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Permalink

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Journal

Materials Research Bulletin, 9(5)

ISSN

0025-5408

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Publication Date

1974

DOI

10.1016/0025-5408(74)90133-0

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REMARKS ON THE MUTUAL SOLUBILITIES AND SUPERCONDUCTIVITY OF HEXABORIDES

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(Received March 18, 1974; Communicated by B. T. Matthias)

ABSTRACT

X-ray diffraction and electron microprobe data indicate that the mutual solubility of LaB_6 and YB_6 depend strongly on the method of alloy preparation. Superconducting transition temperatures of these alloys are reported.

The hexaborides of yttrium, thorium and the light rare earths all crystallize in a cubic structure which can be visualized as a CsCl arrangement of metal atoms and B_6 octahedra. We give our values of a_0 measured on single crystals in a Gandolfi camera in Table 1. Because of the small variations of the lattice constant, one expects, on the basis of the Hume-Rothery rules, complete solid solution between these hexaborides.

In a study of superconductivity in the YB_6 - LaB_6 system, we found that arc-melting of YB_6 - LaB_6 mixtures invariably produced

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Research supported in part by the Office of Naval Research*, Department of the Navy, Contract IPAPS/ONR-N00014-69-A-0200-6031; and in part by the Air Force Office of Scientific Research, Air Force Systems Command, Contract #AROSR-F44620-72-C-0017. Reproduction in whole or in part is permitted for any purpose by the United States Government.

TABLE 1

Compound	$a_o (\text{\AA})$	
	Experiment	Literature ¹
LaB ₆	4.156	4.154
CeB ₆	4.141	4.141
PrB ₆	4.133	4.130
NdB ₆	4.126	4.126
SmB ₆	4.133	4.133
GdB ₆	4.109	4.108
ThB ₆	4.110	4.113
YB ₆	4.102	4.113

material with two distinct cubic lattice parameters, as well as tetraboride contamination. Metallurgical examination showed that three phases were present. Further examination in an electron-beam microprobe showed that a nominal $(\text{La}_{.5}\text{Y}_{.5})\text{B}_6$ arc-melted button contained two distinct B₆ phases, the LaB₆-rich phase containing 15 ± 5 a/o YB₆, and the YB₆-rich phase containing no LaB₆ within counting statistics. Microprobe scans for La L _{α} - and Y L _{α} -radiation are shown in Fig. 1.

This lack of solubility of LaB₆ in YB₆ is surprising, especially in view of the rapid quenching on the water-cooled arc-furnace hearth and the almost identical lattice parameter. Attempts were also made to prepare LaB₆-YB₆ solid solutions by sintering a pressed pellet of the mixed oxides and boron at 1600°C in vacuum. A possible reaction is:²

Initially, we prepared YB₆ via this reaction. X-ray diffraction analysis showed both YB₄ and YB₆ present, and the material was not superconducting to 1.5°K, although arc-melted YB₆ is superconducting at 6.8°K. The results of increasing the B/Y₂O₃ ratio on T_c are given in Table 2. It appears from these results that there is some

FIG. 1

Microprobe scans of $\text{La}_{.5}\text{Y}_{.5}\text{B}_6$. Left, LaL_α radiation; right Y L_α radiation. The field of view is approximately $150\mu \times 150\mu$. Regions of inexact registry contain tetraboride.

variation in the stoichiometry which has a marked effect on T_c . A very slight variation in a_o ($\Delta a_o \sim 0.001 \text{ \AA}$) was observed on varying the $\text{B}/\text{Y}_2\text{O}_3$ ratio.

The T_c and lattice parameter data for YB_6 - LaB_6 mixtures prepared from oxides as above are given in Fig. 2. These data indicate the formation of a solid solution and the fact that the T_c extrapolates to zero near 25 a/o YB_6 . X-ray analysis indicates that now only one cubic phase is present and that Vegard's law is reasonably well obeyed.

TABLE 2

moles B/moles Y_2O_3	Phases Present	T_c ($^\circ\text{K}$)
14	YB_4, YB_6	None to 1.5°K
20	$\text{YB}_4, \text{YB}_6, \text{YB}_{12}$	6.8 ± 0.1
26	$\text{YB}_4, \text{YB}_6, \text{YB}_{12}$	6.3 ± 0.3

FIG. 2

Lattice parameters and superconducting transition temperatures of (La, Y)B₆ solid solutions.

Since LaB₆ is congruently melting and YB₆ is incongruently melting, a possible explanation for the observed insolubility of La in YB₆ in arc-melted material is that the morphology of the appropriate ternary diagram is such that LaB₆ solidifies first from the (La, Y)B₆ melt, and that the liquidus-solidus separation is large enough to result in nearly complete fractionation.

Finally, we note that ThB₆ dissolves readily in both YB₆ and LaB₆ in the arc-furnace. The size factor certainly favors ThB₆-YB₆ solid solution, and our low temperature electrical resistivity measurements suggest that ThB₆ and LaB₆, but not YB₆, are electronically very similar. Insufficient data on the Th-B phase diagram exist to conclude whether ThB₆ melts congruently.

References

1. See compilation by J. L. Hoard and R. E. Hughes in *The Chemistry of Boron and Its Compounds* [ed. E. L. Muetterties; New York, 1967], p. 118.
2. See discussion in G. V. Samsonov, *High-Temperature Compounds of Rare Earth Metals with Nonmetals* (New York: 1965), p. 56.
3. B. T. Matthias, T. H. Geballe, K. Andres, E. Corenzwit, G. W. Hull, and J. P. Maita, *Science* **159**, 530 (1968).