HEAT CAPACITY MEASUREMENTS OF $RbAg_4I_5$ AND Rb_2AgI_3

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Solid-state superionic conductors with general formula MAg_4I_5 (Me = K, Rb, NH_4) are known as solid electrolytes with very high (~10^{-1} $Ohm^{-1}\times cm^{-1}$) silver-ion conductivity at room temperature and below. Discovered in 1960s, $RbAg_4I_5$ is still the most interesting among them as it has the highest silver ion conductivity of 0.33 $Ohm^{-1}\cdot cm^{-1}$ at 25 °C. Moreover, it was experimentally confirmed unambiguously that high values of conductivity remain in the wide temperature range due to the low activation energy of conduction (0.10 eV), being 0.11 $Ohm^{-1}\times cm^{-1}$ at -50 °C [1]. However, accumulated over decades experimental information contradicts the available literature data. It was stated [2] that $RbAg_4I_5$ is thermodynamically unstable below 27 °C and tends to decompose to low-conductive phases according to the reaction

$$RbAg_4I_5 \rightleftarrows Rb_2AgI_3 + AgI$$

In order to solve this contradiction and theoretically confirm experimentally observed rather high stability of $RbAg_4I_5$ one need to obtain full thermodynamical characterization of the system RbI – AgI. In addition to $RbAg_4I_5$, it contains another compound Rb_2AgI_3. The goal of this work was to determine temperature dependencies of heat capacity from -196 to 230 °C ($RbAg_4I_5$) and 290 °C (Rb_2AgI_3), using differential scanning calorimetry (DSC) experimental techniques. The temperature dependences of the molar heat capacity at constant pressure $C_p(T)$ for the compounds $RbAg_4I_5$ and Rb_2AgI_3 were measured by the comparison method [3] using high-purity silver as a heat capacity standard. The obtained results relate to reference thermodynamic data and can be used in thermodynamic calculations.

1. Reznitskikh O.G., Yaroslavtseva T.V., Glukhov A.A., Popov N.A., Urusova N.V., Bukun N.G., Dobrovolsky Yu.A., Bushkova O.V. Synthesis and Comparative Investigation of the Electrochemical Characteristics of $CsAg_4Br_{2.5}I_{2.5}$ and $RbAg_4I_5$ Solid Electrolytes // Russ. J. Electrochem. 2022. Vol. 58, Nr 10. P. 927–937. https://doi.org/10.1134/S102319352210010X

2. Topol L.E., Owens B.B. Thermodynamic Studies in the High-Conducting Solid Systems RbI-AgI, KI-AgI, and NH_4I-AgI // J. Phys. Chem. 1968. Vol. 72, Nr 6. P. 2106-2111. https://doi.org/10.1021/j100852a038

3 GOST R 56754-2015 (ISO 11357-4:2005) "Plastics. Differential scanning calorimetry (DSC). Part 4. Determination of specific heat capacity".

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