Oxygen-Deficient Perovskite, $(CaLa)(MgMn)O_{5.43}$
Prepared Under Oxygen Gas Pressure of 1 Bar[†]

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산소 1기압하에서 합성된 산소결함 Perovskite
$(CaLa)(MgMn)O_{5.43}$의 물리화학적 특성연구

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ABSTRACT

An oxygen deficient perovskite $(CaLa)(MgMn)O_{5.43}$, with the cubic unit cell parameter of 3.826 Å, was prepared at 1150℃ for 10 hrs under the ambient oxygen gas pressure. The average oxidation state of manganese was determined to be 3.86 by the iodometric titration, so that the perovskite could be formulated as $(CaLa)$ $(MgMn_x^{II}Mn_y^{III}Mn_{1-x-y}^{IV})O_{5.43}$ $(2x+y=0.14)$. From X-ray photoelectron spectroscopy, the manganese ions in the lattice are mostly tetravalent, but two paramagnetic configurations were observed in the EPR spectrum: One sharp isotropic signal with hyperfines $(\Delta H \simeq 50$ G, $g=1.997 \pm 0.002$ and $|A|=82(4) \times 10^{-4}$ cm^{-1}) and a broad isotropic one $(\Delta H \simeq 1600$ G and $g=1.994 \pm 0.002)$, those which correspond respectively to Mn(II) and Mn(IV) ions. According to the magnetic susceptibility measurement, it follows the Curie-Weiss law from 20 K up to room temperature with $\mu_{eff}=5.23$ μ_B, which is relatively larger than spin-only value $(\mu_{eff}^{SO}=4.04$ $\mu_B)$ due to the effect of weak ferromagentic coupling. Such a result is in accord with a theory of semicovalence exchange.

요 약

격자상수 3.826 Å을 갖는 입방정계의 산소결함 perovskite $(CaLa)(MgMn)O_{6-x}(x=0.57)$가 산소 1기압하, 1150℃, 10시간의 반응에 의하여 합성되었다. 요오드 적정법에 의하면, 망간이온의 평균산화 상태는 3.86으로서 다음과 같은 일반식 $(CaLa)(MgMn_x^{II}Mn_y^{III}Mn_{1-x-y}^{IV})O_{5.43}$ $(2x+y=0.14)$으로 나타낼 수 있다. X선 광전자 분광분석법에 의하면 격자내의 망간이온이 대부분 +4라는 것을 알 수 있었으나, EPR 스펙트럼에서는 두 개의 서로 다른 paramagnetic configuration이 있음을 알 수 있었다.; 즉 한 개의 초미세 구조를 갖는 sharp한 등방성 피크($\Delta H \simeq 50$ G, $g=1.997 \pm 0.002$, $A=82(4) \times 10^{-4}$ cm^{-1})와 또다른 broad한 등방성 피크($\Delta H \simeq 1600$ G, $g=1.994 \pm 0.002$)가 관측되었으며 이들은 각각 Mn(II)와 Mn(IV) 이온에 의한 것들이다. 자화율 측정에 의하면 이 화합물은 20 K에서 상온에 이르기까지 Curie-Weiss 법칙을 따르며, 이때 관측된 유효자기 모멘트는 5.23 μ_B으로서, 스핀만 고려된 값 (4.04 μ_B)보다 다소 크다는 것을 알 수 있었다. 이러한 현상은 약강자기성 상호작용에 의한 것으로서 semicovalence exchange 이론으로써 설명할 수 있었다.

1. Introduction

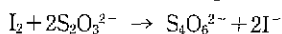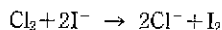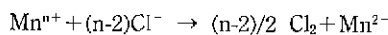The manganese(IV) is frequently found in the octa-hedral (O_h) site in a perovskite structure due to its preferential crystal field stabilization energy[1]. In some ternary or quarternary oxides with perovskite structure such as $AMnO_3$[2](A = alkaline earth metal ion), $Ca_xLa_{1-x}MnO_3$[3], or $ATi_{1-x}Mn_xO_3$[4], etc, the manganese is stabilized in the site with a tetravalent state, where the strong magnetic dipole-dipole interaction has often been observed.

Recently we have tried to stabilize the manganese(V) in a perovskite lattice with an ideal formula of (CaLa)(MgMn)O_6 using high oxygen pressure ($\sim$60 Kbar)[5], but the oxygen deficient perovskite (CaLa)($Mg_{1-x}^{IV}Mn_x^{IV}$) $O_{5.5+x}$ has been reproducibly prepared due to the disproportionation reaction of $Mn^V \rightleftharpoons Mn_{Oh}^{IV} + Mn_{Td}^{VI}$. In addition, an effort has been made to prepare the perovskite having only Mn(IV) under 1 Kbar oxygen gas pressure, but the mixed valence state of Mn(III) and Mn (IV) were observed[6]. Thus it could be concluded that the valence states of manganese ions in the perovskite lattices are quite dependent upon the synthetic condition such as the partial oxygen pressure. In the present study, our attention was made to characterize the magnetic property and the valence state of the manganese ions in (CaLa)(MgMn)O_{6-x} prepared under an ambient oxygen gas pressure, using powder X-ray diffraction, chemical redox titration, electron paramagnetic spectroscopy and magnetic susceptibility measurement.

2. Experimental

The perovskite (CaLa)(MgMn)O_{6-x} was prepared from high purity $CaCO_3$, La_2O_3, $Mg(NO_3)_2 \cdot 6H_2O$ 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. Ths sample was reground and repelleted and sintered at 850 °C for 12 hours and finally sintered at 1150°C for 10 hrs under oxygen flowing atmosphere of 1 bar. After the reaction was completed, the resultant phase was identified by powder X-ray diffraction method with a Philips-Norelco diffractometer using Ni filtered Cu-Kα radiation (λ = 1.5418 Å). The oxidation state of manganese was determined by indirect iodometric method.

After dissolution of the sample in a KI solution, the evolved free iodine was titrated by sodium thiosulfate. These procedures are summarized as follows:

$$Mn^{n+} + (n-2)Cl^- \rightarrow (n-2)/2 \; Cl_2 + Mn^{2-}$$
$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

(n$\geq$2: average oxidation state of the manganese ion)

X-ray photoelectron spectra were recorded on a 550 XPS/AES Perkin-Elmer spectrometer, where unmonochromatized Mg-Kα and Al-Kα radiation were used. The magnetic susceptibility has been measured by Faraday-type magnetobalance in the temperature range of 4.2 K and 300 K and the EPR spectrum could be obtained at 4.2 K and room temperature using Bruker-ER 200tt X-band spectrometer.

3. Results and Discussion

3.1. Crystallographic analysis

The powder X-ray diffraction pattern indicates that the perovskite (CaLa)(MgMn)O_{6-x} has a simple cubic unit cell with a = 3.823 Å. In Table 1 the observed lattice spacings and intensities of diffraction lines are compared with those calculated. The intensity calculation is based upon the assumptions that calcium and lanthanium are randomly distributed at cuboctahedral site, and also magnesium and manganese at octahedral site in the perovskite lattice. Reliability factor in this calculation is close to 12%. It should be noted that no superlattice lines are observed in the XRD pattern indicating the disordered arrangement of Mg and Mn

Table 1. The Powder X-ray Diffraction Data for (CaLa)(MgMn)$O_{5.4}$ Prepared Under Ambient Oxygen Pressure

hkl	d_{obs}(Å)	d_{cal}(Å)	I_{obs}	I_{cal}
100	3.854	3.847	13	10
110	2.720	2.720	100	100
111	2.219	2.221	20	25
200	1.923	1.924	31	40
210	1.722	1.720	3	5
211	1.569	1.571	37	39
220	1.360	1.360	13	22
221 300	1.281	1.282	2	5

cations. According to Galasso et al.[7], 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 A$_2$(BB')O$_6$ and (AA') (BB')O$_6$. Considering that the differences in charges and radii of Mg and Mn ions are not so small (a large part of Mn ions are quartet and the ionic radii of Mg^{2+} and Mn^{4-} is 0.720 and 0.530 Å, respectively[8]), the disordering might be attributed to the mixed valence state of manganese ion and formation of oxygen vacancy, which might reduce the additional Madelung energy.

3.2. Chemical analysis

In order to form an ideal stoichiometric perovskite (CaLa)(MgMn)O$_6$, all the manganese ion in the lattice must be pentavalent Mn(V) by the charge neutrality condition. However, the average valence state of manganese was estimated to be 3.86 according to the iodometric titration, indicating the existence of oxygen deficiency and also implying that a large part of manganese ions are stabilized as Mn(IV), and a few of them as Mn(III) or Mn (II). For this reason such a perovskite can be formulated as (CaLa)(MgMn)O$_{5.43}$.

3.3. Paramagnetic resonance spectroscopic study

EPR and magnetic susceptibility measurements have been carried out to confirm the oxidation state of the manganese ions. The EPR spectra at room temperature indicate the existence of two kinds of paramagnetic species in the perovskite lattice (Fig. 1). The Fig. 1(a) shows that the observed signal is a superposition of two isotropic components; one sharp signal ($\Delta H \simeq 50$ G, $g=1.997 \pm 0.002$) and a broad isotropic signal ($\Delta H \simeq 1600$ G, $g=1.994 \pm 0.002$). They might correspond respectively to Mn(II) and Mn(IV) ions. As shown in Table 2 the observed g-values are very close to those of Mn(II) and Mn(IV) ions in various oxides. Any signal corresponding to Mn(III) was not observed at 300 K and even at 4.2 K due to its very short spin-lattice relaxation time. Fig. 1(b) is an enlarged spectrum of the sharp signal appeared in a resonance range of 2700~4100 cm^{-1} of Fig. 1(a). Here we could observe the hyperfine structure clearly, which corresponds to the Mn(II). The hyperfine coupling constant is estimated as $|A| = 82(4) \times 10^{-4}$ cm^{-1}, which is well consis-
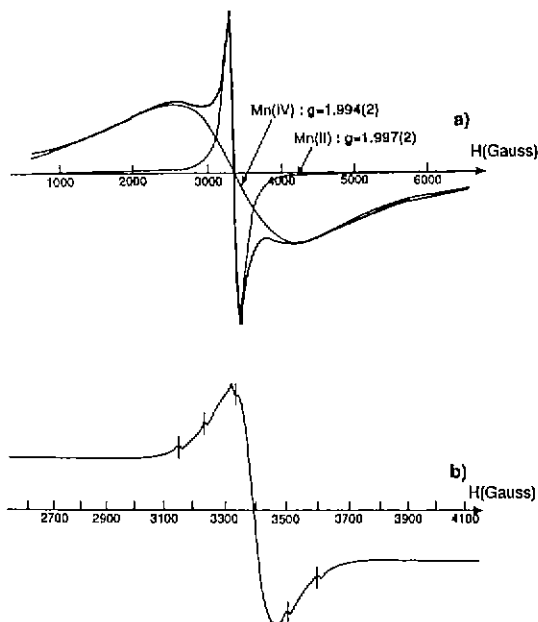

Fig. 1. EPR spectrum for (CaLa)(MgMn)O$_{5.43}$ at room temperature.
(a) It is shown that the observed signal can be separated into two Lorentzian isotropic signals. (b) The enlarged spectrum of (a), showing the hyperfine structure, which could not clearly be observed in total spectrum.

tent with those for Mn(II) ions stabilized in various oxides (Table 2). Though any signal corresponding to Mn(III) could not be detectable in EPR spectrum, an existence of a small Mn(III) fraction in the lattice should be taken into account, which will be discussed in magnetic section in detail along with the experimental confirmation[6]. Therefore we can formulate the perovskite as (CaLa)(MgMn$_x^{II}$Mn$_y^{III}$Mn$_{1-x-y}^{IV}$)O$_{5.43}$, $(2x+y=0.14)$.

3.4. X-ray photoelectron spectroscopic analysis

In order to obtain the useful information concerning the distribution of valence state of manganese ions, X.P.E spectra are obtained (Fig. 2). From the X.P.E. spectrum of Mn 2p$_{1/2}$ and 2p$_{3/2}$ electrons, it has been found that the peak shape and the binding energies (corrected by carbon 1s electron, 284.6 eV) are almost the same as those for MnO$_2$[16]. It thus appears that the content of Mn(III) and Mn(II) in the sample is

Table 2. g-values and Hyperfine Coupling Constant of Mn(IV) and Mn(II) Stabilized in Various Oxide Lattices

Compound	g(room temp)	$\mid A \mid \times 10^4$ cm^{-1}	Ref.
(CaLa)(MgMn)O$_{5.43}$	1.997(2)	82(4)	This work
	1.994(2)	—	
Mn(IV) in (CaLa)(MgMn)O$_{5.45}$	1.996	—	5, 6
Mn(IV) in SrTiO$_3$	1.994(1)	69(1)	9
Mn(IV) in CaZrO$_3$	1.994	73	10
Mn(IV) in α-Al$_2$O$_3$	1.994	70(0.5)	11
Mn(IV) in SrLa$_3$LiMnO$_8$	1.995(1)	—	12
Mn(IV) in (BaLa)(MgMn)O$_{5.5}$	1.995	—	13
Mn(II) in LiNbO$_2$	1.998(1)	78	14
Mn(II) in ZnMoO$_4$	1.999(1)	82	15
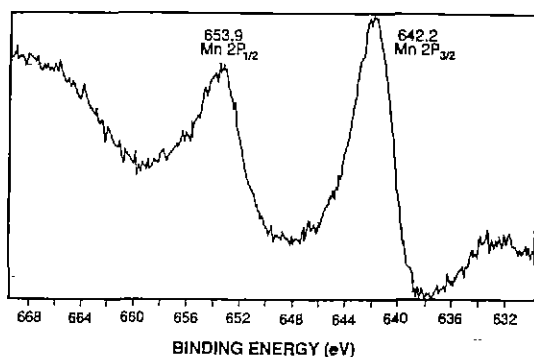
Fig. 2. X-ray photoelectron spectrum for (CaLa)(MgMn)O$_{5.43}$ in the kinetic energy region corresponding to the excitation of Mn2P$_{1/2}$ and Mn2P$_{3/2}$ orbital electrons.

small enough for the corresponding spectra to be superimposed in the Mn(IV) spectra. This fact is consistent with the result of the redox titration.

3.5. Effect of covalency and distribution of oxygen vacancy

The structural distortion, local symmetry preference of transition metal ions and abnormal magnetic properties in various oxides with spinel[17] and perovskite[3]-type structures were explained excellently by the theory of semicovalence proposed by Goodenough[18]. As will be shown later, the semicovalent model is quite appropriate for predicting the distribution of oxygen vacancy as well as explaining the magnetic property of CaLaMgMnO$_{5.43}$. Because the concept is not a fami-

liar one, a brief review for the semicovalence will be helpful for understanding the following discussion in this article.

Generally it is believed that the cation d-orbitals are perturbed by internal electric fields in solids, but there has been no serious consideration of the perturbation of the empty cation orbitals. In semicovalence model, it is pointed out that because of the strong perturbations of neighboring atoms on one another, the empty energy levels correspond to lattice orbitals, not atomic orbitals, and these lattice orbitals may have energies which are nearly degenerated with the atomic d orbitals. The most stable hybrid lattice orbitals are listed for various valence state of manganese ions in Table 3. If the most stable of the empty cation orbitals strongly overlap the full orbitals of neighboring anions, the anion p electrons may spend some of their time in the cation orbitals. The full anion p orbital contains two electrons of opposite spin. If the cation has an oriented net moment, these electrons will not have an equal probability of being shared by the cation. Because of the presence of exchange forces, that anion electron whose spin is parallel to the net cation spin will spend more time on the cation than that with anti-parallel spin. Because a single electron predominates in this bond, it is called semicovalent. Another postulate for semicovalence is that it occurs only below Curie or Neel temperature where the net cation magnetic moment is oriented. Above T$_C$ or T$_N$ there is normal coordinate covalence.

Now let us consider the distribution of oxygen vaca-

Table 3. The Most Hybrid Lattice Orbitals for Various Valence States of Manganese Ions in $CaLaMgMnO_{5.43}$, and the Types of Chemical Bonding Between the Cations and Oxygen Ion

Ions	Outer electron configuration	Empty stable hybrid orbital	Possible Mn-O bonding types	Orbitals participating in covalent bond
Mn(IV)	d^3	d^2sp^3 (octahedral)	covalent or semicovalent	$Mn^{IV}(d^2sp^3)$-$O(2p)$
			metallic-like	$Mn^{IV}(d^2sp^3)$-$O(2p)$
Mn(III)	d^4	dsp^2 (square planar)	covalent or semicovalent	$Mn^{III}(dsp^2)$-$O(2p)$
			metallic-like	—
Mn(II)	d^5	sp^3(tetrahedral)	ionic	—

ncies. Because the total content of Mn(II) and Mn(III) is so small (about 14%), it can be reasonably assumed that they must be diluted in the lattice. In addition Mn and Mg ions are distributed randomly in the octahedral site of the perovskite. Therefore, there are four possible Mn-O bonding types in this perovskite which are also listed in Table 3.

Based upon the postulate of formation of stable hybrid orbitals, it is easily deduced that Mn(IV) ions prefer the 6-coordinated octahedral site and Mn(III) ions favor the oxygen vacant site having square planar symmetry. On the other hand, Mn(II) ions have no symmetry preference because they might form less covalent bond in this perovskite. Of course, the sp^3 orbitals of Mn(II) may form covalent bonds with its four neighboring oxygen ions. As we have shown in the figure[5], an octahedral site with oxygen cis-vacancies can be transformed into a tetrahedral one through a slight displacement of manganese ion. However, in this case, the formation of $Mn^{II}(sp^3)$-$O(p)$ covalent bond on one side of an oxygen ion may weaken the orbital overlap between the $Mn^{IV}(d^2sp^3)$-$O(p)$ covalent bond on the opposite side of the anion, for the Mn(II)-O-Mn(IV) bond is no longer linear. Therefore it is concluded that Mn(II)-O bond may be less covalent in this perovskite, and the Mn(II) ion would have various local symmetries caused by oxygen vacancies. The relative energies for various symmetries around the Mn(II) ion would not greatly differ in magnitude due to the depression of covalency.

The broad E.P.R. signal for Mn(IV) ion supports the existence of strong covalency in Mn(IV)-O bond, and the sharp signal for Mn(II) ion may result from the ionic character of Mn(II)-O bond. And the doublet-like signals of hyperfine structure for Mn(II) ion might be
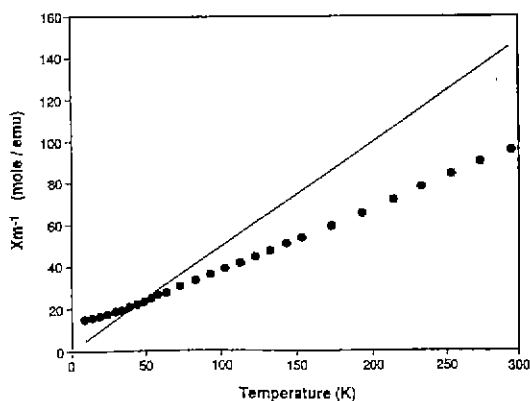
Fig. 3. Temperature dependence of inverse molar susceptibility for $(CaLa)(MgMn)O_{5.43}$.

caused by the presence of different local symmetries of the ions.

3.6. Magnetic property

In Fig. 3, the temperature dependence of inverse molar magnetic susceptibility is shown. Diamagnetic contribution of energy ion is corrected according to Selwood[19]. $(CaLa)(MgMn)O_{5.43}$ follows the Curie-Weiss law between 20 K to 300 K., with Curie constant of $C = 3.42$, Weiss constant of $\theta = -34$ K and the effective magnetic moment of $\mu_{e.f} = 2.828\sqrt{C} = 5.23$ μ_B. The C and θ were obtained from the least square fit of $\chi_m^{-1} = (T-\theta)/C$

Generally the orbital motions of 3d electrons in crystal lattice are quite quenched by ligand ions[20]. Thus, in the absence of magnetic interaction between 3d metal ions, the observed moments are well consistent with the spin-only values. Therefore, the spin-only value of the effective magnetic moment for $(CaLa)(MgMn_x^{II}Mn_y^{III}Mn_{1-x-y}^{IV})O_{5.43}$ $(2x+y=0.14)$ can be calcu-

lated as 4.04 ± 0.01 μ_B.; Consider two extreme cases, where $x=0$ and $y=0$.

(1) $x=0$ or $y=0.14$

$\mu_{eff,1}^2=0.14\times\mu_{eff}^2(Mn^{III})+0.86\times\mu_{eff}^2(Mn^{IV})=16.3$, or $\mu_{eff}=4.03$ μ_B.

(2) $y=0$ or $x=0.07$

$\mu_{eff,2}^2=0.07\times\mu_{eff}^2(Mn^{II})+0.93\times\mu_{eff}^2(Mn^{IV})=16.4$, or $\mu_{eff}=4.05$ μ_B.

Then it should be noted that the observed moment of 5.23 μ_B is quite larger than the spin-only value, implying the existence of magnetic coupling between manganese ions through the shared oxygen ions in the perovskite lattice. The solid curves in Fig. 3 are the theoretical spin-only values of inverse magnetic susceptibility when $\mu_{eff}=4.04$ μ_B is used. Note that the theoretical line intercepts the observed line at 47 K (T_I). Above T_I the observed magnetic susceptibilities are larger than those of spin-only values. On the other hand below T_I the situation is reversed. The fact, that the Weiss constant calculated from the data set above 20 K is negative, implies an antiferromagnetic interaction at low temperature domain. However, the large magnetic moment 5.23 μ_B and relatively large magnetic susceptibilities above T_I could not be understood by considering pure antiferromagnetism only. Thus it has been proposed that the anomalous magnetism may be due to small ferromagnetic domain in the lattice, and the semicovalent model can be used to explain the simultaneous occurrence of antiferro- and ferromagnetism. Here it is necessary to point out that above T_C or T_N, most of magnetic materials show paramagnetism obeying the Curie-Weiss law. However, the ferro- or

antiferromagnetic properties below T_C or T_N are still reflected even in this paramagnetic temperature region.; i.e. the ferro- and the antiferromagnetic materials still have relatively large and small magnetic susceptibilities above T_C and T_N, respectively, compared to the coupling free susceptibilities.

There might be three kinds of manganese pairs which may produce magnetic interactions in the lattice of the perovskite: Mn(IV)-O-Mn(IV), Mn(IV)-O-Mn(III), and Mn(IV)-O-Mn(II) (see Table 4). Because of the small content of Mn(II) and Mn(III) (about 14%), it can be assumed reasonably that the interactions between Mn(II) and Mn(III) can be neglected. Then major magnetic interactions in this lattice should be originated from Mn(IV)-O-Mn(IV) interaction.

Four mechanisms, known as direct exchange, double exchange[21], superexchange[22], and semicovalent exchange[18] have been used to explain the interaction between electron spins. The direct exchange tends to align the net spin on neighboring lattice elements antiparallel to each other. Double exchange requires the transfer of electrons between two kinds of ions, particularly two of the same elements but with different charges. It tends to align spins parallel to each other. Superexchange predicts that the two cations orient their spin parallel if their d-shell are less than half filled, antiparallel if the d-shells are more than half filled. The semicovalent exchange model is based upon the postulate for semicovalence discussed in the previous section. The five possible magnetic couplings between manganese ions in $CaLaMgMnO_{5.43}$ are summarized in Table 4. This exchange model predicts that if an anion p orbital forms semicovalent bond with two

Table 4. Possible Magnetic Interactions Between Manganese Ions in $CaLaMgMnO_{5.43}$.

Mn−O−Mn' bonding type	magnetic coupling type	covalency	case
Mn(IV)−O−Mn(IV)	antiferromagnetic	semicovalent on both sides	1
Mn(IV)−O−Mn(III)	antiferromagnetic	semicovalent on both sides	2
Mn(IV)−O---Mn(III)	weak ferromagnetic	semicovalent on one side only	3
Mn(IV)−O---Mn(II)	weak ferromagnetic	semicovalent on one side only	4
Mn(IV)−O---Mn(III) + Mn(III)---O−Mn(IV)	ferromagnetic	metallic-like	5

If Mn and O ions form covalent bonding, they are joined by a solid line, and if they form ionic bonding, they are joined by a dotted line.

neighboring cations on opposite side of the anion, an antiferromagnetic coupling may result in (case 1 and 2 in Table 4), and if semicovalence occurs with one cation only, the interaction between the anion and other cations is confined to direct exchange, and consequently a weak ferromagnetic coupling may occur (case 3 and 4 in Table 4). If both two neighboring Mn(IV) and Mn(III) ions are stabilized in octahedral symmetry and covalence occurs only in Mn(IV)-O bond, then the state Mn(IV)−O---Mn(III) is degenerated with the state Mn(III)−O---Mn(IV), so that below T_c double exchange takes place between the manganese ions, namely, one electron being free to jump through the anion between the two manganese ions to form a metallic-like bond (case 5). As can be seen in Table 4, the semicovalent exchange model predicts that there must be simultaneous occurrence of antiferromagnetism and ferromagnetism in $CaLaMgMnO_{5.43}$. Of course the antiferromagnetic coupling must be a major interaction due to the large content of Mn(IV)-O-Mn(IV) interaction. In the superexchange model there is no way for atoms to couple ferromagnetically in one direction, antiferromagnetically in another as it contains no anisotropy. From superexchange model, $CaLaMgMnO_{5.43}$ should be ferromagnetic. This is not consistent with the observed magnetic data. Therefore, based upon the semicovalent magnetic exchange model, the anomalous magnetic property of $CaLaMgMnO_{5.43}$ in its paramagnetic temperature region might result from the simultaneous occurrence of antiferromagntism and ferromagnetism below T_C or T_N.

4. Conclusion

An oxygen deficient perovskite $(CaLa)(MgMn)O_{5.13}$ was prepared at 1150°C under ambient oxygen gas pressure. From iodometric titration, EPR and ESCA measurements, the sample could be formulated as $(CaLa)(MgMn^{II}_xMn^{III}_yMn^{IV}_{1-x-y})O_{5.43}$ ($2x+y=0.14$). The anomalous magnetic property of the perovskite might result from the simultaneous occurence of antiferromagnetism and ferromagnetism below T_C or T_N, which can be explained by semicovalence magnetic exchange model.

Acknowledgement

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