Electronic properties of the novel 4d metallic oxide SrRhO$_3$

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The novel 4d perovskite compound SrRhO$_3$ was investigated by isovalent doping studies. The solubility limits of Ca and Ba onto Sr-site were below 80% and 20%, respectively. Although SrRhO$_3$ was chemically compressed, approximately 5.7% by the Ca doping, no significant influence was observed on the magnetic and electrical properties.

Novel 4d electronic compounds in the rhodium-oxide system with perovskite- and Ruddlesden-Popper-type structures were found recently, followed by intensive experimental investigations. An essential chemical reaction in synthesis of the compounds was provoked by a high-pressure and high-temperature heating (6 GPa and 1500 °C) in our originally developed apparatus. The structure characteristics of the compounds were studied by means of powder neutron and x-ray diffraction. The structural data clearly indicate them to be isostructural to the analogous ruthenium oxides with approximately the same degree of local structural distortions. The perovskite SrRhO$_3$ is metallic with enhanced paramagnetism as is the analogous ruthenium oxide CaRuO$_3$. A comprehensive picture, however, for the magnetic and transport properties has not been fully established yet. The quadratic temperature dependence, for example, of the magnetic susceptibility data of SrRhO$_3$ is unexpected, and it does not follow, even qualitatively, the models of conventional paramagnetism or self-consistent-renormalization.

In this short paper, we report the data of isovalent substitution studies on the perovskite SrRhO$_3$. The Ca substitution was achieved onto the Sr site up to approximately 80%, resulting in 5.7% compression in unit-cell volume.

Variable composition precursors Sr$_{1-x}$Ca$_x$RhO$_2$ ($x = 0$ to 1 in 0.2 steps) were prepared from SrCO$_3$ (99.9 %), CaCO$_3$ (99.9 %) and Rh (99.9 %) powders. Mixtures were heated at 1200 °C for 48 hrs in oxygen after a couple of pre-heatings. Each of those (~0.3 g) was then mixed with KClO$_4$ (8 wt.%), and placed into Pt capsules. The capsules were compressed at 6 GPa and heated at 1500 °C for 1 hr, followed by quenching to room temperature at the elevated pressure. Quality of the final products was examined by powder x-ray diffraction in a regular manner. The magnetic susceptibility of the selected samples was measured in a commercial apparatus (Quantum Design, MPMS-XL). The electrical resistivity was measured by a conventional dc-four-terminal technique.

It appeared that the Ca doped samples ($x = 0.2–0.6$) were of high-quality as well as pure SrRhO$_3$. At $x = 0.8$, a small fraction of an unknown phase was detected, indicating a limit on the Ca solubility. At the Ca-end ($x = 1.0$), the sample consisted of multiple phases, which were unidentified. The various lattice parameters and the unit-cell volumes measured in the x-ray study are arranged in Fig. 1. They decrease smoothly with increasing Ca concentration, consistent with Ca having a smaller ionic radius than Sr. The perovskite SrRhO$_3$ was chemically compressed ~ 5.7% by the Ca substitution.

The temperature dependence of the electrical resistivity of the sample pellets were measured between 2 K and 380 K. Metallic behavior was observed for the samples between $x = 0$ and 0.8 in the temperature range. Although the data were probably influenced somewhat by polycrystalline nature of the samples, the essential elec-
FIG. 2: The inverse magnetic susceptibility vs temperature squared at 50 kOe for the polycrystalline samples of (Sr,Ca)RhO$_3$. The plots show a notably linear dependence as the solid lines indicate. Contribution from the sample holder was negligible. The Curie-Weiss law ($1/\chi \sim T$) was unable to fit the magnetic data.

with increasing Ca concentration, rather generally a rigid shift to higher values of $1/\chi$. Neither antiferromagnetic nor ferromagnetic order was observed, and therefore, the data do not provide sufficient evidence to determine the dominant influence on the rather unusual magnetic character ($1/\chi \sim T^2$) in the metallic state.

The Ca-doping shifts the system away from a long-range magnetically ordered state, as the intersection between the horizontal axis and the extrapolated linear fit (Fig.2) moves away from the origin with increasing Ca concentration. Long-range order is expected to appear when the point intersects the origin, as found in the solid solution of the Ru analogue, (Ca,Sr)RuO$_3$. We were then motivated to try Ba-doping in the perovskite, essentially a study in negative compression (Ba has a larger ionic size than Sr). The amount of Ba substituted was, however, too insignificant to test the expectation. The orthorhombic structure quickly transformed to a hexagonal type with increasing Ba concentration; the Ba-solubility limit was less than 20% at the synthesis conditions.

In summary, we reviewed investigations of the isovalent doping studies on SrRhO$_3$. The data indicate no remarkable change in the magnetic and electrical properties of SrRhO$_3$, either qualitatively or quantitatively; the rather unusual magnetic character, quadratic temperature dependence of the magnetic susceptibility ($1/\chi \sim T^2$) was robust against the 5.7% chemical compression. Hence, the open question still remains as to what mechanism is responsible for the magnetic characteristics. Further investigations, including testing aliovalent doping effects on SrRhO$_3$, would be of interest.

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