

High-Pressure Phase Transition of Hexagonal Alkali Pnictides

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Abstract—High-pressure studies of Li_3P , Na_3Sb , and Na_3Bi at room temperature show that these compounds undergo a reversible transition from a hexagonal phase to a denser, cubic phase. The lattice parameters of the cubic phases are determined at pressures of up to 9.0 GPa.

INTRODUCTION

Most of the alkali pnictides with the general formula A_3B ($\text{A} = \text{Li}-\text{Cs}$, $\text{B} = \text{N}-\text{Bi}$) [1–6] crystallize in four structure types: three hexagonal (AlB_2 , Na_3As , and Cu_3P types) and one cubic (Li_3Bi type). The properties of these compounds at atmospheric pressure have been studied in detail, but little is known about their high-pressure behavior. Hexagonal Li_3N with the AlB_2 structure is known to undergo an irreversible transformation into a hexagonal phase with the Na_3As structure near 100°C at pressures in the range 0.4–0.7 GPa [3, 6]. At the same time, hexagonal Na_3Sb and Na_3Bi , isostructural with Na_3As , undergo a reversible transformation into a cubic phase at room temperature and pressures of 2.3 and 1.0 GPa, respectively [1].

The objective of this work was to study the structural phase transitions of Li_3P , Na_3Sb , and Na_3Bi at

room temperature and pressures of up to 9.0 GPa and to establish the temperature stability range of hexagonal Li_3Sb (α phase) at atmospheric pressure.

EXPERIMENTAL

Samples for this investigation were prepared from Li, Na, Sb, and Bi metals and red phosphorus at high temperatures and atmospheric or high pressures. All manipulations with the starting reagents and synthesis products were carried out in a hermetically sealed chamber filled with dry argon. The starting mixtures with components in the ratio 3 : 1 ($3\text{A} + \text{B} = \text{A}_3\text{B}$; $\text{A} = \text{Li, Na}$; $\text{B} = \text{P, Sb, Bi}$) were placed in an argon-filled Fe or Nb reactor and slowly heated to the preset temperature. The synthesis conditions and lattice parameters of the resultant materials are summarized in Table 1.

Table 1. Synthesis conditions and lattice parameters of hexagonal and cubic lithium and sodium pnictides

Compound	Structure	a , Å	c , Å	p , GPa	t , °C	τ , h
Li_3N	<i>H</i>	3.654	3.880	10^{-4}	400–500	1
Li_3N	<i>H</i>	3.580	6.362	0.4–0.6	20–100	0.5
Li_3P	<i>H</i>	4.263	7.543	10^{-4}	750	20–25
Li_3P	<i>C</i>	5.93		4.0	700	1
Li_3Sb	<i>H</i>	4.71	8.32	10^{-4}	50	1
Li_3Sb	<i>C</i>	6.57		10^{-4}	680–1000	1
Li_3Bi	<i>C</i>	6.722		10^{-4}	1050	1
Na_3Sb	<i>H</i>	5.366	9.516	10^{-4}	950	1
Na_3Bi	<i>H</i>	5.459	9.674	10^{-4}	850	1

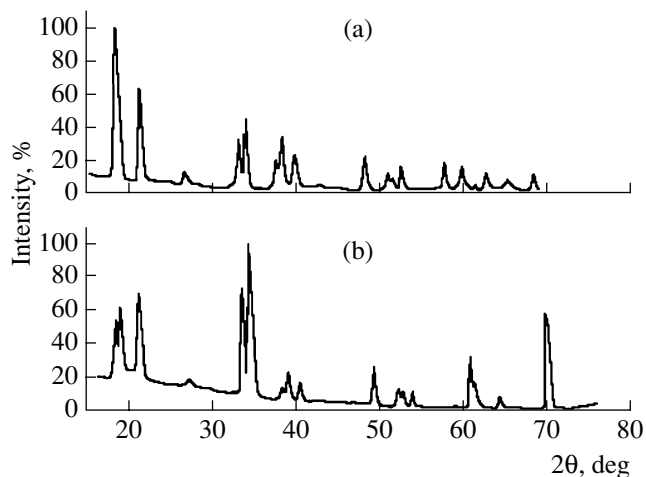


Fig. 1. XRD patterns of (a) Na_3Bi and (b) Na_3Sb at atmospheric pressure.

High-pressure synthesis was carried out in a toroid-type cell [7] at a pressure of 8.0 GPa and a temperature of 900°C, as described in [8]. The phase composition of the samples was determined by x-ray diffraction (XRD) on a DRON-2 powder diffractometer (CuK_α radiation).

The polymorphism of alkali pnictides was studied by in situ XRD (DRON-2, MoK_α radiation, graphite monochromator) at room temperature and pressures from 10^{-4} to 9.0 GPa generated in a diamond-anvil cell [9].

RESULTS AND DISCUSSION

All of the samples studied were single-phase as determined by XRD. The XRD patterns of Na_3Bi and

Na_3Sb (Fig. 1) are typical of hexagonal phases; Li_3P is isostructural with Na_3Sb [10–13].

Li_3Bi crystallizes in a cubic structure with $a = 6.722 \text{ \AA}$ [3].

Heating a 3 : 1 mixture of Li and Sb to 650°C at atmospheric pressure yields hexagonal Li_3Sb (Na_3As -type structure) with $a = 4.71 \text{ \AA}$ and $c = 8.32 \text{ \AA}$ (Fig. 2a). Further heating leads to an irreversible phase transition to cubic Li_3Sb (Li_3Bi structure) with $a = 6.57 \text{ \AA}$ (Fig. 2b). Detailed phase-diagram data for Li_3Sb are still missing; the reported information is contradictory in some respects. Cubic Li_3Sb was variously reported to be stable below 650°C [2, 14] or above 650°C [15]. At the same time, it is well known that K_3Sb and Rb_3Sb have a hexagonal structure at room temperature and atmospheric pressure but may have a cubic structure when prepared in thin-film form [16, 17]. Cubic K_3Bi and Rb_3Bi are stable above 280 and 230°C, respectively [18, 19]. The present results provide clear evidence that cubic Li_3Sb is a high-temperature phase. Li_3P , Na_3Sb , and Na_3Bi undergo no such transformations at atmospheric pressure.

Li_3P was prepared by reacting a mixture of red phosphorus powder and lithium metal at 750°C for 20–25 h in a closed iron reactor. The resultant compound was found to have a hexagonal structure of the Na_3As type with $a = 4.28 \text{ \AA}$ and $c = 7.52 \text{ \AA}$. The measured lattice parameters differ slightly from the calculated ones ($a = 4.272 \text{ \AA}$, $c = 7.594 \text{ \AA}$), which is probably due to structural imperfection. Cubic Li_3P was obtained by heating the hexagonal polymorph to 700°C at a pressure of 4.0 GPa [10]. Figure 3 displays the calculated and experimental XRD

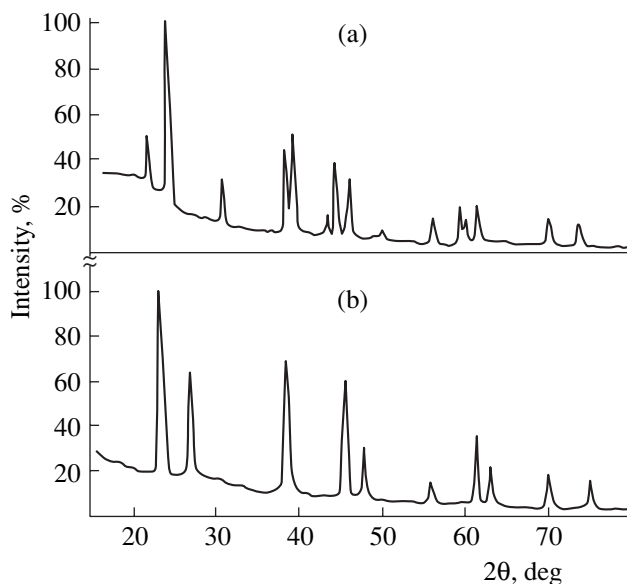


Fig. 2. XRD patterns of (a) hexagonal and (b) cubic Li_3Sb at atmospheric pressure.

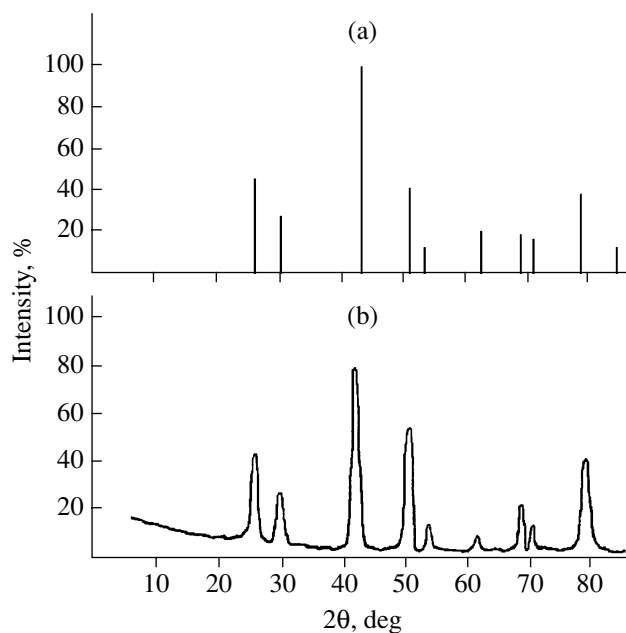


Fig. 3. (a) Calculated and (b) experimental XRD patterns of Li_3P at atmospheric pressure.

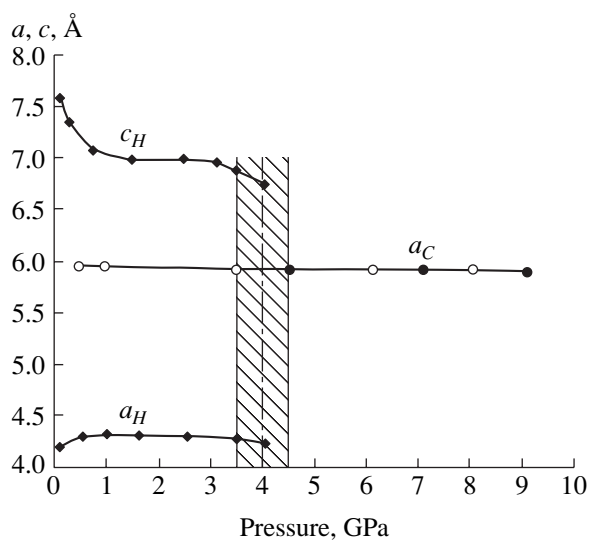


Fig. 4. Lattice parameters of hexagonal and cubic Li_3P as functions of increasing (solid circles) and decreasing (open circles) pressure.

patterns of cubic Li_3P . The experimentally determined lattice parameter of quenched cubic Li_3P ($a = 5.93 \text{ \AA}$) is close to the one predicted theoretically (5.905 \AA). Cubic Li_3P , obtained by quenching at high pressure, is a metastable phase. At atmospheric pressure, the cubic phase gradually (1–2 h) transforms into the stable, hexagonal phase. The phase transition of Li_3P exhibits an appreciable hysteresis (Table 2). Figure 4 shows the lat-

tice parameters of Li_3P as functions of pressure. Hexagonal Li_3P disappears at 4.5 GPa, and only the cubic phase exists at higher pressures. Judging from the variation of the lattice parameter with pressure, the compressibility of cubic Li_3P is rather low.

Cubic Na_3Sb and Na_3Bi could not be stabilized to room temperature and atmospheric pressure even by quenching from temperatures of up to 950°C at pressures of up to 8.0 GPa, which confirms that the cubic forms of these compounds are unstable at atmospheric pressure. Attempts to obtain cubic Na_3Sb and Na_3Bi by other methods (mechanochemical synthesis or dissolution of elemental mixtures in aqueous ammonia) were also unsuccessful. Nevertheless, the hexagonal-to-cubic phase transitions of Na_3Sb and Na_3Bi could be observed by in situ XRD at room temperature and pressures in the range 10^{-4} to 9.0 GPa. Figure 5 shows the XRD patterns of Na_3Sb at high pressures. At 1.3 GPa, the reflections from the cubic phase are very weak (Fig. 5a). With increasing pressure, the reflections from the hexagonal phase become weaker, while those from the cubic phase grow. At 3.3 GPa, only the reflections from cubic Na_3Sb are present. It is also seen in Fig. 5 that, with increasing pressure, the reflections from the cubic phase shift to larger diffraction angles, indicating a decrease in lattice parameter.

The hexagonal-to-cubic phase transition of Na_3Bi was observed at a lower pressure, in the range 0.5–1.0 GPa [11, 12].

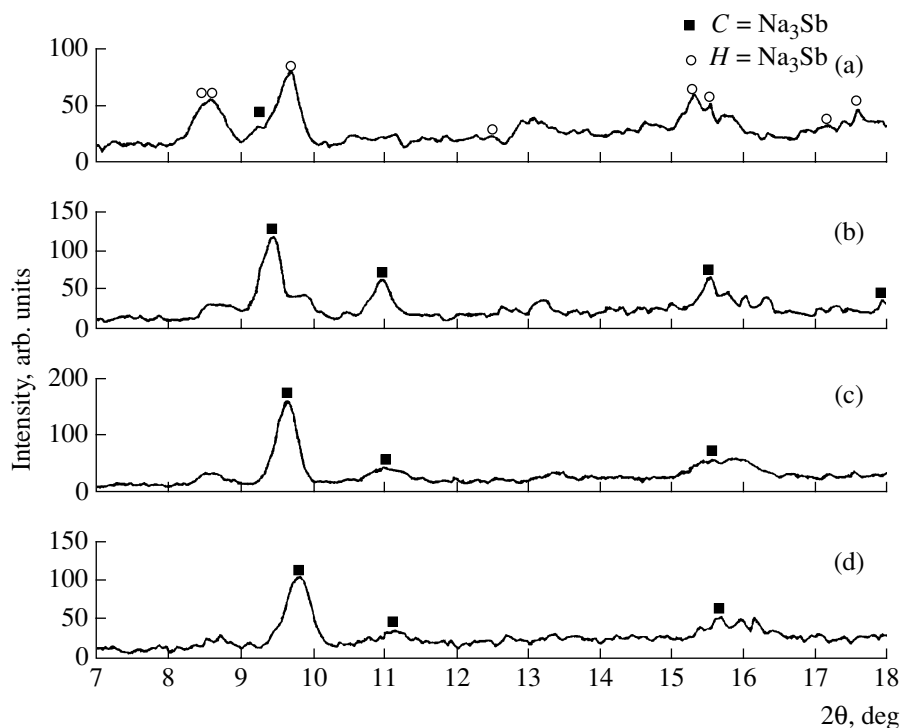


Fig. 5. XRD patterns of Na_3Sb at (a) 1.3, (b) 3.3, (c) 4.3, and (d) 5.2 GPa.

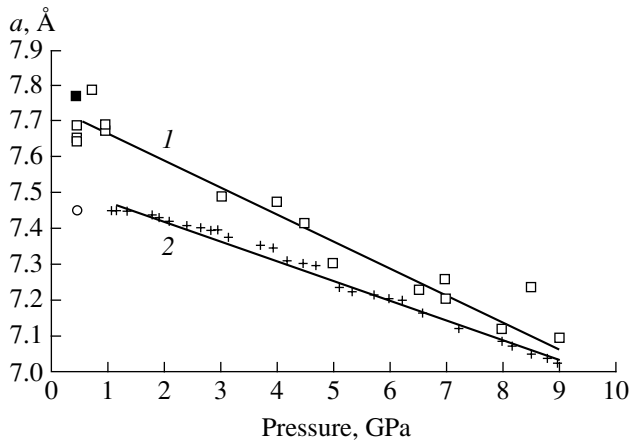


Fig. 6. Lattice parameters of cubic (1) Na_3Bi and (2) Na_3Sb as functions of pressure.

Three loading–unloading cycles confirmed that the phase transition occurred in a range of pressures, through a two-phase region, without decomposition of the compounds.

Table 2. Stability limits of hexagonal and cubic pnictides in the course of loading (\uparrow) and pressure release (\downarrow)

Compound	Structure	$p\uparrow$, GPa	$p\downarrow$, GPa
Li_3P	<i>H</i>	<3.5	10^{-4}
	<i>H + C</i>	3.5–4.5	$1.0\text{--}10^{-4}$
	<i>C</i>	>4.5	>1.0
Na_3Sb	<i>H</i>	<2.3	10^{-4}
	<i>H + C</i>	2.3–3.2	$1.5\text{--}10^{-4}$
	<i>C</i>	>3.2	>1.5
Na_3Bi	<i>H</i>	<0.5	10^{-4}
	<i>H + C</i>	0.5–1.0	$0.5\text{--}10^{-4}$
	<i>C</i>	>1.0	>0.5

Table 3. Lattice parameters (increasing and decreasing pressure) and compressibility of cubic Na_3Bi , Na_3Sb , and Li_3P

Compound	p , GPa	a , Å	V , Å ³	ΔV , Å ³	$\chi \times 10^{-2}$, GPa ⁻¹
Li_3P	4.0	5.875	202.78	19.53	1.2
	9.0	5.68	183.25		
	1.0	5.875	202.78		
Na_3Sb	2.3	7.40	405.22	56.54	2.5
	9.0	7.025	358.62		
	0.5	7.46	415.16		
Na_3Bi	1.0	7.65	447.7	120.51	3.2
	9.0	7.05	350.4		
	0.5	7.78	470.91		

Table 2 lists the pressure ranges of the hexagonal–cubic phase transition in the pnictides studied. The large width of the high-pressure phase transition is related to kinetic factors. Consequently, the pressure range of the phase transition must be narrower at higher temperatures. Indeed, it is well known that the rate of such processes is temperature-dependent [20]. The existence of a two-phase region was also reported by Beister *et al.* [1]. The pressures at which we observed the phase transition (2.3 GPa in Na_3Sb and 0.75 GPa in Na_3Bi) differ somewhat from those reported earlier. The discrepancy is attributable to differences in the sample preparation procedures and techniques of high-pressure studies.

A characteristic feature of the high-pressure phase transition in the alkali pnictides is a large hysteresis in loading–unloading cycles. Our results (Table 2) demonstrate that, during the unloading process, the two-phase region is observed at lower pressures. The hysteresis is larger at higher transition pressures. This correlates with the finding that, after unloading to atmospheric pressure, the cubic-to-hexagonal phase transition of Na_3Sb and Na_3Bi takes several minutes, whereas that of Li_3P takes about 2 h.

The lattice parameters of cubic Na_3Bi and Na_3Sb as functions of pressure are shown in Fig. 6, and those of Li_3P are shown in Fig. 4. These data were used to evaluate the compressibility of the cubic phases: $\chi = \frac{\Delta V}{V_0} \times$

$\frac{1}{\Delta p}$ (Table 3). Compressibility was found to decrease in going from Na_3Bi ($3.2 \times 10^{-2} \text{ GPa}^{-1}$) to Na_3Sb ($2.5 \times 10^{-2} \text{ GPa}^{-1}$) and to Li_3P ($1.2 \times 10^{-2} \text{ GPa}^{-1}$), which seems to be due to the decrease in the atomic number of the Group V element.

Thus, the alkali pnictides studied undergo a transition from a hexagonal phase (Na_3As structure, sp. gr. $P6_3/mmc$) to a denser, cubic phase (Li_3Bi structure, sp. gr. $Fm\bar{3}m$) as the temperature or pressure is raised. The lattice parameters of the cubic phases fit in with the dependence of a on the atomic radius R_A of the alkali metal reported earlier for the A_3B ($\text{A} = \text{Li–Cs}$, $\text{B} = \text{Sb–Bi}$) pnictides [21].

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REFERENCES

- Beister, H.J., Klein, J., Schewe, J., and Syassen, K., Structural Phase Transitions of Alkali Metal Pnictides and Chalcogenides under Pressure, *High Pressure Res.*, 1991, vol. 7, no. 1, pp. 91–95.
- Brauer, G. and Zintl, E., Konstitution von Phosphiden, Arseniden, Antimoniden und Wismutiden des Lithiums,

- Natriums und Kaliums, *Z. Phys. Chem. Abstr.*, 1937, vol. 37B, no. 5/6, pp. 323–352.
3. Beister, H.J., Haag, S., Kniep, R., *et al.*, Structural Phase Transitions in Lithium Pnictides under Pressure, *Angew. Chem.*, 1988, vol. 100, p. 1116.
 4. Gnutzmann, V.G., Dorn, F.W., and Klemm, W., Über einige A3B- und AB2-Verbindungen der schweren Alkalimetalle mit Elementen der V Gruppe, *Z. Anorg. Allg. Chem.*, 1961, vol. 309, no. 3/4, pp. 210–225.
 5. Hafner, P. and Range, K.-J., Na₃As Revised: High-Pressure Synthesis of Single Crystals and Structure Refinement, *J. Alloys Compd.*, 1994, vol. 216, no. 1, p. 7.
 6. Mitrokhina, S.V., Burdina, K.P., and Semenenko, K.N., A New Polymorph of Li₃N, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1990, vol. 31, no. 6, pp. 612–614.
 7. Khvostantsev, L.G., Vereshchagin, L.F., and Novikov, F.P., Device of Toroid Type for High Pressure Generation, *High Temp.–High Pressures*, 1977, vol. 9, no. 6, pp. 637–639.
 8. Burdina, K.P., Mechanism of Cubic Boron Nitride Formation, *Wide Bandgap Mater.*, 2000, vol. 8, pp. 137–153.
 9. Degtyareva, V.F., Bdikin, I., and Khasanov, S., BCC High-Pressure Phase in the SnBi Alloy, *Solid State Commun.*, 1996, vol. 99, no. 12, p. 907–909.
 10. Kalinin, V.B., Donchak, A.A., Burdina, K.P., *et al.*, High-Pressure Phase of Lithium Phosphide, Li₃P, *Materialovedenie*, 1999, no. 2, pp. 40–42.
 11. Leonova, M.E., Kulinich, S.A., Sevast'yanova, L.G., *et al.*, Synthesis of Sodium Bismuthide Na₃Bi under a High Pressure, *Exp. Geosci.*, 1998, vol. 7, no. 2, pp. 55–56.
 12. Kulinich, S.A., Leonova, M.E., Sevast'yanova, L.G., *et al.*, High-Pressure Synthesis of Sodium Bismuthide, Na₃Bi, *Zh. Obshch. Khim.*, 1999, vol. 69, no. 5, pp. 681–683.
 13. Leonova, M.E., Sevast'yanova, L.G., Gulish, O.K., and Burdina, K.P., New Cubic Phases in the Li–Na–Sb–Bi System, *Neorg. Mater.*, 2001, vol. 37, no. 12, pp. 1488–1492 [*Inorg. Mater.* (Engl. Transl.), vol. 37, no. 12, pp. 1270–1273].
 14. Samsonov, G.V., *Antimonidy* (Antimonides), Kiev: Naukova Dumka, 1977, p. 53.
 15. *Termodinamicheskie konstanty veshchestv: Spravochnik* (Thermodynamic Constants of Substances: A Handbook), Moscow: VINITI, issue 10, 1965–1981.
 16. Sommer, A.H. and McCarroll, W.H., A New Modification of the Conducting Compound K₃Sb, *J. Appl. Phys.*, 1966, vol. 37, pp. 174–178.
 17. Chiikava, C.C., The Crystal Structure of Rb₃Sb, *J. Phys. Soc. Jpn.*, 1961, vol. 16, pp. 1175–1180.
 18. Chuntunov, K.A., Yatsenko, S.P., Kuznetsov, A.N., *et al.*, Polymorphic Transformation of Rb₃Bi, *Kristallografiya*, 1977, vol. 22, no. 3, pp. 641–647.
 19. Sands, D.E., Wood, D.H., and Ramsey, W.J., The Crystal Structure of β-K₃Bi, *Acta Crystallogr.*, 1963, vol. 16, no. 4, p. 316.
 20. Ishchuk, V.M., Zavadskii, E.A., and Gulish, O.K., Diffuse Phase Transitions in PZT Solid Solutions due to the Coexistence of Ferro- and Antiferroelectric Phases, *Fiz. Tverd. Tela* (Leningrad), 1986, vol. 28, no. 5, p. 1502.
 21. Leonova, M.E., Bdikin, I.K., Sevast'yanova, L.G., *et al.*, Heavily Compressed Phases in M–Bi Systems, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2000, vol. 41, no. 5, pp. 334–337.