

Original paper

Agardite-(Nd), $\text{NdCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$, from the Hilarion Mine, Lavrion, Greece: mineral description and chemical relations with other members of the agardite–zálesiite solid-solution system

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Agardite-(Nd), ideally $\text{NdCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$, has been approved by the IMA Commission on New Minerals, Nomenclature and Classification as a new mineral species, a Nd-dominant analogue of agardite-(Y), -(La) and -(Ce), a member of the mixite group. The material considered as the holotype was found in the Hilarion Mine, Agios Konstantinos (Kamariza), Lavrion District, Attiki Prefecture, Greece. Agardite-(Nd) occurs as thin, acicular to hair-like crystals up to 0.5 mm long and up to 5 μm thick, elongate along [001], with hexagonal cross section. More commonly, agardite-(Nd), agardite-(Y) and/or agardite-(La) form rims (up to 3 μm thick) of zoned acicular crystals (up to 0.015 \times 1.2 mm) with a core consisting of zálesiite. They are usually combined in sprays or radiating clusters up to 2 mm. Gradual compositional transitions among zálesiite, agardite-(Nd), agardite-(Y) and agardite-(La) are typical. The minerals of the agardite–zálesiite solid-solution system are associated here with zincolivenite, azurite, malachite and calcite in cavities of an oxidized ore mainly consisting of goethite and in cracks of supergene altered mica schist. Agardite-(Nd) is transparent, light bluish green, with white streak, and lustre vitreous in crystals and silky in aggregates. Crystals are brittle, cleavage is none observed, and fracture is uneven. Calculated density is 3.81 g/cm³. Optically, agardite-(Nd) is uniaxial positive, $\omega = 1.709\text{--}1.712$, $\epsilon = 1.775\text{--}1.780$. Pleochroism is strong: $O =$ pale turquoise-coloured, $E =$ bright green-blue. Chemical composition of agardite-(Nd) (averaged of 6 electron microprobe analyses, H₂O by difference) is: CuO 42.63, ZnO 3.52, CaO 2.15, Y₂O₃ 1.27, La₂O₃ 2.16, Ce₂O₃ 0.38, Pr₂O₃ 0.79, Nd₂O₃ 3.05, Sm₂O₃ 0.32, Gd₂O₃ 0.40, Dy₂O₃ 0.31, As₂O₃ 33.65, H₂O_{calc.} 9.37, total 100.00 wt. %. The empirical formula based on 3 As atoms is: $[(\text{Nd}_{0.19}\text{La}_{0.14}\text{Y}_{0.12}\text{Pr}_{0.05}\text{Gd}_{0.02}\text{Ce}_{0.02}\text{Sm}_{0.02}\text{Dy}_{0.02})_{\Sigma\text{REE}0.58}\text{Ca}_{0.39}]_{\Sigma 0.97}(\text{Cu}_{5.49}\text{Zn}_{0.44})_{\Sigma 5.93}(\text{AsO}_4)_3(\text{OH})_{5.38} \cdot 2.64\text{H}_2\text{O}$. Chemical data on other minerals of the agardite–zálesiite system from the Hilarion Mine are also given and discussed. Agardite-(Nd) is hexagonal, space group $P6_3/m$; unit cell parameters are: $a = 13.548(8)$, $c = 5.894(6)$ Å, $V = 937(2)$ Å³, $Z = 2$. The strongest reflections of the X-ray powder diagram ($d, \text{Å} - [hkl]$) are: 11.70–100[100]; 4.443–22[111, 120]; 3.545–18[211, 121]; 2.935–18[221, 400]; 2.695–13[112, 320, 230], 2.559–10[410], 2.453–30[212, 122, 231]. The type specimen is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow.

Keywords: agardite-(Nd), new mineral, mixite group, Lavrion, oxidized zone of ore deposit

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1. Introduction

The mixite group includes hexagonal arsenates and phosphates with the general formula $ACu_6(\text{TO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ in which $T = \text{As}^{5+}$, P^{5+} and $A = \text{REE}^{3+}$, Bi^{3+} , Al^{3+} , Ca^{2+} , Pb^{2+} . Agardites, the REE arsenate members, are the most widespread minerals of the group, common in the oxidation zone of many ore deposits. They are rare earth minerals proper, in which the sum of REE (lanthanides + Y) prevails over any other constituent (Ca, Pb, Bi and Al) in the A site, in accordance with the Levinson rule (Levinson 1966; Bayliss and

Levinson 1988). Three agardites with different species-defining REE were known as valid, IMA-approved mineral species before this work: agardite-(Y) with the idealized formula $\text{YCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ (Dietrich et al. 1969), agardite-(La) $\text{LaCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ (Fehr and Hochleitner 1984; Anthony et al., 2000), and agardite-(Ce) $\text{CeCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ (Walenta and Theye 2004).

Agardite with dominant Nd has been reported in literature several times for different localities. These included several mines in the Schwarzwald, Germany, namely Käfersteige near Pforzheim, Daniel im Töss, Wittichen

(Johann am Burgfelsen), Silberbrünnle near Gengenbach and Gottesehre near Urberg (Walenta 1992, 2003), the Osenovlak deposit in Bulgaria (Kunov et al. 2002), the Simon and Big 3 mines in Nevada, USA (Castor and Ferdock 2004), Cobar in New South Wales, Australia (Frost et al. 2004, 2005), and the Tefler Mine, Western Australia (Downes et al. 2006). Thus, it is probably not a very rare mineral in the oxidized zone of ore deposits. However it has not been explicitly characterized and not approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC). Agardite-(Nd) was present in the official IMA-CNMNC List of Mineral Names (posted on the IMA-CNMNC website) with status “N = published without approval of the CNMNC”.

We have studied agardite-(Nd) from famous ancient Lavrion mining district in Greece and submitted formal proposal on this “old new” mineral to the IMA-CNMNC. Both the mineral and its name have been approved by the Commission (IMA no. 2010-056). The type specimen is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, with registration no. 4020/1.

In this paper, we give a description of agardite-(Nd) from Lavrion, considered as the holotype of this mineral species, and other intimately associated members of the agardite $REECu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$ – zálesiite $CaCu_6(AsO_4)_2(AsO_3OH)(OH)_6 \cdot 3H_2O$ solid-solution system.

2. Occurrence

The Lavrion district is located *c.* 50 km southeast of Athens, in Attici Prefecture, Greece, and is famed for the exploitation of Pb–Ag-rich ore during ancient times. It belongs to the Attic–Cycladic Belt, which is a polymetamorphic terrane within the Alpine orogen of the Hellenides and includes three Mesozoic tectono-metamorphic units, which are, from bottom to top, the Basal Unit, the Cycladic–Blueschist Unit and the Upper Unit. Neogene and Quaternary sediments also occur in the area (Marinos and Petrascheck 1956; Altherr and Siebel 2002; Skarpelis 2007; Liati et al. 2009).

The “Basal Unit” consists of a metamorphosed volcano-sedimentary mélange (Kessariani Schists) sandwiched between two calcic and rarely mica-bearing marble horizons (“Upper” and “Lower” marbles). Geochronological data and fossils indicate a late Triassic–early Jurassic age for the protoliths (Marinos and Petrascheck 1956; Liati et al. 2009). A detachment fault separates the Basal Unit from the Cycladic–Blueschist Unit, even though the original contact formed a major thrust fault (Marinos and Petrascheck 1956; Skarpelis 2007). The Cycladic–Blueschist

Unit consists of HP–LT metapelites and metasandstones with minor intercalations of carbonates and blueschist-facies basic metaophiolites retrogressed to greenschists (Baltatzis 1996; Photiades and Saccani 2006).

Miocene igneous rocks intruded the Basal Unit causing intense contact metamorphism and ore deposition. Brittle tectonics in the Basal Unit facilitated emplacement of subvertical dykes of granodiorite to granite porphyries and subvolcanic andesite (Marinos and Petrascheck 1956; Altherr and Siebel 2002; Skarpelis et al. 2008; Voudouris et al. 2008a, b). Intrusion of a granodiorite stock caused a contact metamorphism of the surrounding Kessariani Schists accompanied by hornfelses and Ca-scarns formation. The K–Ar dating on orthoclase from a dyke rock provides a minimum age of 9.4 ± 0.3 Ma for the igneous activity (Skarpelis et al. 2008). Two more K–Ar ages of 8.8 ± 0.5 Ma and 8.27 ± 0.11 Ma have been reported for a whole-rock sample of the granodiorite and its biotite (Marinos 1971; Altherr et al. 1982).

The Miocene igneous activity was also temporally associated with ore formation and detachment fault operation (Liati et al. 2009). A variety of mixed sulphide ore types including intrusion-hosted, skarn-, vein- and mainly manto carbonate-replacement-type ores were deposited mostly along the contacts between the two marble horizons and the intercalated schists (Marinos and Petrascheck 1956; Skarpelis 2007; Voudouris et al. 2008a, b). The manto-type ores consist primarily of pyrite, sphalerite, galena, arsenopyrite and chalcopyrite.

Two extensive mining centers, Plaka and Agios Konstantinos (Kamariza), as well as several smaller ones, cover *c.* 150 km² of the Lavrion area. The (Pb–Zn–Ag) ± Au sulphide deposits of the Kamariza area are genetically related to the emplacement of the Miocene east–west trending subvolcanic andesitic dykes, the only magmatic rock in the area (Marinos and Petrascheck 1956; Voudouris and Economou-Eliopoulos 2003; Solomos et al. 2004; Skarpelis 2007; Voudouris et al. 2008b). Replacement veins as well as chimneys and mantos of massive sulphides are the major orebody types. Ores are developed along the contact between Kessariani Schists and Lower Marbles or within the marbles themselves, always close to the andesitic dykes. The main ore minerals are sulphides and sulphoarsenides, native metals (Au, Bi), sulphosalts of Ag, Cu, Pb with As, Sb and Bi. Ore mineralogy demonstrates that most of the Kamariza ore has formed by moderately to low-saline hydrothermal fluids at intermediate to high sulphidation conditions. Subsequent oxidation of the primary sulphides resulted in a development of an extensive supergene minerals zone from which hundreds of mineral species have been described (Katerinopoulos and Zissimopoulou 1994; Baumgartl and Burow 2002; Skarpelis and Argyraki 2009). Formation of the different supergene mineral species and assemblages

was controlled mainly by near-neutral to mildly acidic conditions, variable P_{CO_2} , metal and sulphate ion activities and Eh (Skarpelis and Argyraki 2009).

Agardite-(Nd) and other minerals of the agardite-zálesiite solid-solution system were found in the Hilarion Mine, Agios Konstantinos (Kamariza). They are supergene minerals formed in the oxidation zone of a sulphide-rich orebody situated at the contact between calcite Lower Marble and mica schist of Kessariani. These minerals occur in cavities of a lode (up to 1 m thick) of oxidized ore composed by goethite (limonite) with subordinate clay minerals, mainly kaolinite, quartz, and calcite. Also they are observed in cracks of supergene altered mica schist contacted with this oxidized ore. Agardite-zálesiite system members are closely associated with zincolivenite, azurite, malachite, and calcite.

3. Appearance, physical properties and optical data

Agardite-(Nd) occurs as thin, acicular to hair-like, commonly divergent crystals up to 0.5 mm long and 1–3 μm , rarely up to 5 μm thick, with hexagonal cross section.

They are elongated along [001], the prismatic belt is formed by faces {100} or {110}. Twinning was not observed. More typically, agardite-(Nd), as well as agardite-(Y) and agardite-(La), form marginal zones (up to 3 μm thick) of larger (up to 1.2 mm long and 10–15 μm thick) zoned acicular crystals with a core consisting of zálesiite. Crystals of both types are usually combined in sprays or radiating clusters (Figs 1 and 2) up to 2 mm across. In some cavities occur soft, cotton-like open-work fibrous aggregates of agardite-zálesiite system minerals, visually indistinguishable from each other.

Agardite-(Nd) is transparent, light bluish green (turquoise-coloured) in aggregates to almost colourless in separate thin needles or fibres. Streak is white. Lustre is vitreous in relatively thick crystals and silky in aggregates. It is non-fluorescent in UV light and cathode rays. Mohs' hardness is < 3. Crystals are brittle, cleavage or parting are none observed, fracture is uneven. Density could not be measured because crystals are too thin and form open-work aggregates; density calculated from the empirical formula is 3.81 g/cm^3 .

Optically, agardite-(Nd) is uniaxial positive. Refractive indexes for one sample are: $\omega = 1.709(3)$, $\varepsilon = 1.775(5)$; for another sample, they are slightly

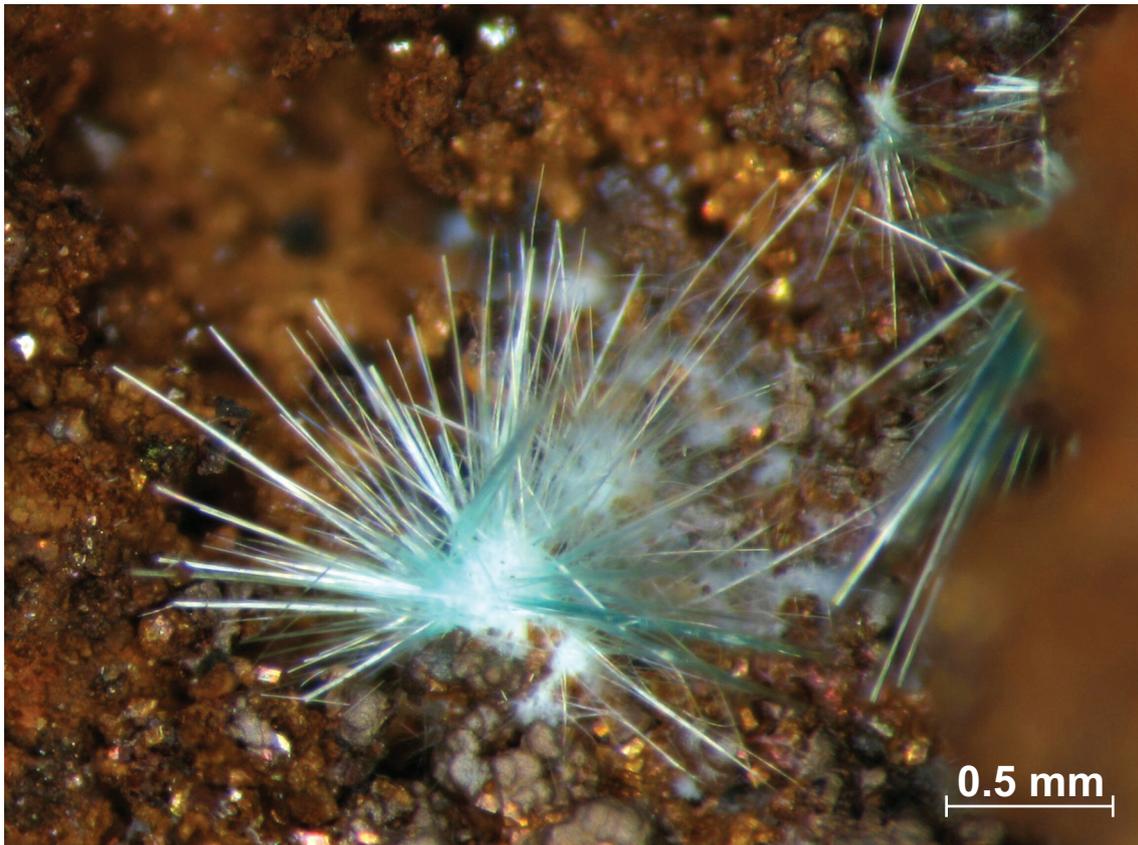


Fig. 1 Radiating cluster (1.5 mm in diameter) of zoned crystals consisting of a zálesiite core and agardite-(Nd) peripheral parts. Hilarion Mine, Lavrion.



Fig. 2 Radiating clusters (up to 1.5 mm in diameter) of zoned crystals consisting of a zálesiite core and agardite-(Y)/agardite-(Nd)/agardite-(La) peripheral parts associated with compact spherulite of zincolivenite. Hilarion Mine, Lavrion.

higher: $\omega = 1.712(3)$, $\epsilon = 1.780(5)$. Pleochroism is strong: O = pale turquoise-coloured, E = bright green-blue. The absorption scheme is: $E > O$.

4. Chemical composition

Chemical analyses were performed using a Camebax SX 50 electron microprobe instrument operating at a voltage of 20 kV and a beam current of 2 nA; the electron beam diameter was 2 μm . As standards were used FeAsS (Fe, As), CuO (Cu), ZnO (Zn), diopside (Ca), YPO_4 (Y), LaPO_4 (La), CePO_4 (Ce), PrPO_4 (Pr), NdPO_4 (Nd), SmPO_4 (Sm), GdPO_4 (Gd), DyPO_4 (Dy). Other elements with atomic numbers higher than O were below detection limits. The water was not measured directly because of scarcity of pure material. Analytical data are given in Tab. 1. The empirical formula of agardite-(Nd) based on 3 As atoms is $[(\text{Nd}_{0.19}\text{La}_{0.14}\text{Y}_{0.12}\text{Pr}_{0.05}\text{Gd}_{0.02}\text{Ce}_{0.02}\text{Sm}_{0.02}\text{Dy}_{0.02})_{\Sigma\text{REE}0.58}\text{Ca}_{0.39}]_{\Sigma 0.97}(\text{Cu}_{5.49}\text{Zn}_{0.44})_{\Sigma 5.93}(\text{AsO}_4)_3(\text{OH})_{5.38} \cdot 2.64\text{H}_2\text{O}$. Its simplified, end-member formula is $\text{NdCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$, which requires CuO 43.45, Nd_2O_3 15.32, As_2O_5 31.39, H_2O 9.84, total 100.00 wt. %.

Most of “agardite” crystals studied here show chemical heterogeneity. The most significant variations are

found for large A cations, in the $\text{Ca}/\Sigma\text{REE}$ and the $\text{Y}/\text{La}/\text{Nd}$ ratios. Commonly a crystal consists of zones corresponding to two, three or, in some cases, even four mineral species. Zálesiite typically occurs in core of a crystal whereas agardite-(Y), agardite-(Nd) and/or agardite-(La) form its peripheral parts. As a rule, no sharp boundaries are observed between chemically different areas: gradual compositional transitions between zálesiite, agardite-(Nd), agardite-(Y) and agardite-(La) are common instead. Typical compositions of four minerals forming here the continuous solid-solution system are given in Tab. 1. Ca-free agardites were not found at this locality, and neither was a REE -free zálesiite. Some analyses of the latter show low contents of lanthanides (close to their detection limits) but never less than 0.5 wt. % Y_2O_3 .

All minerals of the agardite–zálesiite solid-solution system at this locality are Ce-depleted, obviously as a result of cerium fractionation from other REE because of its oxidation from Ce^{3+} to Ce^{4+} . The main reason may represent the influence of oxygen-rich meteoric water and sulphuric acid produced by oxidation of primary ore sulphides.

Another characteristic chemical feature of the agardite–zálesiite system minerals from the Hilarion mine is the presence of zinc admixture, typically ranging from

Tab. 1 Chemical composition of minerals of the agardite-zálesiite solid-solution system from the Hilarion mine, Lavrion

Constituent	Agardite-(Nd)*	Agardite-(La)	Agardite-(Y)	Zálesiite
		wt. %		
FeO	0.00 [0.00–0.02]	<i>bdl</i>	3.04	<i>bdl</i>
CuO	42.63 [41.3–41.5]	42.18	41.86	44.92
ZnO	3.52 [3.1–3.8]	3.35	1.02	0.95
CaO	2.15 [1.9–2.3]	2.02	2.06	3.14
Y ₂ O ₃	1.27 [0.7–1.4]	1.48	3.21	1.77
La ₂ O ₃	2.16 [1.6–2.6]	3.40	2.68	2.01
Ce ₂ O ₃	0.38 [0.0–0.6]	0.39	0.27	<i>bdl</i>
Pr ₂ O ₃	0.79 [0.4–0.9]	0.74	<i>bdl</i>	0.83
Nd ₂ O ₃	3.05 [2.8–3.5]	2.54	1.48	1.59
Sm ₂ O ₃	0.32 [0.0–0.5]	<i>bdl</i>	0.22	<i>bdl</i>
Gd ₂ O ₃	0.40 [0.3–0.6]	0.30	0.31	<i>bdl</i>
Dy ₂ O ₃	0.31 [0.0–0.5]	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
As ₂ O ₅	33.65 [32.1–34.4]	33.09	33.18	33.49
H ₂ O _{calc.} **	(9.37)	(10.51)	(10.67)	(11.30)
Total	(100.00)	(100.00)	(100.00)	(100.00)
formulae calculated on the basis of 3 As atoms				
Ca	0.39	0.38	0.38	0.58
Y	0.12	0.14	0.30	0.16
La	0.14	0.22	0.17	0.13
Ce	0.02	0.02	0.02	–
Pr	0.05	0.05	–	0.05
Nd	0.19	0.16	0.09	0.10
Sm	0.02	–	0.01	–
Gd	0.02	0.02	0.02	–
Dy	0.02	–	–	–
ΣREE	0.58	0.61	0.61	0.44
Σ(Ca+REE)	0.97	0.99	0.99	1.02
Fe	–	–	0.44	–
Cu	5.49	5.52	5.47	5.82
Zn	0.44	0.43	0.13	0.12
Σ(Cu+Zn+Fe)	5.93	5.95	6.04	5.94
As	3	3	3	3
OH***	5.38	5.49	5.67	5.36
H ₂ O***	2.64	3.33	3.32	3.79

* Average data for six point-analyses obtained from two crystals of agardite-(Nd) with thickness 0.005 mm and outer zone (0.003 mm thick) of one crystal with zálesiite core; ranges are in square brackets. ** By total difference. *** The OH/H₂O ratio is calculated by charge balance with (AsO₄)₃. *bdl* – below detection limit.

1.0 to 3.5 wt. % ZnO. Moreover, in some analyses, up to 3 wt. % FeO was detected (Tab. 1).

5. X-ray crystallography

Single-crystal X-ray studies of agardite-(Nd) were not carried out because crystals are very thin and typically divergent. A STOE IPDS II single-crystal diffractometer equipped with an image plate detector was used to obtain X-ray powder data, by means of the Gandolfi method

(MoK_α radiation). X-ray powder diffraction pattern of agardite-(Nd) (Tab. 2) is close to those of other arsenates of the mixite group. Unit-cell parameters calculated from the powder data are: $a = 13.548(8)$, $c = 5.894(6)$ Å, $V = 937(2)$ Å³, $Z = 2$.

All crystallographic and structural studies of “agardites” and related arsenates of the mixite group show the same space group, $P6_3/m$, and identical structure (Hess 1983; Aruga and Nakai 1985; Mereiter and Preisinger 1986; Sejkora et al. 1999; Walenta and Theye

Tab. 2 X-ray powder diffraction data of agardite-(Nd) from the Hilarion mine, Lavrion

I_{obs}	d_{obs}	I_{calc}^*	d_{calc}	hkl
100	11.70	100	11.73	100
4	5.291	2	5.267	101
22	4.443	3, 13	4.446, 4.435	111, 120
7	4.173	4	4.158	201
5	3.921	2	3.911	300
18	3.545	2, 17	3.544, 3.544	211, 121
6	3.397	5	3.387	220
8	3.255	1, 7	3.254, 3.254	130, 310
18	2.935	9, 10	2.937, 2.933	221, 400
9	2.815	1, 4	2.849, 2.849	131, 311
13	2.695	3, 4, 5	2.702, 2.692, 2.692	112, 320, 230
10	2.559	11	2.560	410
30	2.453	11, 16, 4	2.454, 2.454, 2.449	212, 122, 231
3	2.223	2, 1	2.223, 2.217	222, 240
3	2.185	1, 1	2.184, 2.180	312, 501
4	2.104	3, 1	2.107, 2.107	510, 150
3	2.078	1, 1	2.079, 2.075	402, 241
3	1.983	1, 1	1.987, 1.987	322, 232
2	1.935	2	1.929	430
3	1.835	2	1.833	431
8	1.776	2, 5	1.772, 1.772	422, 242
4	1.714	6	1.714	152
4	1.701	1, 2	1.700, 1.694	223, 440
2	1.683	1	1.682	313
6	1.623	5, 1	1.629, 1.628	602, 441
3	1.584	3	1.584	522
1	1.557	2	1.554	710
3	1.529	3	1.529	612
6	1.467	3, 3	1.473, 1.468	004, 442
3	1.432	1, 2	1.433, 1.433	720, 270
1	1.397	1, 1	1.398, 1.393	124, 721
1	1.376	1	1.376	433
2	1.340	1	1.337	181
3	1.317	1, 1, 1	1.320, 1.317, 1.313	730, 404, 802
3	1.280	2	1.277	414
2	1.233	1	1.231	552
1	1.210	1	1.208	514

* I_{calc} values are calculated from structural data for agardite-(Ce) (Hess 1983); for this calculated pattern, only reflections with intensities ≥ 1 are given.

2005). In the X-ray powder pattern of agardite-(Nd) from the Hilarion Mine, the measured intensities of reflections are close to ones calculated for agardite-(Ce) structurally studied by Hess (1983) (see Tab. 2). From this similarity, we consider for agardite-(Nd) the same space group $P6_3/m$ and the same structure as for other mixite-group arsenates.

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