(4)\\ - Cl(1) 3.243(4)\\ - Cl(4) 3.487(4)\\ - Cl(4) 3.490(4)\\ \end{array}$	$\begin{array}{l} K(3)\mbox{-}polyhedron \\ K(3)\mbox{-}Cl(6)\ 3.021(4) \\ \mbox{-}Cl(7)\ 3.106(4) \\ \mbox{-}Cl(3)\ 3.145(4) \\ \mbox{-}Cl(3)\ 3.145(4) \\ \mbox{-}Cl(2)\ 3.281(4) \\ \mbox{-}Cl(2)\ 3.500(5) \\ \mbox{-}Cl(2)\ 3.500(5) \\ \mbox{-}Cl(2)\ 3.688(4) \\ \mbox{-}K(3)\mbox{-}Cl\ 3.272 \\ \hline Zn(1)\mbox{-}square \\ Zn(1)\mbox{-}Cl(5)\ 2.243(3) \\ \mbox{-}Cl(3)\ 2.251(3) \\ \mbox{-}Cl(4)\ 2.321(3) \\ \mbox{-}Cl(4)\ 2.336(3) \\ \mbox{-}Zn(1)\mbox{-}Cl(4)\ 2.348 \\ \hline Zn(2)\mbox{-}tetrahedron \\ Zn(2)\mbox{-}Cl(1)\ 2.249(3) \\ \mbox{-}Cl(2)\ 2.263(3) \\ \hline \end{array}$
- Cl(4) 3.48/(4) - Cl(4) 3.490(4) - Cl(1) 3.723(4) <k(2) -="" 3.285="" cl=""></k(2)>	- Cl(2) 2.263(3) - Cl(7) 2.268(3) - Cl(6) 2.289(3) <zn(2) -="" 2.267="" cl=""></zn(2)>

Table 5. Bond-valence calculations for mellizinkalite. Parameters are taken from Brese & O'Keeffe (1991).

	K(1)	K(2)	K(3)	Zn(1)	Zn(2)	\sum
Cl(1)	0.13	0.14 0.04			0.52	0.83
Cl(2)	0.03	0101	0.13 0.07		0.50	0.77
Cl(3)	0.15 0.12	0.19	0.04	0.52		1.16
Cl(4)		0.07 0.07		0.43 0.41		0.98
Cl(5)	0.14 0.12	0.21	0.17	0.53		1.17
Cl(6) Cl(7)	0.22 0.10 0.04	0.26 0.21	0.26 0.20		0.47 0.50	1.21 1.05
\sum	1.05	1.19	1.05	1.89	1.99	



Fig. 4. The crystal structure of mellizinkalite. The unit cell is outlined.

Mellizinkalite, being anhydrous chloride, is closely associated with OH- and H₂O-bearing minerals: avdoninite, belloite, eriochalcite, mitscherlichite, carnallite, gypsum, kainite, chrysothallite and romanorlovite. This fact, as well as the temperature of 110°C measured in this zone when collecting, show that these minerals were probably formed not as a result of direct deposition from the gas phase (hot gases in the fumaroles of the Second scoria cone contain no more than 1 % H₂O: Zelenski *et al.*, 2012) but as products of the interactions involving earlier formed, high-temperature sublimate minerals, HCl – bearing fumarolic gas and atmospheric components (at first, water vapor) at relatively low temperatures, presumably not higher than 110–150°C.

It was experimentally found that $K_3Zn_2Cl_7$ melts incongruently at 250°C under atmospheric pressure (Nikonova *et al.*, 1941). Thermodynamic calculations for the KCl–ZnCl₂ system show that $K_3Zn_2Cl_7$ is stable at temperatures below 230–250°C (Baxter & Heikinheimo, 2005). This in agreement with our assumption on the temperature range of mellizinkalite formation.

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