

Alloriite, $\text{Na}_5\text{K}_{1.5}\text{Ca}(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{SO}_4)(\text{OH})_{0.5} \cdot \text{H}_2\text{O}$, a New Mineral Species of the Cancrinite Group¹

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Abstract—Alloriite, a new mineral species, has been found in volcanic ejecta at Mt. Cavalluccio (Campagnano municipality, Roma province, Latium region, Italy) together with sanidine, biotite, andradite, and apatite. The mineral is named in honor of Roberto Allori (b. 1933), an amateur mineralogist and prominent mineral collector who carried out extensive and detailed field mineralogical investigations of volcanoes in the Latium region. Alloriite occurs as short prismatic and tabular crystals up to 1.5×2 mm in size. The mineral is colorless, transparent, with a white streak and vitreous luster. Alloriite is not fluorescent and brittle; the Mohs' hardness is 5. The cleavage is imperfect parallel to $\{10\bar{1}0\}$. The density measured with equilibration in heavy liquids is 2.35 g/cm^3 and calculated density (D_{calc}) is 2.358 g/cm^3 (on the basis of X-ray single-crystal data) and 2.333 g/cm^3 (from X-ray powder data). Alloriite is optically uniaxial, positive, $\omega = 1.497(2)$, and $\epsilon = 1.499(2)$. The infrared spectrum is given. The chemical composition (electron microprobe, H_2O determined using the Penfield method, CO_2 , with selective sorption, wt %) is: 13.55 Na_2O , 6.67 K_2O , 6.23 CaO , 26.45 Al_2O_3 , 34.64 SiO_2 , 8.92 SO_3 , 0.37 Cl , 2.1 H_2O , 0.7 CO_2 , 0.08 $-\text{O} = \text{Cl}_2$, where the total is 99.55. The empirical formula ($Z = 1$) is $\text{Na}_{19.16}\text{K}_{6.21}\text{Ca}_{4.87}(\text{Si}_{25.26}\text{Al}_{22.74}\text{O}_{96})(\text{SO}_4)_{4.88}(\text{CO}_3)_{0.70}\text{Cl}_{0.46}(\text{OH})_{0.76} \cdot 4.73\text{H}_2\text{O}$. The simplified formula (taking into account the structural data, $Z = 4$) is: $[\text{Na}(\text{H}_2\text{O})][\text{Na}_4\text{K}_{1.5}(\text{SO}_4)] \cdot [\text{Ca}(\text{OH}, \text{Cl})_{0.5}](\text{Si}_6\text{Al}_6\text{O}_{24})$. The crystal structure has been studied ($R = 0.052$). Alloriite is trigonal, the space group is $P31c$; the unit-cell dimensions are $a = 12.892(3)$, $c = 21.340(5)$ Å, and $V = 3071.6(15)$ Å³. The crystal structure of alloriite is based on the same tetrahedral framework as that of afghanite. In contrast to afghanite containing clusters $[\text{Ca}-\text{Cl}]^+$ and chains $\dots\text{Ca}-\text{Cl}-\text{Ca}-\text{Cl}\dots$, the new mineral contains clusters $[\text{Na}-\text{H}_2\text{O}]^+$ and chains $\dots\text{Na}-\text{H}_2\text{O}-\text{Na}-\text{H}_2\text{O}\dots$. The strongest reflections in the X-ray powder diffraction pattern [d , Å (I , %)(hkl)] are: 11.3(70)(100), 4.85(90)(104), 3.76(80)(300), 3.68(70)(301), 3.33(100)(214), and 2.694(70)(314, 008). The type material of alloriite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. The registration number is 3459/1.

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A new mineral from the cancrinite group was identified in a sample from the south-southeastern slope of Mt. Cavalluccio located in the northern part of caldera of the volcano Sacrofano (the last eruption happened presumably 400 to 500 ka ago). This volcano pertains to the Sabatini volcanic complex, Latium, Italy. The new mineral was found and kindly placed at the disposal of Russian scientists for investigation by Roberto Allori, Italian amateur mineralogist and prominent mineral collector. The mineral is named *alloriite* in his honor. R. Allori (born 1933) made a great contribution to field investigations and the documentation of volca-

nic complexes in Latium. He has conducted his studies since 1960, and the mineralogical dataset of this region is largely based on the results of his investigations. Observations made by Allori and his collections of rocks and minerals are widely used for research purposes at the Roma University. In particular, two new mineral species, willhendersonite and piergorite, were discovered in his collections.

The sample containing the new mineral is a spherical volcanic bomb 4.5 cm in diameter composed of sanidine syenite. In addition to sanidine, this rock contains small amounts of biotite, andradite, and apatite. Alloriite occurs as transparent colorless and pale violet crystals up to 1.5×2 mm in size lining the walls of small miarolitic cavities (Fig. 1).

The alloriite crystals are hexagonal, short prismatic, isometric or flattened on pinacoid $\{0001\}$. They are

¹ A new mineral alloriite and its name were accepted by the Commission on New Minerals and Mineral Names, Russian Mineralogical Society, May 8, 2006. Approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association, August 2, 2006.

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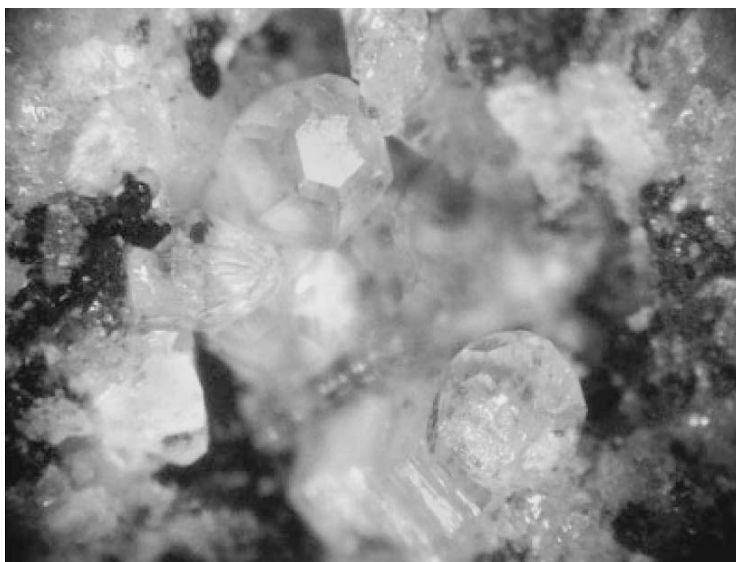


Fig. 1. Crystals of alloriite.

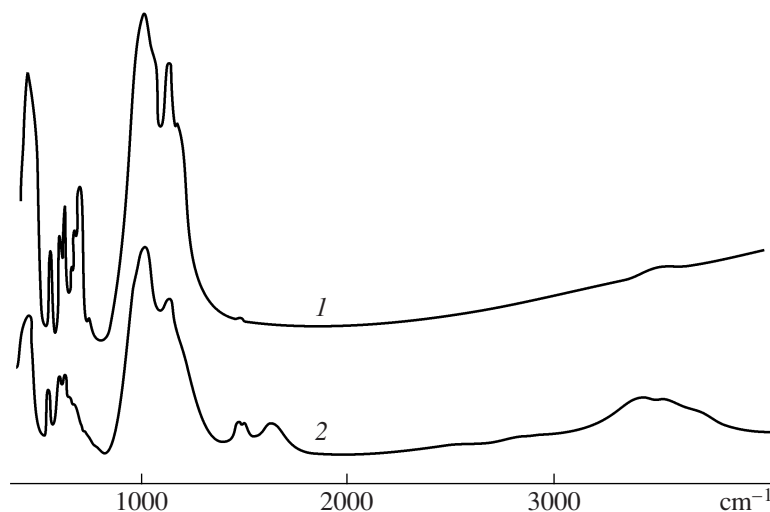


Fig. 2. IR spectra of (1) afghanite from the Ladjvardara lazurite deposit, Pamirs, Tadjikistan and (2) alloriite from Mt. Cavalluccio, Latium, Italy.

formed by unit forms $\{0001\}$, $\{10\bar{1}0\}$, $\{10\bar{1}3\}$, $\{10\bar{1}4\}$, and $\{11\bar{2}0\}$. The mineral is brittle; the imperfect cleavage is parallel to $\{10\bar{1}0\}$; the fracture is conchoidal. The Mohs' hardness is 5. The alloriite density measured with equilibration in heavy liquids is $2.35(1) \text{ g/cm}^3$. The calculated density values 2.358 g/cm^3 (from X-ray single-crystal data) and 2.333 g/cm^3 (from empirical formula and X-ray powder data).

The wavenumbers of the absorption bands in the infrared spectrum of alloriite and their attribution are (cm^{-1} ; sh is shoulder; the wavenumbers of the strongest bands (Fig. 2) are underlined): 3660sh (O–H-stretching vibrations of OH-groups ?); 3500 , 3430 (O–H-stretching

vibrations of H_2O molecules); 1630 (bending vibrations of the CO_3^{2-} ions), 1490 , 1463 (stretching vibrations of CO_3^{2-} ions); 1185sh , 1123 (SO_4^{2-} stretching vibrations); 1105sh , 1006 (stretching vibrations of the tetrahedral framework); 750sh , 710sh (planar bending vibrations of the CO_3^{2-} ions ?); 670 , 646 , 619 , 596 , 543 (bending vibrations of the SO_4^{2-} ions and tetrahedral framework); and 445 , 425sh (bending vibrations of Si–O–Si). According to the locations of most bands, the IR spectrum of alloriite is close to that of afghanite (Ballirano et al., 1996) and differs from the latter mainly in the presence of fairly strong bands of H_2O

Table 1. Chemical composition of alloriite

Component	Content, wt %	Range	Standard deviation	Standard
Na ₂ O	13.55	12.76–14.27	0.65	Albite
K ₂ O	6.67	6.20–7.04	0.3	Microcline
CaO	6.23	5.42–7.01	0.6	Wollastonite
Al ₂ O ₃	26.45	26.08–26.93	0.3	Al ₂ O ₃
SiO ₂	34.64	34.26–35.15	0.3	SiO ₂
SO ₃	8.92	8.30–9.92	0.6	FeS ₂
Cl	0.37	0.15–0.64	0.2	NaCl
H ₂ O	2.1 ± 0.2			
CO ₂	0.7 ± 0.1			
–O=Cl ₂	–0.08			
Total	99.55			

Note: Mg, Mn, Fe, Sr, Ba, Pb, P, and F contents are below detection limits (<0.05 to 0.3 wt %)

molecules and CO₃ groups and the other proportions of band intensities. The important distinction of alloriite is the absence of a band at 685 cm^{–1} in the IR spectrum that is characteristic of afghanite from both volcanic assemblages and lazurite skarn deposits.

According to the microscopic study, the new mineral is optically uniaxial and positive. Refractive indexes are $\omega = 1.497(2)$ and $\epsilon = 1.499(2)$. Under a microscope, alloriite is colorless and is not pleochroic.

The chemical composition was determined with electron microprobe (average over 5 point analyses)

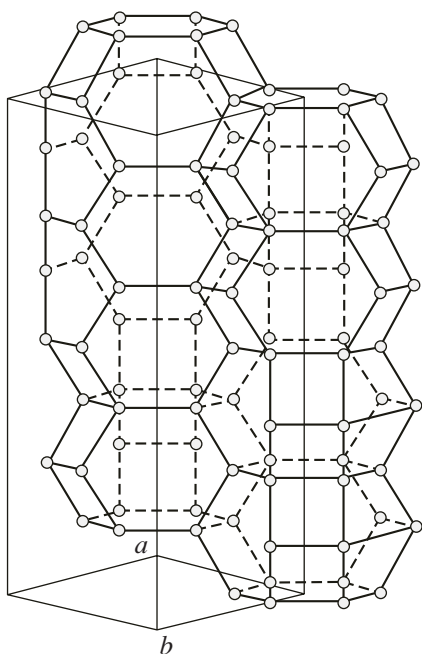


Fig. 3. A fragment of the afghanite-type framework of alloriite.

(Table 1). The water content was measured with the Penfield method, and the CO₂ content with selective sorption on the ascarite sorbent from gaseous products of glowing in the oxygen flux at 1000°C and atmospheric pressure.

The empirical formula calculated on the basis of (Si, Al)₄₈ (Z = 1) with allowance for the charge balance is: Na_{19.16}K_{6.21}Ca_{4.87}(Si_{25.26}Al_{22.74}O₉₆)(SO₄)_{4.88}(CO₃)_{0.70}Cl_{0.46}(OH)_{0.76} · 4.73H₂O. The simplified formula (Z = 4) is as follows: [Na(H₂O)][Na₄K_{1.5}(SO₄)] · [Ca(OH,Cl)_{0.5}](Si₆Al₆O₂₄). In the latter formula, the atoms are grouped according to the structural data (see below).

The idealized formula of alloriite is Na₅K_{1.5}Ca(Si₆Al₆O₂₄)(SO₄)(OH_{0.5}) · H₂O. The theoretical chemical composition calculated from this formula is (wt %): 14.75 Na₂O, 6.72 K₂O, 5.34 CaO, 29.11 Al₂O₃, 34.31 SiO₂, 7.62 SO₃, 2.14 H₂O, where the total is 99.99.

The crystal structure of alloriite was studied on a single crystal (an ENRAF-NONIUS autodiffractometer, Mo radiation, 3040 reflections with $F > 6\sigma F$) to $R = 0.052$. The mineral is trigonal, and the space group is $P31c$. The unit-cell dimensions are $a = 12.892(3)$, $c = 21.340(5)$ Å, and $V = 3071.6(15)$ Å³.

The tetrahedral framework corresponding to that of afghanite (Pobedinskaya et al., 1991; Rastsvetayeva et al., 1993; Ballirano et al., 1997) fits Si_{6.65}Al_{5.35}O₂₄ in terms of composition, with an ordered Si and Al distribution inherent to the alloriite structure (Figs. 3 and 4). The strongest layer reflections are a multiple of 4, indicating that the period of alloriite, as well as afghanite, is a multiple of cancrinite. From four independent sites of Al, three are with Al–O distances ranging from 1.718 to 1.731 Å; the fourth distance, 1.702 Å, implies that Al is partially replaced with Si in the tetrahedron. The framework of alloriite and afghanite is characterized by a tetrahedron sequence of the ABABACAC type and contains two types of channels, broad and narrow.

The channels of the first type running along 3-fold axes ($1/3, 2/3, z$) and ($2/3, 1/3, z$) consist of alternating large (liottite type) and small (cancrinite type) cages, which are divided by shrinkages of the channels at their intersections with tetrahedral layers of type C (Ballirano et al., 1997). A cavity of the liottite type ABABAC can incorporate as much as three SO₄ groups. A part of the SO₄ groups in alloriite is replaced by the carbonate group, 0.3CO₃, in each liottite cage. Cancrinite cavities AC contain clusters [Ca · Cl]⁺ (in davyne, microsomalite, quadridavyne, and afghanite) or clusters [Na · H₂O]⁺ (in cancrinite, vishnevite, piglianoite, and alloriite). Thus, the predominance of OH-groups over Cl in small (cancrinite type) cages of broad channels is one of the distinctive features of alloriite in comparison with afghanite. A composition of these cavities is Ca₄Cl₂ for afghanite (Ballirano et al., 1997) and Ca₄(OH)_{1.66}Cl_{0.34} for alloriite (this study). The position of Cl is reliably fixed on the 3-fold axis in the cancrinite cage with the population 0.2. The position of O fills up around the axis.

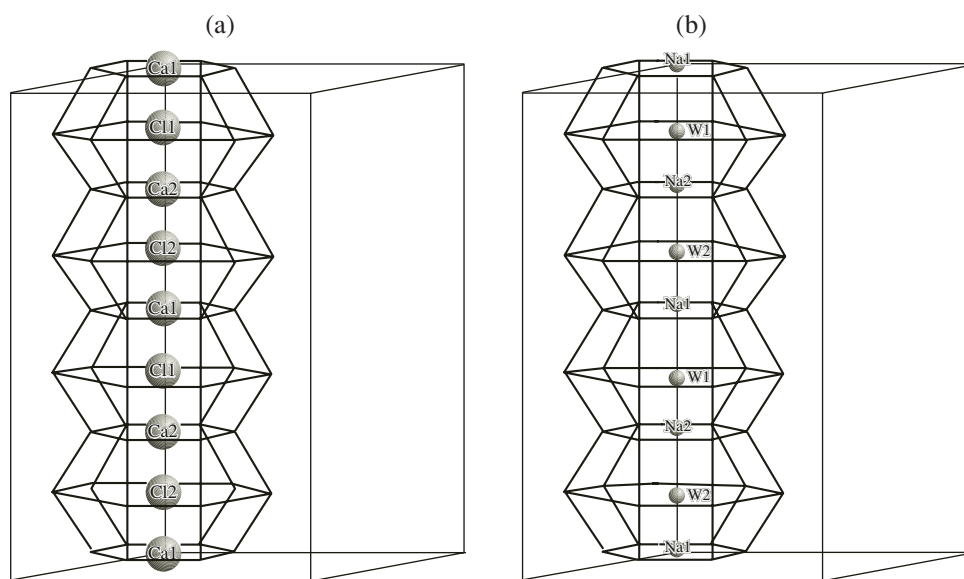


Fig. 4. Narrow cancrinite-type channel in (a) afghanite and (b) alloriite.

The second-type channels [narrow, running along the 3-fold axes (00 z)] are formed by the sequence of cancrinite cages. A part of Ca and Cl in afghanite is hosted in these channels and forms chains ...Ca–Cl–Ca–Cl..., whereas H₂O–Na chains (idealized ...–Na–H₂O–Na–H₂O–...) are hosted in the narrow channels of alloriite. A small amount of Na in the narrow channels is replaced with calcium; therefore, the composition of the chains is described as [(Na_{3.54}Ca_{0.46})(H₂O)_{3.5}(OH)_{0.5}]. Thus, the second (and the most important) difference between alloriite and afghanite is similar to the differences between other pairs of allied cancrinite-group minerals: davyne (with chains ...Ca–Cl–Ca–Cl...) and members of the cancrinite–vishnevite series (with chains ...–Na–H₂O–Na–H₂O–...), as well as microsommite (with chains ...Ca–Cl–Ca–Cl...) and piglianoite (with chains ...–Na–H₂O–Na–H₂O–...) (Table 2).

The oxygen position is split into subpositions on the axis and around it in both columns of the cancrinite cavities and cancrinite cages of the broad channels. While the O positions on the axis and around it are approximated by OH-groups and H₂O molecules, respectively, it is taken into account that OH-groups are comparable with Cl atoms in size and, hence, can locate on the axis, whereas water molecules are much larger and tend to localize around the axis, as was frequently observed in the structures of eudialyte, for example. An excess of positive charges requires the substitution of H₂O with OH; however, a predominance of Si over Al prevents the replacement of framework oxygen atoms with OH-groups, because, in this case, the Si–OH–Si framework fragments disturb the local charge balance. In addition, the IR spectrum of alloriite does not show bands of the acid Si–OH groups (range 1800–3200 cm^{–1}).

Table 2. Comparative characteristics of sulfate minerals belonging to the cancrinite group*

Sequence of tetrahedral layers	a , Å b , Å	Minerals with the chain ...Ca–Cl–Ca–Cl... in the cancrinite channel	Minerals with the chain ...–Na–H ₂ O–Na–H ₂ O–... in the cancrinite channel
<i>AB</i>	12.7–13.0 5.3–5.4	Davyne	Vishnevite
<i>AB</i>	22.1–22.2 5.2–5.3	Microsommite	Piglianoite
<i>ABABACAC</i>	12.8–12.9 21.3–21.5	Afghanite	Alloriite

* Minerals presented in the table contain cages of cancrinite and liottite types and their combinations (Pobedinskaya et al., 1991; Ballirano et al., 1996, 1997; Bonaccorsi and Merlino, 2005; Della Ventura et al., 2005).

Table 3. X-ray powder diffraction data for alloriite

$I_{\text{meas}}, \%$	$D_{\text{meas}}, \text{\AA}$	$D_{\text{calc}}, \text{\AA}$	hkl
70	11.3	11.21	100
20	10.7	10.705	002
30	6.53	6.470	110
20	6.03	6.019	103
40	5.35	5.421	201
90	4.85	4.830	104
20	4.36	4.407	203
40	4.15	4.155	211
60	4.03	4.000	105
80	3.76	3.736	300
70	3.68	3.680	301
100	3.33	3.321	214
50	3.096	3.125, 3.108, 3.097, 3.076	116, 310, 222, 311
40	2.970	2.985, 2.951	312, 107
30	2.855	2.850	313
60	2.795	2.802, 2.778, 2.769	400, 401, 224
70	2.694	2.688, 2.676	314, 008
30	2.626	2.608	403
10	2.528	2.515	315
40	2.488	2.482	404
20	2.390	2.397, 2.384	226, 412
60	2.165	2.176, 2.157	308, 330
30	2.070	2.074, 2.066, 2.062	219, 407, 228
20	2.010	2.017, 2.000	510, 334
40	1.941	1.935	408
30	1.890	1.889, 1.884	319, 514
50	1.812	1.813, 1.805	409, 418
30	1.766	1.769, 1.763, 1.763, 1.762	2.1.11, 604, 3.1.10, 1.0.12
30	1.745	1.746, 1.742	329, 434
30	1.647	1.655, 1.655, 1.644	525, 606, 2.1.12
30	1.619	1.618	440
10	1.564	1.562, 1.562, 1.562	2.2.12, 533, 703
10	1.551	1.554, 1.552, 1.550, 1.548, 1.547	620, 3.2.11, 621, 444, 3.1.12
30	1.532	1.534, 1.534, 1.532	534, 704, 608
20	1.506	1.505	4.0.12
50	1.386	1.384	448
50	1.357	1.355	804
20	1.339	1.338	0.0.16
20	1.311	1.310	1.1.16
30	1.299	1.298	718
10	1.283	1.282	4.3.12
10	1.275	1.274, 1.274, 1.272	814, 807, 4.0.15
40	1.248	1.254, 1.249, 1.248, 1.245	815, 638, 3.2.15, 900

The X-ray powder pattern of alloriite (Table 3) was obtained using an RKG-86 camera, Fe radiation. The unit-cell dimensions refined from the powder pattern are $a = 12.940(2) \text{ \AA}$, $c = 21.409(5) \text{ \AA}$, and $V = 3104.5(20) \text{ \AA}^3$.

Comparative characteristics of alloriite and afghanite are given in Table 4. As can be seen, these minerals are significantly different in both chemical composition and physical properties (IR spectra, refraction indexes, and density).

Table 4. Comparative characteristics of alloriite and afghanite

Mineral	Alloriite	Afghanite
Formula	$\text{Na}_2\text{K}_{1.5}\text{Ca}(\text{Si}_6\text{Al}_6\text{O}_{24})$ $(\text{SO}_4)(\text{OH})_{0.5} \cdot \text{H}_2\text{O}$	$(\text{NaK})_{0.5}\text{Ca}_{2.5}(\text{Si}_6\text{Al}_6\text{O}_{24})$ $(\text{SO}_4)_{1.5}\text{Cl}_{1.5}$
Symmetry	Trigonal	Trigonal or hexagonal
Space group	$P31c$	$P31c$ or $P6_3mc$
a , Å	12.892	12.77–12.88
c , Å	21.340	21.35–21.46
V , Å ³	3072.1	3015–3086
Z	4	4
Strong reflections in X-ray powder pattern, d , Å (I %)	11.3(100), 4.85(90), 4.03(60), 3.76(80), 3.68(70), 3.33(100), 2.795(60), 2.694(70), 2.165(60)	4.8257(30), 3.9993(12), 3.6943(100), 3.3009(56), 2.7495(12), 2.6775(25), 2.1339(18)
Wave numbers of strong (by integral intensities) bands of IR spectrum, cm^{-1} *	<u>3500</u> , <u>3430</u> , 1123, 1006, 619, 596, 543, 445	1121, 1004, <u>685</u> , <u>667</u> , 613, 595, 542, 430
Optical parameters		
ω	1.497	1.522–1.528
ϵ	1.499	1.528–1.533
Density, g/cm^3	2.358 (calculated from structural data) 2.334 (calculated from empirical formula and unit-cell dimensions refined from X-ray powder pattern) 2.35 (measured)	2.65 (calculated) 2.55 (measured)
Source	This study	Bariand et al., 1968; Pobedinskaya et al., 1991; Rastsvetaeva et al., 1993. Ballirano et al., 1994, 1996, 1997; Bonaccorsi, Merlino, 2005

* Wave numbers of the diagnostic bands are underlined.

The accuracy of the determination of the chemical composition, refractive indexes, and density is confirmed by a good compatibility index calculated from the Gladstone–Dale equation: $1 - (K_p/K_c) = -0.033$ for the measured density, $1 - (K_p/K_c) = -0.041$ for the density estimated from the empirical formula and X-ray powder pattern, and $1 - (K_p/K_c) = -0.029$ for the density calculated from the structural data.

The type material of alloriite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. The registration number is 3459/1.

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