Synthèse des solutions solides cubiques ZnO-LiMeO$_2$ (Me = Sc^{3+}, Ti^{3+}, Fe^{3+}, In^{3+}) sous hautes pressions et hautes températures

P.S. Sokolov,[a] A.N. Baranov,[b] V.A. Tafeenko,[b] V.L. Solozhenko [a*]

[a] LPMTM-CNRS, Université Paris Nord, Villetaneuse, France
[b] Chemistry Department, Moscow State University, Moscow, Russia

Zinc oxide belongs to the family of wide-band-gap semiconductors and possesses high exciton binding energy (60 meV). At ambient conditions ZnO has a hexagonal wurtzite structure (space group P6$_3$mc) which transforms into cubic rock-salt one (space group Fm3m) at pressures above 6 GPa and reverts to wurtzite phase at pressure release. Recently a number of metastable Me$_{1-x}$Zn$_x$O solid solutions (Me = Ni^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+}) with rock-salt structure have been synthesized by quenching from 7.7 GPa and 1450-1650 K [1]. Quenched Ni$_{1-x}$Zn$_x$O rock-salt solid solutions show remarkable stability at ambient conditions in a wide concentration range ($0 < x \leq 0.8$) [1].

In the present work we report the synthesis of metastable rock-salt (LiMeO$_2$)$_{1-x}$(ZnO)$_x$ solid solutions (Me = Sc^{3+}, Ti^{3+}, Fe^{3+}, In^{3+}) obtained in the wide concentration range up to $x = 0.8$ by quenching from 7.7 GPa and 1350-1550 K. Lattice parameters of solid solutions have been calculated from X-ray diffraction patterns taken at temperatures up to 1073 K on B2 beamline (HASYLAB-DESY). It was found that the lattice parameters of all synthesized rock-salt solid solutions perfectly follow the Vegard's law. Samples with $x > 0.8$ consist of two-phase mixtures of solid solutions with wurtzite and rock-salt structure. As was shown in the series of preliminary experiments at ambient pressure concentration range of rock-salt (LiFeO$_2$)$_{1-x}$(ZnO)$_x$ solid solutions is limited for $x < 0.3$, thus the synthesis at high pressure and high temperature substantially extends the concentration range of rock-salt phase.

For all the studied systems the onset of thermal decomposition depends on concentration. For example, at $x = 0.8$ (LiFeO$_2$)$_{1-x}$(ZnO)$_x$ rock-salt phase is stable at ambient pressure up to 673 K, but at $x = 0.6$ temperature increases up to 773 K. The nature of Me^{3+} cation seriously influence on the thermal stability of rock-salt phase too. Rock-salt solid solution (LiScO$_2$)$_{0.3}$(ZnO)$_{0.7}$ is stable up to 823 K whereas of (LiFeO$_2$)$_{0.3}$(ZnO)$_{0.7}$ is stable up to 723 K.

[1] A.N. Baranov, P.S. Sokolov, O.O. Kurakevych, V.A. Tafeenko, D. Trots, V.L. Solozhenko, *High Press. Res.* **28**, 515 (2008).

* e-mail of the corresponding author: vladimir.solozhenko@univ-paris13.fr