



JOURNAL OF  
APPLIED  
CRYSTALLOGRAPHY

**Volume 54 (2021)**

**Supporting information for article:**

**Formation and characterization of an Al-rich metastable phase in the Al–B phase diagram**

**Alexander I. Malkin, Vladimir V. Chernyshev, Alena A. Ryazantseva, Alexander L. Vasiliev, Maximilian S. Nickolsky and Andrei A. Shiryaev**

## Content

1. High-Temperature X-ray measurements.
2. Crystal structure determination from two-phase powder pattern.

## 1. High-Temperature X-ray measurements

High temperature X-ray powder diffraction patterns were measured *in vacuo* at Empyrean (Panalytical BV) diffractometer equipped with an HTK-1200N oven (Anton Paar).

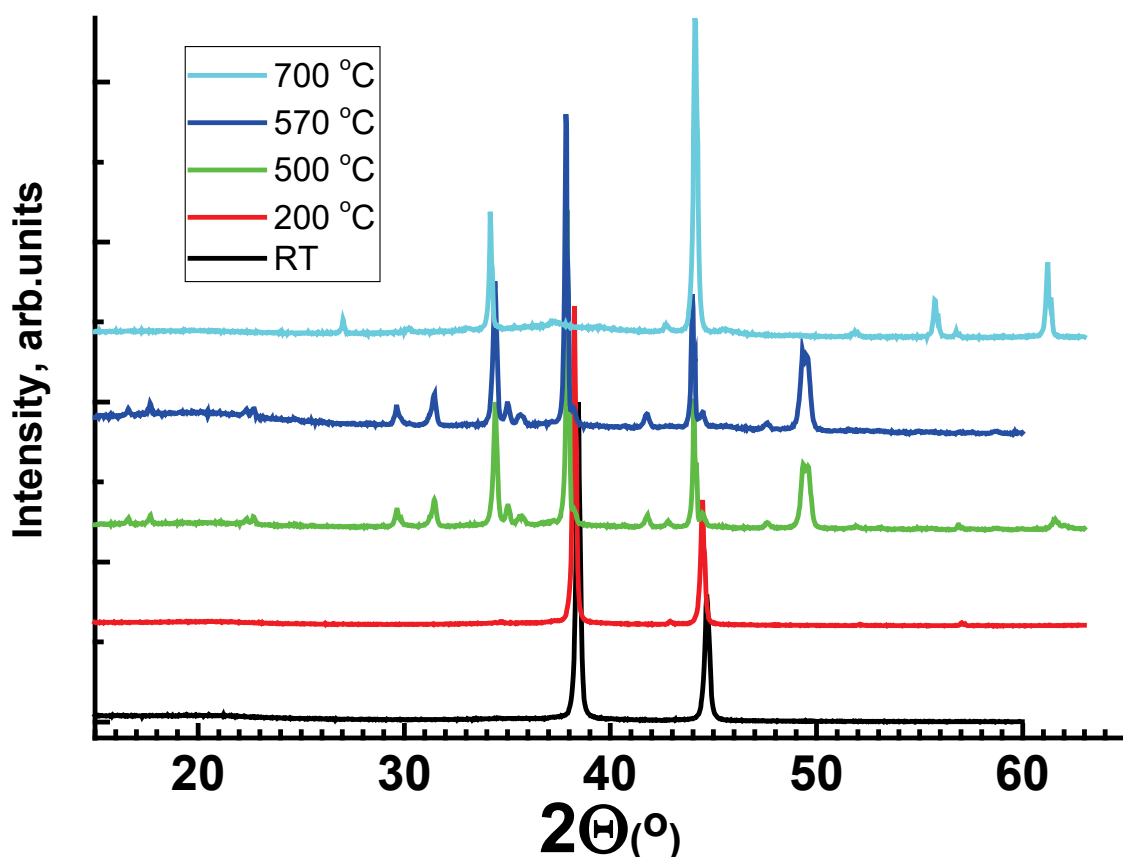


Figure S1. Powder patterns measured *in situ* at  $T = 25, 200, 500$  and  $570$  °C.

## 2. Crystal structure determination from two-phase powder patterns.

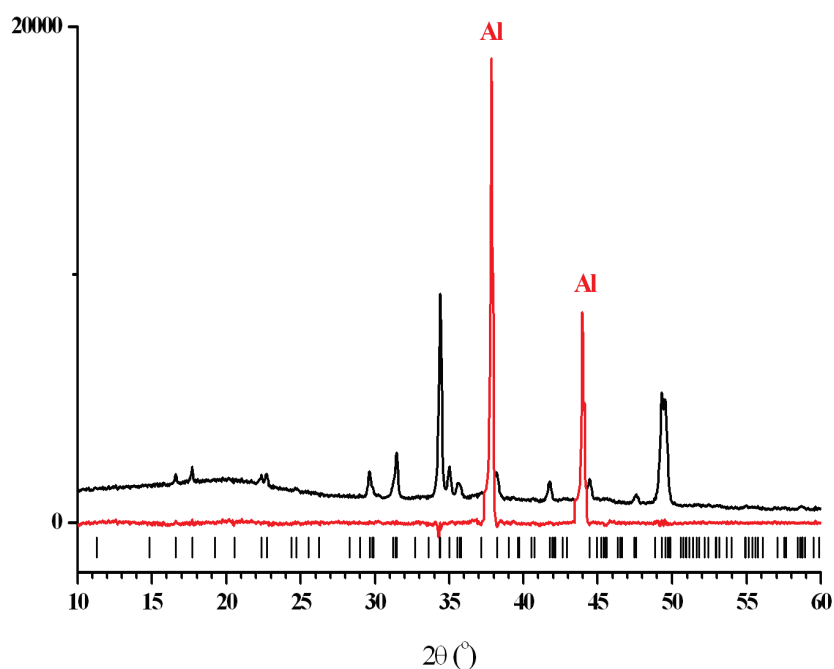
X-ray powder diffraction pattern measured at  $570$  °C *in vacuo* (**HT** pattern) was used for initial indexing and structure solution of metastable phase  $\text{AlB}_x$  (phase **M**). Powder pattern measured in air at  $25$  °C after the quenching and boron removal (**N** pattern) was used for the **M**-phase crystal structure completion and final two-phase refinement. In both cases, sample contained two crystalline phases – **M** and Al metal (cubic phase **cubA**).

In the **HT** pattern, in the  $10\text{--}60^{\circ} 2\theta$  range, 23 peaks were selected (Table S1).

**Table S1.** List of peaks observed in the **HT** pattern in the 10-60° 2 $\theta$  range.

No.	$d$ (Å)	2 $\theta$ (°)	I <sub>rel</sub> (%)
1	5.3316	16.61	2
2	5.0099	17.69	3
3	3.9737	22.35	2
4	3.9145	22.70	3
5	3.6082	24.65	1
6	3.0121	29.63	5
7	2.9950	29.81	2
8	2.8636	31.21	2
9	2.8435	31.43	9
10	2.6051	34.40	43
11	2.5617	35.00	5
12	2.5239	35.54	2
13	2.5114	35.72	2
14	2.3748	37.85	100 ( <b>Al</b> )
15	2.3542	38.20	5
16	2.1616	41.75	4
17	2.0566	43.99	42 ( <b>Al</b> )
18	2.0360	44.46	4
19	1.9098	47.57	2
20	1.8462	49.32	23
21	1.8376	49.56	18
22	1.6701	54.93	1
23	1.5732	58.63	1

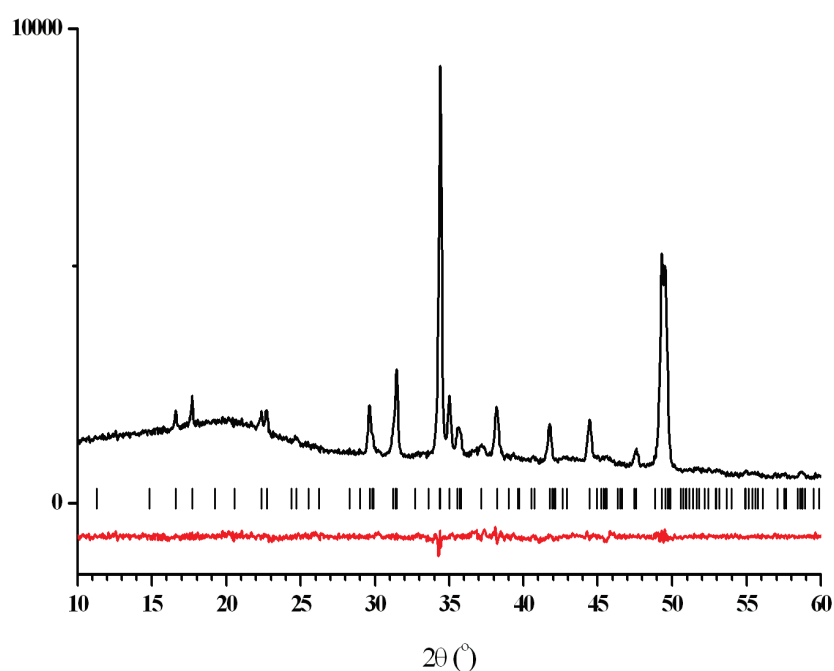
After excluding two peaks from the **cubA** phase (Al metal), the positions of twenty one diffraction peaks from the M-phase were indexed using TREOR90 (Werner et al., 1985) and AUTOX (Zlokazov, 1992, 1995) software in hexagonal *R*-centered lattice with the following parameters:  $a = 18.46$  Å and  $c = 8.98$  Å. Application of the Pawley fitting (Pawley, 1981) (Fig. S2) narrowed the search to the following five space groups (s.g.): *R3*, *R-3*, *R32*, *R3m* and *R-3m*.



**Figure S2.** The result of the Pawley fitting of the **HT** pattern (black) with two excluded regions under two peaks (red) of the **cubA** phase. Vertical bars denote calculated positions of the peaks in *R*-centered hexagonal unit cell.

As a consequence of Pawley fitting, one can see that two peaks from **cubA** phase – at  $2\theta$  angles  $37.85^\circ$  ( $hkl = 111$ ) and  $43.99^\circ$  ( $hkl = 200$ ) – do not overlap with the neighboring peaks from the **M** phase (at  $2\theta$  angles  $37.13$ ,  $38.25$ ,  $42.94$ ,  $44.46$ ), which are separated from them by more than  $0.4^\circ$ . This observation allows us to modify the experimental pattern **HT**, replacing two strong narrow Al peaks with the calculated background, and work further with this modified high-temperature pattern (**mHT**) shown in Fig. S3.

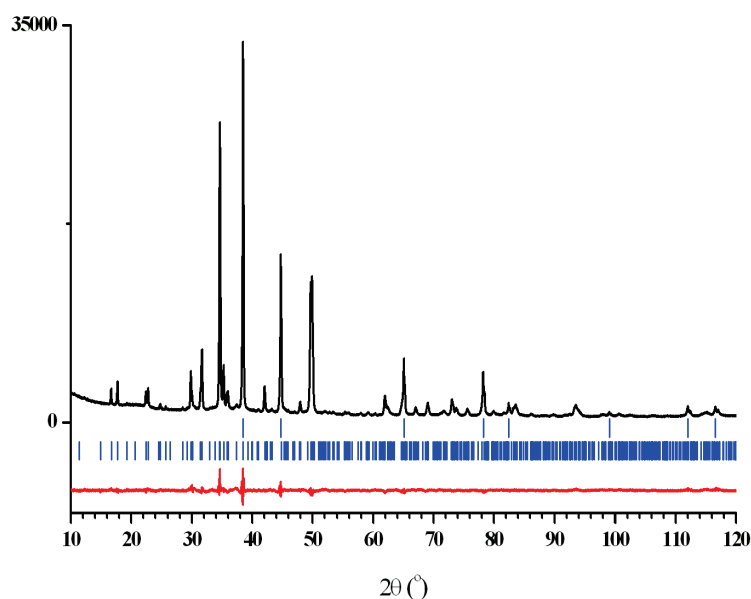
In the initial search for the structural motif, the **mHT** pattern was used, and two algorithms were applied – simulated annealing implemented in MRIA (Zlokazov, Chernyshev, 1992) and parallel tempering realized in FOX (Favre-Nicolin, Cerny, 2002). Based on electronic microscopy data, the Al:B ratio was estimated as  $1 - 1.5$ . Therefore, we assumed this ratio as  $\sim 1.2$  and calculated the number of Al and B atoms in the asymmetric part for each from five aforementioned space groups to satisfy this ratio. In addition, we also assumed the volume per atom as  $12-14 \text{ \AA}^3$ . For example, in *R*-3, in the asymmetric part of we tried to position 6 atoms of aluminum and 5 boron atoms. All solutions selected at this stage were refined in program MRIA with the  $U_{\text{iso}}$  fixed to  $0.05 \text{ \AA}^2$  for all atoms. Subsequent crystal chemistry analysis narrowed the solutions to those with Al–Al, Al–B and B–B interatomic distances not less than  $2.4$ ,  $2.0$  and  $1.8 \text{ \AA}$ , respectively.



**Figure S4.** The result of the Pawley fitting of the **mHT** pattern.

All remaining structural models belonged to two space groups,  $R-3$  and  $R-3m$ . They were further used in the two-phase Rietveld refinements with the room temperature pattern **N**, which resulted in one structural motif only with the sharply better fitting in space group  $R-3$ . The refinement of 7 Al and 4 boron atoms in the asymmetric part was stable and led to  $\chi^2 = 2.901$ . However, the Al:B ratio in this structural model exceeded the measured range of 1.0 – 1.5. Consequently, analysis of difference Fourier maps was performed to locate possible additional boron sites. Required values of  $F^2_{hkl}$  were taken from the Pawley fit of the room temperature pattern. A boron atom was placed into every electron density maximum stronger than  $1 \text{ e}/\text{\AA}^3$  and its position and occupancy were refined. This procedure allowed us to localize an additional boron site on the axis 3. On the following steps of the Rietveld refinement coordinates of all atoms and a common isotropic displacement parameter  $U_{iso}$  were analysed. This allowed to determine the site occupancies and to reveal two sites simultaneously occupied by Al and B atoms.

In the final two-phase Rietveld refinement, for the **M**-phase in space group  $R-3$  the following parameters were refined: the cell parameters  $a$  and  $c$ ; peak profiles accounting for anisotropic line broadening (Popa, 1998); coordinates of 5 Al and 4 B sites with occupancies fixed to 1; coordinates of two sites occupied by Al and B simultaneously with the refinement of their occupancies (with the sum of occupancies constrained to 1); coordinate  $z$  and occupancy of the  $(0, 0, z)$  boron site; common isotropic displacement parameter  $U_{iso}$ . The refinement was stopped at  $\chi^2 = 2.362$  (see also Fig. S4 and Fig. 3 of the manuscript). Atomic coordinates and occupancies are given in Table 2 (see main text), from which it follows that the Al:B ratio in **M** is equal to 1.28.



**Figure S4.** Rietveld plot of the N pattern showing the experimental (black) and difference (red) curves after two-phase refinement. Vertical bars denote calculated positions of the peaks of **cubA** (1<sup>st</sup> row) and **M** (2<sup>nd</sup> row) crystalline phases.

## References

- Favre-Nicolin, V., Cerny, R. (2002). FOX, 'free objects for crystallography': a modular approach to ab initio structure determination from powder diffraction. *J. Appl. Cryst.*, **35**, 734-743.
- Pawley, G. S. (1981) Unit-cell refinement from powder diffraction scans. *J. Appl. Cryst.*, **14**, 357-361.
- Popa, N. C. (1998) The (hkl) Dependence of Diffraction-Line Broadening Caused by Strain and Size for all Laue Groups in Rietveld Refinement, *J. Appl. Cryst.* **31**, 176-180.
- Werner, P.-E., Eriksson, L., Westdahl, M. (1985) TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries. *J. Appl. Cryst.* **18**, 367-370.
- Zlokazov, V. B. (1992) MRIAAU - a program for autoindexing multiphase polycrystals, *J. Appl. Cryst.*, **25**, 69-72.
- Zlokazov, V. B. (1995) AUTOX — A program for autoindexing reflections from multiphase polycrystals, *Comput. Phys. Commun.*, **85**, 415-422.
- Zlokazov, V. B., Chernyshev, V. V. (1992) MRIA - a program for a full profile analysis of powder multiphase neutron-diffraction time-of-flight (direct and Fourier) spectra, *J. Appl. Cryst.* **25**, 447-451.