CHEMISTRY LETTERS, pp. 1201-1206, 1972. Published by the Chemical Society of Japan

SYNTHESIS AND PROPERTIES OF ORDERED PEROVSKITES $A_2(Ln^{3+}M^{5+})O_6$ (A=Ba,Sr, Ln=Y,Gd,Dy,Er, M=Mo,W)[1]

Kiichiro KAMATA, Masahiro YOSHIMURA, Tetsuro NAKAMURA and Toshiyuki SATA
Research Laboratory of Engineering Materials,
Tokyo Institute of Technology, Ookayama, Tokyo

Ordered perovskites, $Ba_2(LnMo)O_6$, $Sr_2(LnMo)O_6$ and $Ba_2(LnW)O_6$, were newly synthesized. The crystallographic, electrical and magnetic properties for these compounds were investigated. The magnetic moments of Mo^{5+} and W^{5+} were determined. Magnetic properties indicated that the interaction between $Ln^{3+}(4f^n)$ and $Mo^{5+}(4d^1)$ or $W^{5+}(5d^1)$ was fairly weak in these compounds.

Several ordered perovskites $A_2(B'B'')O_6$ which contain two paramagnetic cations in the B site of the perovskite lattice have been synthesized[2-5]. These compounds have interesting properties, 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], $Sr_2(CrMo)O_6$ and $Sr_2(CrW)O_6$[4]. In these reports the interaction between $3d^n$ electrons and $4d^1(Mo^{5+})$ or $5d^1(W^{5+}, Re^{6+})$ electrons were studied.

We tried to prepare new perovskites, $A_2(LnMo)O_6$ and $A_2(LnW)O_6$ with A=Ba,Sr and Ca, in order to study the magnetic interaction between $4f^n(Ln^{3+})$ and $4d^1(Mo^{5+})$ or $5d^1(W^{5+})$. Lanthanide ions, $Gd^{3+}(4f^7)$, $Dy^{3+}(4f^9)$ and $Er^{3+}(4f^{11})$ with large magnetic moments and Y^{3+} with no magnetic moment, were chosen for B' cations in this work.

Appropriate mixtures of reagent-grade $BaCO_3$ (or $Ba(NO_3)_2$), $SrCO_3$, $CaCO_3$, Y_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, MoO_3 and WO_3 were heated at 1200-1300°C for 2hr, and reground and reheated at 1250-1350°C for 5hr in the atmosphere of wet hydrogen. The oxygen partial pressure in this atmosphere was determined to be 10^{-14} atm[6]. X-ray powder diffraction analysis showed that only the compounds $Ba_2(LnMo)O_6$, $Sr_2(LnMo)O_6$, and $Ba_2(LnW)O_6$ had been synthesized with perovskite structures. $Ba_2(LnMo)O_6$ and $Sr_2(LnMo)O_6$ were black and $Ba_2(LnW)O_6$ was deep blue.

X-ray powder diffraction patterns were taken at room temperature using CuKα radiation. Super-structure lines showing the alternating arrangement in B site were observed in $Sr_2(LnMo)O_6$ and $Ba_2(LnW)O_6$, but not observed in $Ba_2(LnMo)O_6$. The d.c. conductivities were measured over a temperature range from 80 to 600K. The measurements were made by the four-probe method for ceramic samples in a stream of hydrogen. The magnetic susceptibilities were measured using a magnetobalance in a temperature range from 80 to 300K.

The crystallographic, electrical and magnetic properties of the synthesized perovskites are summarized in Table I.

Table I. Physical properties for $A_2(LnM^{5+})O_6$ compounds at room temperature

Compound	Tolerance factor	Symmetry	Lattice constant (Å)	Conductivity $(\Omega cm)^{-1}$	Activation energy * (eV)	P_{eff} ** (μ_B)	P_{Ln} *** (μ_B)	asympt. Curie temp. (K)
Ba_2YMoO_6	0.98	cubic	8.388	1.6×10^{-2}	0.15	1.5	0	-110
Ba_2GdMoO_6	0.97	cubic	8.452	2.8×10^{-2}	0.13	7.8	8.0	+5
Ba_2DyMoO_6	0.98	cubic	8.406	1.1×10^{-2}	0.13	10.4	10.6	-13
Ba_2ErMoO_6	0.98	cubic	8.376	7.3×10^{-2}	0.11	9.5	9.5	-10
Sr_2YMoO_6	0.93	p.cubic	8.180	1.7×10^{-2}	0.13	1.5	0	-100
Sr_2GdMoO_6	0.92	p.cubic	8.260	2.3×10^{-2}	0.12	7.8	8.0	-3
Sr_2DyMoO_6	0.93	p.cubic	8.230	9.3×10^{-3}	0.13	10.4	10.6	-10
Sr_2ErMoO_6	0.93	p.cubic	8.132	3.8×10^{-2}	0.12	9.5	9.5	-12
Ba_2YWO_6	0.98	cubic	8.378	1.5×10^{-7}	0.2-0.3	0.96	0	-70
Ba_2GdWO_6	0.97	cubic	8.431	1.5×10^{-7}	0.2-0.3	7.5	8.0	+4
Ba_2DyWO_6	0.98	cubic	8.392	2.5×10^{-7}	0.2-0.3	10.4	10.6	-13
Ba_2ErWO_6	0.98	cubic	8.366	5.0×10^{-7}	0.2-0.3	9.4	9.5	-10

* from 200 to 500K. ** Effective magnetic moment observed: Diamagnetism were corrected according to Selwood[7]. *** Effective magnetic moment for lanthanide ion: from Kittel, " Introduction to Solid State Physics", John Wiley & Sons, (1967) 3rd Ed., p.437.

The lattice constants observed in these perovskites were closely related to the ionic radii of constituent ions. The lattice constants for $Ba_2(LnMo)O_6$ were in agreement with the previous values[5]. The difference between the lattice constant of $Ba_2(LnMo)O_6$ and that of $Ba_2(LnW)O_6$ should result from the difference between the ionic radius of Mo^{5+} and that of W^{5+} which was absent in recent works[9-10]. The plot of cell volumes vs. ionic radii (Fig. I) gave 0.625Å for the radius of W^{5+}. The tolerance factors[8)] for the perovskites $Ba_2(LnW)O_6$ were calculated using this value. The tolerance factors were 0.97-0.98 for cubic perovskites and 0.92-0.93 for pseudo-cubic perovskites. The value(0.89) estimated for Ca compounds suggests a difficulty in the formation of the perovskite phase.

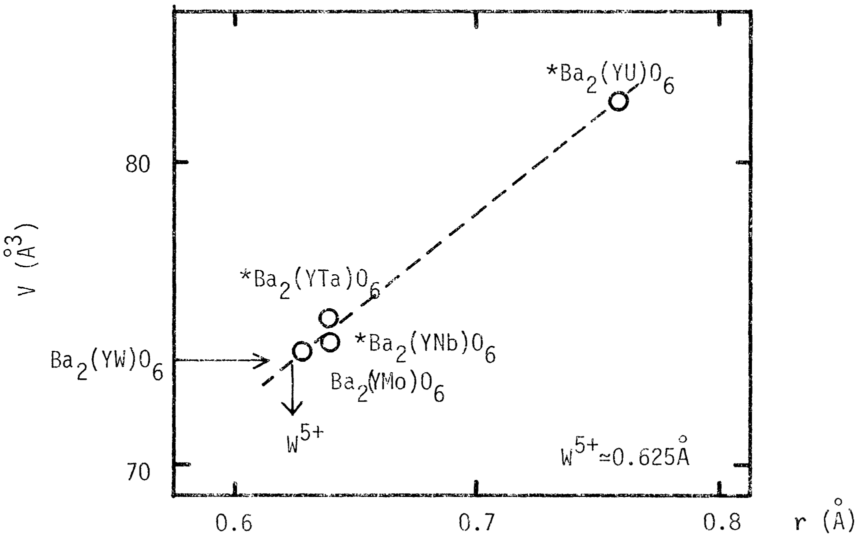


Fig. I. Plot of the cell volumes $Ba_2(YM^{5+})O_6$ vs. the ionic radii of M^{5+} ions after Shannon[9-10)]. * the cell volume derived from Galasso[11)].

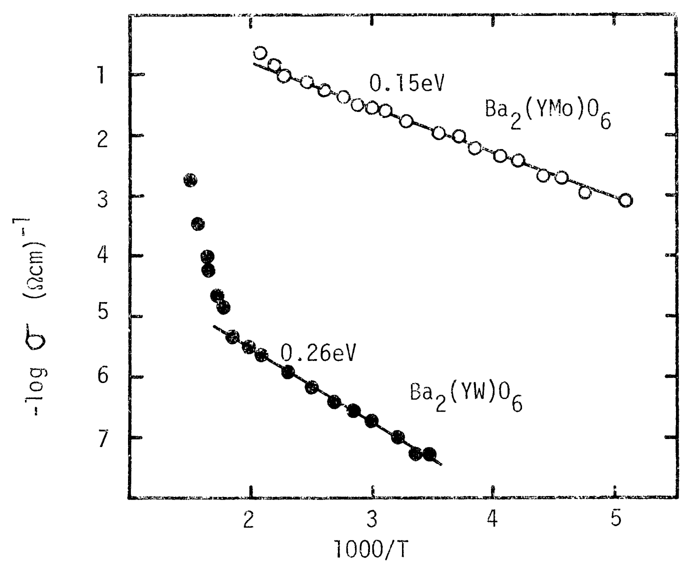


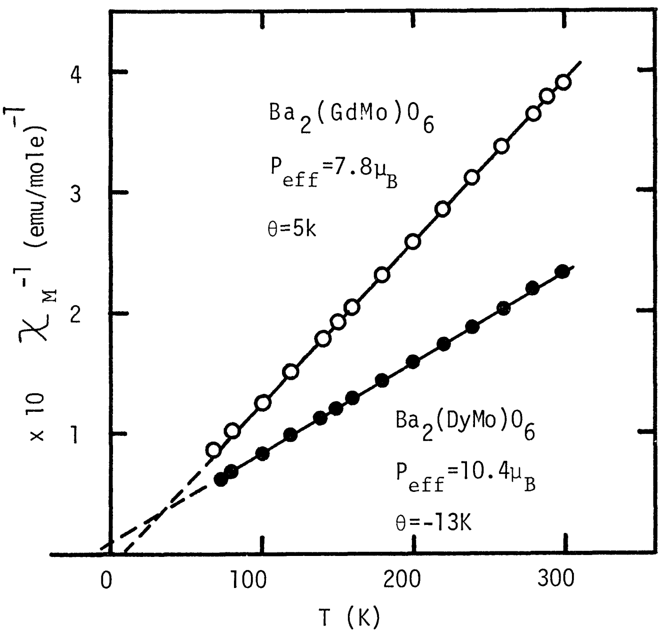
Fig. II. Electrical conductivity vs. temperature

Fig. II shows the electrical conductivities of $Ba_2(YMo)O_6$ and $Ba_2(YW)O_6$. Similar semiconducting behaviors were observed in the other perovskites obtained. The electrical conductivities at room temperature, 10^{-2}-10^{-3} $(\Omega cm)^{-1}$, and their activation energies, 0.1-0.2eV(200-500K), were observed in the perovskites containing Mo^{5+}, $A_2(LnMo)O_6$. Similarly, the values, 10^{-6}-10^{-7} $(\Omega cm)^{-1}$ and 0.2-0.3eV, respectively, were observed in those containing W^{5+}, $A_2(LnW)O_6$. From these results it can be said that perovskites $A_2(LnMo)O_6$ are better electrical conductors than perovskites $A_2(LnW)O_6$.

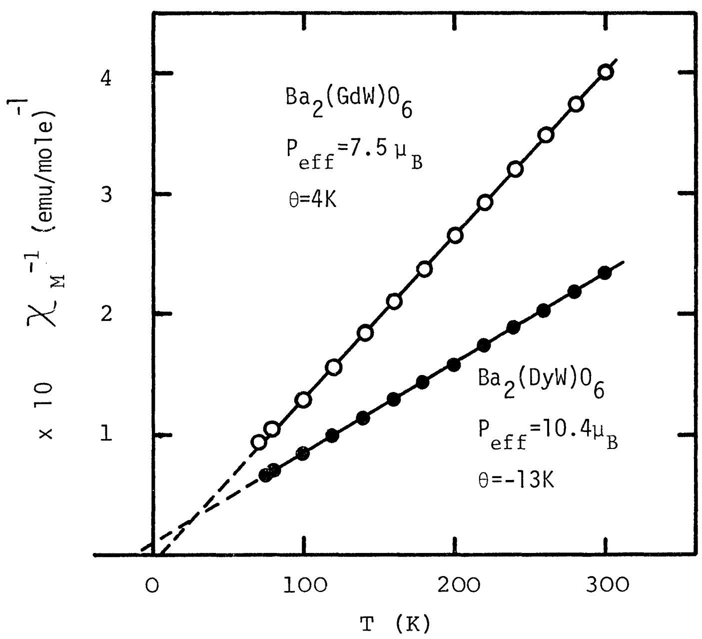
All perovskites obtained showed paramagnetic behaviors obeying the Curie-Weiss law. Fig. III shows the reciprocal susceptibility vs. temperature relations of several perovskites. No Néel points of them were observed over a temperature range from 80 to 300K. The magnetic moment $0.96\mu_B$ of $Ba_2(YW)O_6$ is in good agreement with that of $SrLa(MgW)O_6$[6]; therefore the magnetic moment should be attributed to W^{5+} ion. The magnetic moment $1.5\mu_B$ of $Ba_2(YMo)O_6$ and $Sr_2(YMo)O_6$ might be attributed to Mo^{5+} ion. Since the effective moment was calculated by the formula: $P_{eff}=\sqrt{P_{Ln}^2 + P_{M5+}^2}$, the contribution of P_{M5+} was relatively small on the total moment P_{eff}. When P_{Ln} was large in particular, the magnetic moment of each perovskite became nearly equal to that of the lanthanide ion as seen in Table I. The values of the asymptotic Curie temperature for all perovskites were very small. From above results it can be deduced that the magnetic interaction between $Ln^{3+}(4f^n)$ and $Mo^{5+}(4d^1)$ and $W^{5+}(5d^1)$ is very weak in these compounds.

Fig. III Reciprocal susceptibility vs. temperature

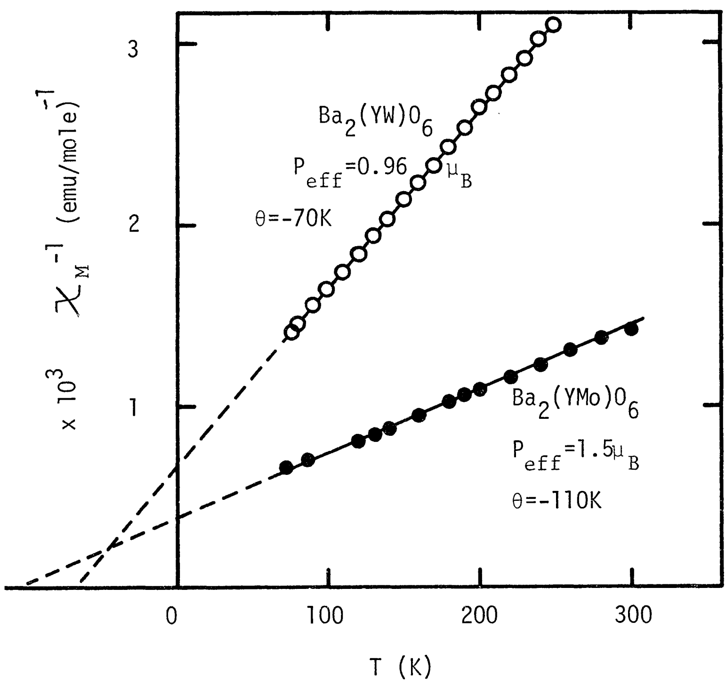
(a) $Ba_2(DyMo)O_6$ and $Ba_2(GdMo)O_6$



(b) $Ba_2(DyW)O_6$ and $Ba_2(GdW)O_6$



(c) $Ba_2(YMo)O_6$ and $Ba_2(YW)O_6$



Acknowledgment. The authors wish to thank Mr. W.H.Cheng, Union Industrial Research Institute in the Republic of China, for his faithful assistance in the preparation and determination of lattice parameters of the $Ba_2(YMo)O_6$ and $Sr_2(YMo)O_6$ compounds.

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(Received August 21, 1972)