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Norilskite, $(Pd,Ag)_7Pb_4$, a new mineral from Noril`sk -Talnakh deposit, Russia

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ABSTRACT

Norilskite, $(Pd,Ag)_7Pb_4$ is a new platinum-group mineral discovered in the Mayak mine of the Talnakh deposit, Russia. It forms anhedral grains in aggregates (up to about 400 μm) with polarite, zvyagintsevite, Pd-rich tetra-auricupride, Pd-Pt bearing auricupride, Ag-Au alloys, (Pb,As,Sb) bearing atokite, mayakite, Bi-Pb rich kotulskite and sperrylite in pentlandite, cubanite and talnakhite. Norilskite is brittle, has a metallic lustre and a grey streak. Values of VHN_{20} fall between 296 and 342 kg/mm^2, with a mean value of 310 kg/mm^2, corresponding to a Mohs hardness of approximately 4. In plane-polarized light, norilskite is orange-brownish pink, has moderate to strong bireflectance, orange-pink to greyish-pink pleochroism, and strong anisotropy; it exhibits no internal reflections. Reflectance values of norilskite in air (R_o, R_e, in %) are: 51.1, 48.8 at 470nm, 56.8, 52.2 at 546nm, 59.9, 53.5 at 589nm and 64.7, 55.5 at 650nm. Sixteen electron-microprobe analyses of natural norilskite gave an average

composition: Pd 44.33, Ag 2.68, Bi 0.33, and Pb 52.34, total 99.68 wt.%, corresponding to the empirical formula $(Pd_{6.56}Ag_{0.39})_{\sum 6.95}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$ based on 4 Pb+Bi atoms; the average of eight analyses on synthetic norilskite is: Pd 42.95, Ag 3.87, and Pb 53.51, total 100.33 wt.%, corresponding to $(Pd_{6.25}Ag_{0.56})_{\sum 6.81}Pb_{4.00}$. The mineral is trigonal, space group $P3_121$, with a 8.9656(4), c 17.2801(8) Å, V 1202.92(9) Å^3 and Z = 6. The crystal structure was solved and refined from the powder X-ray-diffraction data of synthetic $(Pd,Ag)_7Pb_4$. Norilskite crystallizes in the $Ni_{13}Ga_3Ge_6$ structure type, related to nickeline. The strongest lines in the X-ray powder diffraction pattern of synthetic norilskite [d in Å (I) (hkl)] are: 3.2201(29)(023,203), 2.3130(91)(026,206), 2.2414(100)(220), 1.6098(28)(046,406), 1.3076(38)(246,462), 1.2942(18)(600), 1.2115(37)(22.12,12.13), 0.9626(44)(06.12,60.12). The mineral is named for the locality, the Noril`sk district in Russia.

Keywords: norilskite, platinum-group mineral, $(Pd,Ag)_7Pb_4$ phase, electron-microprobe data, reflectance data, X-ray-diffraction data, crystal structure, Mayak mine, Talnakh deposit, Noril`sk district, Russia.

Introduction

The holotype specimen (polished section), that contains norilskite, ideally $(Pd,Ag)_7Pb_4$, comes from the massive pentlandite-cubanite-talnakhite ore from the Mayak mine in the Talnakh deposit of the Noril`sk district, Russia. The sample was found at coordinates: 69° 30′ 20′′ N and 88° 27′ 17′′ E. The phase with the corresponding chemical composition, described as unnamed $(Pd,Ag)_2Pb$, has been also observed in the massive pentlandite-cubanite-talnakhite ore in Komsomolsky mine of the Talnakh deposit and in the massive pentlandite-talnakhite ore in Zapolyarny (Trans-Polar) mine of the Noril`sk I deposit (Sluzhenikin and Mokhov, 2015). Norilskite formed in post magmatic conditions, with decreasing temperature (Sluzhenikin and Mokhov, 2015), most likely below 400°C.

The ore deposits of the Noril'sk-Talnakh district are associated with hypabyssal intrusions related to the Siberian flood basalt province. Different types of ore can be distinguished in terms of sulphide content, metal proportions and position within the host intrusion. Extensive studies have been dedicated to Noril`sk ores and deposits (e.g. Genkin *et al.*, 1981, Distler *et al*., 1988, Naldrett *et al*., 1992, Czamanske *et al*., 1992, Komarova *et al*., 2002, Sluzhinikin, 2011, Sluzhinikin and Mohkov, 2015, among others).

Almost half of all known named platinum-group minerals were reported from the Noril`sk ores, and also a number of unidentified phases. Furthermore, around 17 new platinum-group minerals, among other minerals, were discovered from the Noril`sk deposits.

Mineral name and type material

Both mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA No 2015-008). The

mineral is named for the locality, the Noril`sk district, Russia. The mineral name norilskite was proposed for an alloy of Pt-Pd-Fe-Ni-Cu found in places near the Noril`sk deposits by Zviagincev (1940). Nevertheless, Genkin (1968) proved that it was a mixture of several PGE minerals. Since that time no mineral species with the name norilskite was proposed.

The holotype (polished section) is deposited at the Department of Earth Sciences of the Natural History Museum, London, UK, catalogue No BM 2015, 1 and co-type material (polished section) is deposited in the Fersman Mineralogical Museum, Moscow, Russia, catalogue No 4694/1.

Appearance, physical and optical properties

Norilskite forms anhedral grains (about 10 to 20 μm in diameter, in case of type material the grain reaches almost 400 μm) in aggregates with polarite, zvyagintsevite, Pd-rich tetra-auricupride, Pd-Pt bearing auricupride, Ag-Au alloys, (Pb,As,Sb) bearing atokite, mayakite, Bi-Pb rich kotulskite and sperrylite in pentlandite, cubanite and talnakhite. The image of norilskite (No 229) with associated minerals of the type material from the Mayak mine is shown in Fig. 1.

Norilskite is opaque with a metallic lustre and grey streak. The powder of synthetic norilskite is grey in colour. The mineral is brittle. Values of VHN_{20} measured from 9 indentations is in the range from 296 to 342 kg/mm^2, with a mean value of 310 kg/mm^2, which corresponds to a Mohs hardness of about 4. The density calculated on the basis of the empirical formula is 12.99 g/cm^3. In plane-polarized reflected light, norilskite is orange-brownish pink, has moderate to strong bireflectance, strong from orange-pink (R_o) to greyish orange-pink ($R_{e'}$) pleochroism, and strong anisotropy with rotation tints from dull yellow to dull blue in partially crossed polars. It exhibits no internal reflections.

Reflectance measurements were made in air relative to a WTiC standard on both natural and synthetic norilskite using a J & M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. The results are tabulated (Table 1) and illustrated in Fig. 2. With $R_o > R_e$ norilskite is uniaxial negative.

Chemical composition

Chemical analyses were performed with a CAMECA SX-100 electron probe microanalyser (EPMA) in wavelength-dispersive mode using an electron beam focussed to 1-2 μm. Pure elements were used as standards. Concentrations were quantified on the PdL_α, AgL_α, BiM_α and PbM_α (with overlap correction on AgL_α and BiM_α) with an accelerating voltage of 15 keV, and a beam current of 10 nA on the Faraday cup. Other elements were below detection limit.

The electron-microprobe results are given in Table 2. The analyses of three grains from the Mayak mine, Talnakh deposit gave close compositions with slightly variable Pd:Ag ratio (based on 4 Pb+Bi atoms): $(Pd_{6.56}Ag_{0.42})_{\sum 7.01}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$ (No 229), $(Pd_{6.47}Ag_{0.38})_{\sum 6.87}(Pb_{3.98}Bi_{0.02})_{\sum 4.00}$ (No 208), $(Pd_{6.66}Ag_{0.37})_{\sum 7.06}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$ (No 136) with the empirical formulae for the average analysis (n=16) $(Pd_{6.56}Ag_{0.39})_{\sum 6.97}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$. The proposed simplified formulae for norilskite is $(Pd,Ag)_7Pb_4$ with Z = 6. The Table 2 also shows alternative recalculations of empirical formulae of norilskite based one Pb+Bi atoms per formulae unit (Z = 24) and on 11 atoms per formulae unit (Z = 6). Nevertheless in accordance with the crystal structure investigations (see "*Structure description*" section) we are favourable to $(Pd,Ag)_7Pb_4$ formulae based on 4 Pb+Bi atoms.

Synthetic analogue

Tiny intergrowths of norilskite with lamellae of polarite and other minerals listed above embedded in pentlandite prevented its extraction and isolation in an amount sufficient for the relevant crystallographic and structural investigations. Therefore these investigations were performed on the synthetic phase $(Pd_{6.25}Ag_{0.56})_{\sum 6.81}Pb_{4.00}$.

The synthetic phase $(Pd_{6.25}Ag_{0.56})_{\sum 6.81}Pb_{4.00}$ was prepared in an evacuated and sealed silica-glass tube in a horizontal furnace in the Laboratory of Experimental Mineralogy of the Czech Geological Survey in Prague. To prevent loss of material to the vapour phase during the experiment, the free space in the tube was reduced by placing a closely fitting glass rod against the charge. The temperature was measured with Pt-PtRh thermocouples and is accurate to within ± 3 °C. A charge of about 200 mg was carefully weighed out from the native elements. We used, as starting chemicals silver powder (Aldrich Chem. Co., 99.999% purity), lead ingot (Aldrich Chem. Co., 99.999% purity), and palladium powder (Aldrich Chem. Co., 99.95% purity). The starting mixture was first melted at 1000°C for two days. The product was then (from melting at 1000°C) ground in an agate mortar under acetone and reheated to 300°C for 113 days. The sample was quenched by dropping the capsule in cold water.

X-ray crystallography

A few grains of synthetic material were tested using single-crystal diffraction, however all crystals examined were found unsuitable for single-crystal analysis. Therefore, the crystal structure and unit cell parameters of synthetic norilskite were refined from the powder X-ray diffraction data.

151 The powder X-ray diffraction pattern used for the Rietveld refinement and refinement of
152 lattice parameters was collected in Bragg-Brentano geometry on an X´Pert Pro PANalytical
153 diffractometer, equipped with X´Celerator detector and a Co*K*α radiation source. The data
154 were collected in the range between 15 and 135° 2θ. The details of data collection and basic
155 crystallographic data are given in Table 3.

156 Inspection of the powder diffraction pattern of the synthetic analogue of norilskite
157 indicated a positive match with the PDF-2 card no. 42-798 (ICDD 2002) denoted as the
158 Pd_6AgPb_4 phase and the Pd_3Pb phase as a minor admixture (PDF-2 card no. 50-1631). The
159 existence of a synthetic phase Pd_6AgPb_4 is mentioned in the work of Sarah *et al*. (1981),
160 where it is referred to as having the $Ni_{13}Ga_3Ge_6$ structure type. However, neither crystal
161 coordinates nor chemical data for the Pd_6AgPb_4 phase have been published. The card no.
162 605653 for the Pd_6AgPb_4 phase, which can be found in the Inorganic Crystal Structure
163 Database (ICSD 2015), contains the same structural data (i.e. atomic coordinates) as has the
164 card no. 52177 for the $Ni_{13}Ga_3Ge_6$ phase. Moreover, in the card 605653 is also a remark, that
165 the coordinates were estimated by the database editor by the analogy to isotypic compounds.
166 Therefore, the starting structure model of synthetic norilskite for subsequent Rietveld
167 refinement was derived from the published data for the $Ni_{13}Ga_3Ge_6$ phase (Nover and
168 Schubert, 1981). In this structure model, the Ni atoms (8 independent positions) were
169 substituted by the Pd atoms, the Ge atoms (3 independent positions) by the Pb atoms and the
170 Ga atoms (2 independent positions) by the Ag atoms. This initial structure model of synthetic
171 norilskite (Pd39 Ag9 Pb18 atoms in the unit-cell) was refined by the Rietveld method for the
172 powder X-ray diffraction data by means of the FullProf program (Rodríguez-Carvajal, 2006).
173 The background was determined by the linear interpolation between consecutive breakpoints
174 in the pattern. The refined parameters include those describing the peak shape and width, peak

asymmetry, unit cell parameters, fractional coordinates, occupancy parameters and an overall isotropic displacement parameter.

The occupancy parameters were carefully tested during the refinement (Pb against Pd, Ag against Pb), taking into account that it is not possible to distinguish between Ag and Pd atoms from conventional powder X-ray diffraction data (Co*K*α radiation). Consequently, the occupancy at the Ag(2) position (6*c*) was changed from Ag to Pb atoms, as was suggested by a significant drop of an R_{Bragg} factor (from 0.144 to 0.121) and a more reasonable coordination sphere for the other Ag atoms (octahedral coordination by Pb atoms). This substitution influences the chemical composition of the structure model. Whereas the former model contains Pd39 Ag9 Pb18 atoms in the unit-cell, the new one has Pd39 Ag3 Pb24 atoms in the unit-cell (result of Ag → Pb substitution on position 6*c*). After recalculation for $Z = 6$, the structure-derived formula is $(Pd_{6.50}Ag_{0.50})_{\Sigma 7.00}Pb_{4.00}$, which is in a very good agreement with the chemical composition obtained from electron microprobe analysis of the synthetic phase $(Pd_{6.25}Ag_{0.56})_{\sum 6.81}Pb_{4.00}$.

The final cycles of refinement converged to the residual factors: $R_{Bragg} = 0.098$, $R_{wp} = 0.045$ and $R_p = 0.034$. The crystal structure data are presented in Table 4, Fig. 3 shows the Rietveld plot. The crystal structure is depicted in Fig. 4 and 5, respectively. Since it is not possible to differentiate between Ag and Pd atoms in refinement from conventional powder X-ray diffraction data, all non-Pb positions are denoted as M1-M9. Table 5 presents an indexed powder-diffraction pattern of norilskite.

Structure description

The norilskite crystal structure can be viewed as a superstructure of the partially filled nickeline (NiAs) structure with doubled *a* and tripled *c* lattice parameters relative to the basic

unit-cell of the nickeline structure. In this basic structure, the As atoms form a hexagonal close packed (hcp) arrangement and Ni atoms occupy the octahedral interstices. Such structure contains also trigonal-bipyramidal voids. If all of these voids are occupied, one arrives at the Ni_2In structure type. In the norilskite crystal structure, the Pb atoms show a distorted hexagonal close packing and all octahedral voids are occupied by M atoms (more specifically by M1, M2, M3, M4, M8 and M9 positions). Stoichiometry of such hypothetical compound is MPb and its crystal structure has the NiAs structure topology. However, 75 % of available trigonal-bipyramidal voids are occupied by additional M atoms (M5, M6, M7 positions) in the norilskite crystal structure. This partial occupation results in (Pd+Ag)/Pb = 1.75 ratio which corresponds very well with such ratio 1.70 obtained from electron microprobe analysis of synthetic material.

The partial occupation of trigonal-bypiramidal voids in norilskite implies short interatomic distances between M and Pb atoms, by comparison with the Pd-Pb distances observed in zvyagintsevite (2.85 Å; Ellner, 1981) and the $PdPb_2$ phase (2.95 Å; Havinga, 1972). The shortest interatomic contacts observed in the norilskite structure are 2.66 Å and 2.69 Å for M(7)-Pb(5) and M(5)-Pb(5) bonds, respectively. However, similar short metal-metal contacts were reported for the fully occupied Ni_2In compound (Bhattacharya and Masson, 1976), so there seems to be no way to avoid such short interatomic distances in these compounds. On the other hand, partial occupancy of the trigonal bipyramidal voids might be a way to help the structure to relax (Norén *et al*., 2000). The presence of vacancies seems to be an important stabilizing factor for the crystal structure of norilskite.

The alternative formulae of norilskite $(Pd,Ag)_{1.70}Pb_{1.00}$ based on one Pb atom per formula unit (Z = 24) clearly indicates its structural relationship with the NiAs and Ni_2In structures. It also shows a proportion of trigonal-bipyramidal voids, which are occupied by Ag and Pd atoms (i.e. 75% of available voids). However, we have decided for $(Pd,Ag)_7Pb_4$ ideal

formulae (Z = 6), which reflects the fact that norilskite is an ordered superstructure relative to the NiAs and Ni_2In structures. The presentation with $Pd_6(Pd,Ag)Pb_{4.00}$ formulae can also be considered as another alternative. Nevertheless, since we were not able to reveal a distinct Ag site from conventional X-ray diffraction data, we prefer the $(Pd,Ag)_7Pb_4$ ideal formulae for norilskite. The EMPA data of natural sample are also supportive for the $(Pd,Ag)_7Pb_4$ ideal formulae (Table 2).

Proof of identity of natural and synthetic norilskite

The structural identity between the synthetic $(Pd,Ag)_7Pb_4$ and the natural material was confirmed by electron back-scattering diffraction (EBSD). For that purpose, we used a TESCAN Mira 3GMU scanning electron microscope combined with EBSD system (NordlysNano detector, Oxford Instruments). The natural sample was prepared for investigation by the re-polishing the surface with colloidal silica (OP-U) for 5 minutes to reduce the surface damage. The EBSD patterns were collected and processed using a proprietary computer program AZtec HKL (Oxford Instruments). The solid angles calculated from the patterns were compared with a synthetic $(Pd,Ag)_7Pb_4$ match containing 100 reflectors to index the patterns. The Kikuchi patterns obtained from the natural material (seven measurements on different spots on natural norilskite) were found to match the patterns generated from the structure of synthetic $(Pd,Ag)_7Pb_4$ provided by our crystal structure determination (Fig. 6). The values of the mean angular deviation (MAD goodness-of-fit in the solution) between the calculated and measured Kikuchi bands range between 0.58° and 0.39°. These values reveal a very good match; mean angular deviations <1° are considered as indicators of an acceptable fit.

The EBSD study, chemical identity and optical properties confirmed the correspondence between natural and synthetic materials and thereby legitimise the use of the synthetic phase for the complete characterization of norilskite.

Acknowledgements

The authors acknowledge Ulf Hålenius, Chairman of the CNMNC and its members for helpful comments on the submitted data. They also acknowledge the helpful comments of Louis J. Cabri and an anonymous reviewer. The authors are grateful to Patricie Halodová and Jakub Haloda for carrying out the EBSD measurements. This work was supported by the internal project No. 337800 from the Czech Geological Survey.

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TABLES

TABLE 1. Reflectance data for norilskite

TABLE 2. Electron-microprobe analyses of natural and synthetic norilskite and three recalculations of norilskite stoichiometry (based on Pb+Bi = 4 apfu, Pb+Bi = 1 apfu, and11 apfu).

TABLE 3. Powder X-ray diffraction experimental details and Rietveld analysis of norilskite

TABLE 4. Atomic positions for synthetic norilskite (space group $P3_121$, $B_{iso(overall)}$ = 0.12(2) $Å^2$), M(1)-M(7) represent Pd or/and Ag atoms.

TABLE 5. X-ray powder-diffraction data for synthetic norilskite (Co$K\alpha$ radiation). Reflections with intensities ≥ 1% are shown.

FIGURES

FIG. 1. Images of norilskite (nor) from the type locality Mayak mine of the Talnakh deposit, Noril`sk district (Sample No 229) and associated minerals (*a*) Back-scattered electron (BSE) image (*b*) reflected light photomicrograph of the same grain, zvyagintsevite (zvy), auricupride (aur), tetra-auricupride (tet), polarite (pol) and Ag-Au alloys.

FIG. 2. Reflectance data for natural norilskite compared to synthetic in air. The reflectance values (R %) are plotted versus wavelength λ in nm.

FIG. 3. Observed (circles), calculated (solid lines) and difference Rietveld profiles for norilskite. The upper reflection markers correspond to norilskite and the lower markers to a Pd_3Pb (7 wt. %) impurity.

FIG. 4. Polyhedral representation of (a, b) the norilskite crystal structure showing the $[MPb_6]$ distorted octahedra (M = Pd or Ag) and (c) the NiAs (nickeline) structure. Unit-cell edges are highlighted.

FIG. 5. (a) View along the *c* axis showing a layer composed of $[MPb_6]$ edge-sharing octahedra (green) and trigonal-bipyramidal sites (brown) occupied by additional M atoms (M=Pd,Ag), (b) detailed view of the trigonal-bipyramidal site.

FIG. 6. EBSD image of natural norilskite; in the right pane, the Kikuchi bands are indexed.

TABLE 1. Reflectance data for natural and synthetic norilskite.

	natural		synthetic	
λ (nm)	Ro (%)	Re' (%)	Ro (%)	Re' (%)
400	46.6	44.9	47.1	45.1
420	47.9	45.9	48.4	46.1
440	49.0	46.9	49.6	47.3
460	50.4	48.2	51.1	48.7
470	**51.1**	**48.8**	**51.8**	**49.4**
480	51.8	49.4	52.5	50.0
500	53.3	50.4	53.9	51.2
520	54.7	51.2	55.3	52.2
540	56.3	52.0	56.7	53.2
546	**56.8**	**52.2**	**57.1**	**53.5**
560	57.9	52.5	58.1	54.1
580	59.7	53.1	59.6	54.9
589	**59.9**	**53.5**	**59.9**	**55.2**
600	61.1	53.8	61.2	55.6
620	62.7	54.4	62.3	56.5
640	64.0	55.1	63.9	57.2
650	**64.7**	**55.5**	**64.4**	**57.7**
660	65.4	55.8	65.0	58.1
680	66.6	57.0	66.4	59.0
700	67.8	58.1	67.5	60.0

Note: The values required by the Commission on Ore Mineralogy are given in bold.

TABLE 2. Electron-microprobe analyses of natural and synthetic norilskite and three recalculations of norilskite stoichiometry (based on Pb+Bi = 4 apfu, Pb+Bi = 1 apfu, and11 apfu).

Natural sample						$(Pd,Ag)_7Pb_4$ (Z=6)			$(Pd,Ag)_{2-x}Pb$ (Z=24)			$(Pd,Ag)_7Pb_4$ (Z=6)			
No	Pd	Ag	Pb	Bi	Total	Pb=4			Pb=1			apfu 11			
	wt.%					Pd	Ag	Pb+Bi	Pd	Ag	Pb+Bi	Pd	Ag	Pb	Bi
229 (2)	45.01	2.91	52.30	0.44	100.66	6.65	0.42	4.00	1.66	0.11	1.00	6.60	0.42	3.94	0.03
229 (2)	44.39	3.20	52.42	0.32	100.34	6.56	0.47	4.00	1.64	0.12	1.00	6.54	0.46	3.97	0.02
229 (2)	44.65	2.78	52.71	0.39	100.53	6.55	0.40	4.00	1.64	0.10	1.00	6.58	0.40	3.99	0.03
229 (2)	44.02	2.84	52.35	0.43	99.63	6.50	0.41	4.00	1.62	0.10	1.00	6.55	0.42	4.00	0.03
229 (2)	44.80	2.85	53.07	0.36	101.07	6.53	0.41	4.00	1.63	0.10	1.00	6.57	0.41	3.99	0.03
avg (*n*=5)	*44.57*	*2.91*	*52.57*	*0.39*	*100.44*	*6.56*	*0.42*	*4.00*	*1.64*	*0.11*	*1.00*	*6.57*	*0.42*	*3.98*	*0.03*
208	44.84	2.88	52.94	0.25	100.91	6.57	0.42	4.00	1.64	0.10	1.00	6.58	0.42	3.99	0.02
208	43.56	2.60	52.62	0.19	98.97	6.43	0.38	4.00	1.61	0.09	1.00	6.54	0.39	4.06	0.01
208	44.21	2.52	52.47	0.34	99.54	6.52	0.37	4.00	1.63	0.09	1.00	6.59	0.37	4.02	0.03
208	44.35	2.52	53.09	0.35	100.31	6.46	0.36	4.00	1.62	0.09	1.00	6.57	0.37	4.04	0.03
208	43.64	2.76	53.14	0.25	99.80	6.37	0.40	4.00	1.59	0.10	1.00	6.51	0.41	4.07	0.02
208	44.59	2.48	53.21	0.29	100.57	6.49	0.36	4.00	1.62	0.09	1.00	6.58	0.36	4.03	0.02
avg (*n*=6)	*44.20*	*2.63*	*52.91*	*0.28*	*100.02*	*6.47*	*0.38*	*4.00*	*1.62*	*0.09*	*1.00*	*6.56*	*0.38*	*4.03*	*0.02*
136-2	44.25	2.31	51.23	0.12	97.91	6.71	0.35	4.00	1.68	0.09	1.00	6.68	0.34	3.97	0.01
136-2	44.04	2.39	50.53	0.45	97.41	6.73	0.36	4.00	1.68	0.09	1.00	6.68	0.36	3.93	0.04
136-2	44.09	2.46	52.06	0.31	98.92	6.56	0.36	4.00	1.64	0.09	1.00	6.61	0.36	4.01	0.02
136-2	44.73	2.61	51.68	0.49	99.51	6.68	0.38	4.00	1.67	0.10	1.00	6.64	0.38	3.94	0.04
136-2	44.12	2.82	51.57	0.35	98.86	6.62	0.42	4.00	1.65	0.10	1.00	6.60	0.42	3.96	0.03
avg (*n*=5)	*44.24*	*2.52*	*51.41*	*0.35*	*98.52*	*6.66*	*0.37*	*4.00*	*1.66*	*0.09*	*1.00*	*6.64*	*0.37*	*3.96*	*0.03*
avg (*n*=15)	44.33	2.68	52.34	0.33	99.68	6.56	0.39	4.00	1.64	0.10	1.00	6.59	0.39	3.99	0.03
Std. dev.	0.39	0.22	0.72	0.09											

Synthetic sample					$(Pd,Ag)_7Pb_4$ (Z=6)			$(Pd,Ag)_{2-x}Pb$ (Z=24)			$(Pd,Ag)_7Pb_4$ (Z=6)		
	Pd	Ag	Pb	Total	Pb=4			Pb=1			apfu 11		
	wt.%				Pd	Ag	Pb	Pd	Ag	Pb	Pd	Ag	Pb
Exp33	43.28	3.64	53.94	100.85	6.25	0.52	4.00	1.56	0.13	1.00	6.38	0.53	4.09
Exp33	42.63	4.34	53.07	100.03	6.26	0.63	4.00	1.56	0.16	1.00	6.32	0.63	4.04
Exp33	42.21	4.18	53.48	99.87	6.15	0.60	4.00	1.54	0.15	1.00	6.29	0.61	4.09
Exp33	43.19	3.63	53.67	100.50	6.27	0.52	4.00	1.57	0.13	1.00	6.39	0.53	4.08
Exp33	42.88	4.66	53.09	100.63	6.29	0.67	4.00	1.57	0.17	1.00	6.31	0.68	4.01
Exp33	42.80	3.43	53.25	99.48	6.26	0.49	4.00	1.57	0.12	1.00	6.40	0.51	4.09
Exp33	42.88	3.92	53.71	100.50	6.22	0.56	4.00	1.55	0.14	1.00	6.35	0.57	4.08
Exp33	43.72	3.19	53.89	100.79	6.32	0.45	4.00	1.58	0.11	1.00	6.45	0.46	4.08
avg (*n*=8)	42.95	3.87	53.51	100.33	6.25	0.56	4.00	1.56	0.14	1.00	6.36	0.57	4.07
Std. dev.	0.42	0.46	0.32	0.45									

TABLE 3. Powder X-ray diffraction experimental details and Rietveld analysis of norilskite

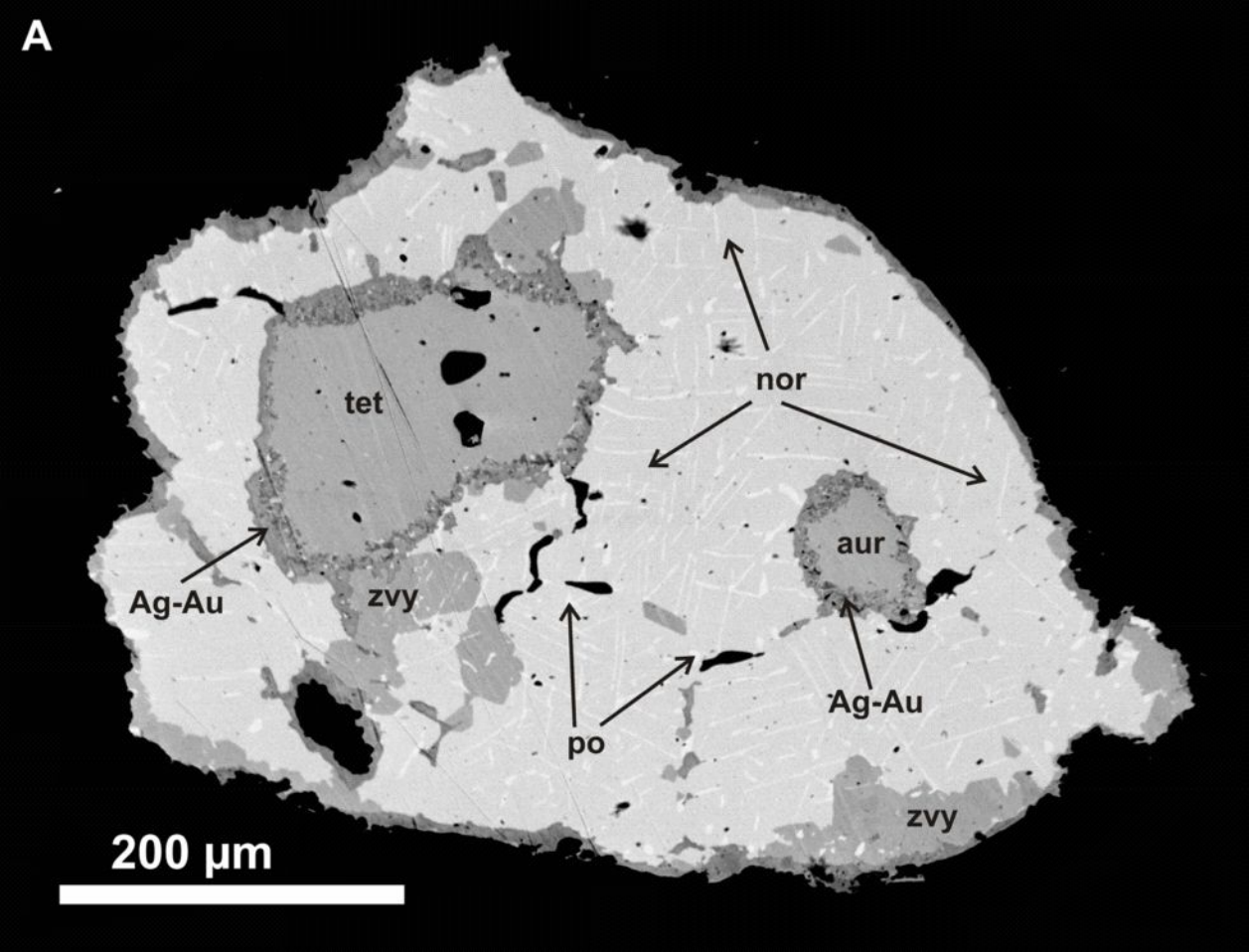
Data collection	
Radiation type, source	X-ray, Co$K\alpha$
Generator settings	40kV, 30mA
Range in 2θ (°)	15 -135
Step size (°)	0.02
Crystal data	
Space group	$P3_121$
Unit-cell content	$Z = 6$
Unit-cell parameters (Å)	$a = 8.9656(4)$
	$c = 17.2801(8)$
Unit-cell volume (Å^3)	1202.92(9)
Rietveld analysis	
No. of reflections	531
No. of structural parameters	31
No of. profile parameters	4
R_{Bragg}	0.098
R_p	0.034
R_{wp}	0.045
Weighting scheme	$1/y_o$

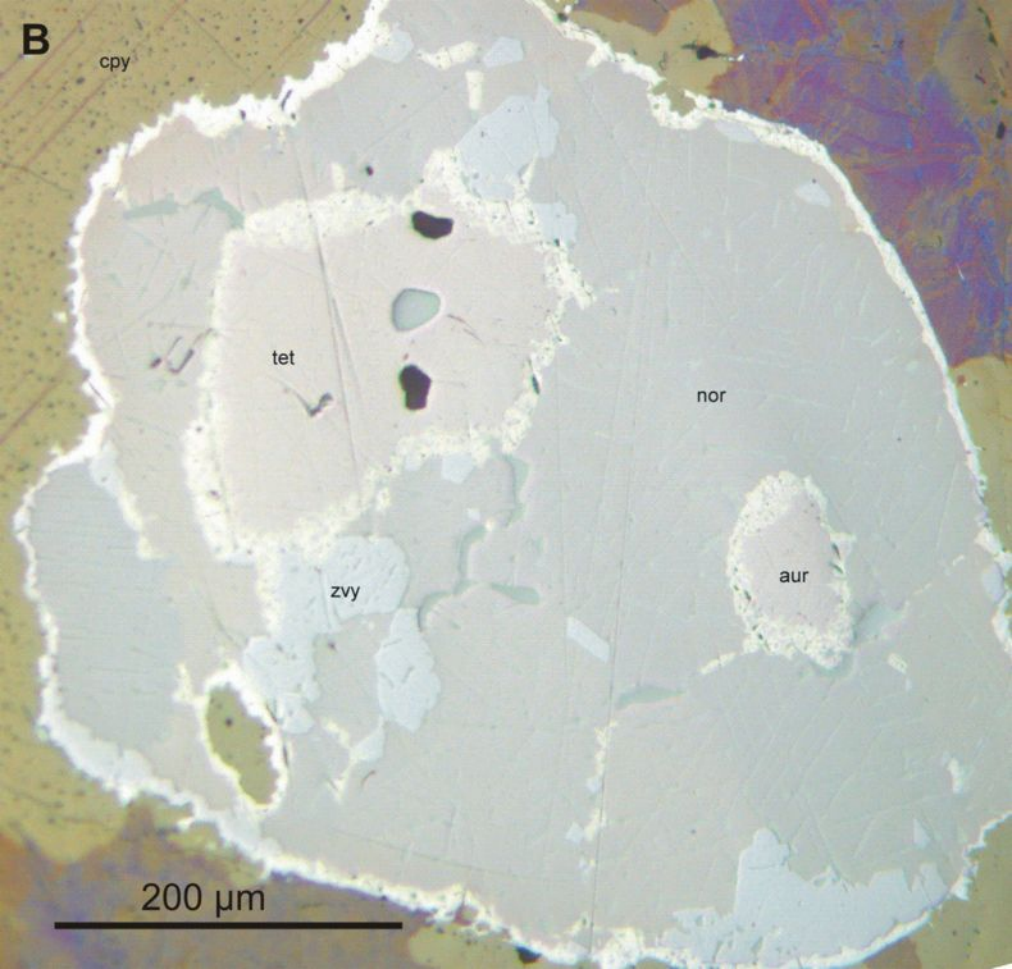
TABLE 4. Atomic positions for synthetic norilskite (space group $P3_121$, $B_{iso(overall)}$ = 0.12(2) $Å^2$), M(1)-M(7) represent Pd or/and Ag atoms.

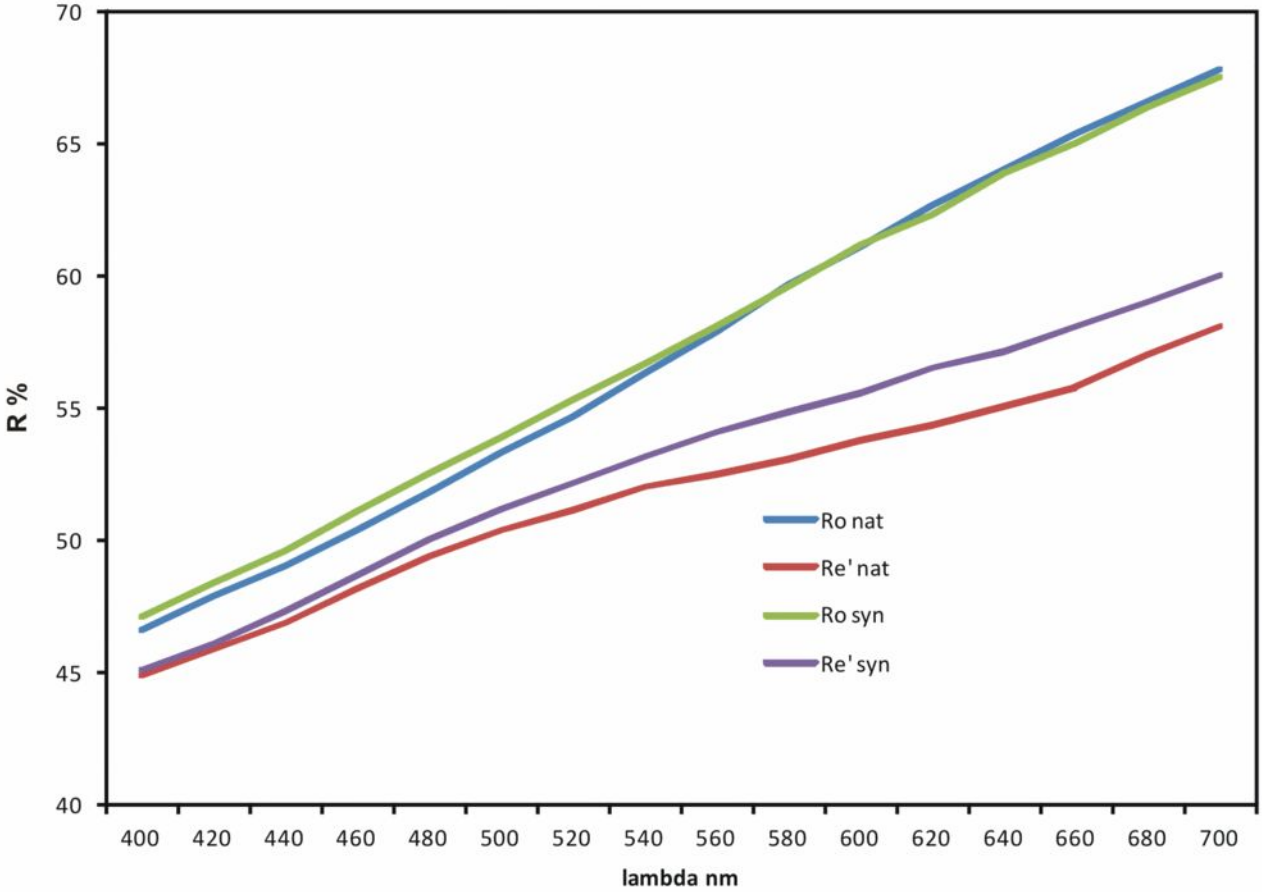
Atom	Wyckoff letter	*x*	*y*	*z*
M(1)	3*a*	0.492(5)	0	1/3
M(2)	3*b*	0.996(6)	0	5/6
M(3)	6*c*	0.998(7)	0.503(5)	0.3213(9)
M(4)	6*c*	0.507(5)	0.006(5)	0.162(1)
M(5)	6*c*	0.315(4)	0.658(3)	0.0930(9)
M(6)	6*c*	0.333(4)	0.178(4)	0.420(1)
M(7)	6*c*	0.153(3)	0.343(4)	0.259(1)
M(8)	3*a*	0.012(4)	0	1/3
M(9)	3*b*	0.497(7)	0	5/6
Pb(1)	6*c*	0.184(4)	0.309(4)	0.0839(6)
Pb(2)	6*c*	0.623(2)	0.305(2)	0.0852(7)
Pb(3)	6*c*	0.340(2)	0.169(2)	0.2545(5)
Pb(4)	6*c*	0.123(1)	0.316(3)	0.4129(7)

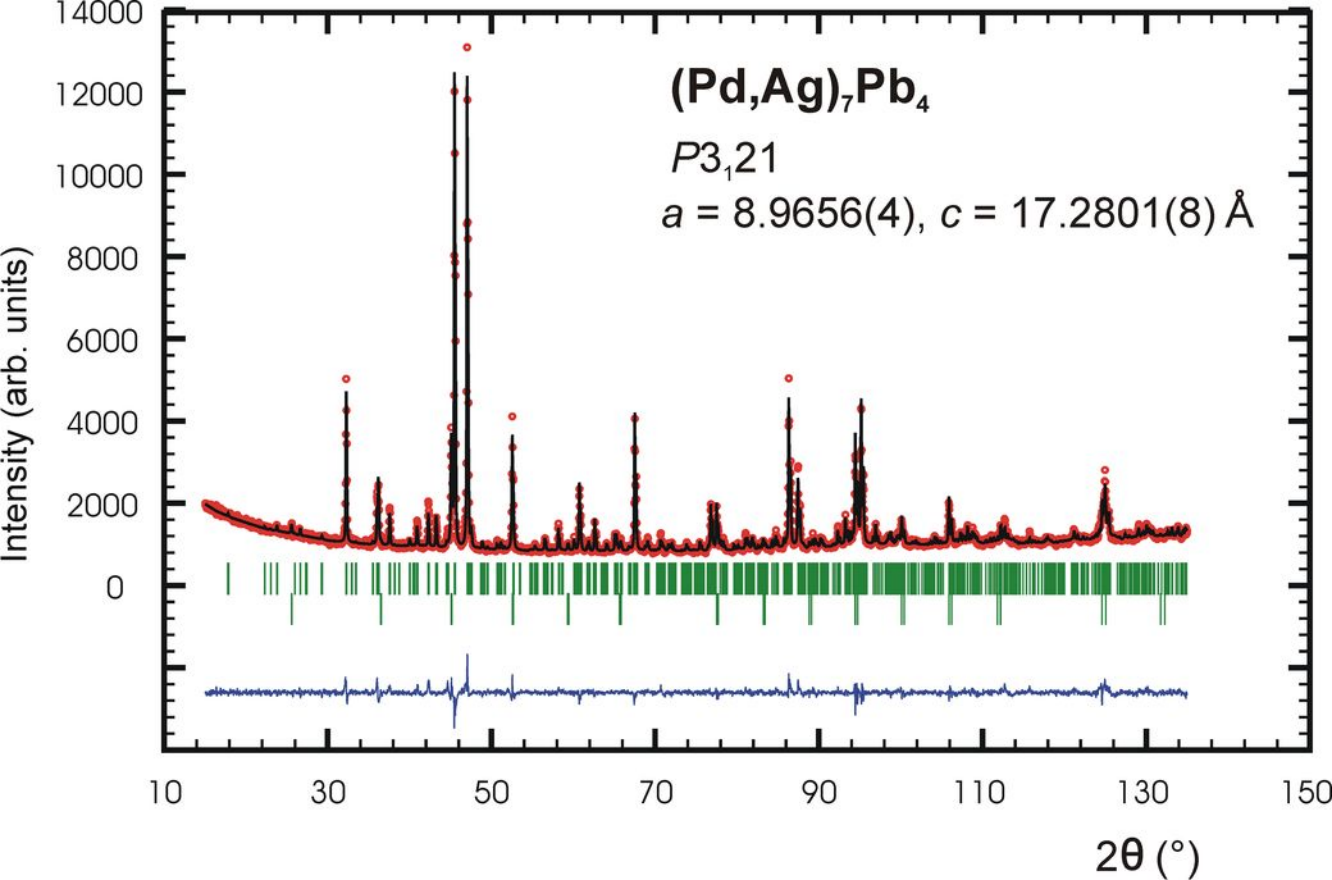
TABLE 5. X-ray powder-diffraction data for synthetic norilskite (Co*K*α radiation). Reflections with intensities ≥ 1% are shown.

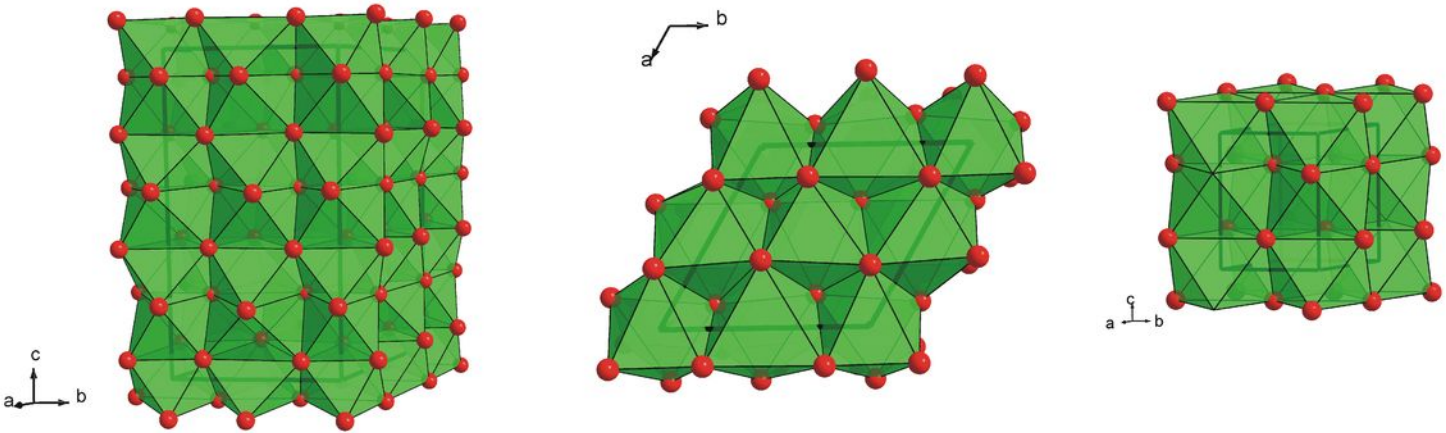
h	k	l		$I_{(obs)}$	$I_{(calc)}$	$d_{(obs)}$	$d_{(calc)}$
0	2	3	}	29	13	3.2201	3.2192
2	0	3			15		3.2192
1	2	1		8	7	2.8905	2.8932
0	0	6		11	13	2.8819	2.8801
1	2	2		7	6	2.7788	2.7787
0	3	1		4	4	2.5584	2.5595
0	3	2	}	8	2	2.4790	2.4792
3	0	2			5		2.4792
1	2	4	}	6	1	2.4274	2.4275
2	1	4			6		2.4275
0	2	6	}	91	59	2.3130	2.3131
2	0	6			40		2.3131
2	2	0		100	100	2.2414	2.2413
1	2	7		2	3	1.8886	1.8891
0	4	3	}	6	3	1.8396	1.8394
4	0	3			2		1.8394
2	2	6		13	15	1.7690	1.7688
0	2	9	}	6	4	1.7212	1.7211
2	0	9			4		1.7211
1	4	2	}	4	2	1.6626	1.6626
4	1	2			2		1.6626
0	4	6	}	28	12	1.6098	1.6096
4	0	6			19		1.6096
5	0	1		3	3	1.5467	1.5466
0	0	12		11	11	1.4402	1.4401
1	5	2	}	3	2	1.3767	1.3767
5	1	2			2		1.3767
5	1	4		2	2	1.3271	1.3271
2	4	6	}	38	23	1.3076	1.3074
4	6	2			15		1.3074
6	0	0		18	18	1.2942	1.2941
2	5	2		3	3	1.2307	1.2306
2	2	12	}	37	36	1.2115	1.2115
1	2	13			3		1.2108
2	5	4	}	4	3	1.1950	1.1948
5	2	4			2		1.1948
4	4	0		11	11	1.1208	1.1207
5	2	8		4	3	1.0776	1.0776
2	6	6	}	15	5	1.0086	1.0085
6	2	6			9		1.0085
0	6	12	}	44	20	0.9626	0.9625
6	0	12			20		0.9625


A
tet
nor
aur
Ag-Au
zvy
po
Ag-Au
zvy
200 µm

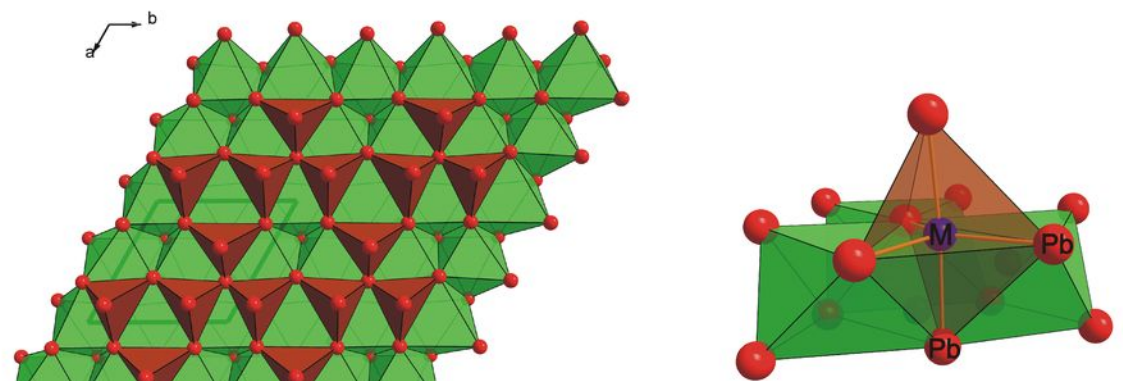

B
cpy
tet
nor
zvy
aur
200 µm


70
65
60
55
50
45
40
R %
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700
lambda nm
Ro nat
Re' nat
Ro syn
Re' syn

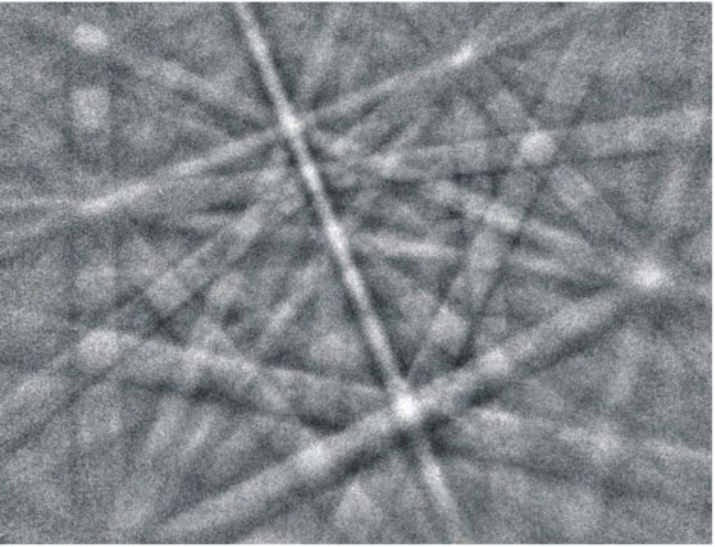

(Pd,Ag)7Pb4
P3121
a = 8.9656(4), c = 17.2801(8) Å
Intensity (arb. units)
14000
12000
10000
8000
6000
4000
2000
0
10
30
50
70
90
110
130
150
2θ (°)

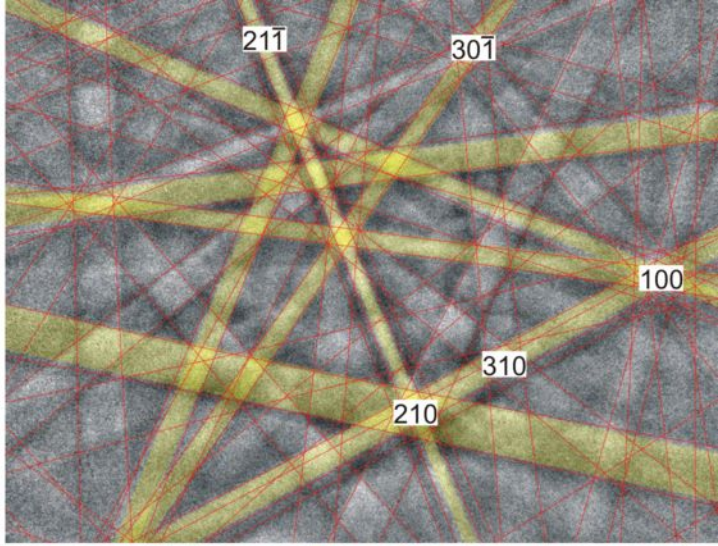


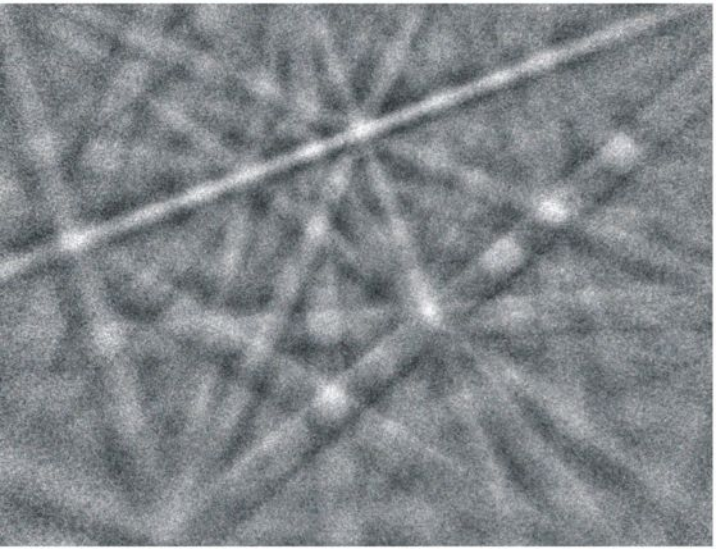
(a) (b) (c)

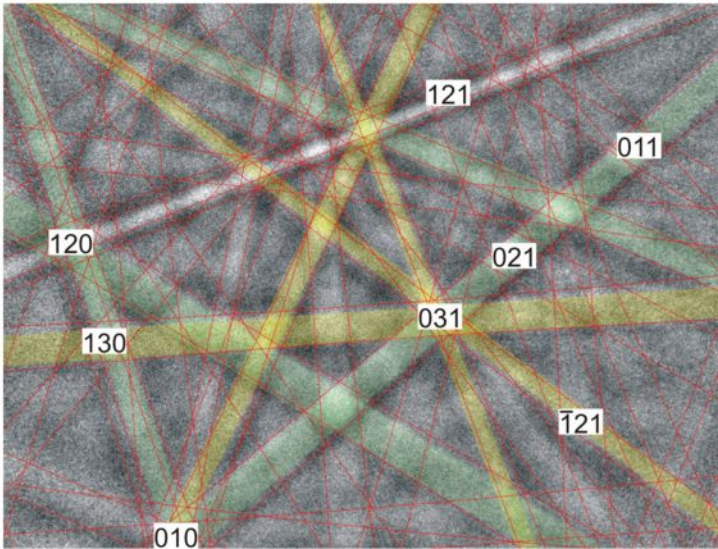


(a) (b)




$21\bar{1}$
$30\bar{1}$
100
310
210




121
011
120
021
031
130
$\bar{1}21$
010