Phase equilibria and thermal stability of $CuMo_{1-x}W_xO_4$ and $CuW_{1-y}Mo_yO_4$ in the $CuMoO_4$–$CuWO_4$ system

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The increasing interest in discovering of new energy sources during the last decades has greatly stimulated scientific research in finding new renewable sources of energy. In the field of energy conversion, photovoltaic batteries (conversion of a light into electricity) and electrochemical cells (intraconversion of chemical and electrical energy) have traditionally been investigated. Recently, batteries with high energy and power density as well as miniaturized sizes are wanted with larger interest and specialized applications for microcells (e.g. integrated power supplies for microelectromechanical systems). Nowadays, all efforts are focused on fabrication and investigations of so-called *3-dimentional solid-state lithium batteries*. The solid-state cells with Li/LiPON (Lithium Phosphorous Oxonitride)/$CuWO_4$ layers show high-volume rate capacity and overcome unfavorable electrochemical degradation in liquid electrolyte [1]. The thin film of copper tungstate could be a promising positive electrode material for high-performance rechargeable lithium batteries [1]. $CuWO_4$ belongs to the triclinic distorted wolframite type crystals (s.g. $P\bar{1}$) [2]. The $CuWO_4$ structure can be described as the hexagonal close-packed framework of oxygen ions with copper and tungsten ions occupying half of the octahedral sites [2]. Copper molybdate, $CuMoO_4$, shows thermochromism in the 175-260 K range depending strongly on the heating/cooling rate [1]. A several $CuMoO_4$ polymorphs have been reported, i.e. α-$CuMoO_4$ (s.g. $P\bar{1}$) stable under ambient conditions, high temperature polymorphs β-$CuMoO_4$ and ε-$CuMoO_4$ (s.g. $P2_1/n$), γ-$CuMoO_4$ (s.g. $P\bar{1}$) existing below 200 K, as well as $CuMoO_4$-II and $CuMoO_4$-III, both high pressure modifications [3,4].

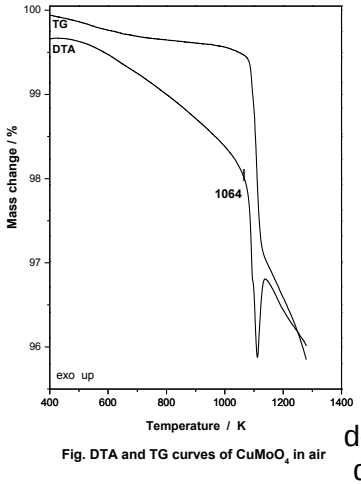

Fig. DTA and TG curves of $CuMoO_4$ in air

Interesting properties of copper molybdate and tungstate have motivated us to an investigation of their mutual reactivity in the solid state. For this purphose, $CuMoO_4$/$CuWO_4$ mixtures with different contents of initial reactants were prepared and heated in air at selected temperatures form the 823–1073 K range. The XRD results showed the existence of two solid solutions, i.e. $CuMo_{1-x}W_xO_4$ (where $0 < x < 0.10$) crystallizing in the α-$CuMoO_4$ structure and $CuW_{1-y}Mo_yO_4$ for $0 < y < 0.35$ crystallizing in the distorted wolframite structure. DTA-TG measurements in air showed that $CuMoO_4$ and $CuMo_{1-x}W_xO_4$ solid solution melt at ~1064 K and the resulting liquid immediately decomposes. Copper tungstate and $CuW_{1-y}Mo_yO_4$ solid solution melt in air at ~1223 K and, analogously as for $CuMo_{1-x}W_xO_4$, the resulting liquid decomposes. Melting point of all phases significantly moves down in an inert atmosphere.

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