Thematic Section: Thermodynamic Research. **Full Paper**
Subsection: Inorganic Chemistry. *Reference Object Identifier* – ROI: jbc-02/18-55-7-37
Publication is available for discussion in the framework of the on-line Internet conference "*Butlerov readings*".
http://butlerov.com/readings/
Submitted on May 25, 2018.

Chemical and phase models of a ternary reciprocal system Li,K||F,CrO_4

© **Alexander V. Burchakov**,*+ **Dmitry V. Timoshin**, **Ekaterina M. Egorova**, **Igor M. Kondratyuk**, and **Andrey S. Kirsanov**
Samara State Technical University. Molodogvardeyskaya St., 244. Samara, 443100. Russia. E-mail: turnik27@yandex.ru

*Supervising author; +Corresponding author

Keywords: physical-chemical analysis, modeling, multicomponent system, molten salt, chromates and halides of alkali metals, differential thermal analysis, phase equilibria, eutectic, breakdown point, saddle point, KOMPAS-3D, T-x-y phase diagram, phase complex.

Abstract

Phase equilibria of the "liquid-solid" type in the three-component mutual system Li, K || F,CrO_4 was experimentally studied in this work. Method of study is differential thermal analysis (DTA) using the projection-thermographic method (PTGM). Experimental data on the system made it possible to construct a 3D model of the phase complex of the system and a chemical model. Under the model means the combination of chemical equations establishing communication amounts of reactants and reaction products in the system. Using the combination "chemical model + phase model" allows the forecasting of physicochemical processes for arbitrary composition of the system that occur during alloy fusion and further crystallization.

Analysis of the elements of faceting – binary systems – gives the following information: two systems LiF-Li_2CrO_4 and LiF-KF are eutectic-type systems, a congruent melting type compound is formed in the systems Li_2CrO_4-K_2CrO_4 and KF-K_2CrO_4. Before starting an experimental study of the ternary reciprocal system, the total number of individual components of which is six (two compounds $LiKCrO_4$ and K_3FCrO_4 are formed in the Li,K||F,CrO_4 system), the system is partitioned into stable simplexes – subsystems containing stable crystallizing phases. These systems can be studied separately. The tree of the phases of the system has a linear structure and consists of three stable triangles, separated by two stable secant (segments). The compound K_3FCrO_4 (D_2) is unstable in the LiF melt (the decomposition of this compound takes place on K_2CrO_4 and KF Information on the stable elements and chemical reactions taking place in the system made it possible to create a chemical model of the system based on the equivalent balance of the components of the system. The model allows for a mixture with an arbitrary ratio of the components of the system to determine the stable phases formed during alloy fusion and crystallization, and the chemical reactions that proceed. The quasibinary system $LiKCrO_4$-LiF, which is a stable secant, the stable diagonal LiF-K_2CrO_4, as well as the stable triangles D1-LiF-Li_2CrO_4, D_1-LiF-K_2CrO_4 and LiF-KF-K_2CrO_4 have been experimentally studied. These systems, apart from the latter, are eutectic-type systems. In the latter system, due to the nonvariant transformation at the point R 520: L + K_3FCrO_4 = K_2CrO_4 + KF, the K_3FCrO_4 compound changes the melting type from congruent to incongruent. The compounds K_2CrO_4, KF and LiF crystallize in the ternary eutectic E 490, so there is no triangulation in the system LiF-KF-K_2CrO_4.

References

[1] Determination and analysis of experimental and calculated values of specific melting enthalpies for nonvariant compositions in binary systems from alkali metal halides. M.O. Shashkov, E.I. Frolov. *Student-scientific journal "The Edge of Science".* **2013**. Vol.1. P.69-74. (russian)
[2] V.A. Alexeyev. Cooling of electronic equipment using melting substances. *Moscow: Energy.* **1975**. 80p. (russian)
[3] E.I. Ardashnikova. Physicochemical analysis is the basis of directed inorganic synthesis. *Soros Education Journal.* **2004**. Vol.8. No.2. P.30. (russian)
[4] A.V. Burchakov. Modeling of phase complex of multicomponent systems involving alkali metals chromates and halides. Dissertation for the degree of candidate of chemical sciences. *Samara.* **2016**. (russian)

[5] A.V. Burchakov, E.M. Dvoryanova, I.M. Kondratyuk. Phase Equilibria in the Ternary Reciprocal System Li,K||I,CrO_4. *Russian Journal of Inorganic Chemistry.* **2015**. Vol.60. No.8. P.999-1007. (russian)
[6] A.V. Burchakov, E.M. Dvoryanova, and I.M. Kondratyuk. Liquid compound stratification details in quasi-ternary system LiF–RbI–Li_2CrO_4. *Butlerov Communications.* **2014**. Vol.38. No.5. P.72-77. ROI: jbc-02/14-38-5-72
[7] A.V. Burchakov, E.M. Dvoryanova, and I.M. Kondratyuk. Phase complex of stable tetrahedron LiF–RbI–Rb_2CrO_4–Li_2CrO_4 of quaternary reciprocal system Li,Rb||F,I,CrO_4. *Butlerov Communications.* **2014**. Vol.39. No.8. P.40-49. ROI: jbc-02/14-39-8-40
[8] A.V. Burchakov, E.M. Dvoryanova, I.M. Kondratyuk. Phase equilibria in the stable tetrahedron LiF-RbI-Rb_2CrO_4-RbF of the quaternary reciprocal system Li, Rb || F, I, CrO_4. Journal "Izvestiya Saratov University. *Series Chemistry. Biology. Ecology".* **2014**. Vol.14. Iss.4. P.42-47. (russian)
[9] A.V. Burchakov, E.M. Dvoryanova, and I.M. Kondratyuk. Experimental research and computer modeling of stable triangle LiF–KI–K_2CrO_4 of quaternary reciprocal system Li,K||F,I,CrO_4. *Butlerov Communications.* **2015**. Vol.42. No.6. P.59-67. ROI: jbc-02/15-42-6-59
[10] A.V. Burchakov, E.M. Dvoryanova, I.M. Kondratyuk. Computer 3D-modelling of phase complex for ternary system. XX International Conference on Chemical Thermodynamics in Russia (RCCT-2015) (June 22-26, 2015, Nizhni Novgorod): Abstracts. *Nizhni Novgorod: Nizhni Novgorod University Press.* **2015**. 407p.
[11] Thermal Constants of Substances: Handbook, Issue X, part 1: Tables of Accepted Values: Li, Na, Ed. by V. P. Glushko (VINITI, *Moscow*, **1981**).
[12] Thermal Constants of Substances: Database (Institute of Thermal Physics of Extreme States, Joint Institute for High Temperatures, Russian Academy of Sciences; Chemical Faculty, Lomonosov Moscow State University, Moscow, Russia), http://www.chem.msu.su/cgibin/tkv.pl?show=welcom.html (accessed July 13, **2017**) (russian).
[13] J.M. Sangster and A.D. Pelton. *J. Phys. Chem.* Ref. **1987**. Vol.16. No.3. P.509-561.
[14] ACerS-NIST. Phase Equilibria Diagrams. CD-ROM Database. Version 3.1.0. American Ceramic Society. National Institute of Standards and Technology. Order online: www.ceramics.org.
[15] G.A. Bukhalova, Z.N. Topshinoeva, and V.G. Akhtyrskii. *Zh. Neorg. Khim.* **1974**. Vol.19. P.235.
[16] Melting Diagrams of Salt Systems: Binary Systems with Common Cation, Ed. by V. I. Posypaiko, E. A. Alekseeva, and N.A. Vasina (Khimiya, Moscow, **1977**). Vol.III.
[17] I.N. Belyaev. Physicochemical analysis of salt systems. Rostov n. D, ed. *Rostov-on-Don. State. University.* **1962**. P.37. (russian)
[18] Belyaev I.N. Zh. Neorg. Khim. 6 [5] 1178-1188 (1961); Russ. J. Inorg. Chem. (Engl. Transl.), 6 [5] 602-608 (**1961**).
[19] G.A. Bukhalova, Z.N. Topshinoeva, and V.G. Akhtyrskii. *Zh. Neorg. Khim.* **1974**. Vol.19. P.235. (russian)
[20] Melting Diagrams of Salt Systems: Ternary Reciprocal Systems, Ed. by V.I. Posypaiko and E.A. Alekseeva (Khimiya, Moscow, **1977**). (russian)