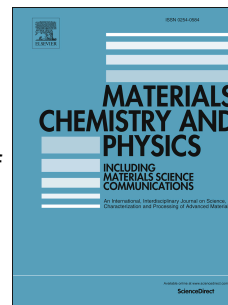


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Discontinuous transition from insulator to semiconductor induced by phase change of the new organic- inorganic hybrid $[(\text{CH}_2)_7(\text{NH}_3)_2]\text{CoBr}_4$

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Abstract

$[(\text{CH}_2)_7(\text{NH}_3)_2]\text{CoBr}_4$, triclinic crystal has a space group P1 with two molecules per asymmetric unit cell ($Z = 2$). Unit cell dimensions are: $a = 7.6588$ (3) Å, $b = 10.5160$ (3) Å, $c = 11.3319$ (5) Å, $\alpha = 66.745$ (2) °, $\beta = 77.2258$ (13) °, $\gamma = 88.001$ (2) °, volume = 816.37(5) Å³ and calculated density = 2.078 Mg m⁻³. The structure consists of $[\text{CoBr}_4]^{2-}$ tetrahedra separated by heptane diammonium layers. The organic hydrocarbon layers pack in a stacked herring-bone manner hydrogen bonded to the halide ions. Lattice potential energy is $U_{\text{pot}} = 1827.7$ kJ/mol, and molecular volume $V_m = 0.408$ nm³. Calorimetric (DSC) measurements indicate phase transitions at $T_1 = 350 \pm 1$ K ($\Delta S = 22.7$ J/K-mol) and 335 K ($\Delta S = 10.5$ J/K-mol). Dielectric and conductivity as a function of temperature ($300 < T < 420$) and frequency ($0.21 < f \text{ (kHz)} < 60$) were investigated. Abrupt change from an insulator to semiconductor behavior takes place around T_1 . At low temperatures, thermally activated Arrhenius behavior is observed with frequency dependent, temperature independent activation energy. At high temperatures conductivity and activation energy are frequency and temperature dependent implying non-Arrhenius type behavior where the charged particles experience different potentials for local and long distance movements. Conduction takes place via correlated barrier hopping with maximum barrier height $W_M = 0.015$ eV.

Key words: X-ray crystal structure, Phase transition, Dielectric constant, conductivity.

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†In partial fulfillment of Ph.D.

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