

Oxygen Deficient Perovskite, $(\text{CaLa})(\text{MgMn})\text{O}_{6-x}$ Prepared Under High Oxygen Gas Pressure of 1000 Bar

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Recently we have tried to synthesize the novel perovskite with an ideal formula of $(\text{CaLa})(\text{MgMn})\text{O}_6$ under the oxygen gas pressure of 1 bar¹, but the oxygen deficient perovskite $(\text{CaLa})(\text{MgMn})\text{O}_{5.43}$ has been reproducibly prepared. It has also been proposed that manganese ions in the lattice are in the mixed valence state with major contribution of Mn(IV) and minor Mn(III) and Mn(II), which are thought to be strongly dependent upon the oxygen pressure of preparation process.

In the present study, an attention was made to prepare $(\text{CaLa})(\text{MgMn})\text{O}_{6-x}$ under the oxygen gas pressure of 1000 bar in order to stabilize Mn(IV) only in the lattice, which was characterized by powder X-ray diffraction, chemical redox titration, electron paramagnetic resonance spectroscopy and magnetic susceptibility measurement.

The perovskite $(\text{CaLa})(\text{MgMn})\text{O}_6$ was prepared from high purity CaCO_3 , La_2O_3 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and MnO_2 . Equimolar mixture was homogeneously ground in an agate mortar, pelleted and calcined at 700°C in order to decompose the carbonate and nitrate. The sample was reground, repelleted and calcined under the oxygen gas pressure of 1 bar at 850°C and 950°C for 12 hours, and finally treated under the high oxygen gas pressure² of 1000 bar at 950°C for 48 hours.

The powder X-ray diffraction pattern indicates that $(\text{CaLa})(\text{MgMn})\text{O}_{6-x}$ has a simple cubic unit cell with a lattice parameter of $a = 3.864(2)$ Å. In Table 1 the observed lattice spacings and intensities of diffraction lines are compared with those calculated. Agreement between observed and calculated intensities is quite good as shown in Table 1. Reliability factor in this calculation is close to 10%.

For a lot of compounds reported previously³ with the formula of $(\text{CaLa})(\text{BB}')\text{O}_6$ type perovskites such as $\text{BB}' = \text{MgTa}$, MgRu , MgIr , CaTa , MnMo and MnTa , the superlattice lines were found in the XRD patterns due to an ordered arrange-

Table 1. The Powder X-ray Diffraction Data for $(\text{CaLa})(\text{MgMn})\text{O}_{5.5}$ Prepared Under High Oxygen Gas Pressure of 1000 bar

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}
1	0	0	3.8643	3.8640	15	10
1	1	0	2.7317	2.7323	100	100
1	1	1	2.2298	2.2309	20	26
2	0	0	1.9329	1.9320	27	41
2	1	0	1.7267	1.7280	8	5
2	1	1	1.5772	1.5775	41	38
2	2	0	1.3660	1.3661	16	22
3	1	0	1.2222	1.2219	15	16
3	2	1	1.0324	1.0327	19	21

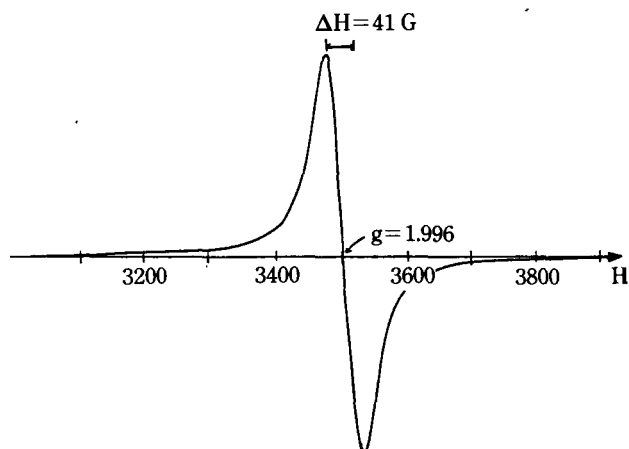


Figure 1. EPR spectrum for $(\text{CaLa})(\text{MgMn}_{0.1}\text{Mn}_{0.9})\text{O}_{5.45}$ at room temperature.

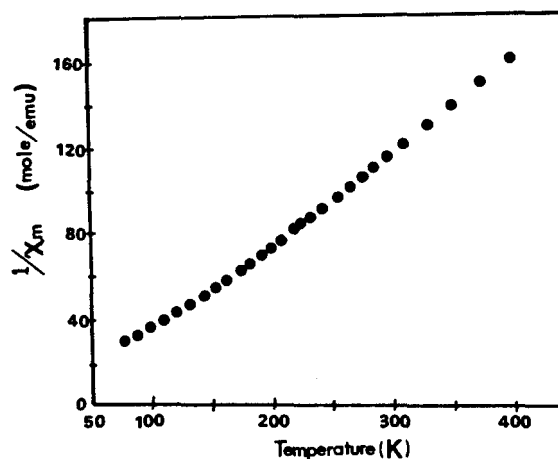


Figure 2. Temperature dependence of inverse molar susceptibility X_m^{-1} for $(\text{CaLa})(\text{MgMn}_{0.1}\text{Mn}_{0.9})\text{O}_{5.45}$.

ment of B and B' ions in the oxygen-octahedral sites. However, it can be noted that $(\text{CaLa})(\text{MgMn})\text{O}_{6-x}$ has no superlattice lines indicating the disordered arrangement of Mg and Mn cations in the B and B' sites. According to Galasso *et al.*,⁴ the differences in the valence and the size between B and B' cations are the important factors for controlling the ordering in perovskite-type compounds like $\text{A}_2(\text{BB}')\text{O}_6$ and $(\text{AA}')(\text{BB}')\text{O}_6$. Considering that the differences in charges and radii of Mg and Mn ions are not so small, the disordering might be due to the formation of oxygen vacancy and mixed valence state of manganese ions, which might reduce the additional Madelung energy. In order to form an ideal perovskite structure $(\text{CaLa})(\text{MgMn})\text{O}_6$, all the manganese ion in the lattice must be pentavalent by the charge neutrality condition. However, the average valence state of manganese was estimated to be 3.90 according to the iodometric titration, indicating the existence of oxygen deficiency and also implying that the most of manganese ions are stabilized as Mn(IV), and a few of them as Mn(III) or Mn(II). But the EPR spectrum excludes the possibility of Mn(II) ion. The EPR spectrum at room temperature shows a sharp isotropic signal with $g = 1.996$ and $\Delta H = 41$ G (Figure 1). The observed g -value of 1.996 is very close to those of Mn(IV) in the various

oxides such as $\text{SrTiO}_3^{5,6}$ ($g=1.994\pm 0.001$), calcium zirconate ($g=1.994$)⁷, $\alpha\text{-Al}_2\text{O}_3$ ($g=1.994$)⁸, $\text{SrLa}_3\text{NiMnO}_8$ ($g=1.995\pm 0.001$)⁹ and $(\text{BaLa})(\text{MgMn})\text{O}_{5.5}$ ($g=1.995$)¹⁰. There are no additional signal which might be attributed to Mn(II), Mn(V), or Mn(VI) ions. The g -values of Mn(II) in various oxides are ranging from 1.998 to 2.003¹¹ at room temperature, which is not found in our spectrum. In case of Mn(III), however, its relaxation time is so short that any signal cannot be found at room temperature. Thus, considering the results of redox titration and EPR spectrum, it is concluded that a small amount of Mn(III) ions are stabilized in $(\text{CaLa})(\text{MgMn})\text{O}_{5.45}$, which can therefore be formulated as $(\text{CaLa})(\text{MgMn}_{0.1}^{\text{III}}\text{Mn}_{0.9}^{\text{IV}})\text{O}_{5.45}$. Goodenough¹² postulated that Mn(III) hybridizes the stable d_{sp^2} lattice orbitals (favoring the square planar symmetry) and Mn(IV) the stable d^2sp^3 orbitals (favoring the octahedral symmetry). Based on this postulate, it is most probable that Mn(III) ions in $(\text{CaLa})(\text{MgMn}_{0.1}^{\text{III}}\text{Mn}_{0.9}^{\text{IV}})\text{O}_{5.45}$ favor the oxygen vacant site having square planar symmetry. In order to confirm the valence states of manganese ions, the magnetic susceptibility was measured as a function of temperature. The variation of X_m^{-1} vs T is shown in Figure 2. Diamagnetic contribution of every ion in $(\text{CaLa})(\text{MgMn})\text{O}_{5.45}$ to X_m is corrected according to Selwood¹³. $(\text{CaLa})(\text{MgMn})\text{O}_{5.45}$ follows the Curie-Weiss law above 200 K with Curie constant $C=2.32$, Weiss constant $\theta=29$ K and effective magnetic moment $\mu_{\text{eff}}=2.828 \sqrt{C}=4.31 \mu_B$. The Curie and Weiss constants were obtained from the least square fit of $X_m^{-1}=(T-\theta)/C$ in the temperature domain from 200 K to 400 K. Generally the orbital motions of 3d electrons in crystal lattice are quite quenched by ligand ions¹⁴. Thus, in the absence of magnetic interaction between 3d metal ions, the observed moments are well consistent with the spin-only values. Therefore, the effective magnetic moment of $(\text{CaLa})(\text{MgMn}_{0.1}^{\text{III}}\text{Mn}_{0.9}^{\text{IV}})\text{O}_{5.45}$ can be calculated as the followings: $\mu_{\text{eff}}^2=0.1 \times \mu_{\text{eff}}^2(\text{Mn}^{\text{III}}) + 0.90 \times \mu_{\text{eff}}^2(\text{Mn}^{\text{IV}}) = 0.1 \times (4.90)^2 + 0.9 \times (3.87)^2 = 15.9$ or $\mu_{\text{eff}} \approx 4.0 \mu_B$. Then it should be noted that the observed moment of 4.31 is somewhat larger than the spin-only value, which implies the existence of magnetic coupling between manganese ions in the crystal lattice. There might be two kinds of possible magnetic interactions in the lattice: Mn(III)-O-Mn(IV) and Mn(IV)-O-Mn(IV). According to Goodenough¹², the manganese ions can ferromagnetically coupled in the former case, and antiferromagnetically coupled in the latter case. Therefore the somewhat larger value of observed magnetic moment might result from the possible ferromagnetic interaction between Mn(III) and Mn(IV) ions in $(\text{CaLa})(\text{MgMn}_{0.1}^{\text{III}}\text{Mn}_{0.9}^{\text{IV}})\text{O}_{5.45}$, which is consistent with the positive value of the observed Weiss constant. But the antiferromagnetic coupling (Mn(IV)-O-Mn(IV)) at low temperature could not be excluded completely, because of the small positive curvature, indicating the antiferro-paramagnetic transition, in the X_m^{-1} vs T plot (Figure 2) below 200 K.

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Synthesis of $[\{\eta^6\text{-C}_6\text{H}_5\text{NPhC(O)R}'\}\text{Mn}(\text{CO})_3]\text{PF}_6$ and Its Reactivity toward Nucleophiles

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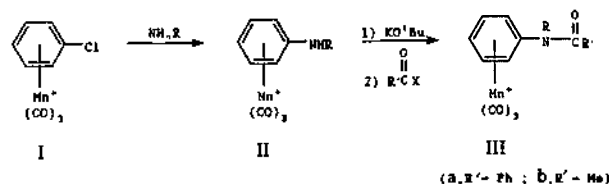
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$[(\text{Halobenzene})\text{Mn}(\text{CO})_3]^+$ is a versatile starting compound. The high reactivity of the manganese complex is utilized in the preparation of other functionally substituted arene complexes by substitution of chloride with anionic or neutral nucleophiles¹.

Several years ago, (aromatic amide)FeCp⁺ cations were made by using (haloarene)FeCp⁺ cations². However, no attempts were made to synthesize (aromatic amide)Mn(CO)₃⁺ cations. When we compared the electrophilicity of FeCp⁺ and Mn(CO)₃⁺, we expected that the (aromatic amide)Mn(CO)₃⁺ compounds would be potentially more versatile synthetic reagents. We decided to make the (aromatic amide)Mn(CO)₃⁺ and to study the reaction between (aromatic amide)Mn(CO)₃⁺ and nucleophiles. In this note, we report the formation of $[\{\eta^6\text{-C}_6\text{H}_5\text{NPhC(O)R}'\}\text{Mn}(\text{CO})_3]\text{PF}_6$ (R' = Ph and Me) and its reaction with H⁻, PhMgBr, MeMgBr, LiCH₂CN, and LiCMe₂CN.

$[\{\eta^6\text{-C}_6\text{H}_5\text{NPhC(O)R}'\}\text{Mn}(\text{CO})_3]\text{PF}_6$ was prepared according to the following scheme. The first step was reported



(a, R' = Ph; b, R' = Me)