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

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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, $K_3In(PO_4)_2$, $K_3In_3(PO_4)_4$ and $KInP_2O_7$ 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 KInP₂O₇ 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 K₂MoO₄ and K₄P₂O₇ after cooling leads to the full separation of InO_n polyhedral in the framework of K₃In(PO₄)₂, while more acidic ones give a corner-sharing groups In₃O_n in case of K₃In₃(PO₄)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_2MoO_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.

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