(P2-13)

Physical properties of the copper oxides $RCu_3Ru_4O_{12}$ (R=Ca, La, Pr) with similar structures to filled skutterudite

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We report the physical properties of the quaternary oxides $RCu_3Ru_4O_{12}$ (R=Ca, La, Pr) and their solid solutions. These oxides crystallize in the cubic structure (space group Im3) closely related to the filled-skutterudite structures where the R atoms are located at the center of the icosahedral cage of oxygen atoms[1]. The similarity of the crystal structure let us expect for $RCu_3Ru_4O_{12}$ appearance of novel magnetic properties, such as Pr-based heavy Fermion superconductivity in $PrOs_4Sb_{12}$, as well as good candidates for thermoelectric materials.

We have prepared polycrystalline sample by heat treating the mixture of CuO, RuO_2, and R_2O_3 or $CaCO_3$ at 1000 °C for 4 days. For the samples obtained as single-phase, the electrical resistvity, thermoelectric power, thermal conductivity, specific heat and magnetization were measured.

The low temperature physical properties of $RCu_3Ru_4O_{12}$ (R=La and Ca) are basically the same to the results of previous report by Ramirez et al.[2], where the enhanced electronic specific heat coefficient γ reaches 20 mJ/K^2.mol–Ru for $CaCu_3Ru_4O_{12}$ and 40 mJ/K^2.mol–Ru for $LaCu_3Ru_4O_{12}$, respectively, suggesting the presence of the strong correlation effect of Ru–4d conduction electrons. The low temperature magnetic susceptibility data indicates the valence of Cu is nonmagnetic monovalent Cu^+.

Magnetic susceptibility χ of $PrCu_3Ru_4O_{12}$ does not follow the Curie-Weiss law over the whole experimental region. The Pr atoms have normal $4f^2$ state (Pr^{3+}) from the Curie-Weiss fitting. The χ and the magnetic specific heat divided by temperature $C_{\rm mag}/T$ keep increasing with decreasing temperature down to 2 K, suggesting the degenerate $4f$ state of Pr under the T_h crystalline electric field symmetry. The $C_{\rm mag}/T$ shows a broad maximam at 0.74 K and decreases gradually with decreasing temperature down to 0.28 K. The absolute value of the $C_{\rm mag}/T$ at 0.28 K is 2.1 J/K^{2}mol–Pr.

The room temperature thermoelectric power and electrical resistivity of $RCu_3Ru_4O_{12}$ are 30–60 μV/K and 300–800 $\mu\Omega$cm, respectively, and the maximum thermoelectric power factor is estimated at 5×10^{-4} W/mK^2. $RCu_3Ru_4O_{12}$ are promising thermoelectric materials and their properties can be improved by substitution of chemical element and single-crystallization.

[1] M.Labeau, et al. J. Solid State Chem., **33** (1980) 257.

[2] A.P. Ramirez, et al., Solid State Commun. **131** (2004) 251.