Effect of elemental substitutions on ruthenates with pyrochlore-type structure

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Abstract. Synthesis and physical properties of Pb$_{2-x}$Ln$_x$Ru$_2$O$_{7-δ}$ (Ln = Y, Eu, Lu) phase are reported. The pyrochlore ruthenates Pb$_{2-x}$Ln$_x$Ru$_2$O$_{7-δ}$ (Ln = Y, Eu, Lu) have been successfully synthesized by the solid-state reaction. The solid-solution compounds of Pb$_{2-x}$Lu$_x$Ru$_2$O$_{7-δ}$ undergo a crossover from metallic (x = 0) to insulating (x = 2) with increasing x. Owing to a localized magnetic moment on Ru site, these compounds with x > 0 also indicate the spin-glass (SG) like behaviors at low temperature (T < $T_{SG}$). From electric resistivity measurements for the Y-substituted system, the sample of x = 0.0 shows metallic behaviors and that of x = 1.0 shows insulating properties. In Pb$_{2-x}$Eu$_x$Ru$_2$O$_{7-δ}$ system, the solid-solution compounds show from metallic (x = 0) behaviors to insulating (x = 2) behaviors with increasing x. In a similar manner as Pb$_{2-x}$Lu$_x$Ru$_2$O$_{7-δ}$ system, it was found that $T_{SG}$ decreases monotonously with decreasing x and goes to zero at x = 0.6. As a result of electric resistivity measurements, the samples with 0.4 ≤ x ≤ 0.8 show the metal-insulator (MI) transition at 10-30 K where the slope of temperature dependence of electrical resistivity ($\rho$) changes. In the metallic region, values of $\rho$ obey $T^2$-dependencies which indicate the strongly correlated electron behaviors in this system.

1. Introduction
Pyrochlore oxides constitute a large family of transition metal oxides with a chemical formula of $A_2B_2O_7$ [1–3], where $A$ is a larger cation and $B$ is a smaller transition metal. Both $A$ and $B$ ions individually form a three dimensional sub-lattices consisting of corner-shared tetrahedra. When the exchange interaction between the nearest-neighbor atoms is antiferromagnetic, the magnetic moments on the atoms in such sub-lattice are expected to be geometrically frustrated. As a result, the system shows a freezing into a spin glass state which has been found in several pyrochlores or a disordered ground state instead of a magnetically ordered state. Electric and magnetic properties of pyrochlores with $B$ sites of $4d$ elements are especially attractive, since the $4d$ electrons generally indicate the variety of localized and itinerant behaviors [4–8]. For example, the bismuth ruthenate Bi$_2$Ru$_2$O$_7$ is metallic and Pauli paramagnetic with a nearly temperature-independent resistivity, while the rare earth ruthenates Ln$_2$Ru$_2$O$_7$ (Ln represents lanthanoids from Pr to Lu) are all semiconductors with localized magnetic moment on the ruthenium atoms. In order to clarify the transport behaviors of pyrochlore ruthenates near the boundary of the metal-insulator crossover, detailed investigations of the physical properties have been performed for the Ln-substituted system Bi$_{2-x}$Ln$_x$Ru$_2$O$_7$ [9, 10]. Although Pb$_2$Ru$_2$O$_{6.5}$ is known to show a Pauli paramagnetism with a metallic behavior similar to Bi$_2$Ru$_2$O$_7$, there
have been a few reports on Ln-substituted system Pb_{2-x}Ln_xRu_2O_7-δ because of the difficulty in synthesizing a single phase [11]. In this paper, the synthesis and physical properties of Pb_{2-x}Ln_xRu_2O_7-δ (Ln = Y, Eu, Lu) phase are reported [12].

2. Experimental
The lead-lanthanoid pyrochlores Pb_{2-x}Ln_xRu_2O_7-δ have been synthesized by the solid-state reaction method. The raw materials of PbO, Ln_2O_3 and Ru with 99.99% purity were mixed thoroughly, pelleted and heated in air at 850 °C for 24 hours. Then the sample was ground, pelleted and heated in air at 850 – 1200 °C for 48 hours. Several samples with Pb rich composition were sealed in Pt tubes to prevent the sublimation at high temperatures. Obtained samples were characterized by X-ray diffraction measurements (Rigaku, RINT-2200). Magnetic susceptibilities were measured by SQUID magnetometer (Quantum Design, MPMS-5T). Electric resistivity measurements were performed by a conventional four-terminal method.

Figure 1 shows XRD patterns of Pb_{2-x}Lu_xRu_2O_7-δ compounds. All the sample is successfully indexed by the pyrochlore structure. As shown in Fig. 2, lattice parameters were found to decrease linearly with increasing Lu content x. This indicates that the solid solution compounds of Pb_{2-x}Lu_xRu_2O_7-δ were obtained as single phases. Eu and Y substituted compounds were also synthesized as single phases in the range of 0 ≤ x ≤ 2.

Figure 3 shows temperature dependences of magnetic susceptibility (χ) for Pb_{2-x}Lu_xRu_2O_7-δ compounds. Pb_2Ru_2O_6.5 compound (x = 0) shows temperature-independent Pauli paramagnetism as previously reported [13,14]. The other end material, Lu_2Ru_2O_7 indicates spin-glass like behavior at T = T_{SG} of about 80 K where values of χ for zero-field cooling (ZFC) and field cooling (ZFC) diverge [15]. Values of χ for the samples of x > 1.0 are well analyzed by
Figure 2. Lu composition dependence of lattice parameters in Pb$_{2-x}$Lu$_x$Ru$_2$O$_{7-\delta}$ compounds.

Figure 3. Temperature dependences of magnetic susceptibility for Pb$_{2-x}$Lu$_x$Ru$_2$O$_{7-\delta}$ compounds. Open and solid marks corresponds to FC and ZFC measurements.

Curie-Weiss law with negative values of Weiss temperatures which indicates a localized-moment character with antiferromagnetic interactions. The spin freezing temperature, $T_{SG}$, slightly decreases with Lu content $x$ and disappears for $x = 0.2$. In the case of Ln = Y and Eu, similar behaviors were observed [12]. In the case of Pb-Eu system, another anomalies in $\chi$-T plot were observed at lower temperatures of about 25 K for samples with $0.2 < x < 1.8$. These anomalies were attributed to the magnetic order of rare-earth atoms in other compounds [13], although the ground state of Eu$^{3+}$ is non-magnetic. These anomalies may be caused by magnetic Eu$^{3+}$ ions due to the oxygen deficiency and/or an impurity phase.

In Fig. 4, we show temperature dependences of electric resistivity ($\rho$) of Pb$_{2-x}$Y$_x$Ru$_2$O$_{7-\delta}$ system. It was found that the conductivity of the system changes from metallic to semiconducting with increasing $x$. From a preliminary analysis, it was found that Ru-O-Ru bond angles of about 130° increases with decreasing $x$. These structural distortions can be caused by the 6$s^2$ lone-pair electrons on Pb sites, leading to the band mixture with Ru 4$d$ band at the Fermi surface via the framework of oxygen atoms.

Fermi liquid behaviors such as $T^2$-dependence of electric resistivity and linear heat-capacity coefficient ($\gamma$) are reported for a single crystal of Pb$_2$Ru$_2$O$_{6.5}$ [14]. It was found that the ratio of $T^2$ coefficient, $A$, to $\gamma^2$ of Pb$_2$Ru$_2$O$_{6.5}$ corresponds to the universal Kadowaki-Woods relation as shown in other strongly correlated transition metal oxides [16]. From this viewpoint, it is of interest to study $A/\gamma^2$ of the Ln substituted system which will be reported elsewhere.

4. Summary
The lead-lanthanoid pyrochlores Pb$_{2-x}$Ln$_x$Ru$_2$O$_{7-\delta}$ (Ln = Y, Eu, Lu) have been successfully synthesized by the solid-state reaction. Obtained samples were characterized by X-ray diffraction, magnetic susceptibility, and electrical resistivity measurements. Magnetic susceptibility measurements indicated that the spin freezing temperature, $T_{SG}$, decreases with Ln content $x$ and goes to zero at $x = 0.2$ for Lu and Y. From electric resistivity measurements, a crossover from metallic to semiconducting behaviors was observed in the Pb$_{2-x}$Y$_x$Ru$_2$O$_{7-\delta}$ compounds.
system. These boundaries between metallic and insulating phases mostly correspond to values of $x$ with $T_{SG} = 0$. Further microscopic experiments such as NMR or neutron diffraction measurements should be necessary to clarify the effect of the geometrical frustration near $x = 2.0$ on the crossover to itinerant behaviors around $x = 1.0$.

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