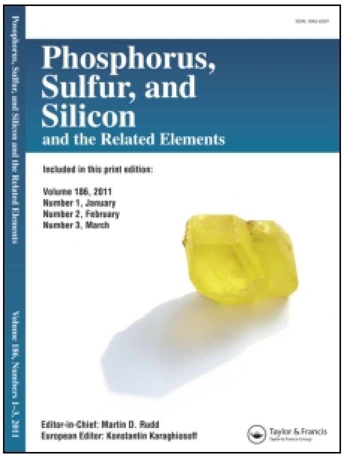

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SYNTHESIS, CRYSTAL STRUCTURES AND PROPERTIES OF $M_3B_3S_6$ (M = Na, K, Rb) AND $LiSrB_3S_6$

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Abstract The thioborates $M_3B_3S_6$ (M = Na[1,2], K[1,2], Rb) and $LiSrB_3S_6$ were prepared from stoichiometric amounts of the metal sulfides, boron and sulfur. The crystal data for the isotypic $M_3B_3S_6$ (M = Na, K, Rb) compounds are: space group $R\bar{3}c$; a = 15.118(1), 15.520(5), 15.813(4) Å; c = 7.512(1), 8.424(3), 8.804(1) Å (hexagonal). The crystal data for the first quarternary thioborate $LiSrB_3S_6$ are: space group Cc; a = 14.933(6), b = 8.703(4), c = 7.866(3) Å, $\beta = 116.76(3)^\circ$. All four metathioborates contain isolated $B_3S_6^{3-}$ anions which form B_3S_3 rings with three exocyclic sulfur atoms.

INTRODUCTION

In recent years considerable progress has been observed in the chemistry and structural chemistry of thioborates as well as in the knowledge of their interesting physical properties. This was possible by the development of appropriate and novel methods for their synthesis and crystallization[1].

Unexpected tetrahedral BS_4 coordination has been observed in the heavy metal thioborate $Pb_4B_4S_{10}$[1], in $TlBS_3$[1] (the first perthioborate) as well as in $Ag_6B_{10}S_{18}$[1] and $Li_{6+2x}[B_{10}S_{18}]S_x(x \approx 2)$[3]. Compared to those ternary phases which have trigonal planar BS_3 coordination like $H_3B_3S_6$[1], Tl_3BS_3[4], and $Sr_3[BS_3]_2$[5] these tetrahedral compounds are considerably more stable towards nucleophilic attack by water or oxygen.

SAMPLE PREPARATION AND PROPERTIES

The synthesis of well-defined and highly pure thioborates is difficult because of the high reactivity of the boron sulfides towards a variety of container materials at elevated temperatures. The fused silica tubes usually employed are attacked by boron sulfide at temperatures above 300–400°C, with B–Si exchange and formation of

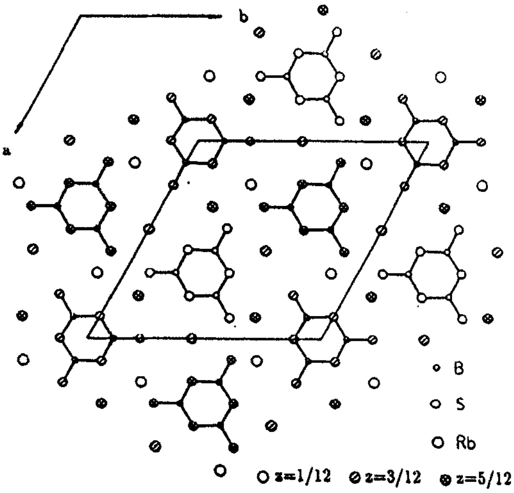

Figure 1 Projection of the unit cell of $Rb_3B_3S_6$ along [0 0 1] ($1/12 \leq z \leq 5/12$)

silicon–sulfur compounds resulting. Two general methods have proven to be suitable for the preparation of pure samples: (a) the inner surface of the quartz glass crucible is coated with a tight layer of glassy carbon, or (b) crucibles made of glassy carbon, of pressed graphite, or of boron nitride, furnished with a tight screw cap, are used as sample containers. For the high-temperature experiment they are inserted into a coated silica tube. In the following the conditions for the synthesis of pure crystalline samples of $M_3B_3S_6$ and $LiSrB_3S_6$ are described:

The thioborates were prepared in high temperature reactions from stoichiometric amounts of the metal sulfides, boron, and sulfur using method (a) for $Rb_3B_3S_6$ and $LiSrB_3S_6$ and method (b) for $Na_3B_3S_6$ and $K_3B_3S_6$. Table I shows the time–temperature program for the preparation of the four metathioborates.

TABLE I Time–Temperature Program for the Preparation of

$Na_3B_3S_6$:	RT $\xrightarrow{2h}$ 700°C (10h) $\xrightarrow{1h}$ 580°C $\xrightarrow{160h}$ 500°C $\xrightarrow{48h}$ RT
$K_3B_3S_6$:	RT $\xrightarrow{2h}$ 625°C (10h) $\xrightarrow{1h}$ 520°C $\xrightarrow{120h}$ 460°C $\xrightarrow{44h}$ RT
$Rb_3B_3S_6$:	RT $\xrightarrow{2h}$ 600°C (1.5h) $\xrightarrow{1/2h}$ 550°C (16h) $\xrightarrow{1/2h}$ 400°C (72h) $\xrightarrow{240h}$ RT
$LiSrB_3S_6$:	RT $\xrightarrow{1/2h}$ 600°C (1.5h) $\xrightarrow{1/2h}$ 800°C (3h) $\xrightarrow{1/4h}$ 700°C (16h) $\xrightarrow{2h}$ RT

All four compounds are very sensitive to moisture and have to be handled under dry inert gas.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

The crystal structures were determined from single crystal X-ray diffraction data. The refinement converged to R values given in Table II. The final atomic coordinates and thermal parameters are given in the Tables III and IV. In the crystal structures of $M_3B_3S_6$ all atoms occupy the special position 18e (x 0 1/4) (hexagonal).

TABLE II R values for the structure solutions

	$Na_3B_3S_6$	$K_3B_3S_6$	$Rb_3B_3S_6$	$LiSrB_3S_6$
R	0.028	0.030	0.032	0.053
R_w	0.027	0.037	0.028	0.046

TABLE III Atomic coordinates and isotropic thermal parameters ($Å^2$) with standard deviations for $M_3B_3S_6$

Atom	$Na_3B_3S_6$		$K_3B_3S_6$		$Rb_3B_3S_6$	
	x	U_{eq}*	x	U_{eq}*	x	U_{eq}*
M	0.46108(8)	0.0420(5)	0.45011(7)	0.0368(4)	0.44703(6)	0.0252(4)
S(1)	0.87666(4)	0.0291(3)	0.88080(8)	0.0472(6)	0.88289(16)	0.0391(9)
S(2)	0.23469(4)	0.0294(3)	0.22824(7)	0.0320(4)	0.22438(16)	0.0247(8)
B	0.1177(2)	0.0225(9)	0.1138(3)	0.027(2)	0.1131(7)	0.021(4)

* U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

The isotypic compounds $M_3B_3S_6$ (M=Na, K, Rb) consist of M^+ cations and of isolated, planar $B_3S_6{}^{3-}$ anions which form B_3S_3 six-membered rings with three exocyclic sulfur atoms. The B-S bond lengths are typical for trigonally coordinated boron (Table V). The exocyclic bond lengths (B-S(2)) are significantly shorter than the bond

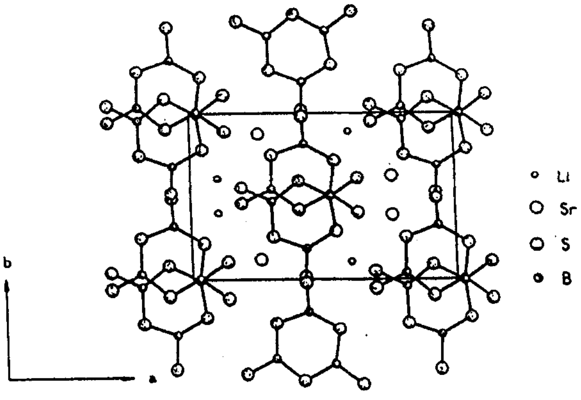

Figure 2 Projection of the unit cell of $LiSrB_3S_6$ along [0 0 1]

TABLE IV Atomic coordinates and isotropic thermal parameters (Å^2) with standard deviations for $LiSrB_3S_6$

Atom	x	y	z	U_{eq}^*
Li	0.5967(15)	0.1091(23)	0.5585(30)	0.030(4)
Sr	0.25940	0.12067(10)	0.52460	0.0135(3)
S(1)	0.12784(18)	0.10642(28)	0.10197(37)	0.0141(9)
S(2)	0.80252(19)	0.24762(27)	0.43095(40)	0.0144(8)
S(3)	0.04147(19)	0.21392(27)	0.56856(43)	0.0201(10)
S(4)	0.42134(18)	0.01765(25)	0.40736(39)	0.0129(8)
S(5)	0.68562(19)	0.04912(27)	0.92310(40)	0.0153(9)
S(6)	0.90428(21)	0.08878(28)	0.01137(55)	0.0276(13)
B(1)	0.4256(8)	0.1785(11)	0.9732(15)	0.008(2)
B(2)	0.0206(9)	0.0081(13)	0.5583(18)	0.017(2)
B(3)	0.7997(8)	0.0405(12)	0.4606(16)	0.011(2)

TABLE V B–S bond lengths with standard deviations for $M_3B_3S_6$ (Å)

	$Na_3B_3S_6$	$K_3B_3S_6$	$Rb_3B_3S_6$	Symmetry Code
B–S(1a)	1.824(1)	1.810(3)	1.821(6)	a: y, x-1, 0.5-z
B–S(2)	1.768(3)	1.776(5)	1.760(12)	

lengths in the ring. The coordination sphere of the M^+ cations consists of seven sulfur atoms with M···S distances between 2.969(1)–3.423(1) Å (Na), 3.206(1)–3.443(2) Å (K), and 3.306(2)–3.521(3) Å (Rb). In the crystal structure of $LiSrB_3S_6$ similar B–S bond lengths are observed(average: exocyclic: 1.778 Å, ring: 1.817 Å). Li^+ is tetrahedrally coordinated by sulfur, the coordination sphere of Sr^{2+} consists of nine sulfur atoms with average distances of 2.51 Å (Li···S) and 3.202 Å (Sr···S).

Structurally equivalent six-membered rings are observed in the crystal structures of $M_3B_3O_6$[6] (M=Na, K, Rb, Cs) which are isotypic with $M_3B_3S_6$ (M=Na, K, Rb).

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