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Crystal structure and thermal stability of $Ni_{151.5}Pb_{24}S_{92}$. Search for selenium- and tellurium-containing analogs

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The crystal structure of the subvalent nickel—lead sulfide, which has been described previously as $Ni_{60}Pb_9S_{31}$, was established and the composition of this sulfide was refined based on powder X-ray diffraction data. The true $Ni_{151.5}Pb_{24}S_{92}$ composition of this compound was confirmed by the EDX techniques. The temperature range of stability of this compound (490—578 °C) was refined by differential thermal analysis. In the search for analogs, the triangulation of the Ni—Pb—Se and Ni—Pb—Te systems at 540 °C was carried out for the first time. No new ternary phases were detected.

Key words: nickel, lead, subvalent chalcogenides, mixed chalcogenides, heterometallic bonds, crystal structure.

Crystalline subvalent mixed chalcogenides of transition and main-group metals remain poorly studied. Only several compounds of the general formula $M_3E_2Ch_2$ (M = Co, Rh, Ni, or Pd; E = In, Tl, Sn, or Pb, Bi; Ch = S or Se)[1] with parkerite- or shandite-type structures and a few representatives of other compositions, for example, Ni_6BiS_3, $Ni_{11}Bi_5S_4$,[2] $Ni_{60}Pb_9S_{31}$,[3] and $Ni_{6-x}SnCh_2$ (Ch = Se or Te),[4] are known. The crystal structures of only several compounds with parkerite- or shandite-type structures[5,6] as well as of mixed nickel-tin selenides and tellurides[4] were established. All known structures of this class contain infinite networks of main-group metal—transition metal bonds. The characteristic features of the formation and stabilization of these bonds are of considerable interest from the viewpoint of fundamental inorganic chemistry. In addition, compounds of this type might exhibit unusual electrophysical or magnetic properties.

The aim of the present study was to determine the crystal structure, refine the temperature range of existence of $Ni_{60}Pb_9S_{31}$, which has been described previously, and perform an experimental search for other stable subvalent mixed nickel—lead chalcogenides.

Earlier,[3] the phase equilibria in the Ni—Pb—S system have been studied by isothermal annealing in the tem-

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perature range of 340—700 °C. Powder X-ray phase analysis of the samples annealed over a very long period of time (15 months) revealed two phases, *viz.*, $Ni_3Pb_2S_2$ with the shandite structure, which is stable throughout the temperature range under study, and a phase, to which the $Ni_{60}Pb_9S_{31}$ composition has been previously assigned.[3] The latter phase exists only in the temperature range of 554—615 °C and its structure is unknown.

To our knowledge, there have been no systematic studies of the phase relations in the Ni—Pb—Se and Ni—Pb—Te ternary systems. The only nickel—lead selenide, *viz.*, $Ni_3Pb_2Se_2$, isostructural with $Ni_3Pb_2S_2$ was described.[5] According to the thermal analysis data for the quasibinary Ni_3Te_4—PbTe [7] and $NiTe_2$—PbTe [8] systems, no ternary phases were formed in these systems.

Results and Discussion

Composition, thermal stability, and crystal structure of "$Ni_{60}Pb_9S_{31}$." Attempts to synthesize the $Ni_{60}Pb_9S_{31}$ compound led us to the conclusion that the published data[3] on the composition and the temperature range of stability of this compound called for the further refinement. The powder X-ray diffraction analysis[3] of the samples with the above-mentioned stoichiometry, which were annealed at 554—615 °C for 200—300 h and quenched by rapid cooling in water, demonstrated that the desired phase was obtained only at temperatures close to the lower boundary of this temperature range and always contained $Ni_3Pb_2S_2$ and Ni as impurities.

With the aim of refining the range of existence of $Ni_{60}Pb_9S_{31}$, we carried out a DTA study of the following three types of samples: the $Ni_3Pb_2S_2$ + Ni + Ni_3S_2 and Ni + Pb + S mechanical mixtures of stoichiometric compositions and annealed samples containing the required phase with insignificant impurities of $Ni_3Pb_2S_2$ and Ni.

The differential thermal curves of both mechanical mixtures showed a small reversible thermic effect at 490 °C (endothermic effect upon heating), which was absent from the differential thermal curve of the annealed sample. In addition, the differential thermal curves of all samples showed reversible effects at 578 and 583 °C. According to visual observations, the latter effects are associated with melting of the samples. The assumption that the effects at 490 and 578 °C correspond to the lower and upper temperature boundaries of existence of the phase, respectively, was confirmed by the data from powder X-ray diffraction analysis for the samples, which were annealed at different temperatures in the range of 490—578 °C and quenched in water.

Attempts to grow single crystals of this compound from the gas phase by chemical transport reactions in sealed tubes failed. A noticeable mass transfer was observed in none of the reactions. In some cases, small crystals appeared on the surface of the charge. The investigation of these crystals on a single-crystal diffractometer demonstrated that they were Ni or Ni_3S_2.

The crystal structure of the nickel—lead sulfide under study was established based on the powder X-ray diffraction data. To prepare a sample as pure as possible, a mixture of composition 63 Ni + 7 Pb + 30 S was annealed at 540 °C for 16 days with one intermediate grinding. Then, small impurities of Ni_3S_2 and Ni were separated by a magnet from a thoroughly ground annealed sample. However, the powder X-ray diffraction analysis showed that the Ni_3S_2 impurity was removed incompletely (the intensity of the strongest line of Ni_3S_2 was *ca.* 3%).

The X-ray diffraction data were indexed (except for the lines of Ni_3S_2) within the face-centered cubic lattice. Since no additional absences were observed, the structure was solved in the space group *Fm*3*m* (No. 225).

Initially, the structure was solved with the use of 41 reflections, whose intensities were determined based on the results of profile analysis. The positions of the heavy atoms (Pb) were revealed by examining the Patterson function (SHELXS-97).[9] Then calculations of Fourier syntheses were alternated with the least-squares cycles of the parameter refinement with the use of the GSAS program[10] to locate the remaining atoms with the simultaneous refinement of the newly revealed positions with fixed thermal parameters (B_{iso} = 0.2 Å^2). Since the structural model thus obtained contained two partially occupied nickel positions, we attempted to refine the structure within the space groups *F*23 (No. 196), *F*432 (No. 209), and *F*-43*m* (No. 216) using the CSD program package.[11] However, the structure solutions obtained in these groups were characterized by too high *R* factors and no ordering was observed.

The final Rietveld refinement for the two-phase sample (the structural parameters of Ni_3S_2 were taken from the literature[12]) was carried out with the use of the RIETAN-94 program.[13] The thermal parameters of all Ni atoms were

Table 1. Parameters of the refinement of the crystal structure of $Ni_{151.5}Pb_{24}S_{92}$

Parameter	Characteristic
Composition	$Ni_{151.5(1)}Pb_{24}S_{92}$
Space group	*Fm*-3*m* (No. 225)
a/Å	15.51349(5)
V/Å^3	3733.61(2)
Z	1
2θ/deg	6.0 < 2θ < 104.99
Number of atomic parameters refined	14
R_I, R_p*, R_{wP}*	0.030, 0.037, 0.051
Type of the profile function	Modified pseudo-Voigt
Program	RIETAN-94

* The values are given after subtraction of the background.

Table 2. Positional parameters in the crystal structure of $Ni_{151.5}Pb_{24}S_{92}$

Atom	Position	x/a	y/b	z/c	Occupancy	$B_{iso}/Å^2$
Pb	24(d)	0	0.25	0.25	1	0.246(9)
Ni(1)	96(k)	0.25108(8)	0.08356(3)	y	1	0.34(1)
Ni(2)	24(e)	0.3739(1)	0	0	1	0.34
Ni(3)	32(f)	0.3069(7)	x	x	0.704(1)	0.34
Ni(4)	32(f)	0.0821(1)	x	x	0.281(2)	0.34
S(1)	24(e)	0.1664(1)	0	0	1	0.22(2)
S(2)	32(f)	0.16404(8)	x	x	1	0.22
S(3)	32(f)	0.39315(7)	x	x	1	0.22
S(4)	4(a)	0	0	0	1	3.9(2)

refined simultaneously with the occupancies of the Ni(3) and Ni(4) positions. The thermal parameters of the S(1), S(2), and S(3) atoms were refined analogously. The crystallographic parameters are given in Table 1. The positional and thermal parameters are listed in Table 2. The experimental, calculated, and difference X-ray profiles are shown in Fig. 1.

The composition of the $Ni_{151.5}Pb_{24}S_{92}$ compound determined from the structure refinement (Ni, 56.64; Pb, 8.97; and S, 34.39 at.%) is consistent with the results of elemental analysis of individual grains in the annealed samples (Ni, 57.3±0.6; Pb, 9.5±0.6; and S, 33.0±0.2 at.%). Apparently, slight differences resulted from the complexity of analysis of the Pb—S pair due to the fact that the peaks of the M series belonging to the lead atoms fall on the absorption band edge of sulfur. The determined composition was also qualitatively confirmed by the fact that the annealed sample with composition 60 Ni + 9 Pb + 31 S contained the Ni and Ni_3S_2 impurities (region of the three-phase equilibrium $Ni_{151.5}Pb_{24}S_{92}$ + Ni + Ni_3S_2). The refined composition differs substantially from that published in the literature[3] (Ni, 60.0; Pb, 9.0; and S, 31.0 at.%).

The overall view of the crystal structure of $Ni_{151.5}Pb_{24}S_{92}$ is shown in Fig. 2. It is convenient to consider the structure as composed of several structural fragments.

Primarily, these are square pyramids (Fig. 3, *a*) formed by the Ni(1) and Ni(2) atoms (Ni(1)—Ni(2), 2.654(1) Å; Ni(1)—Ni(1), 2.5927(9) Å). The pyramids are coordinated by the S(3) atoms at side edges, by the Pb atoms at the base edges, and by the S(2) atoms at the base vertices. The Pb atoms are shared by four adjacent pyramids and each Pb atom is coordinated by eight Ni(1) atoms at the

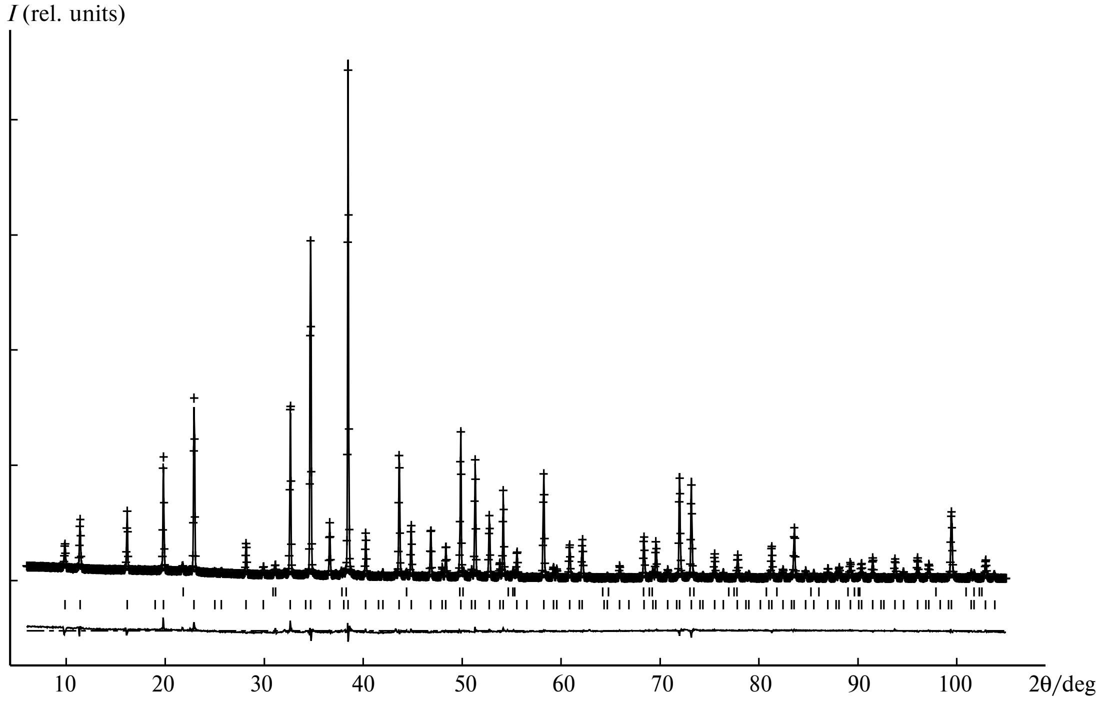

Fig. 1. Experimental, calculated, and difference X-ray diffraction patterns of $Ni_{151.5}Pb_{24}S_{92}$.

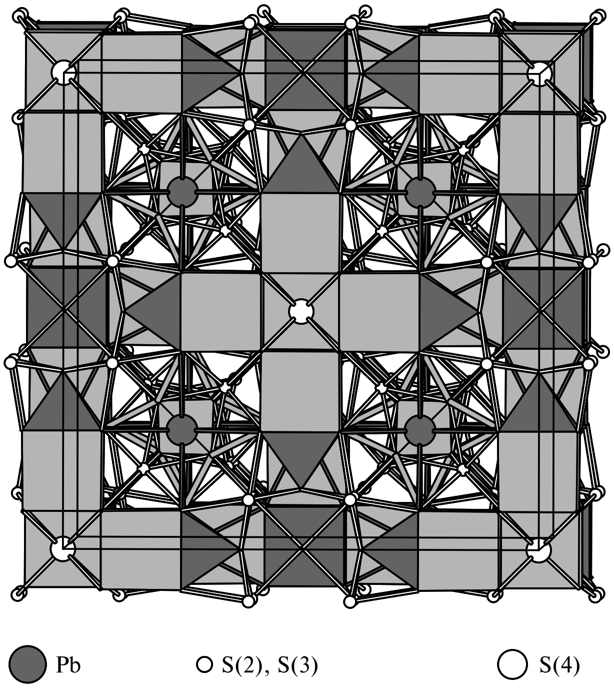

Fig. 2. Overall view of the crystal structure of $Ni_{151.5}Pb_{24}S_{92}$. The figure shows the square pyramids, which are composed of the Ni(1) and Ni(2) atoms and fused with the cubes formed by the Ni(1) and Ni(4) positions (the centers of the cubes are occupied by the S(1) atoms), as well as the tetrahedra composed of the Ni(3) atoms.

Pb—Ni(1) distances of 2.8892(2) Å. These distances are comparable with the Ni—Ni distances in metallic nickel[14] (2.49 Å) and with the Ni—Pb distances in the mixed nickel—lead selenide $Ni_3Pb_2Se_2$ (2.808 Å).[5] Therefore, the structure contains an infinite three-dimensional network of the heterometallic Ni—Pb bonds.

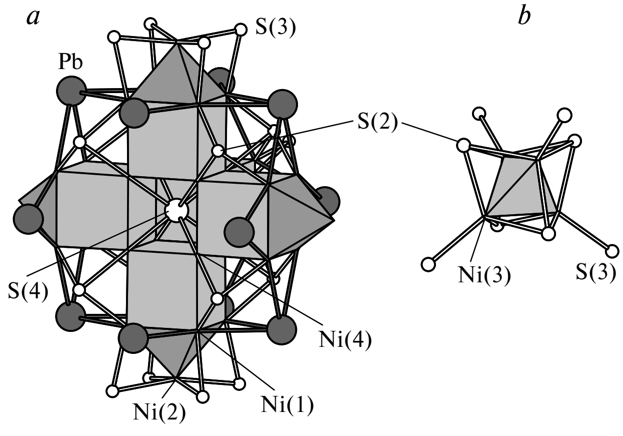

Fig. 3. Fragments of the crystal structure of $Ni_{151.5}Pb_{24}S_{92}$: the three-dimensional cross composed of the nickel cubes and square pyramids (*a*) and the tetrahedron formed by the nickel atoms (*b*). The Ni(1) atoms bound to Ni(3) in the vicinity of the tetrahedron are omitted for simplicity. The S(1) atom is hidden by the center of the distorted cube composed of the Ni(1) and Ni(4) atoms.

Eight positions of the Ni(4) atoms (each position is occupied by 0.281) are located in the vertices of a cube. In addition, the positions of the Ni(4) and Ni(1) atoms form six cubes elongated along the fourfold axes. These cubes share opposite faces with the cube composed of the Ni(4) atoms and the pyramids (their bases) formed by the Ni atoms. Hence, the structural fragments can be described as three-dimensional crosses (see Fig. 3, *a*) containing square pyramids of the Ni atoms at the ends.

The centers of the cubes formed by the Ni(4) atoms are occupied by the S(4) atoms. The centers of the cubes composed of the Ni(1) and Ni(4) atoms are occupied by the S(1) atoms. The distance between two Ni(4) atoms is 2.546(5) Å, and the distance between the Ni(1) and Ni(4) atoms is 2.622(3) Å. Due to the partial occupancy of the Ni(4) positions, only two Ni positions are, on the average, actually occupied in each cube formed by these atoms. Because of this, the coordination polyhedron of the S(4) atom is open resulting, apparently, in the large thermal displacement of this atoms and, as a consequence, in the large thermal parameter (3.9 $Å^2$). It should be noted that the refined occupancy of the S(4) position was equal to unity in all cases.

A regular tetrahedron formed by the Ni(3) positions with the occupancies of 0.704 (see Fig. 3, *b*) is another structural fragment. The Ni(3)—Ni(3) distance is 2.498(3) Å. The tetrahedra are located between the "crosses" and are linked to the latter by the Ni(1) and Ni(2) atoms *via* the S(2) and S(3) atoms, which coordinate the tetrahedra at the edges and vertices, respectively. In addition, there are also rather short bonds between the vertices of the tetrahedra and the Ni(1) atoms (2.554(1) Å).

All Ni—S distances are in the range of 2.203(5)—2.363(1) Å typical of the Ni—S bonds (*d*(Ni—S) = 2.25—2.40 Å in NiS[15] and Ni_3S_2;[16] *d*(Ni—S) = 2.184 Å in Ni_9S_8).[17] Since the distances *d*(Pb—S) = 3.1675(1) and *d*(S—S) = 2.581(2) Å are long compared to the analogous distances in PbS (*d*(Pb—S) = 2.957 Å)[18] or NiS_2 (*d*(S—S) = 2.059 Å),[19] they can be assigned to nonbonded contacts.

A characteristic feature of the crystal structure of $Ni_{151.5}Pb_{24}S_{92}$ is the presence of small 14-vertex (8 S(3) + 6 Ni(2)) cavities (into which spheres with the radius of ~3.9 Å can be fitted) with the centers having the coordinates (0, 0, 1/2).

Square pyramids formed by Ni atoms were also found in other structures, for example, in subvalent nickel telluride $Ni_{2.86}Te_2$ [20] or mixed nickel—tin chalcogenides,[4] the vertices in these compounds being occupied only partially. The tetrahedra formed by Ni atoms were observed, for example, in the $CeNi_4In$ structure,[21] where these tetrahedra are linked in a three-dimensional framework by sharing their vertices.

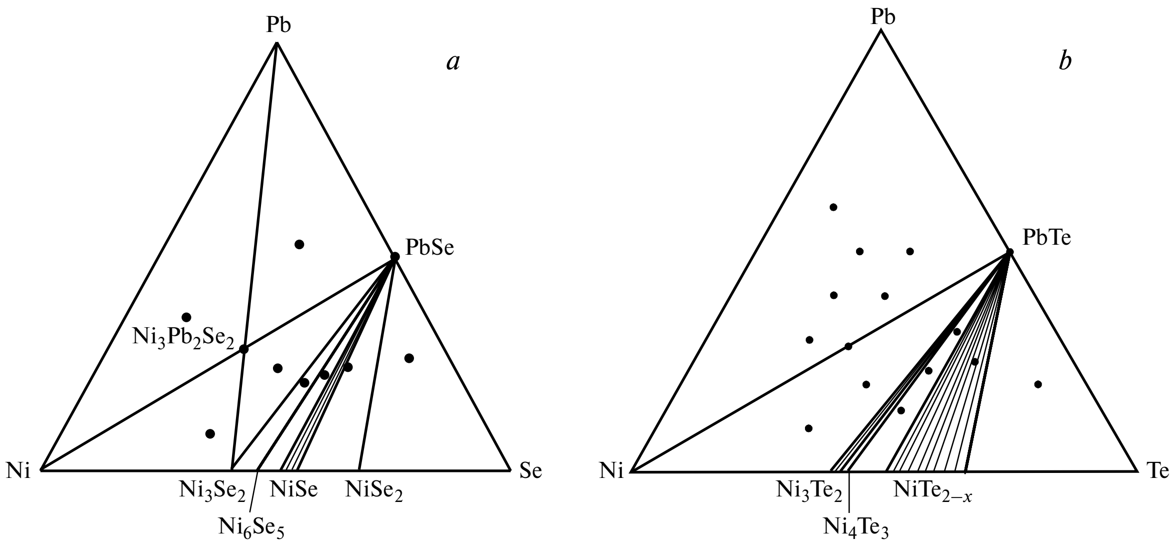

Fig. 4. Phase equilibria in the Ni—Pb—Se (*a*) and Ni—Pb—Te (*b*) systems at 540 °C. The studied compositions are denoted by points. The compounds in the binary systems stable at 540 °C are constructed based on the published data.[23] The two-phase regions are dashed.

The crystal structure of $Ni_{151.5}Pb_{24}S_{92}$ differs substantially from the structure of another known mixed nickel—lead sulfide, *viz.*, $Ni_3Pb_2S_2$. In the latter structure, the Ni atoms do not form well-defined clusters and are separated by rather large distances (d(Ni—Ni) = 2.783 Å). In the $Ni_3Pb_2S_2$ structure, the Pb and S atoms, which form a distorted octahedron, are the nearest neighbors of the Ni atoms. Apparently, the absence of nickel clusters in the latter compound is attributed to the low nickel content as compared to that in $Ni_{151.5}Pb_{24}S_{92}$.

Search for mixed nickel—lead selenides and tellurides was carried out by studying the phase equilibria in the N—Pb—Se and Ni—Pb—Te systems at 540 °C. In each system, several samples, which were annealed at this temperature for ~20 days, were studied by powder X-ray diffraction analysis. The triangulation did not afford new ternary compounds (Fig. 4).

Hence, the "selenide" and "telluride" analogs of $Ni_{151.5}Pb_{24}S_{92}$ and the "telluride" analog of $Ni_3Pb_2S_2$ were not formed at 540 °C. This fact can be associated with the geometry factor. The replacement of the S atoms in the $Ni_{151.5}Pb_{24}S_{92}$ structure by the larger Se and Te atoms would be expected to lead to an increase in the Ni—Ni distances both in the tetrahedra formed by the Ni(3) atoms and the pyramids formed by the Ni(1) and Ni(2) atoms to which the sulfur atoms are coordinated at the faces and edges, respectively. This tendency is clearly seen in phases with shandite-like structures in which the chalcogen atoms are coordinated to the triangles consisting of Ni atoms. The Ni—Ni distance in $Ni_3Pb_2Se_2$ (2.809 Å) is much longer than that in $Ni_3Pb_2S_2$ (2.783 Å). Apparently, the necessity of increasing the Ni—Ni distance, which can be achieved in the structures of the "selenide" and "telluride" analogs of $Ni_{151.5}Pb_{24}S_{92}$ and the "telluride" analog of $Ni_3Pb_2S_2$, is responsible for instability of the corresponding subvalent nickel—lead selenides and tellurides.

Experimental

Synthesis of $Ni_{151.5}Pb_{24}S_{92}$ and study of the phase relations in the Ni—Pb—Ch systems (Ch = S, Se, or Te). Lead (99.99%), powdered Ni (99.99%, Aldrich), S (special purity grade), Se (special purity grade), and Te (special purity grade) were used as the starting compounds. A nickel powder was preheated under a stream of hydrogen at 500 °C for 3 h. Weighed samples (~1 g) were vacuum-sealed in quartz tubes. The tubes were annealed in temperature-controlled shaft furnaces. The temperature was maintained within ±3°. All samples were rapidly quenched by plunging into cold water.

Single-crystal growth. Crystals were grown with the use of I_2 (special purity grade), $PbCl_2$ (reagent grade; dried at 125 °C), NH_4Cl (high-purity grade; sublimed under Ar), Br_2 (reagent grade; purified by distillation over P_2O_5), $(NH_4)_2PbCl_6$, and $AlCl_3$ (the latter two reagents were synthesized according to known procedures[22]) as the carriers. The concentrations of the carriers were in the range from $1 \cdot 10^{-3}$ to $4 \cdot 10^{-2}$ mol L^{-1}.

In the experiments on single-crystal growth, evacuated sealed tubes (120—150 mm in length and 5—6 mm in diameter) containing a weighed sample (~0.5 g) and a carrier (~$1 \cdot 10^{-6}$ mol cm^{-3}) were placed in a temperature-controlled gradient two-temperature horizontal furnace. The temperatures of the hot (charge) and cold zones were maintained within the temperature range of the phase existence. The growth time was 300—400 h. Then the tubes were quenched into water.

Methods of investigations. The powder X-ray diffraction analysis of the products was carried out and X-ray patterns were measured on a STADI/P (Stoe) diffractometer equipped with a linear detector (Cu-$K_{\alpha 1}$ radiation, transmission mode, Ge monochromator). The measured powder X-ray patterns were analyzed with the use of the WinXpow program package (version 1.0) and the PDF base. Single crystals were studied on a CAD4 (Enraf—Nonius) diffractometer.

The differential thermal curves of the samples were recorded on a PRT-1000M instrument in the temperature range of 25—800 °C; the rate of heating was 5 °C min^{-1}; Al_2O_3 (high-purity grade) was used as the standard; the temperature was determined with an accuracy of 5 °C.

Elemental analysis was carried out on a CAMEBAX Type MB1 instrument equipped with an energy dispersive detector. The analysis was performed with the use of individual crystallites from quenched samples, which contained (according to the powder X-ray diffraction data) the $Ni_{60}Pb_9S_{31}$ phase as the major component. The contents of the elements were determined with the use of the K series of the S and Ni atoms and the M series of the Pb atom.

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References

1. S. Natarajan, G. V. Subba Rao, R. Baskaran, and T. S. Radhakrishnan, *J. Less-Common Met.*, 1988, **138**, 215.
2. K. Mariolacos, *Chem. Erde*, 1987, **46**, 315.
3. K. Mariolacos, *Chem. Erde*, 1986, **45**, 338.
4. A. L. Lyubimtsev, A. A. Isaeva, A. I. Baranov, A. Fischer, and B. A. Popovkin, 6*th Intern. Workshop on High Temperature Superconductors and Novel Inorganic Materials Engeneering (June 2001), Book of Abstracts*, Moscow—St. Petersburg, 2001, PIII-10.
5. K.-J. Range, F. Rau, M. Zabel, and H. Paulus, *Z. Kristallogr.*, 1997, **212**, 50.
6. A. I. Baranov, A. V. Olenev, and B. A. Popovkin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 337 [*Russ. Chem. Bull.*, 2001, **50**, 353 (Engl. Transl.)].
7. Ch. I. Abilov and P. G. Rustamov, *Izv. Akad. Nauk, Neorg. Mater.*, 1984, **20**, 582 [*Inorg. Mater., Proceed. Acad. Sci. USSR*, 1984, **20**, No. 4 (Engl. Transl.)].
8. M. A. Alidzhanov, S. G. Agdamskaya, and Ch. I. Abilov, *Izv. Akad. Nauk, Neorg. Mater.*, 1991, **27**, 2437 [*Inorg. Mater., Proceed. Russ. Acad. Sci.*, 1991, **27**, No. 11 (Engl. Transl.)].
9. (a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen (Germany), 1997; (b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen (Germany), 1997.
10. A. C. Larson and R. B. Von Dreele, *GSAS, General Structure Analysis System*, LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos NM 87545, 2000.
11. L. G. Akselrud, Yu. N. Gryn, P. U. Zavalij, V. K. Pecharsky, and V. S. Fundamentsky, *Abstrs. of Papers, 12th European Crystallographic Meeting*, Moscow, 1989, 155.
12. J. B. Parise, *Acta Crystallogr.*, *Sect. B*, 1980, **36**, 1179.
13. (a) F. Izumi, *The Rietveld Method*, Ed. R. A. Young, Oxford University Press, Oxford, 1993, Ch. 13; (b) Y.-I. Kim and F. Izumi, *J. Ceram. Soc. Jpn.*, 1994, **102**, 401.
14. H. E. Swanson and E. Tatge, *Natl. Bur. Stand. (U.S.)*, 1953, Circular 539, 13.
15. V. Rajamani and C. T. Prewitt, *Canadian Mineralogist*, 1974, **12**, 253.
16. J. B. Parise, *Acta Crystallogr.*, *Sect. B*, 1980, **36**, 1179.
17. M. E. Fleet, *Acta Crystallogr.*, *Sect. C*, 1987, **43**, 255.
18. Y. Noda, K. Masumoto, S. Ohba, Y. Saito, K. Toriumi, Y. Iwata, and I. Shibuya, *Acta Crystallogr.*, *Sect. C*, 1987, **43**, 1443.
19. S. Furuseth and A. Kjekhus, *Acta Chem. Scand.*, 1969, **23**, 2325.
20. R. B. Kok, G. A. Wiegers, and F. Jellinek, *Rec. Trav. Chim. Pays-Bas*, 1965, **84**, 1585.
21. M. D. Koterlin, B. S. Morokhivskii, R. R. Kutyan´skii, I. D. Shcherba, and Ya. M. Kalychak, *Fiz. Tverd. Tela*, 1998, **40**, 7 [*Russ. Solid State Phys.*, 1998, **40** (Engl. Transl.)].
22. *Handbuch der Präparativen Anorganischen Chemie*, Ed. H. von G. Brauer, Ferdinand Enke Verlag, Stuttgart, 1978.
23. *Diagrammy sostoyaniya dvoinykh metallicheskikh sistem* [*Phase Diagrams of Binary Metal Systems*], Ed. N. P. Lyakishev, Mashinostroenie, Moscow, 1999, **3**, Pt. 1, 880 pp. (in Russian).

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