Application of Combined Molten Salts for Tailoring Crystal Growth of Indium Phosphates

D.V. Kyselov, K.V. Terebilenko, M.S. Slobodyanik

Taras Shevchenko National University of Kyiv, Chemistry Department, Ukraine

The quest for novel oxide materials containing tetrahedral groups has brought forward manifold promising materials, including indium containing oxides [1-2]. Among their various representatives, the ternary In-P-O and quaternary M-In-P-O compounds (M – alkaline metal) excel through their versatile chemical and physical properties [3]. In particular, K$_3$In(PO$_4$)$_2$, K$_3$In$_3$(PO$_4$)$_4$ and KInP$_2$O$_7$ have attracted considerable research attention due to its excellent performance as luminescence hosts for rare-earth metals doping with enhanced emitting under visible light irradiation [4]. Whereas the structural peculiarities of indium phosphates are known for most of them, structural substitution and solid solution formation that can influence band structure, charge-transfer and the morphological properties of the respective material are rarely studied. Herein, the unified method for indium phosphates preparation has been applied for tailoring crystal growth of a number of M-In-P-O crystalline compounds in a pure and doped with europium phases.

As a key reagent molybdate component has been used as a reaction media and a phosphate one as a direct reagent. Indium oxide or indium fluoride has been applied as a source of indium. The crystallization trends has been explored for K –In – P – Mo – O molten system in details. Generally, the melt with a certain composition has been cooled to reach a solidified mixture, whereas crystalline product has been leached out by washing in water. The crystals obtained in this way have been studied by IR spectroscopy and X-Ray powder diffraction. The crystal structure of KInP$_2$O$_7$ has been verified by single crystal X-Ray diffraction. The crystallization trends for the compounds mentioned above and their mixtures have been explored depending on the K/Mo and K/P ratios in the initial melt. As it was shown, there is a relationship between the indium polyhedral condensation and the basic properties of the melt applied. Thus, the most basic melt containing K$_2$MoO$_4$ and K$_4$P$_2$O$_7$ after cooling leads to the full separation of InO$_n$ polyhedral in the framework of K$_3$In(PO$_4$)$_2$, while more acidic ones give a corner-sharing groups In$_3$O$_n$ in case of K$_3$In$_3$(PO$_4$)$_4$. The complicity of molybdate component role is also followed by the change of the crystallization area of different phosphates and the presence of phosphates, which are not common for pure M-In-P-O melts.

Consequently, addition of molybdate salts through MoO$_3$ and K$_2$MoO$_4$ is a challenging multi-parameter process and leaves room for further investigations that are now in progress. The present systematic study demonstrates that the combination of the inert and direct salts is a promising approach towards the construction of new compounds with different crystalline blocks aggregation.