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### A New Ordered Perovskite Oxide, (CaCe)(CaNb)O<sub>6</sub>

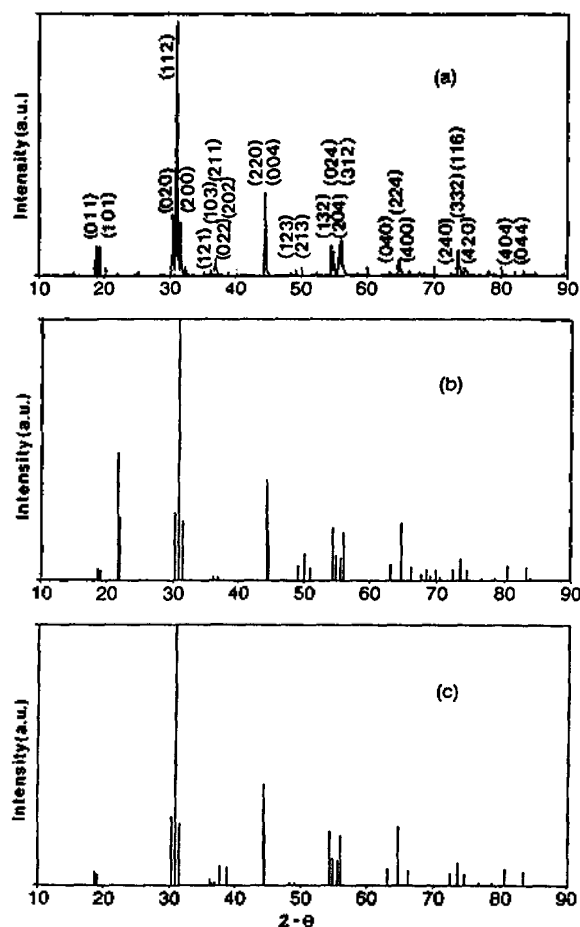
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In the perovskite type oxides like A<sub>2</sub>(BB')O<sub>6</sub> and (AA')(BB')O<sub>6</sub>, the A (or A') cations are coordinated with twelve oxygen ions and the B (or B') cations with six ones. Thus the A-site cation is normally found to be somewhat larger than the B-site one. It is also known that the A-site cations form the competing bonds with the B-site ones by sharing an oxygen ion and the bond strength of the (A-O) bonds should be influenced by the oxidation state of B-cation and the covalency of (B-O) bonds.<sup>1-4</sup> In these perovskites, the substitution of one metal ion for another may induce the evolution of crystal structure and physico-chemical properties. Recently the crystal-field dependency of magnetic property for some lanthanide ions has been studied. According to the previous studies, the octahedral<sup>5</sup> (6-coordination) and the cuboctahedral<sup>6,7</sup> (12-coordination) crystal-fields result in quite different magnetic behaviors. However, no systematic studies on the crystal-field effect for Ce<sup>3+</sup> (f<sup>1</sup>) ion in perovskite lattice have been performed as yet.

There are only a few compounds that contain cerium ion such as Ba<sub>2</sub>(CeM)O<sub>6</sub>, (M=Nb,<sup>8</sup> Ta,<sup>9</sup> Pa<sup>10</sup>), where the B-site cations have a rock-salt arrangement. But the oxidation state of cerium ion in these compounds has not been confirmed so far. Because some compounds have been reported for the formula of Ca<sub>2</sub>LnNbO<sub>6</sub> (Ln=lanthanide ions except for Ce<sup>3+</sup>), our attention was paid to preparing the new perov-

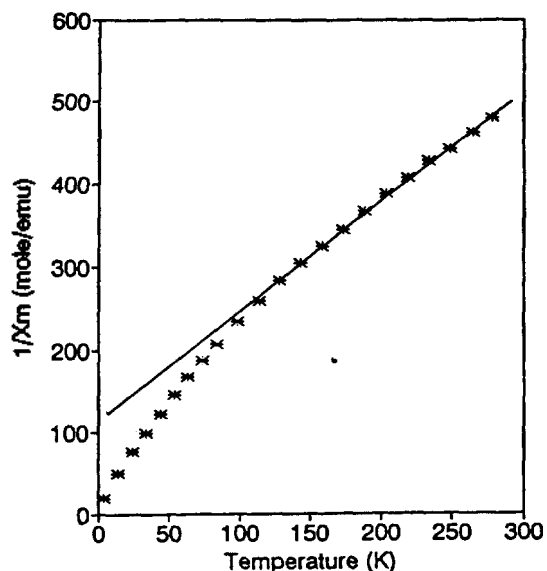


**Figure 1.** (a) The observed powder XRD pattern for (CaCe)(CaNb)O<sub>6</sub>, and the calculated patterns based upon models that, (b) only calcium ions are distributed in A-site, and cerium and niobium ions are completely ordered in B-site, (c) calcium and cerium ions are randomly distributed in A-site and calcium and niobium ions are ordered in B-site.

skite, Ca<sub>2</sub>CeNbO<sub>6</sub> (Ln=Ce<sup>3+</sup>) and performing its structural and magnetic characterizations which will be the stepping-stones for understanding the magnetic properties of Ce<sup>3+</sup> ions stabilized in the different crystal fields.

The polycrystalline sample of Ca<sub>2</sub>CeNbO<sub>6</sub> was prepared by two step solid state reactions under high temperature. At first, the stoichiometric mixture of high purity reactants of CeO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and CaCO<sub>3</sub> was well ground in an agate mortar, pelleted and pre-fired at 900°C for about 10 hours under the flowing hydrogen. Then the sample was finally fired at 1350°C for several days under the flowing hydrogen until a homogeneous product was obtained. The color of the product was yellowish orange.

The powder X-ray diffraction pattern (Figure 1(a)) indicates that Ca<sub>2</sub>CeNbO<sub>6</sub> has a monoclinically distorted perovskite structure with lattice constants of  $a_0=b_0=8.152$  Å,  $c=8.139$  Å and  $\gamma=87.7^\circ$ , which can be reduced to a body-centered orthorhombic unit cell,  $a=5.647$  Å,  $b=5.879$  Å and  $c=8.139$  Å. But in the case of Ce-perovskite (A<sub>2</sub><sup>2+</sup>CeB<sup>5+</sup>O<sub>6</sub>) where Ce<sup>3+</sup> is the largest among lanthanides and even larger than Ca<sup>2+</sup>, cerium ion could be stabilized in the A-site preferentially. Therefore two possible compounds, Ca<sub>2</sub>(CeNb)O<sub>6</sub> and



**Figure 2.** Temperature dependence of inverse molar magnetic susceptibility for  $(\text{CaCe})(\text{CaNb})\text{O}_6$ . Solid line indicates a least square fit in the temperature region obeying the Curie-Weiss law.

$(\text{Ca}^{2+}\text{Ce}^{3+})(\text{Ca}^{2+}\text{Nb}^{5+})\text{O}_6$ , could be postulated at this stage. In order to distinguish the two possible compounds, the ordering type of cations in the lattice is confirmed by calculating the theoretical X-ray diffraction intensity based on two different models, where all the atoms in the cell are assumed to be at their ideal atomic positions; 1) only the  $\text{Ca}^{2+}$  ions are distributed in the oxygen-cuboctahedral A-sites, and the  $\text{Ce}^{3+}$  and  $\text{Nb}^{5+}$  ions are completely ordered over the oxygen-octahedral B-sites (Figure 1(b)); 2) the  $\text{Ca}^{2+}$  and  $\text{Ce}^{3+}$  ions are randomly distributed in the A-sites, whereas the  $\text{Ca}^{2+}$  and  $\text{Nb}^{5+}$  ions are completely ordered over the B-sites, and all the other ions are located at their ideal positions in the perovskite structure (Figure 1(c)). As can be seen clearly in Figure 1, the observed X-ray intensity pattern (Figure 1(a)) is very well consistent with that based on the assumption 2) (Figure 1(c)). Therefore it is concluded that the cerium ions are stabilized in the oxygen cuboctahedral A-sites in the perovskite lattice, so that it can be correctly formulated as  $(\text{CaCe})(\text{CaNb})\text{O}_6$  instead of  $\text{Ca}_2(\text{CeNb})\text{O}_6$ .

Although the cationic distribution in the lattice could be clearly determined from the XRD intensity calculation but the exact oxidation state of cerium ion ( $\text{Ce}^{3+}$  or  $\text{Ce}^{4+}$ ) is not clear due to almost the same atomic scattering factors of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ . However, considering the effective ionic radii of  $\text{Ce}^{3+}$  (1.34 Å) and  $\text{Ce}^{4+}$  (1.14 Å) in the cuboctahedral site by Shannon,<sup>12</sup> it is expected that  $\text{Ce}^{3+}$  ion occupies preferentially the A-site.

In order to confirm the oxidation state and to characterize the magnetic behavior of cerium ion, the magnetic susceptibility was measured as a function of temperature. The variation of  $\chi_m$  vs.  $T$  is shown in Figure 2. Diamagnetic contribution of every ion to  $\chi_m$  was corrected according to Selwood.<sup>13</sup>

The compound follows the Curie-Weiss law above 100 K with Curie constant  $C=0.744$ , Weiss constant  $\theta=-81.7$  K and the effective magnetic moment  $\mu_{\text{eff}}=2.828\sqrt{C}\mu_B=2.44\mu_B$ , which is well agreed with the free ion value of  $\text{Ce}^{3+}$

( $4f^1$ ),  $\mu_{\text{free ion}}=g_f\sqrt{J(J+1)}=2.54\mu_B$ . The Curie and Weiss constants were obtained from the least square fit of  $\chi_m=(T-\theta)/C$  in the temperature domain from 100 K to 300 K. It should be noted that below 100 K the compound exhibits a strong deviation from the Curie-Weiss law. Such an anomalous magnetic behavior has also been observed for some other  $\text{Ce}^{3+}$ -containing compounds like  $\text{CeScO}_3$ ,<sup>6</sup>  $\text{CeBa}_2\text{Cu}_3\text{O}_7$ ,<sup>7</sup>  $\text{CeVO}_3$ ,<sup>14</sup> and  $\text{CeF}_3$ ,<sup>15</sup> etc.

Magnetic moment for  $\text{Ce}^{3+}$  ( $f^1$ ) ion can be affected by the spin-orbit interaction, the crystal-field and the magnetic dipole interaction. Since the  $f$  electrons are shielded from the perturbing effect of crystal-field by the outer-lying  $s$  and  $p$  electrons, the crystal-field effect on the paramagnetic ion is weak and incapable of disturbing the spin-orbit coupling. Thus the states ( $^2F_{7/2}$  for  $\text{Ce}^{3+}$ ) other than the ground state ( $^2F_{5/2}$  for  $\text{Ce}^{3+}$ ) are thermally inaccessible and the ions are essentially free as far as the electrons are concerned.<sup>16</sup> On the other hand, the lower the temperature becomes, the more significant the crystal-field effect will become, and the  $(J+1)$ -fold degeneracy of  $\text{Ce}^{3+}$  free ion is lifted by the crystal-field into some Kramers doublets.<sup>17</sup> Thus it is not surprising that there is a deviation from the Curie-Weiss law at low temperature. Though the magnetic dipole interaction may induce a deviation from the Curie-Weiss law, no evidence for the magnetic dipole interaction on this system was found.

Therefore it can be concluded that the anomalous magnetic property of  $(\text{CaCe})(\text{CaNb})\text{O}_6$  might result from the increase of the crystal-field at low temperature.

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## Electrochemical Studies on the Reduction of Dioxygen by Hexaammineruthenium(II) at High pH

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Recently Anson *et al.*, introduced a new amperometric mode with disk electrode rotated at constant rate and held at constant potential to investigate the reduction of dioxygen by hexaammineruthenium(II) while they were studying the first example of a preactivation catalytic mechanism at a polymer-coated electrode of three components.<sup>1</sup> The method has been since then advantageously applied for the kinetic studies of redox catalysis.<sup>2,3</sup> We thought that this new electrochemical mode would be useful as one method compensating for or excelling other, *e.g.*, spectrophotometric or magnetic resonance, methods to investigate the kinetics of redox reactions in homogeneous solutions and employed it here to investigate the redox reaction between dioxygen and hexaammineruthenium(II) from pH 1 to pH 12 where spectrophotometric studies were not perfected.

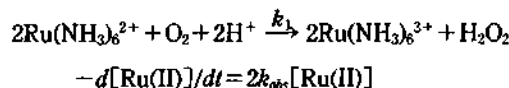
The original spectrophotometric studies of the redox reaction between dioxygen and hexaammineruthenium(II) were initiated by Taube *et al.*,<sup>4</sup> who recognized the fact that Ru(II) among metal ions in the 2+ oxidation state was unique in being the only one forming a series of substitution-inert octahedral complexes,<sup>6</sup> and were extremely carefully and beautifully performed by following the decrease in absorbance at 250 nm where Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> ( $\epsilon_{250}$  540 M<sup>-1</sup>cm<sup>-1</sup>) is oxidized to Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ( $\epsilon_{250}$  300 M<sup>-1</sup>cm<sup>-1</sup>). The results have been believed reliable<sup>1-3</sup> but their studies were limited to the reaction in acidic medium up to pH 6.05. In addition, Taube *et al.*, first investigated the reaction in the acidic medium mainly at low temperatures and reported the bimolecular rate constant 126 M<sup>-1</sup>s<sup>-1</sup> at pH 5.44 and 25.5°C,<sup>4</sup> and later presented a corrected value 63 M<sup>-1</sup>s<sup>-1</sup> at the latter conditions.<sup>5</sup> Thus it was required to have the redox reaction examined at high pH over a decade. In this Note we wish to report the results on kinetic studies of the redox reaction at room temperature up to pH 12 from pH 1 using the amperometric method at rotating disk electrode.

Hexaammineruthenium(III) chloride was prepared by a slight modification of literature procedure.<sup>7-9</sup> Hexaammineruthenium(II) chloride prepared by following the literature method<sup>8</sup> in this laboratory was found to be usually impure

partly because of the oxidation by dioxygen in aqueous solution which is the reaction medium for synthesis and was completely oxidized to be separated as the oxidized form Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> by repeated recrystallization procedure in the air. Electronic absorption spectra were in agreement with the literature and the elemental analysis (Korea Basic Science Center) gave N=26.92% (27.14% calc). Diffusion coefficient of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> measured from the Levich slope of rotating disk voltammograms at several different rotation rates (Pine AFMSRX with RDE4) was 5.4×10<sup>-6</sup> cm<sup>2</sup>/s, which is in good agreement with the value 5.48×10<sup>-6</sup> cm<sup>2</sup>/s reported by Wightman *et al.*<sup>10</sup> Solution was buffered with hydrochloric acid (pH 1-2), phthalate (pH 3-4), acetate (pH 4-5), phosphate (pH 6-8), carbonate (pH 9-11) and sodium hydroxide (pH 12) and contained 0.1 M NaCl. Laboratory distilled water was further purified by passage through Millipore system. All experiments were performed in the electrochemical cell thermostated at 22±1°C.

The method introduced by Anson *et al.*,<sup>1</sup> was employed to investigate the reaction. Solution of hexaammineruthenium(II) was prepared by reduction of hexaammineruthenium(III) with zinc amalgam under nitrogen atmosphere. This procedure typically took an hour.<sup>9</sup> The kinetics of the reaction between Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and O<sub>2</sub> was followed under pseudo-first-order conditions by means of a glassy carbon rotating disk electrode after aliquot of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> was syringed into an air-saturated solution, where the electrode was rotated at 3600 rpm. Air from a gas dispersion tube was passed through the solution throughout each run to ensure that the concentration of O<sub>2</sub> remained constant. The electrode potential was maintained at +0.5 V where the oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> to Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> produced a limiting current proportional to the time-dependent concentration of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>. No significant contributions to the current at this potential observed from the solution containing O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> only.

Figure 1 shows a trace of the current for the oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> at a rotating disk electrode in a solution saturated with air and the corresponding plot of ln(current/ $\mu$ A) vs. time. The magnitude of the current produces a continuous measure of the concentration of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and the linear semi-logarithmic plot confirms that the reduction of O<sub>2</sub> by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> is first-order with respect of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>.<sup>1-6</sup>



Since the redox reaction is also known to be first-order with respect to O<sub>2</sub>,<sup>4,5</sup> the linear slope 3.8×10<sup>-2</sup> s<sup>-1</sup> gives rise to a second-order rate constant of 68 M<sup>-1</sup>s<sup>-1</sup> under the present experimental conditions ([O<sub>2</sub>]=0.28 mM and pH 5.5). The measured value of the rate constant is in good agreement with the 63 M<sup>-1</sup>s<sup>-1</sup> value by Taube *et al.*,<sup>4,5</sup> indicating that the present amperometric method with disk electrode rotated at the constant rate 3600 rpm and held at the constant potential +0.5 V is a reliable technique to investigate the kinetics of the reaction as was first demonstrated at pH 4.5 by Anson *et al.*<sup>1-3</sup>

The procedure is applied to the reaction in the medium from pH 1 up to pH 12 and the results are shown in Figure 2. It is interesting to observe that the bimolecular rate con-