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FLUORESCENT X-RAY Kβ SHIFT AND MAGNETIC MOMENT OF Mn^{2+} ION IN ORDERED PEROVSKITES $(BaLa)(MnMo)O_6$, $(SrLa)(MnTa)O_6$ AND $Ba_3(MnTa_2)O_9$

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The rock salt arrangement between Mn and Mo or Ta was found in new compounds $(BaLa)(MnMo)O_6$ and $(SrLa)(MnTa)O_6$. The fluorescent X-ray Kβ shift from Mn in $(BaLa)(MnMo)O_6$ was located between those of MnO and $(SrLa)(MnTa)O_6$. $(SrLa)(MnTa)O_6$ obeyed the Curie - Weiss law above the room temperature, while $(BaLa)(MnMo)O_6$ showed a ferrimagnetism with $T_c = 120$ K. The valency pair (Mn^{2+}, Mo^{5+}) in $(BaLa)(MnMo)O_6$ was verified.

In the perovskite-type compound $(BaLa)(MnMo)O_6$, where Ba^{2+} and La^{3+} ions are randomly distributed among the A - sites of perovskite structure ABO_3, there are two kinds of possible valency pair for the magnetic cations in B - sites, i.e. (Mn^{2+}, Mo^{5+}) and (Mn^{3+}, Mo^{4+}). In compounds $(SrLa)(MnTa)O_6$ and $Ba_3(MnTa_2)O_9$, on the other hand, the Ta^{5+} state is so stable as to drive the paired Mn ion in an Mn^{2+} state. Hence, the compounds $(SrLa)(MnTa)O_6$ and $Ba_3(MnTa_2)O_9$ are suitable for reference materials containing Mn^{2+} ion. In order to determine which valency pair is realized in $(BaLa)(MnMo)O_6$, perovskite-type compounds $(BaLa)(MnMo)O_6$, $(SrLa)(MnTa)O_6$ and $Ba_3(MnTa_2)O_9$ were prepared, and their X-ray powder diffraction patterns, fluorescent X-ray Kβ spectra from Mn and magnetic properties were measured. The former two are new compounds and the third is a known one.$^{1)}$

Polycrystalline samples were prepared from $BaCO_3$ (purity : 99.9 %), $SrCO_3$ (99.9 %), La_2O_3 (99.99 %), MnO_2 (99.9 %), MoO_3 (99.9 %) and Ta_2O_5 (99.5 %). The stoichiometric mixtures of the reagents were reacted at 1250 °C for 3 h in a wet hydrogen flowing atmosphere. The partial pressure of oxygen in this atmosphere was approximately 10^{-14} atm.$^{2)}$ The reacted mixtures were ground, pelletized and reheated at 1320 °C for $(BaLa)(MnMo)O_6$, and at 1350 °C for $(SrLa)(MnTa)O_6$ and $Ba_3(MnTa_2)O_9$ for 4 h in the wet hydrogen atmosphere. The resulted pellet of $(BaLa)(MnMo)O_6$ was black, those of $(SrLa)(MnTa)O_6$ and $Ba_3(MnTa_2)O_9$ were pale-gray.

The X-ray powder diffractometry using Cu Kα radiation(λ =1.5405 Å) indicated that $(BaLa)(MnMo)O_6$ and $(SrLa)(MnTa)O_6$ had perovskite structures with superlattice lines caused by the rock salt arrangement (1:1 ordering) of Mn and Mo or Ta atoms in the B - sites of the perovskite structure ABO_3. Crystal systems were cubic for $(BaLa)(MnMo)O_6$ with the lattice constant of a = 8.119(2) Å and pseudocubic for $(SrLa)(MnTa)O_6$ with the constant of a = 8.079(3) Å. $Ba_3(MnTa_2)O_9$, on the other hand, had a rhombohedrally distorted perovskite structure with superlattice lines due to a layer-like ordering (1:2 ordering) of Mn and Ta atoms in the B - sites. Lattice constants based on the tripled edge of the perovskite unit, a' = 12.359 Å and α' = 89°51', were determined from 666 and 12,0,0 diffraction pairs. The 666 lines were split into an asymmetrical doublet with a stronger higher-angle line. The 12,0,0 was a single line. According to Galasso et al.,[1] this rhombohedral perovskite cell is reduced to a hexagonal unit cell with the space group $P\bar{3}m1$, whose lattice constants are derived as follows:

$$a = \frac{2}{3}(a')\sin\frac{\alpha'}{2} = 5.818\ \text{Å} \quad \text{and} \quad c = a'\left[1 - \frac{4}{3}\sin^2\frac{\alpha'}{2}\right]^{1/2} = 7.154\ \text{Å}.$$

These constants are referred to the reported ones: [1] a = 5.819 Å and c = 7.127 Å.

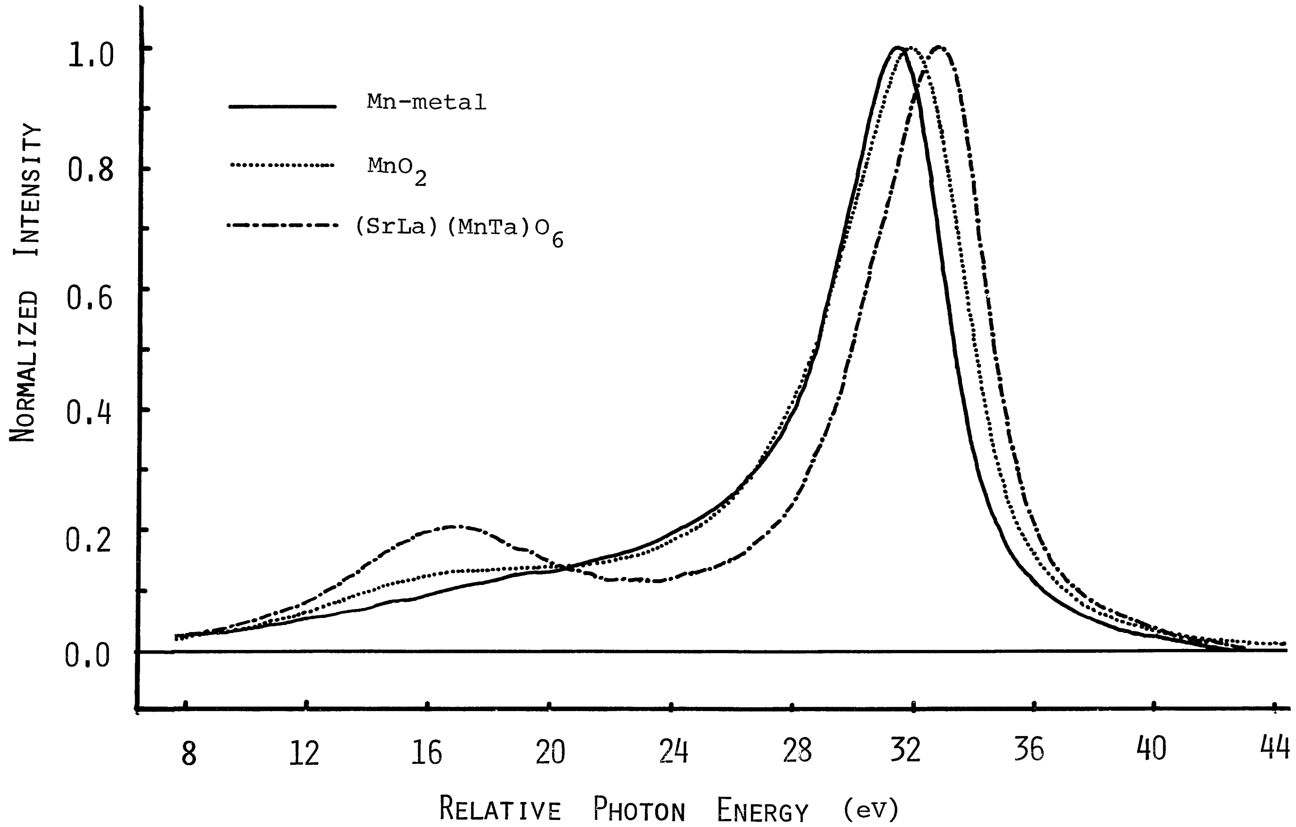

Fig.1 Line profiles of fluorescent X - ray Mn - Kβ spectra from Mn, MnO_2 and $(SrLa)(MnTa)O_6$.

In order to specify the valency state of manganese ions in the B-sites of perovskite structure ABO_3, characteristic X-rays from manganese ions in those compounds were measured with a vacuum two-crystal spectrometer equipped with Ge-(111) analyzer crystals and X-ray excitation method.[3)] Figure 1 shows profiles of the characteristic Mn-Kβ rays from Mn-metal, MnO_2 and $(SrLa)(MnTa)O_6$. Shifts in photon energy of Mn-Kβ lines from the mentioned compounds relative to that in Mn-metal were observed to be 1.06 eV for $(BaLa)(MnMo)O_6$, 1.20 eV for $(SrLa)(MnTa)O_6$, 1.25 eV for $Ba_3(MnTa_2)O_9$ and 0.96 eV for MnO(rock salt structure, green). Figure 2 shows a collation of the Mn-Kβ shifts of several Mn^{4+}-, Mn^{3+}-, and Mn^{2+}- compounds. Since the shift of Mn-Kβ line in $(BaLa)(MnMo)O_6$ is midway between those of $Ba_3(MnTa_2)O_9$ or $(SrLa)(MnTa)O_6$ and MnO, manganese ions in $(BaLa)(MnMo)O_6$ are in an Mn^{2+} state.

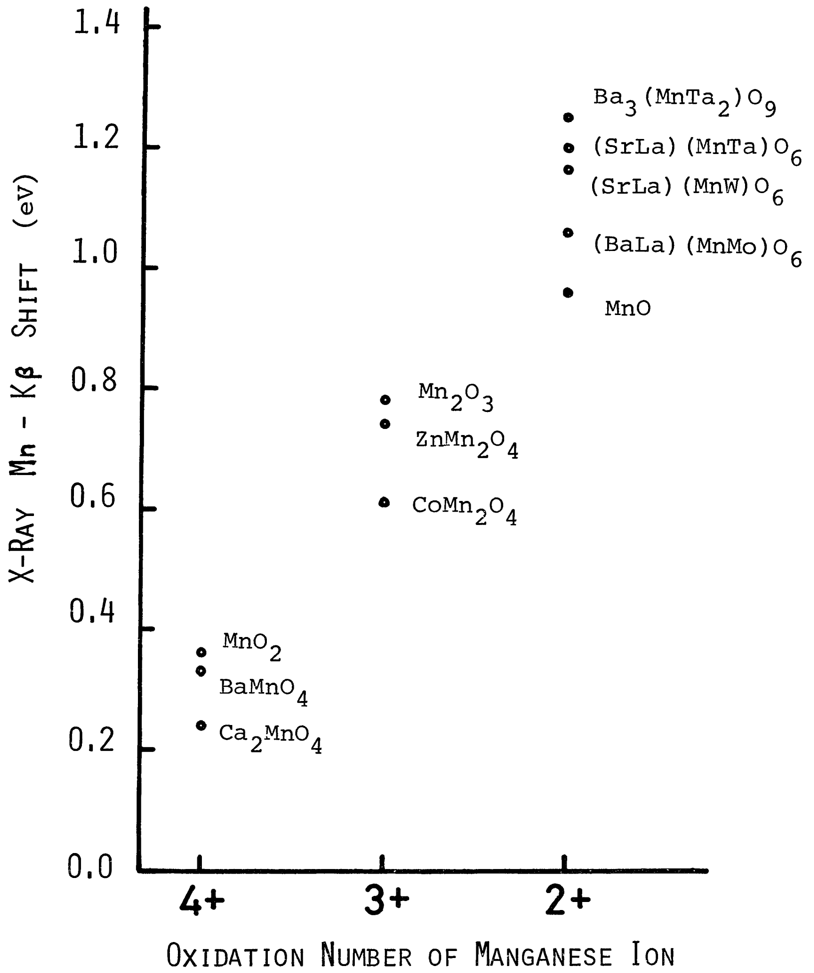

Fig.2 Mn-Kβ shifts relative to metal Mn for various Mn-compounds.

Magnetic susceptibilities of these compounds were measured with a Faraday-type magnetobalance under field-and-gradient product of $H\nabla H = 10^6 - 10^7$ Oe^2/cm. Diamagnetism of individual ions was corrected according to Selwood. 4) Figure 3 shows the $H\nabla H$ dependence of Fm, the force experiencing per formula weight of each sample, at fixed temperatures. The Fm vs. $H\nabla H$ of (SrLa)(MnTa)O_6 is linear and coincides with that of $Ba_3(MnTa_2)O_9$ at 290 K. This paramagnetic behavior is similar for (BaLa)(MnMo)O_6 at room temperature and at 328 K. However, the Fm vs. $H\nabla H$ of (BaLa)(MnMo)O_6 at 77 K is non-linear and is followed by a saturation effect. Figure 4 shows the magnetization $\sigma = \sigma_s + \chi H$ versus field H for (BaLa)(MnMo)O_6 at 77 K. Values ∇H and $H\nabla H$ for this measurement were calibrated independently by use of Ni(99.99 %) and $CuSO_4\,5\,H_2O$(99.9 %), respectively, as standards. The saturation magnetization at 77 K obtained by an extrapolation was approximately $\sigma_s = 2.5$ emu/g, which amounts to 1/17 of the expected saturation value at 0 K for the pair (Mn^{2+}, Mo^{5+}) in the colinear antiparallel spin arrangement.

Figure 5 shows reciprocal magnetic molar susceptibility $1/\chi_m$ plotted against absolute temperature T for the samples at a fixed $H\nabla H$ of $5 - 7 \times 10^6$ Oe^2/cm. (SrLa)(MnTa)O_6 and $Ba_3(MnTa_2)O_9$ obey the Curie - Weiss law above room temperature with an effective magnetic moment per Mn of $P_{eff} = 5.7\,\mu_B$. Although the observed moment is somewhat smaller than the theoretical spin-only value of Mn^{2+} ion $5.9\,\mu_B$, the $5.7\,\mu_B$ moment is presumed to come from an Mn^{2+} state in these compounds because an empirical stability of Ta^{5+} state. The shape of $1/\chi_m$ vs. T of (BaLa)(MnMo)O_6 in Fig.5 is characteristic of a ferrimagnetic substance.

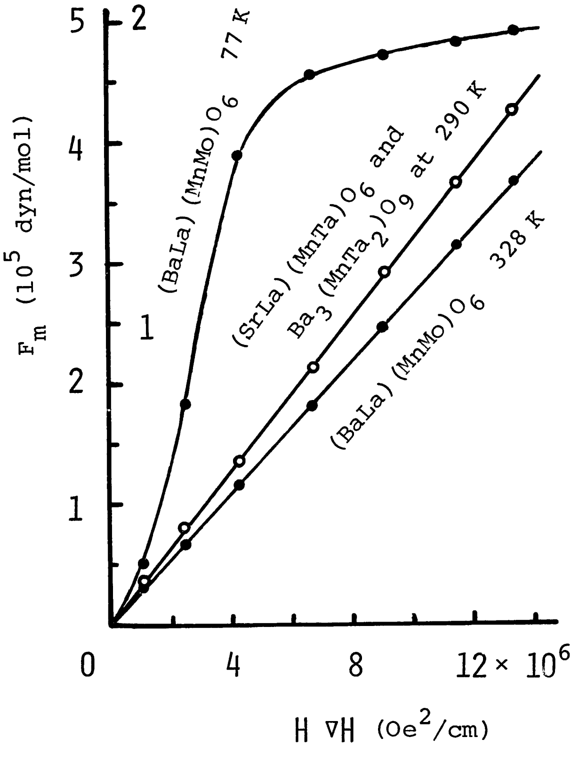

Fig.3 Force per formula weight vs. Field-and-gradient product.

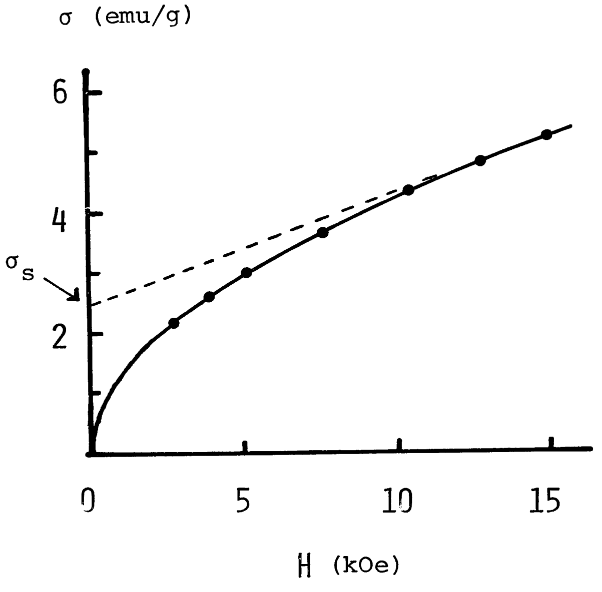

Fig.4 Magnetization vs. magnetic field for (BaLa)(MnMo)O_6 at 77 K .

Effective magnetic moment per formula of (BaLa)(MnMo)O_6, $P_{eff} = 5.9\ \mu_B$, was obtained from the linear part of $1/\chi_m$ vs. T above 800 K. The temperature dependence of magnetization σ for (BaLa)(MnMo)O_6 at the fixed values of H = 12.8 kOe and ∇H = 72.4 Oe/cm was also shown in Fig.5. Curie temperature $T_c = 120$ K of (BaLa)(MnMo)O_6 was derived from the temperature dependence of σ and $1/\chi_m$. The expected effective moments in theoretical spin-only calculations for (BaLa)(MnMo)O_6 are

$$P_{eff}(2,5) = (5.9^2 + 1.7^2)^{1/2}\ \mu_B = 6.15\ \mu_B \quad \text{for valency pair } (Mn^{2+}, Mo^{5+}) \text{ and}$$

$$P_{eff}(3,4) = (4.9^2 + 2.8^2)^{1/2}\ \mu_B = 5.65\ \mu_B \quad \text{for valency pair } (Mn^{3+}, Mo^{4+}).$$

The observed moment $P_{eff} = 5.9\ \mu_B$ from $1/\chi_m$ vs. T, however, lies midway between the calculated moments.

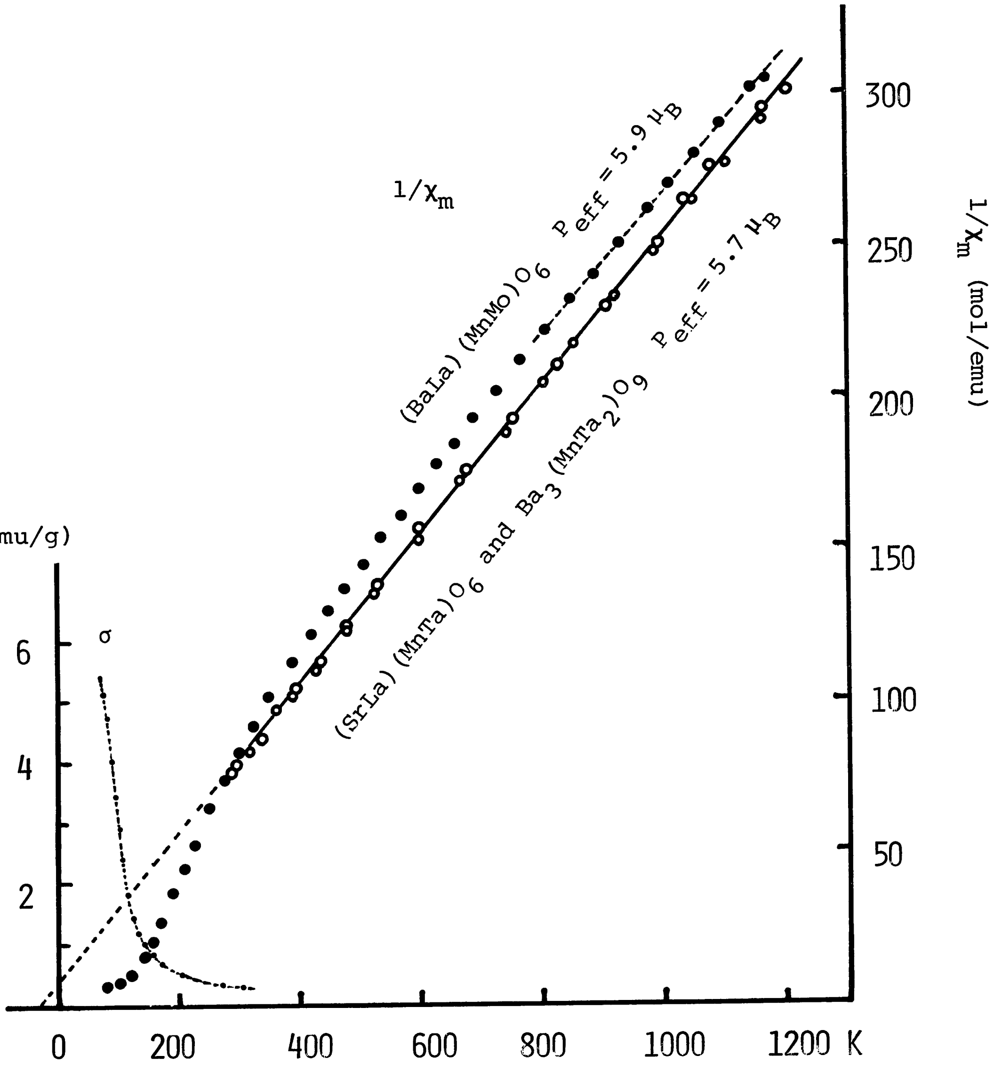

Fig.5 Reciprocal magnetic molar susceptibility versus absolute temperature for (BaLa)(MnMo)O_6, (SrLa)(MnTa)O_6 and $Ba_3(MnTa_2)O_9$.
Temperature dependence of magnetization for (BaLa)(MnMo)O_6 is shown.

However, validity of the valency pair (Mn^{2+}, Mo^{5+}) will be accounted for as follows. Empirical moment of Mn^{2+} ion in B - sites of perovskite-type oxides can be put as $P(Mn^{2+}) = 5.7\ \mu_B$, as mentioned in $(SrLa)(MnTa)O_6$ and $Ba_3(MnTa_2)O_9$, and that moment of Mo^{5+} ion as $P(Mo^{5+}) = 1.5\ \mu_B$, according to the previous work for $Ba_2(YMo)O_6$ and $Sr_2(YMo)O_6$.⁵⁾ These moments give a satisfactory agreement with the data observed:

$$P_{emp}(2,5) = (5.7^2 + 1.5^2)^{1/2}\ \mu_B = 5.9\ \mu_B .$$

Finally, the valency pair (Mn^{2+}, Mo^{5+}) in $(BaLa)(MnMo)O_6$ was verified by the following.

1) The shift of Mn - Kβ line for $(BaLa)(MnMo)O_6$ was among those of Mn^{2+}-compounds.
2) $(BaLa)(MnMo)O_6$ involved the 1:1 ordering of Mn and Mo ions and showed a ferrimagnetism. [The Mn and Mo will be disordered and χ_m will show an antiferromagnetism if the pair is (Mn^{3+}, Mo^{4+}).]
3) The magnetic moment $P_{eff} = 5.9\ \mu_B$ observed in $(BaLa)(MnMo)O_6$ was explained by the empirical moment of Mn^{2+} and Mo^{5+}.

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