CRYSTAL AND ELECTRONIC STRUCTURE OF LiB_xAl_3

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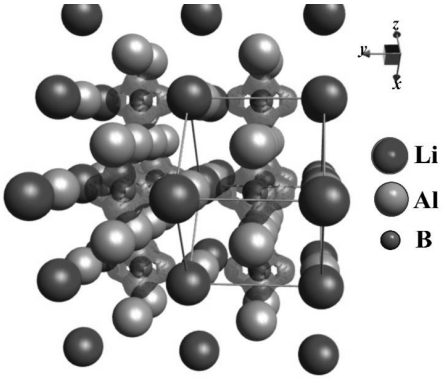
The binary Li–Al system is characterized by formation of 3 stable compounds, namely LiAl (NaTl structure type (ST), space group (SG) *Fd*-3*m*), Li_3Al_2 (own ST, SG *R*-3*m*) and Li_9Al_4 (own ST, SG *C*2/*m*), and one metastable – $LiAl_3$ ($AuCu_3$ ST, SG *Pm*-3*m*). The last compound forms sometimes as a by-product in electrochemical lithiation of Al-contained intermetallics because of stabilization by impurities or electrolyte [1]. In this case small B atoms occupy octahedral voids of the $LiAl_3$ crystal structure.

Studied alloys were synthesized in an arc furnace under high purity argon atmosphere. Lithium (99.8 wt. %, ingots), aluminum (99.99 wt. %, ingots) and boron (98 wt. %, powder) were used as starting materials. Components were pressed before melting. Homogenization annealing was carried out at 200 °C for 30 days in evacuated silica tubes. X-ray data were collected using automatic diffractometer DRON-2.0M (Fe$K\alpha$-radiation).

A LiB_xAl_3 ternary phase was found in a $Li_{22}Al_{73}B_5$ alloy. It is a superstructure of the $LiAl_3$ compound, which crystallizes in the $CaTiO_3$-type structure (SG *Pm*-3*m*). The unit cell parameter of this phase (a = 4.042(1) Å) is bigger than for the binary compound (a = 4.010 Å [2]), which confirms the boron inclusion in Wyckoff site 1*b*. We assume that the boron content could be different for this phase so it may have homogeneity range. For example, cell parameter a is 4.022 Å for $LiAl_3$ compound synthesized by lithiation reactions of metallic aluminum, $TiAl_3$ or VAl_3 phases [1]. Electron localization function (ELF) and density of states (DOS) were calculated by the TB-LMTO-ASA method for the further explanation of the boron influence on the crystal structure and properties of this phase. The significant value of energy interaction (-iCOHP) between six Al atoms (octahedral framework) and B atom in the centre of them was observed (see Fig.). It can be explained by partial covalent contribution in the chemical Al–B bond, so the ternary phase stability increases.



Atom coordinates:
Li 1*a* (0 0 0)
Al 3*c* (0 1/2 1/2)
B 1*b* (1/2 1/2 1/2)

Energy of interactions:
-iCOHP(Al–Al) = 0.401 eV
-iCOHP(Li–Al) = 0.300 eV
-iCOHP(Al–B) = 3.341 eV

[1] V. Kordan, O. Zhyshkovych, O. Zelinska, I. Tarasiuk, V. Pavlyuk, R. Serkiz. Pecularities of electrochemical lithiation of the binary intermetallics of the systems {Ti, V}–Al, Visnyk Lviv Univ. Ser. Chem. 2019. Vol. 60(1). P. 127–139 (in Ukrainian).

[2] T. Yoshi Yama, K. Hasebe, M. Mannami. Al_3Li superlattice in Al-4.5wt. % Li alloy, J. Phys. Soc. Jpn. 1968. Vol. 25. P. 908.