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THE STRUCTURE OF HIGH-TEMPERATURE SOLUTION-GROWN LaB_6: A SINGLE-CRYSTAL DIFFRACTOMETRY STUDY*

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Summary

Three single crystals of LaB_6, prepared from aluminium melts with different [B]/[La] ratios, were investigated using X-ray diffractometry. Final agreement indices were 1.36%, 1.10% and 1.15%. Vacancies at the boron position were indicated, although not conclusively established, for all three crystals. The thermal vibrations of lanthanum are larger than those of boron, which were found to be anisotropic with small inter-octahedral and larger intra-octahedral vibrations.

1. Introduction

In the last few years single crystals of LaB_6 have been widely used as thermionic cathodes in electronic devices with high performance characteristics [1, 2]. In this connection it is of great importance that a reproducible composition can be obtained for LaB_6 crystals prepared by different methods [3]. This problem is closely related to that of the homogeneity range of LaB_6 and its variation with temperature. The reports on this issue are, however, largely contradictory [4]. It has, for instance, been established that the cell dimensions do not vary with composition [5 - 7]. Nevertheless, chemical analyses [5 - 7] as well as thermochemical data [6] indicate the occurrence of a relatively extended range of homogeneity at high temperature. The range which can be quenched to room temperature is narrow but perhaps not zero.

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Several explanations have been presented as regards the atomic mechanism behind this composition variation. The most obvious suggestion is the occurrence of vacancies at the lanthanum position for boron-rich compositions. Another explanation [6] anticipates the occurrence of two phases with compositions LaB_6 and LaB_9 characterized by identical unit cells as well as diffraction intensities, although LaB_9 was assumed to contain ordered vacancies. In particular the latter assumption seems improbable, since some 33% of the ordered vacancies at the lanthanum position are involved and the superstructure X-ray diffraction lines resulting should be easily established. However, the LaB_9 structure may not be present at room temperature and therefore not visible in the X-ray pattern [8]. The problem became even more puzzling after the publication of results from a very careful chemical characterization of zone-refined LaB_6 single crystals [9]. The composition of these crystals proved to be boron-deficient with a [B]/[La] ratio of 5.75. The defect structure was assumed to consist of octahedral complexes of vacancies at the boron positions (from loss of complete boron octahedra) with lanthanum atoms accommodated in some of these holes.

There is one report in the literature on the occurrence of vacancies in boron-rich hexaboride compositions. Using a neutron diffraction technique and density measurements [10], it was found that in $Th_{1-x}B_6$ vacancies occur at the thorium positions to an extent corresponding to $x \approx 0.22$. In this boride the unit cell volume increases with an increasing number of vacancies. In the present paper we report the results of an X-ray investigation of LaB_6 using an automatic single-crystal diffractometer and least-squares refinement of the data corrected for extinction, absorption and Lorentz polarization effects. The three crystals studied were prepared by crystallization from an aluminium melt, containing [B]/[La] ratios corresponding to boron excess or lanthanum excess. The aim of the investigation was to determine the occurrence of vacancies at the lanthanum position and to analyse the thermal vibrations of the atoms. As a by-product the atomic coordinate of boron was obtained with a much higher precision than earlier. However, the X-ray data did not yield any evidence for vacancies at the lanthanum position but rather at the boron position. Owing to the lower X-ray scattering power of boron the sensitivity to vacancies at the boron position is lower. The thermal vibration analysis emerged as maybe the most important result of the investigation.

2. Experimental details

2.1. *Preparation and characterization of single crystals*

Single crystals were prepared by high-temperature solution growth from an aluminium melt [11]. The purities of the starting materials were lanthanum 99.7%, boron better than 99% and aluminium 99.99%. Starting mixtures with various [B]/[La] ratios were placed in alumina crucibles and

TABLE 1

Preparation conditions, cell dimensions and composition for LaB_6 single crystals

Temperature of preparation (°C)	*Atomic ratio B/La in the aluminium melt*	*Cell dimensions*		*Atomic ratio B/La, as analysed in the crystal*
		a (Å)	V (Å^3)	
1400	12	4.1570(1)	71.834(5)	NA
1400	9[a]	4.1569(1)	71.829(7)	5.67
1400	6	4.1570(1)	71.833(4)	6.02
1400	5[a]	4.1566(1)	71.815(6)	NA
1800	9[a]	4.1571(1)	71.841(4)	6.82
1800	6	4.1568(1)	71.827(4)	6.03
1800	5	4.1569(1)	71.833(6)	NA

NA, not available.

[a] Single crystals from these batches have been used for the X-ray intensity measurements.

heated in an argon atmosphere at 1400 °C ([B]/[La] = 5/1, 6/1, 9/1 and 12/1) or at 1800 °C ([B]/[La] = 5/1, 6/1 and 9/1) for 4 h and then slowly cooled to room temperature. The solidified ingots were treated with dilute hydrochloric acid to dissolve the aluminium matrix. Approximately 1 g of LaB_6 single crystals was selected by hand from each batch for further examinations.

The crystals were characterized by X-ray diffraction, chemical and electron microprobe analyses. Powder diffraction patterns were recorded using a Guinier–Hägg focusing camera with Cu Kα_1 radiation (λ = 1.540 598 Å) and semiconductor grade silicon (a = 5.431 065 Å) as an internal calibration substance. The unit cell dimensions were determined from a least-squares refinement of Q-values ($Q = 1/d^2$) using a program developed in Uppsala [12].

The boron and lanthanum contents of the crystals were determined using conventional mannitol and EDTA titration respectively. The results of the cell dimension determinations and the chemical analyses are presented in Table 1.

The lanthanum content of individual single crystals was determined using an ARL electron microprobe. From 3 to 5 single crystals of each batch were mounted in an epoxy resin and the analysis was performed at an accelerating voltage of 20 kV with 3 - 8 points analysed in each crystal. The results were not corrected for absorption, fluorescence and atomic number effects and thus suffer from considerable systematic errors. The results do not, however, show any difference in the lanthanum content of the crystals within an accuracy of ±0.5 wt.%.

2.2. *Single crystal X-ray diffraction experiments*

Intensity data were measured for one single crystal from each of the following batches: [B]/[La] = 9/1, 1400 °C (crystal 1), [B]/[La] = 5/1,

TABLE 2

Scan mode	ω–2θ		
Maximum θ	76°		
Crystal dimensions	Crystal 1	Crystal 2	Crystal 3
(μm)	29 × 23 × 33	46 × 49 × 52	30 × 28 × 34
Total number of reflections recorded	1057	1244	1210
Number of non-equivalent reflections recorded	194	194	194
Colour (as grown)	Violet-blue	Purple	Violet-blue

1400 °C (crystal 2) and [B]/[La] = 9/1, 1800 °C (crystal 3). The intensity data were collected using a PDP8/A-controlled Enraf–Nonius CAD-4 automatic diffractometer, utilizing graphite monochromated Mo Kα radiation. All reflections available with the κ geometry were measured and seven test reflections were used to check the stability of the equipment. A small decrease in the intensities of the test reflections was observed (probably coming from an "ageing" of the X-ray tube) and these were corrected for. Crystal data and parameters referring to intensity measurements are presented in Table 2.

3. Calculations and structure refinements

The crystallographic calculations were carried out on NORD-100 and VAX 11 computers using crystallographic programs described elsewhere [13]. The intensities were corrected for Lorentz polarization, absorption and extinction effects. These calculations as well as least-squares and Fourier calculations have been described in detail elsewhere [14]. The structure of LaB_6 was described in the space group *Pm*3*m* (No. 221) with lanthanum in position 1(a) and boron in position 6(f). The anisotropic thermal vibrations of the boron atoms were indicated in an F_o–F_c Fourier synthesis and subsequently included in the least-squares refinements. The occupancy factors of lanthanum and boron were varied independently of each other. As a result we obtained either an over-occupancy of lanthanum (2% - 3%) or a lower occupancy of the boron position (vacancies) for all three crystals (both occupancies are of course strongly correlated with the scale factor). The over-occupancy, which is displayed in a difference synthesis as well, cannot be explained by lanthanoid impurities, since it would require the assumption of improbably large amounts of impurity. It therefore seems likely that the diffraction data indicate the occurrence of vacancies at the boron position as shown in Table 3, which includes the final structure data and some refinement characteristics. In Table 3 the agreement indices are defined as follows:

TABLE 3

Final structure data and refinement characteristics for three single crystals of LaB_6

Structure data	*Crystal 1 (Nominally LaB_9, 1400 °C)*	*Crystal 2 (Nominally LaB_5, 1400 °C)*	*Crystal 3 (Nominally LaB_9, 1800 °C)*
Boron, occupancy (%)	96.4(7)	97.2(5)	98.2(5)
Boron coordinate: x_B	0.19956(16)	0.19957(15)	0.19948(14)
U_{iso}, lanthanum[a] ($Å^2$)	0.00535(3)	0.00551(2)	0.00525(2)
U_{11}, boron[b] ($Å^2$)	0.0031(2)	0.0032(2)	0.0031(2)
$U_{22} = U_{33}$, boron ($Å^2$)	0.0044(2)	0.0046(1)	0.0046(1)
Refinement characteristics			
R_{conv} (%)	1.36 (935 reflections)	1.10 (1224 reflections)	1.15 (1190 reflections)
$R(F^2)$ (%)	2.48 (935 reflections)	1.93 (1224 reflections)	2.06 (1190 reflections)
$R_w(F^2)$ (%)	3.11	2.61	2.80

Standard deviations are given in parenthesis.

[a] The temperature factor expression is $\exp(-8\pi^2 U_{iso} \sin^2\theta/\lambda^2)$.

[b] The temperature factor expression is $\exp -\{2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)\}$.

$$R(F^2) = \frac{\Sigma ||F_o|^2 - |F_c|^2|}{\Sigma |F_o|^2}$$

$$R_w(F^2) = \frac{\Sigma w(|F_o|^2 - |F_c|^2)^2}{\Sigma |F_o|^2}$$

$$R_{conv} = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}$$

where F_o is the observed and F_c is the calculated structure factor.

The interatomic distances are given in Table 4.

A final F_o–F_c three-dimensional Fourier difference synthesis was calculated. The highest peak density value of the difference map was 1.74 electrons $Å^{-3}$, which is 3.3% of a boron peak in the corresponding F_o electron density map.

It has been shown that structural parameters derived from conventional all-data refinements of structures containing mainly light atoms are in general influenced by non-spherical distributions of the valence electrons. The scattering contributions of such electrons are, however, very small for high-angle reflections ($\sin\theta/\lambda > 0.6$ $Å^{-1}$). The high-angle structure factors can thus be used in a refinement to obtain structural parameters uninfluenced by valence electrons. A Fourier difference synthesis $F_o - F_{c,\text{high-angle}}$, where $F_{c,\text{high-angle}}$ are calculated from structural parameters from the high-angle refinement, will thus reveal charge distributions from the valence electrons.

TABLE 4

Interatomic distances less than 4 Å

Atoms	*Distance* (Å)
La–24B	3.054
B–1B	1.659
B–4B	1.766
B–1B	2.498
B–4La	3.054

The standard deviations are less than 0.001 Å.

Considering the relatively large boron content of LaB_6 and the small systematic errors in the diffraction data (corrected for absorption and extinction), an attempt to carry out a charge density study might be successful. A high-angle refinement of the diffraction data from crystal 2, however, did not show any significant differences from the all-data refinement. All parameters are the same within one standard deviation. No information whatsoever regarding the valence electron distribution can be obtained in this manner, probably because of the high X-ray scattering power of lanthanum.

4. Discussion

The present structural study supports the common description of a hexaboride as consisting of a rigid three-dimensional boron network, built up of interlinked boron octahedra, with the metal atoms accommodated in the interstices of the boron network. The previously observed inequality between inter-octahedral and intra-octahedral B–B distances [15] has been confirmed for LaB_6. The positional coordinate of boron was obtained with a much higher precision than in the earlier study and the interatomic B–B distances were determined with a standard deviation of less than 0.001 Å.

The compositions of the three crystals (1, 2 and 3) as obtained from the crystal structure refinements are $LaB_{5.78 \pm 0.13}$, $LaB_{5.83 \pm 0.09}$ and $LaB_{5.89 \pm 0.09}$ respectively (the errors given correspond to three standard deviations of the boron occupancy). The results do not indicate any partial occupancy of the lanthanum position, but rather a partial occupancy of the boron position, although crystals 1 and 3 should be boron rich and crystal 2 lanthanum rich. The precision of the refinements permit the conclusion that there are no significant differences among the three crystals. The occurrence of vacancies at the boron positions should, however, not be regarded as established but as strongly indicated, since the magnitude of the standard deviations of the occupancy factors calculated might be too small owing to a relatively strong correlation between the scale factor and the occupancy parameter. For crystal 1 the [B]/[La] ratio, as calculated from the structure refinement data, is 5.78 as compared with 5.7 obtained from chemical analysis (Table 2). For crystal 3 the X-ray results indicate a stoichiometric composition while the chemical analysis indicates a boron-rich composition. At present no plausible explanation of this can be given. In this context it must be pointed out that the as-grown colours of the crystals (Table 2) can be altered by etching with dilute HNO_3 as discussed in more detail elsewhere [4, 16].

It is interesting to note that the composition obtained from the refinements, *e.g.* substoichiometry, is in very close agreement with the results for zone-refined single crystals, which were found to have a [B]/[La] ratio of 5.75 [9]. Therefore the question of the occurrence of vacancies at the boron position must be considered, however strange it may seem at first sight. A neutron diffraction study of LaB_6, currently in progress, might give the answer to this question [17].

The most interesting result of the present investigation is perhaps the analysis of the thermal vibrations of the atoms. It is generally agreed that great caution is required with conclusions based on temperature factors, since they often include considerable systematic errors. In the present study, however, where the diffraction data from three different crystals have been used and where different techniques for absorption correction have been used, a greater confidence can be felt for the thermal parameters than in an average structure determination. From Table 2 it is seen that the thermal vibrations of lanthanum are larger than those of boron. This observation may be taken as support for the rigidity of the boron network while the lanthanum ions are relatively free to vibrate in their interstices. A similar observation has been made for the rare earth tetraborides, TbB_4 and ErB_4, which also display a rigid boron network [18].

A significant anisotropy has been found in the thermal vibrations of the boron atoms (see Table 3 and Fig. 1). The inter-octahedral thermal

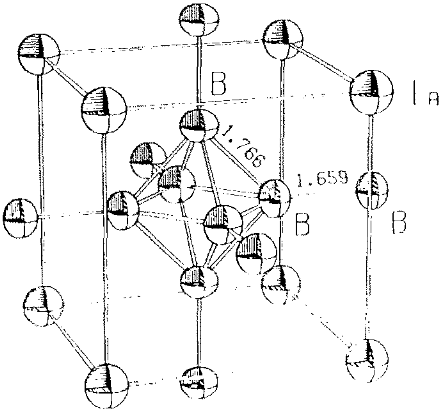

Fig. 1. The structure of LaB_6.

vibrations of a boron atom are smaller than the intra-octahedral ones in agreement with the observation that the inter-octahedral bonds (B–B distance 1.659 Å, Table 4) are stronger than the intra-octahedral ones (B–B distance 1.766 Å, Table 4). The anisotropy of the thermal vibrations is in qualitative agreement with the results from a Raman scattering study of LaB_6 single crystals [19], from which the force constants of the inter- and intra-octahedral B–B bonds were found to be 2.18 mdyne $Å^{-1}$ and 1.28 mdyne $Å^{-1}$, respectively [20].

The measurements of the cell dimensions of LaB_6 have shown no significant deviations between different syntheses (see Table 1). The average of the *a* axes in Table 1 is, however, slightly larger than that recently established for LaB_6 crystals [7], prepared by boro-thermal reduction of La_2O_3. The smaller *a* axis of the material obtained by boro-thermal reduction might be due to small amounts of dissolved carbon, which is known to decrease the cell parameter [21]. In the present synthesis, however, aluminium might dissolve in the LaB_6 crystals. It was shown recently [11] by chemical analysis that the aluminium content of LaB_6 single crystals, prepared by high-temperature solution growth from an aluminium melt, is only 0.02 - 0.056 wt.%. Since the aluminium in this case can occur partially as metallic inclusions, it is not probable that it influences the cell parameters or the structure determination.

After the present contribution was submitted to the Organizing Committee of the 8th International Symposium on Boron in May 1984 a thorough investigation of lanthanum deficient LaB_6 was published by McKelvy *et al.* [8]. The samples were analysed using high-resolution transmission electron microscopy, backscattered electron imaging, nuclear magnetic resonance and other techniques. It was shown that the LaB_9 phase proposed previously does not exist, at least at temperatures below 1800 °C, in agreement with the present results. The homogeneity range extends from $LaB_{6.00}$ to $LaB_{6.13}$ at low temperatures. A width of this order of magnitude for the homogeneity range is in agreement with compositions of the three LaB_6 crystals studied in the present investigation. The main difference between the two studies is that the present diffraction results suggest random vacancies at the boron positions while the study by McKelvy *et al.* indicate random vacancies at the lanthanum positions.

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