REFINEMENT OF THE AgI-Ag_2WO_4 PHASE DIAGRAM

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Silver-conducting solid electrolytes are promising materials for all-solid state batteries with a wide working temperature range, high stability, high safety, and low risk of leakage and corrosion, in contrast to batteries based on liquid organic electrolytes.

The system AgI-Ag_2WO_4 is known since early 1970s. There are two different versions of the phase diagram of the AgI – Ag_2WO_4 system [1, 2]. According to [1], it contains three chemical compounds: $Ag_5IW_2O_8$ (AgI/Ag_2WO_4=1:2), $Ag_4I_2WO_4$ (2:1) and $Ag_6I_4WO_4$ (4:1), while according to [2], there are only two – $Ag_5IW_2O_8$ and $Ag_6I_4WO_4$. All phases are ionic conductors, and the $Ag_6I_4WO_4$ compound exhibits superionic conductivity at ambient temperatures. Later, the composition of the superionic phase was represented by the formula $Ag_{26}I_{18}W_4O_{16}$ (4.5:1) [3]. Our repeated attempts to synthesize $Ag_6I_4WO_4$ and $Ag_{26}I_{18}W_4O_{16}$ compounds using the ampoule method (400°C, furnace cooling to 25°C) from AgI and Ag_2WO_4 each time resulted in non-single-phase products with a small amount of AgI impurity, which contradicts both versions of the phase diagram. Therefore, the goal of this study was to re-examine the phase equilibria in the AgI – Ag_2WO_4 system, refine its phase diagram, and establish the composition of the superionic phase.

Mixtures of the reagents AgI and Ag_2WO_4 in various molar ratios were prepared, sealed in ampoules and annealed according to the selected scheme. The phase composition of the products was analyzed using XRD and DSC. Single-phase products with the $Ag_{26}I_{18}W_4O_{16}$ structure, exhibiting superionic conductivity at room temperature, were obtained in a wide composition range from 3:1 to 3.9:1 (or 20.4…25.0 mol.% Ag_2WO_4); it corresponds to the general formula $Ag_{2+x}I_xWO_4$, where $x = 3 \div 3.9$. This region does not cover any of the superionic phase compositions described in the literature ($Ag_6I_4WO_4$ and $Ag_{26}I_{18}W_4O_{16}$) and is shifted toward a higher Ag_2WO_4 content. It is well known that solid electrolytes based on AgI, stabilized by oxoanions of the XO_4^{2-} type (where X is a transition metal) are prone to metastable states. A test performed by measuring the temperature dependence of conductivity in the thermal cycling mode confirmed the metastability of $Ag_{2+x}I_xWO_4$ except for 3.0:1. Based on the results obtained, it can be concluded that disagreements between the authors [1-3] are due to the fact that the metastable nature of phase equilibria was not taken into account. Changes and clarifications were made to the phase diagram of the AgI – Ag_2WO_4 system, and optimal conditions for the synthesis of single-phase products were selected.

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