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PREPARATION AND PROPERTIES OF ORDERED PEROVSKITES $(LaSr)(MnW)O_6$ AND $(LaSr)(MgW)O_6$ [1)]

Masahiro YOSHIMURA, Kiichiro KAMATA, and Tetsuro NAKAMURA

Research Laboratory of Engineering Materials,
Tokyo Institute of Technology, Ookayama, Tokyo

Ordered perovskites, $(LaSr)(Mn^{2+}W^{5+})O_6$ and $(LaSr)(Mg^{2+}W^{5+})O_6$, were newly prepared. The lattice constants, the electrical conductivities and the magnetic moments were studied. The results indicate that $3d^5$ electrons in Mn^{2+} are almost localized and that the interaction between Mn^{2+} and W^{5+} is fairly weak in this compound.

When both B-site ions have unpaired electrons in ordered perovskites $A_2BB'O_6$, interesting properties have been reported, for example, a ferrimagnetism and a metallic conduction in $Sr_2(FeMo)O_6$ [2)] and $Ba_2(FeRe)O_6$ [3)], a ferrimagnetism and a semiconduction in $Ba_2(MnRe)O_6$ [3)], and an antiferromagnetism and a semiconduction in $Ba_2(CoRe)O_6$ [3)]. Patterson et al.[4)] found a ferrimagnetic perovskite in the case of B = $Cr^{3+}(3d^5)$ and B' = $W^{5+}(5d^1)$. In order to study the case of B = $Mn^{2+}(3d^5)$ and B' = $W^{5+}(5d^1)$, we have newly prepared and investigated the compounds $(LaSr)(MnW)O_6$ and $(LaSr)(MgW)O_6$. The latter which has no 3d electron in B-site was made for comparison. La^{3+} and Sr^{2+} ions were introduced to A-sites in order to attain the valency distribution of B^{2+} and B'^{5+} in B-sites.

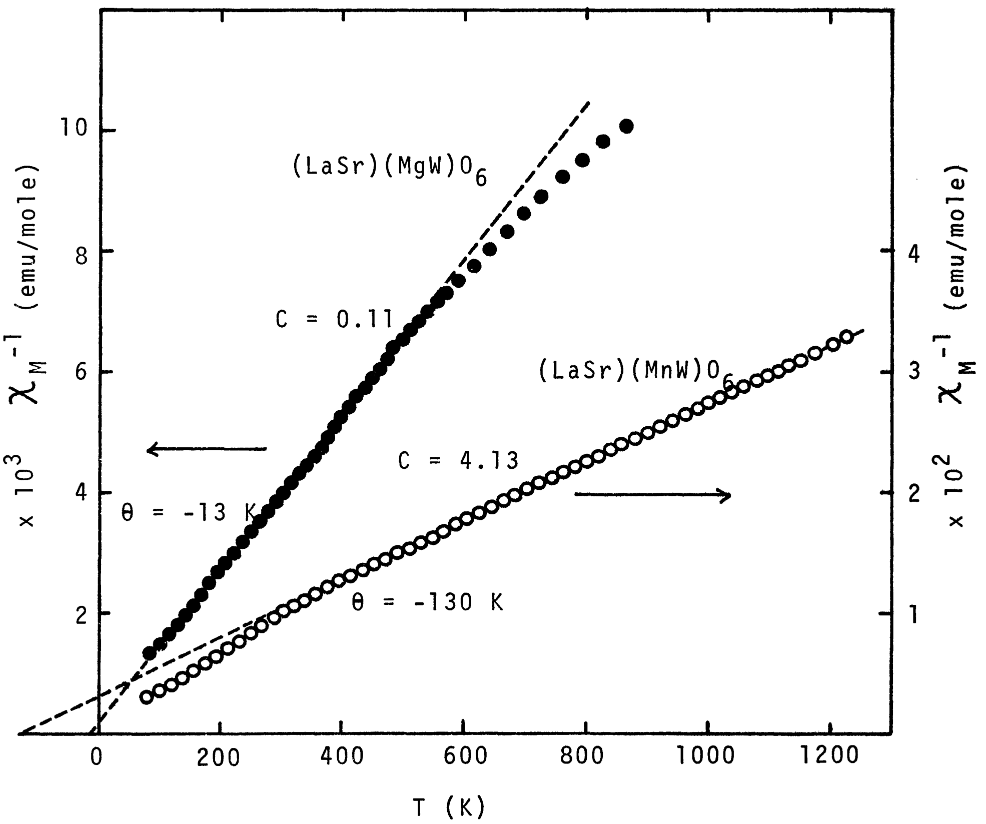
Stoichiometric mixtures of dried La_2O_3, $SrCO_3$, WO_3 and MnO_2 or MgO were fired at 1300 °C for 14 hr, and reground and refired at 1400 °C for 14 hr in the atmosphere of hydrogen gas bubbled through water. The oxygen partial pressure in this atmosphere was determined to be about 10^{-14} atm using a stabilized zirconia cell.

$(LaSr)(MnW)O_6$ was dark brown and $(LaSr)(MgW)O_6$ was deep blue. By the X-ray diffraction, these compounds were found to have ordered perovskite structures, that is, Mn or Mg and W ions occupied B-sites alternately. The lattice constants were determined to be 8.034 Å for $(LaSr)(MnW)O_6$ and 7.922 Å for $(LaSr)(MgW)O_6$ as pseudo-cubic cells. This difference corresponds to that in ionic radii; 0.820 Å for Mn^{2+} and 0.720 Å for Mg^{2+} after Shannon.[5] The Mn^{2+} state in $(LaSr)(MnW)O_6$ was also confirmed by the chemical shift in the fluorescent X-ray analysis. The value of the MnKβ shift of 1.164 eV compared with that of Mn metal was just corresponding to the Mn^{2+} state[6].

Magnetic measurements showed that those compounds exhibited paramagnetic behaviors in the temperature range of 80 - 1200 K (Fig. 1). The reciprocal susceptibility of $(LaSr)(MgW)O_6$ seemed to obey the Curie-Weiss law, $\chi_M = C/(T-\theta)$. Its Curie constant was 0.11 K/mole and the asymptotic Curie temperature was -13 K. The observed value(0.11) was fairly smaller than that(0.37) expected for one d-electron (spin only value). It indicates that $5d^1$ of W^{5+} ion is partly localized in this

Fig. 1 Reciprocal susceptibility vs. temperature

The deviation from the straight line in $(LaSr)(MgW)O_6$ at high temperatures was caused by the temperature-independent correction of diamagnetism (140×10^{-6} emu/mole) after Selwood.[7]

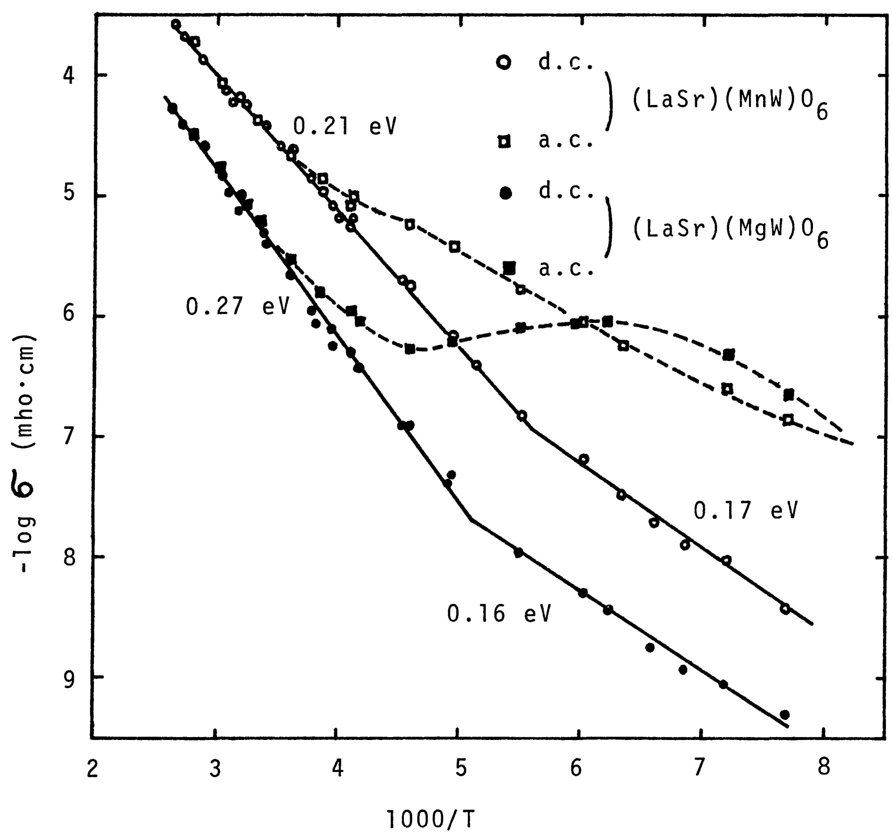


perovskite.

For the compound (LaSr)(MnW)O_6,the Curie-Weiss law was valid in the temperature range above 400 K. Its Curie constant 4.13 was slightly smaller than 4.38 expected for Mn^{2+} ion(spin only value),but it is in good agreement with those observed in $Sr_2(Mn^{2+}W^{6+})O_6$[8] or $Ba_2(Mn^{2+}Re^{6+})O_6$[3]. This indicates that Mn ions are divalent in the high-spin state and that the five 3d-electrons in Mn^{2+} are almost localized in this compound. The deviation from the Curie-Weiss law observed at temperatures below 400 K and the asymptotic Curie temperature of -130 K suggest that a ferrimagnetic ordering will take place at a lower temperature than that studied as seen in the compound $Sr_2(Cr^{3+}W^{5+})O_6$[4].

The electrical conductivity measurements in d.c. and a.c.(1539 Hz) by the usual two-probe method showed that these perovskites were semiconductive (Fig. 2). From the fact that any pronounced differences have not been observed in conductivities and activation energies between (LaSr)(MnW)O_6 and (LaSr)(MgW)O_6,it is presumed that $3d^5$ electrons of Mn^{2+} ion are almost localized,that is,their contributions to the

Fig. 2 Electrical conductivity vs. temperature



electrical conduction are quite small in $(LaSr)(MnW)O_6$. It is also presumed that the conduction in these perovskites is dominated by the direct 5d-5d interaction mechanism as proposed in $Ba_2(MnRe)O_6$ and $Ba_2(MgRe)O_6$[3]. The a.c. conductivities are in agreement with the d.c. conductivities above a room temperature,but showed some dispersions at a low temperature,the cause of which are not known. Measurements for single crystals are desirable to explain the conduction mechanism.

Studies on ordered perovskites containing low valency states of transition elements are in progress. The authors wish to thank Professor T.Sata for his encouragement and support.

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