

Phase equilibria in the ternary system Sm–Al–B at 600°C

Taras SLIVINSKIY^{1,2*}, Yaroslav TOKAYCHUK¹, Roman GLADYSHEVSKI¹

¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

² Scientific Consulting Company “Structure-Properties”, Sakharova St. 33, 79026 Lviv, Ukraine

* Corresponding author. Tel.: +380-32-2394506; e-mail: taras.slivinskiy@gmail.com

Received May 1, 2018; accepted June 27, 2018; available on-line January 1, 2019

The isothermal section of the phase diagram of the system Sm–Al–B at 600°C was constructed. The binary compounds do not dissolve significant amounts the third component. One ternary compound, Sm₃AlB_x ($x \approx 0.1$) was found in the system. The crystal structure of the metal (Sm/Al) sublattice of the new compound belongs to the structure type Cu₃Au (Pearson symbol *cP4*, space group *Pm-3m*, $a = 4.832(2)$ Å). The boron atoms are likely to occupy octahedral voids in the structure, in an arrangement corresponding to the structure type CaTiO₃.

Samarium / Aluminum / Boron / X-ray powder diffraction / Phase diagram

Introduction

The ternary systems *R*–Al–B (*R* = Y, La–Nd, Gd–Tm) have been investigated to a certain extent. For all of them isothermal sections of the phase diagrams at 500°C (for *R* = La, Ce) or 600°C (*R* = Y, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm) have been constructed in the whole (*R* = La, Ce, Pr, Nd, Gd) or partial (*R* = Y, Tb, Dy, Ho, Er, Tm) concentration ranges [1]. No ternary compounds were found in the systems with light rare-earth metals (*R* = La, Ce, Pr, Nd, and Gd), whereas in the systems with *R* = Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu, one or more boron-rich ternary compounds were found and characterized [2–14]. In the systems Dy–Al–B and Ho–Al–B, ternary phases of approximate composition *RA*₃B_{0.5}, were revealed [5]. Crystallographic data of the ternary compounds reported in the systems *R*–Al–B are summarized in Table 1.

The aim of the present work was the experimental investigation of the phase equilibria in the ternary system Sm–Al–B and the construction of the isothermal section of the phase diagram at 600°C in the whole concentration range. The binary systems that delimit the ternary system Sm–Al–B have been studied and the corresponding phase diagrams constructed in the whole concentration ranges [15], even if some questions remain. All the three systems, Sm–Al, Sm–B, and Al–B, are characterized by the formation of binary compounds with finite compositions. Their crystallographic data are summarized in Table 2.

Experimental

One two-component and eight three-component alloys were synthesized from high-purity metals (Sm ≥ 99.9 mass%, Al ≥ 99.985 mass%, B ≥ 99.99 mass%) by arc-melting pressed pellets, using a tungsten electrode and a water-cooled copper hearth under a Ti-gettered argon atmosphere. To achieve homogeneity the samples were melted twice. After the synthesis the alloys were wrapped into tantalum foil, sealed in quartz ampoules under vacuum, and annealed at 600°C for 720 h. Finally the ampoules with the samples were quenched into cold water. The mass losses, which were controlled at all stages of the synthesis, did not exceed 2% of the total mass, which was approximately 1 g for each alloy.

Phase analysis and structure refinements were carried out using X-ray powder diffraction data collected at room temperature on a diffractometer DRON-2.0M (Fe *K*α-radiation). The profile and structural parameters were refined by the Rietveld method, using the program package FullProf Suite [34].

Results and discussion

Isothermal section of the phase diagram of the system Sm–Al–B at 600°C

The isothermal section of the phase diagram of the ternary system Sm–Al–B at 600°C (Fig. 1) was constructed based on the results of the X-ray phase analysis of nine samples.

Table 1 Crystallographic data for ternary compounds reported in the systems R–Al–B, R = Tb–Lu [2].

Compound	Structure type	Pearson symbol	Space group	Unit-cell parameters, Å			Ref.
				<i>a</i>	<i>b</i>	<i>c</i>	
Tb _{1-x} Al _{1-y} B ₁₄	LiAlB ₁₄	<i>oI64</i>	<i>Imma</i>	5.836	10.419	8.189	[3,4,11]
DyAl ₃ B _{0.4-0.5}	BaPb ₃	<i>hR36^a</i>	<i>R-3m</i>	6.149	–	21.090	[5]
Dy _{1-x} Al _{1-y} B ₁₄	LiAlB ₁₄	<i>oI64</i>	<i>Imma</i>	5.846	10.420	8.1982	[3,4,11]
HoAl ₃ B _{0.4-0.5}	BaPb ₃	<i>hR36^a</i>	<i>R-3m</i>	6.132	–	20.986	[5]
Ho _{1-x} Al _{1-y} B ₁₄	LiAlB ₁₄	<i>oI64</i>	<i>Imma</i>	5.816	10.399	8.182 ^b	[3,4,11]
HoAlB ₄	YCrB ₄	<i>oP24</i>	<i>Pbam</i>	5.846	10.405	8.194	[3,4,11]
	YCrB ₄	<i>oP24</i>	<i>Pbam</i>	5.9283	11.5530	3.5306	[6]
				5.839	10.390	8.171	[3,11]
Er _{1-x} Al _{1-y} B ₁₄	LiAlB ₁₄	<i>oI64</i>	<i>Imma</i>	5.842	10.406	8.186	[3,4,11]
				5.848	10.386	8.209	[4]
				5.8157	10.3950	8.1820 ^c	[14]
α-ErAlB ₄	YCrB ₄	<i>oP24</i>	<i>Pbam</i>	5.9955	11.48	3.5284	[6]
β-ErAlB ₄	ThMoB ₄	<i>oS24</i>	<i>Cmmm</i>	5.9213	11.4314	3.5070	[14]
				7.3163	9.3340	3.5301	[8]
Tm _{1-x} Al _{1-y} B ₁₄	LiAlB ₁₄	<i>oI64</i>	<i>Imma</i>	5.826	10.380	8.176	[6]
				5.8212	10.3837	8.1762 ^d	[9]
α-TmAlB ₄	YCrB ₄	<i>oP24^e</i>	<i>Pbam</i>	5.9225	11.4784	3.5224	[10]
β-TmAlB ₄	ThMoB ₄	<i>oS24</i>	<i>Cmmm</i>	7.3057	9.3163	3.5214	[8]
Yb _{1-x} Al _{1-y} B ₁₄	LiAlB ₁₄	<i>oI64</i>	<i>Imma</i>	5.860	10.439	8.222	[3,4,11]
				5.927	11.47	3.492	[11,13]
α-YbAlB ₄	YCrB ₄	<i>oP24</i>	<i>Pbam</i>	5.922	11.473	3.506	[12]
β-YbAlB ₄	ThMoB ₄	<i>oS24</i>	<i>Cmmm</i>	7.3080	9.3150	3.4980	[12]
Yb ₂ AlB ₆	Y ₂ ReB ₆	<i>oP36</i>	<i>Pbam</i>	9.127	11.460	3.584	[11,13]
Lu _{1-x} Al _{1-y} B ₁₄	LiAlB ₁₄	<i>oI64</i>	<i>Imma</i>	5.867	10.364	8.157	[3,4,11]
				5.906	11.440	3.480	[11,13]
α-LuAlB ₄	YCrB ₄	<i>oP24</i>	<i>Pbam</i>	5.9050	11.4440	3.5100	[12]
β-LuAlB ₄	ThMoB ₄	<i>oS24</i>	<i>Cmmm</i>	7.289	9.286	3.504	[12]

^a for the metal atom sublattice; ^b refinement on single crystal, $x = 0.367$, $y = 0.26$; ^c narrow homogeneity range near $x = 0.43$, $y = 0.38$; ^d $x = 0.738(3)$, $y = 0.42(1)$; ^e refinement considering additional cation sites with 2% occupancy, *oP32*

Table 2 Selected crystallographic data for binary compounds reported in the systems Sm–Al, Sm–B, and Al–B [2]. Phases stable at 600°C are marked with bold characters.

Compound	Structure type	Pearson symbol	Space group	Unit-cell parameters, Å			Ref.
				<i>a</i>	<i>b</i>	<i>c</i>	
Sm ₃ Al ^a	Cu ₃ Au	<i>cP4</i>	<i>Pm-3m</i>	4.901	–	–	[16]
Sm₂Al	Co ₂ Si	<i>oP12</i>	<i>Pnma</i>	6.654	5.193	9.631	[17]
SmAl	DyAl	<i>oP16</i>	<i>Pbcm</i>	5.678	11.622	5.678	[18]
SmAl ^a	CsCl	<i>cP2</i>	<i>Pm-3m</i>	3.739	–	–	[19]
SmAl₂	MgCu ₂	<i>cF24</i>	<i>Fd-3m</i>	7.943	–	–	[16]
SmAl₃	Mg ₃ Cd	<i>hP8</i>	<i>P6₃/mmc</i>	6.38	–	4.597	[20]
Sm ₃ Al ₁₁ ^{a?}	La ₃ Al ₁₁	<i>oI28</i>	<i>Immm</i>	4.333	9.97	12.81	[21]
SmAl _{4-x} ^b	BaAl ₄	<i>tI10</i>	<i>I4/mmm</i>	4.287	–	9.905	[20]
				4.281	–	9.906	[22]
SmAl ₄ ^{a?}	UAl ₄	<i>oI20</i>	<i>Imma</i>	4.44	6.38	13.62	[23]
SmAl ₅ ^a	SmAl ₅	<i>hP24</i>	<i>P6₃22</i>	5.548	–	18.118	[24]
Sm ₁₁ Al ₆₀ ^a	Sm ₁₁ Al ₆₀	<i>cI142</i>	<i>Im-3m</i>	14.06	–	–	[25]
SmB ₂ ^c	AlB ₂	<i>hP3</i>	<i>P6/mmm</i>	3.310	–	4.019	[26]
				7.179	7.18	7.205	[27]
Sm₂B₅	Gd ₂ B ₅	<i>mP28</i>	<i>P2₁/c</i>	–	β = 102.02°	–	[27]
SmB₄	UB ₄	<i>tP20</i>	<i>P4/mbm</i>	7.174	7.174	4.0641	[28]
SmB₆	CaB ₆	<i>cP7</i>	<i>Pm-3m</i>	4.128	–	–	[29]
SmB₆₆	YB ₆₆	<i>cF1936</i>	<i>Fm-3c</i>	23.474	–	–	[30]
AlB ₂	AlB ₂	<i>hP3</i>	<i>P6/mmm</i>	3.00	–	3.24	[31]
AlB ₁₀ ^d	Al _{0.61} B _{6.50}	<i>oS88</i>	<i>Cmcm</i>	5.690	8.881	9.100	[32]
Al _{1.67} B ₂₂ ^e	Al _{1.67} B ₂₂	<i>tP216</i>	<i>P4₂2₂</i>	10.161	–	14.283	[33]

^a metastable phase; ^b high-temperature phase stable > 1066°C; ^c prepared at high pressure; ^d stabilized by small amounts of carbon; ^e generally referred to as (α-)AlB₁₂

It contains 14 single-phase, 26 two-phase and 13 three-phase fields. The highest number of equilibria (6) is formed with the binary phase SmB_4 .

The existence of seven binary compounds at 600°C was confirmed: Sm_2Al (structure type Co_2Si), SmAl (DyAl), SmAl_2 (MgCu_2), SmAl_3 (Mg_3Cd), Sm_2B_5 (Gd_2B_5), SmB_4 (UB_4), and SmB_6 (CaB_6). The phase equilibria involving the three other binary phases stable at 600°C, SmB_{66} , AlB_2 , and $\text{Al}_{1.67}\text{B}_{22}$, were estimated by triangulation of the system based on geometrical arguments. The binary compounds of the systems Sm–Al and Sm–B do not dissolve noticeable amounts of the third component. The extent of the solid solution of boron was not investigated; according to literature data rhombohedral β -boron can dissolve approximately 2 at.% Al at 600°C. One ternary compound of composition Sm_3AlB_x ($x \approx 0.1$) was found.

The phase equilibria formed in the isothermal section of the phase diagram of the system Sm–Al–B are similar to those reported for other R–Al–B systems and mainly involve binary phases of the boundary systems. The formation of boron-rich ternary compounds was not observed in the system Sm–Al–B, but the formation of the Sm-rich phase Sm_3AlB_x is a specific feature of the system.

Crystal structure of the ternary compound Sm_3AlB_x

The crystal structure of the ternary compound Sm_3AlB_x was determined using X-ray powder diffraction data for

a sample of nominal composition $\text{Sm}_{70}\text{Al}_{20}\text{B}_{10}$. The sample contained three phases in equilibrium: Sm_2Al (64.9 mass%), Sm_3AlB_x ($x \approx 0.1$) (27.0 mass%), and Sm_2B_5 (8.1 mass%). The positions and the intensities of the Bragg peaks of the ternary phase indicated a Cu_3Au -type structure or a derivative of it.

The existence of a binary aluminide Sm_3Al adopting the structure type Cu_3Au has been reported in the literature [16], however, it is generally considered to be metastable or stabilized by small amounts of impurities. The phase analysis of a sample of composition $\text{Sm}_{75}\text{Al}_{25}$, annealed at 600°C, did not show the formation of such a phase. Hence, Sm_3AlB_x ($x \approx 0.1$) can be considered as a true ternary compound.

A Rietveld refinement confirmed the ordered structure type Cu_3Au ($cP4$, $Pm-3m$, $a = 4.832(2)$ Å) for the metal-atom sublattice. Due to the impossibility to localize the boron atoms from the X-ray diffraction data, we modeled the possible distribution of boron atoms in the structure of Sm_3AlB_x . The boron atoms are likely to occupy octahedral sites in the close-packed metal atom framework. Three structure types, which are filled-up variants of the structure type Cu_3Au ($Pm-3m$, Cu in Wyckoff position 3c and Au in 1a) with the same space group may be considered: CaTiO_3 (additional atoms in Wyckoff position 1b) [35], Mg_3NF_3 (additional atoms in Wyckoff position 3d) [36], and $\text{Na}_{0.3}\text{Li}_{0.2}\text{La}_{0.5}\text{TiO}_3$ (additional atoms in both Wyckoff positions 1b and 3d) [37].

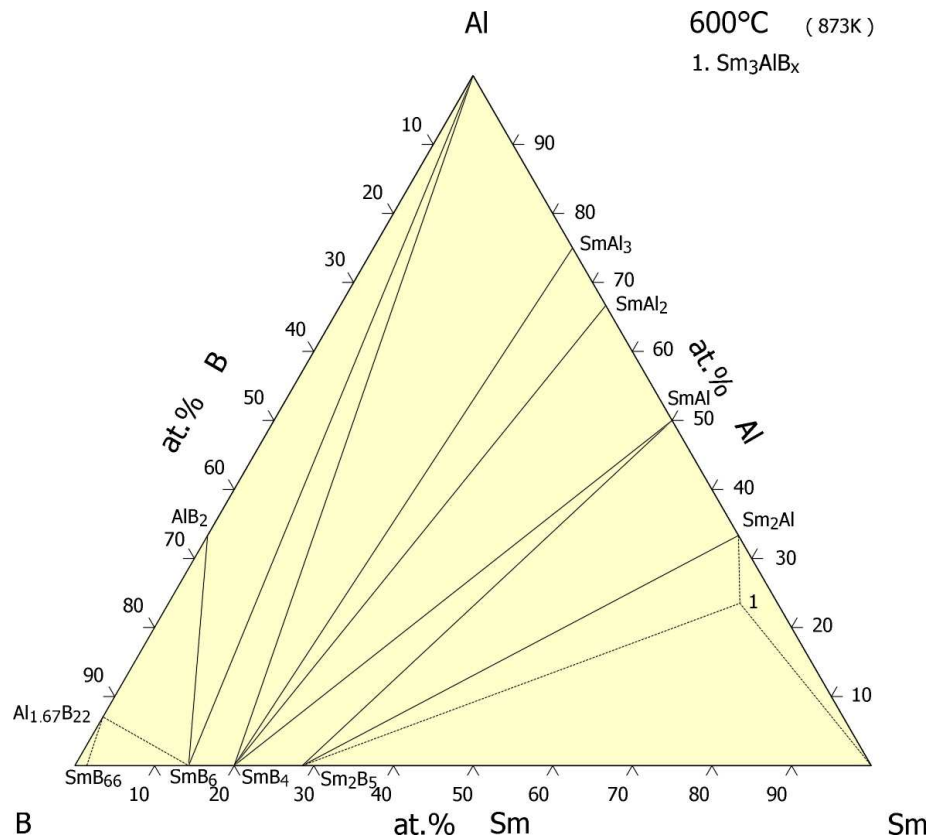


Fig. 1 Isothermal section of the phase diagram of the system Sm–Al–B at 600°C.

The most common of these three types is without contest CaTiO₃; in this case all the B atoms would be surrounded by six Sm atoms and the limiting composition would be Sm₃AlB.

Conclusions

The isothermal section of the phase diagram of the system Sm–Al–B at 600°C is characterized by insignificant solubility of the third component in the binary compounds and by the formation of the ternary phase Sm₃AlB_x ($x \approx 0.1$) with Cu₃Au-type structure of the Sm/Al-sublattice.

Acknowledgements

This work was carried out under the grant of the Ministry of Education and Science of Ukraine No. 0118U003609.

References

- [1] P. Villars, H. Okamoto, K. Cenzual (Eds.), *ASM Alloy Phase Diagram Database*, Release 2006/2018, ASM International, Materials Park, OH, 2018.
- [2] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, Release 2017/18, ASM International, Materials Park, OH, 2017.
- [3] M.M. Korsukova, V.N. Gurin, Y.B. Kuz'ma, N.F. Chaban, S.I. Chykhrij, V.V. Moshchalkov, N.B. Brandt, A.A. Gippius, K.K. Nyan, *Phys. Status Solidi A* 114 (1989) 265-272.
- [4] Y.B. Kuz'ma, V.N. Gurin, M.M. Korsukova, N.F. Chaban, S.I. Chykhrij, *Inorg. Mater.* 24 (1988) 1705-1708.
- [5] S.I. Mikhailenko, S.V. Orishchin, Y.B. Kuz'ma, *Russ. Metall.* 2 (1990) 210-212.
- [6] S.I. Mikhailenko, Y.B. Kuz'ma, N.F. Chaban, *Powder Metall. Met. Ceram.* 33 (1994) 584-587.
- [7] M.M. Korsukova, T. Lundström, L.E. Tergenius, V.N. Gurin, *J. Alloys Compd.* 187 (1992) 39-48.
- [8] T. Mori, R.H. Cardoso-Gil, A. Leithe-Jasper, W. Schnelle, H. Borrmann, Y. Grin, *J. Appl. Phys.* 103 (2008) 07B730.
- [9] M.M. Korsukova, V.N. Gurin, Y. Yu, L.E. Tergenius, T. Lundström, *J. Alloys Compd.* 190 (1993) 185-187.
- [10] T. Mori, H. Borrmann, S. Okada, K. Kudou, A. Leithe-Jasper, U. Burkhardt, Y. Grin, *Phys. Rev. B: Condens. Matter Mater. Phys.* 76 (2007) 064404.
- [11] L.I. Derkhachenko, V.N. Gurin, M.M. Korsukova, A.A. Nechitaïlov, A.P. Nechitaïlov, Y.B. Kuz'ma, N.F. Chaban, *AIP Conf. Proc.* 231 (1991) 451-455.
- [12] R.T. Macaluso, S. Nakatsuji, K. Kuga, E.L. Thomas, Y. Machida, Y. Maeno, Z. Fisk, J.Y. Chan, *Chem. Mater.* 19 (2007) 1918-1922.
- [13] S.I. Mikhailenko, Y.B. Kuz'ma, M.M. Korsukova, V.N. Gurin, *Inorg. Mater.* 16 (1980) 1325-1328.
- [14] Y. Ye, T. Lundström, *J. Alloys Compd.* 210 (1994) 191-196.
- [15] P. Villars, K. Cenzual, J.L.C. Daams, F. Hulliger, T.B. Massalski, H. Okamoto, K. Osaki, A. Prince (Eds.), *Pauling File Binaries Edition*, ASM International, Materials Park (OH), 2002.
- [16] A. Iandelli, *Natl. Phys. Lab. U.K., Symp.* 9 (1958) 3F-2-3F-11
- [17] K.H.J. Buschow, A.S. van der Goot, *J. Less-Common Met.* 24 (1971) 117-120.
- [18] K.H.J. Buschow, *J. Less-Common Met.* 8 (1965) 209-212.
- [19] O.J.C. Runnalls, G.W. Lorimer, *J. Less-Common Met.* 8 (1965) 75-77.
- [20] J.H.N. Van Vucht, K.H.J. Buschow, *Philips Res. Rep.* 19 (1964) 319-322.
- [21] K.H.J. Buschow, J.H.N. Van Vucht, *Philips Res. Rep.* 22 (1967) 233-245.
- [22] S. Delsante, R. Raggio, G. Borzone, R. Ferro, *J. Phase Equilib. Diffus.* 28 (2007) 240-242.
- [23] F. Casteels, *J. Less-Common Met.* 12 (1967) 210-220.
- [24] Z. Ye, C.Z. Wang, K.M. Ho, F. Zhang, Y. Sun, M.I. Mendeleev, R.T. Ott, E. Park, M.F. Besser, M.J. Kramer, Z.J. Ding, C.Z. Wang, K.M. Ho, *Appl. Phys. Lett.* (2015) 106, 101903.
- [25] Z. Ye, F. Zhang, Y. Sun, M.C. Nguyen, S.H. Zhou, L. Zhou, F. Meng, R.T. Ott, E. Park, M.F. Besser, M.J. Kramer, Z.J. Ding, M.I. Mendeleev, C.Z. Wang, R.E. Napolitano, K.M. Ho, *Phys. Rev. Mater.* 1 (2017) 055601.
- [26] J.F. Cannon, D.M. Cannon, H.T. Hall, *J. Less-Common Met.* 56 (1977) 83-90.
- [27] L.V. Zavalii, Y.B. Kuz'ma, S.I. Mikhailenko, *Sov. Powder Metall. Met. Ceram.* 29 (1990) 471-473.
- [28] L.V. Zavalii, V.A. Bruskov, Y.B. Kuz'ma, *Inorg. Mater.* 24 (1988) 5130-1351.
- [29] G.V. Samsonov, N.N. Zhuravlev, Y.B. Paderno, V.R. Melik Adamyan, *Sov. Phys. Crystallogr.* 4 (1960) 507-509.
- [30] G.I. Solovyev, K.E. Spear, *J. Am. Ceram. Soc.* 55 (1972) 475-479.
- [31] W. Hoffmann, W. Jäniche, *Naturwissenschaften* 23 (1935) 851.
- [32] H.G. Will, *Acta Crystallogr.* 23 (1967) 1071-1079.
- [33] J.S. Kasper, M. Vlasse, R.T. Naslain, *J. Solid State Chem.* 20 (1977) 281-285
- [34] J. Rodriguez-Carvajal, *Commission on Powder Diffraction (IUCr), Newsletter* 26 (2001) 12-19.
- [35] T. Barth, *Nor. Geol. Tidsskr.* 8 (1925) 201-216.
- [36] S. Andersson, *Acta Crystallogr. B* 25 (1969) 1009.
- [37] A. Varez, M.T. Fernandez-Diaz, J. Sanz, *J. Solid State Chem.* 177 (2004) 4665-4671.