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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria in the System Li_2O–MgO–B_2O_3

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Abstract—The subsolidus region of the Li_2O–MgO–B_2O_3 system has been studied by X-ray powder diffraction and differential thermal analysis. Isothermal sections at 500–550 and 650–700°C have been designed. The following complex borates have been found to form: at 500–550°C, $Li_2MgB_2O_5$ and $LiMgBO_3$ are formed; at 650–700°C, a new phase $Li_4MgB_2O_5$ is formed along with $LiMgBO_3$; and at 5500–600°, $Li_2MgB_2O_5$ is formed.

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The increasing interest in borates during the last decade is due to their crystal chemistry, which is as rich and varied as silicate crystal chemistry, and their promise for use as materials for nonlinear optics (β–BaB_2O_4, LiB_3O_5, and others) and ionizing-radiation dosimeters (MgB_4O_7 and LiB_4O_7), which is based on thermostimulated luminescence.

The main elements of boron–oxygen frameworks are trigonal BO_3^{3-} and tetragonal BO_4^{5-} groups; their polycondensation produces island, chain, layered, and three-dimensional framework structures.

Frequent building elements of the framework are planar six-membered groups $B_3O_6^{3-}$ and nonplanar six-membered polyanions $B_3O_7^{5-}$ and $B_3O_8^{7-}$. Linkage of these groups through oxygen corners leads to extensive topologic boron–oxygen assemblies. Because of the difficulty of packing the simplest building elements into more complex frameworks, acentric lattices are frequently encountered among the borates; they are promising for polyfunctional materials design.

Borate MgB_4O_7 is used as the base for manufacturing ionizing-radiation detectors due to its thermoluminescence properties. Magnesium borate is formed in the system MgO–B_2O_3. Dysprosium or lithium/dysprosium is an activator for MgB_4O_7. Despite the promise of borates for use as functional materials, studies of complex borates are few.

Therefore, this work studies phase equilibria in the system Li_2O–MgO–B_2O_3 to provide the base for searching and synthesizing new polyfunctional (nonlinear-optical, thermoluminescent, and ion-conducting) borates.

Phase equilibria in the subsystems Li_2O–B_2O_3 and MgO–B_2O_3 have been previously studied in detail.

In the system Li_2O–B_2O_3, nine intermediate compounds were found with the following $Li_2O : B_2O_3$ compositions: 3 : 1, 2 : 1, 3 : 2, 1 : 1, 1 : 2, 2 : 5, 1 : 3, 1 : 4, and 1 : 5 [1, 2]. Of them, the 1 : 1 ($LiBO_2$) and 1 : 2 ($Li_2B_4O_7$) compounds melt congruently at 849 and 917°C, respectively. The 3 : 1, 3 : 2, 2 : 5, 1 : 3, 1 : 4, and 1 : 5 borates melt incongruently at 715, 700, 864, 834, 615, and 475°C, respectively; the 2 : 1 phase exists within a temperature range of 600–645°C. The eutectics in the system Li_2O–B_2O_3 contain 53 and 74 wt % B_2O_3 and melt at 650 and 832°C, respectively. According to [3], $Li_3B_7O_{12}$ exists; according to [1, 2], $Li_4B_{10}O_{17}$ exists in the range 820–864°C; we used the data of [1, 2].

The system MgO–B_2O_3 forms three borates: MgB_4O_7, $Mg_2B_2O_5$, and $Mg_3B_2O_6$ [4].

The ternary oxide system Li_2O–MgO–B_2O_3 forms borates $LiMgBO_3$ [5] and $Li_2MgB_2O_5$ [6]; according to [3], the compound $Li_{2.45}Mg_{0.3}BO_{3.025}$ exists along with $LiMgBO_3$, while the existence of $Li_2MgB_2O_5$ is not confirmed.

We suggested that an $Li_2MgB_2O_5$ phase exists within a limited temperature range up to 650°C, which can explain the fact that Wu and colleagues did not found this compound in the system Li_2O–MgO–B_2O_3 [3]. At 700°C, in addition, a ternary eutectic melts in the system and a metastable phase can form upon melt solidification. The compound $Li_{2.45}Mg_{0.3}BO_{3.025}$ is detected only upon quenching [3]. Because of the above contro-

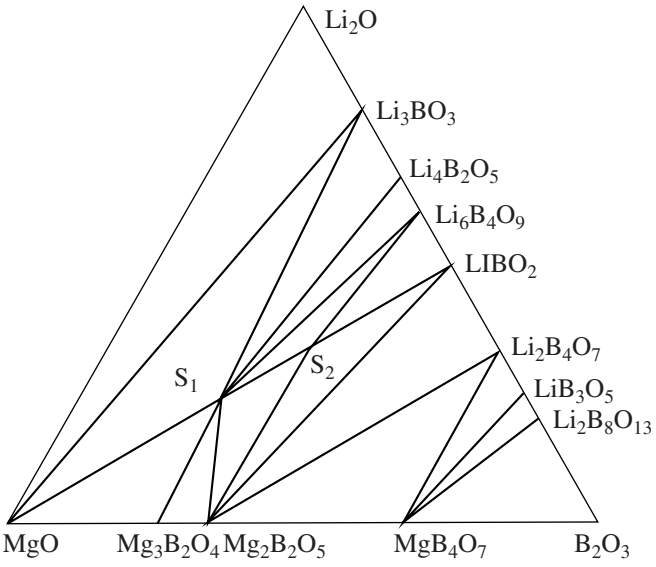

Fig. 1. 550°C isothermal section through the system Li_2O–MgO–B_2O_3. Notations: solid lines, quasi-binary sections; S_1, compound $LiMgBO_3$ (1 : 2 : 1); and S_2, compound $Li_2MgB_2O_5$ (1 : 1 : 1).

versies of the literature data, we restudied the system Li_2O–MgO–B_2O_3 at 500–550 and 600–650°C.

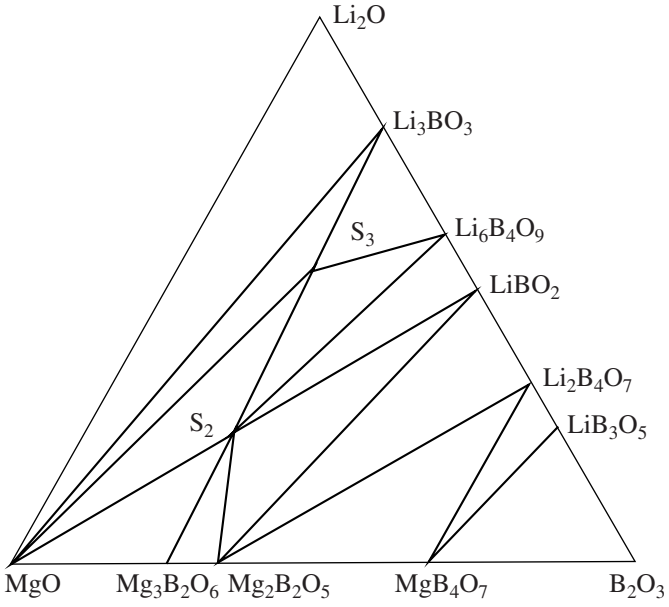

Fig. 2. 650°C isothermal section through the system Li_2O–MgO–B_2O_3. Notations: solid lines, quasi-binary sections; S_1, compound $LiMgBO_3$ (1 : 2 : 1); and S_3, a compound of approximate composition $Li_4MgB_2O_6$ (2 : 1 : 1).

EXPERIMENTAL

The starting chemicals used were H_3BO_3 (high purity grade 12–13), MgO or $MgCO_3$ (pure grade), and Li_2CO_3 (chemically pure grade). Interactions in the system were studied by carrying out solid-state reactions at temperatures in the range of 500–650°C until a liquid appeared. Annealing was carried out in a muffle furnace with programmed cooling. The overall annealing duration was 10 days. Phase formation in the system was studied along crossing sections. Quasi-binary sections were studied in 5–10 mol % steps; in the vicinity of a compound, in 1.5–2 mol % steps, by means of multistep anneals at 500–650°C with intermittent grinding. Equilibration was monitored by X-ray diffraction.

X-ray powder diffraction (XPD) analysis was carried out on an Advance D8 Bruker AXS diffractometer (CuK_α radiation, graphite monochromator). Differential thermal analysis (DTA) was performed on an original setup, which made it possible to record heating curves and thermal events up to 1000°C.

The isothermal sections of the system displayed in Figs. 1 and 2 were designed as a result of XPD of samples whose compositions correspond to the intersection points between all possible sections with double and triple oxide compounds taken into account.

The subsolidus configuration of the phase diagrams for the title system are different because of the thermal stability of double and triple phases.

At 500–550°C, the stable double phases indicated in Fig. 1 are formed in the system Li_2O–MgO–B_2O_3; triple phases $Li_2MnB_2O_5$ and $LiMgBO_3$ are also found to exist under these conditions. The isothermal section of the system at 500–550°C has 16 quasi-binary sections, which break the system to 15 triangles, and the following two triple phases: S_1 – $LiMgBO_3$ (1 : 2 : 1) and S_2 – $LiMgB_2O_5$ (1 : 1 : 1) (Fig. 1). When temperature increases to 650°C, the stable compound $LiMgBO_3$ appears in the system. Along with it, a new triple compound of approximate composition $Li_4MgB_2O_6$ is formed at the point whose composition is 2 : 1 : 1 (Fig. 2); the existence of this compound is verified by X-ray diffraction. Possibly, this compound has a homogeneous region. Its exact composition will be refined in single-crystal experiments. The 2 : 1 and 1 : 4 double phases at 650°C are not involved in equilibrium.

The isothermal section of the system Li_2O–MgO–B_2O_3 at 600–650°C is broken by 14 quasi-binary sections to 13 phase triangles. Analysis of the results of our study with reference to those of work [3] shows that in [3] the system was annealed at 650–800°C without taking into account the stability of double and triple oxides; for this reason, $Li_2MgB_2O_5$, which exists up to 600°C, was not found and $Li_{2.45}Mg_{0.3}BO_{3.025}$ was revealed only by quenching. According to DTA, the

compound $Li_4MgB_2O_6$ exists above 650°C and melts congruently.

To summarize, we have studied subsolidus phase equilibria in the system Li_2O–MgO–B_2O_3 and designed isothermal sections at 500–550 and 650–700°C. A new compound, $Li_4MgB_2O_6$, has been found to exist above 550°C and melt congruently at 800°C.

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