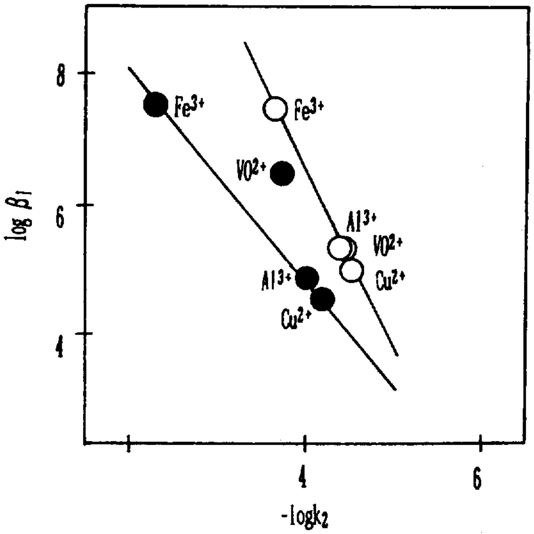

Figure 3. Negative logarithm of k_2 aganist logarithm of first formation constant for metal ion oxalate (●) and malonate complexes (○).

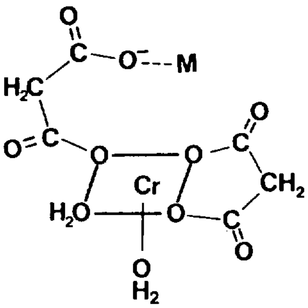

Figure 4. Proposed activated complex in the metal ion catalyzed aquation pathway of $Cr(C_3H_2O_4)_2(H_2O)_2^-$.

and Al^{3+} seems to be quite similar to that of Fe^{3+}-catalyzed aquation previously reported.[15] In previous studies[7,15] of acid catalyzed and Fe^{3+}-catalyzed aquations of these complexes, proton or Fe^{3+} are assumed to make a direct attack on the oxygen atom of oxalate or malonate,[15] forming five coordinated intermediate with only one end of oxalate or malonate bound to chromium (see Figure 4). The role of metal ions is either to help to break the first chromium-oxygen bond and then to help to break the second one or simply to help chelate ring opening.

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Carbonylation of Bromobenzenes having Aldehyde or Protected Aldehyde Groups Catalyzed by Cobalt Carbonyl(I)

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The metal-catalyzed carbonylation of aryl halides is being currently used for many chemicals.[1] Mainly of these, the carbonylation of aryl halides catalyzed by cobalt carbonyl species is successful under mild conditions (room temperature and one atmospheric pressure of carbon monoxide). Many applications were reported by us on the carbonylation of benzal halides (X=Cl, Br),[2-5] halo(halomethyl)benzenes,[6-8]

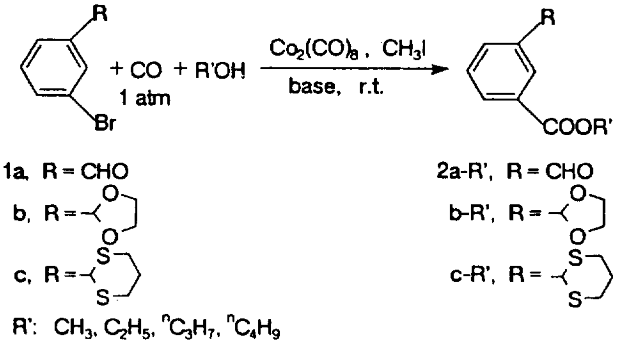
Table 1. Base Effect on the Carbonylation of 3-Bromobenzaldehyde to Ethyl 3-Formylbenzoate Catalyzed by Cobalt Carbonyl[a]

Base	(mmol)	Time[b]	Yield[c]
K_2CO_3	(10)	5	88
K_2CO_3	(5)	8	68
NaOEt	(10)	3	66
CH_3COONa	(5)	3	56
LiOH	(10)	5	46
KOH	(10)	5	14

[a] 3-Bromobenzaldehyde (0.38 g, 2.0 mmol), CH_3I (0.71 g, 5.0 mmol), $Co_2(CO)_8$ (0.034 g, 0.1 mmol), EtOH (20 m*l*), and base were stirred under CO (1 atm) at room temperature. [b] CO absorption is ceased at that time. [c] Isolated yield.

and bis(halomethyl)benzenes[9,10] using cobalt, iron, and palladium complexes at room temperature under one atmospheric pressure of carbon monoxide. However, studies on the carbonylation of aryl halides having other reactive functional groups are rare. We wish to report herein a facile method for cobalt-catalyzed carbonylation of bromobenzenes having aldehyde and protected aldehyde groups.

The carbonylation of 3-bromobenzenes having aldehyde or protected aldehyde groups was conveniently catalyzed in alcohol by dicobalt octacarbonyl in the presence of iodomethane. But, in the absence of iodomethane, this reaction did not proceed at all.



Treatment of 3-bromobenzaldehyde with CH_3I, base, ethanol in the presence of a catalytic amount of $Co_2(CO)_8$ under the atmospheric pressure of carbon monoxide at room temperature gave the corresponding ethyl 3-formylbenzoates in good yields.

Table 1 shows that the product yields depend significantly on bases employed. Potassium carbonate served best among the bases used. Using 5 mmol of potassium carbonate, the yield of ethyl 3-formylbenzoate was reduced compared with 10 mmol of potassium carbonate. Uses of sodium ethoxide, sodium acetate, lithium hydroxide, and potassium hydroxide gave gradually decreased yield of ethyl 3-formylbenzoate. But potassium bicarbonate was inefficient for the present carbonylation. As the results, potassium carbonate might be used as uni-valent base or potassium bicarbonate might be incapable activating catalyst. And, sodium carbonate, sodium bicarbonate, triethylamine, and calcium hydroxide were also inefficient to the present reaction. In case of strong base such as sodium ethoxide, Cannizzaro reaction occurs in a small extents to give 3-bromobenzyl alcohol, which was checked by the GC-Mass spectroscopy.

Table 2. Carbonylation 3-Bromobenzenes having Aldehyde or Protected Aldehyde Groups to 3-Substituted Alkyl Benzoates Catalyzed by Cobalt Carbonyl[a]

Reactant 1	Alcohol R'OH	Product 2-R'	Yield[b] (%)
1a	CH_3OH	**2a**-CH_3	65
1a	C_2H_5OH	**2a**-C_2H_5	88
1a	$^nC_3H_7OH$	**2a**-$^nC_3H_7$	80
1a	$^nC_4H_9OH$	**2a**-$^nC_4H_9$	60
1b	CH_3OH	**2b**-CH_3	96
1b	C_2H_5OH	**2b**-C_2H_5	97
1b	$^nC_3H_7OH$	**2b**-$^nC_3H_7$	92
1b	$^nC_4H_9OH$	**2b**-$^nC_4H_9$	91
1c	CH_3OH	**2c**-CH_3	33
1c	C_2H_5OH	**2c**-C_2H_5	40
1c	$^nC_3H_7OH$	**2c**-$^nC_3H_7$	26
1c	$^nC_4H_9OH$	**2c**-$^nC_4H_9$	36

[a] 3-Bromobenzaldehyde (0.38 g, 2.0 mmol), CH_3I (0.71 g, 5.0 mmol), $Co_2(CO)_8$ (0.034 g, 0.1 mmol), alcohol (20 m*l*), K_2CO_3 (1.50 g, 10.0 mmol) were stirred under CO (1 atm) at room temperature. [b] Isolated yield.

Using potassium carbonate as base and catalyst activator, several alcohols were successively applied into the present reaction (Table 2). Methanol gave methyl 3-formylbenzoate in 65% yield. The higher alcohols gave the lower yields of the corresponding alkyl 3-formylbenzoates and were required the longer reaction time for the cease of the absorption of carbon monoxide. Such trends might be explained in terms of the solubility of K_2CO_3 in the corresponding alcohols. The diversity of methanol might be its high nucleophilicity. In cases of branched alcohols such as ^{i}propanol and ^{t}butanol, the reactions do not proceed.

2-(3-bromophenyl)-1,3-dioxolane was carbonylated to the corresponding 2-(3-carboalkoxyphenyl)-1,3-dioxolanes in excellent yields.

2-(3-Bromophenyl)-1,3-dithiane can also be carbonylated, although chemical yields were not great due to sulfur group known as the catalyst poisoner. In case of ^{n}propanol, 2-(3-acetylphenyl)-1,3-dithiane was observed in a small amount. And cleavage of thioether linkage was observed in a trace amount.

The reaction mechanism is well known according to published results.[7,8,11]

Experimental

A mixture of 3-bromobenzaldehyde (0.49 g, 2.0 mmol), anhydrous potassium carbonate (1.40 g, 10.0 mmol), absolute ethanol (20 m*l*), iodomethane (0.71 g, 5.0 mmol), and dicobalt octacarbonyl (0.034 g, 0.10 mmol) was stirred under the atmospheric pressure of carbon monoxide at room temperature for 5 hours. During reaction, *ca.* 180 m*l* of carbon monoxide was absorbed. After purging carbon monoxide, the mixture was filtered through the short column (silica gel, 5 cm, ether), concentrated, and purified by the preparative thin layer chromatography (silica gel, ethyl acetate : hexane=1 : 10) to give ethyl 3-formylbenzoate (R_f=0.27, R_f=0.44 using ethyl acetate : hexane=3 : 10, 0.29 g, 88%). 3-Bromobenzaldehyde (0.036 g, 10%) was recovered. 2-(3-Bromophenyl)-1,3-dioxolane and 2-(3-bromophenyl)-1,3-dithiane were also similaryl carbonylated.

Analytical data of alkyl formylbenzoates were as follows

Methyl 3-formylbenzoate. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 3.98 (s, 3H CH$_3$), 7.66 (t, 1H, J=8 Hz, aromatic H-5), 8.13 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.33 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.56 (t, 1H, J=2 Hz, aromatic H-2), 10.17 (s, 1H, CHO); mass (m/e) 165 (7), 164 (M$^+$, 74), 163 (29), 133 (100), 105 (60), 77 (44), 51 (46), 50 (36); IR (ν_{CO}) 1728 and 1704 cm^{-1}.

Ethyl 3-formylbenzoate. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 1.41 (t, 3H, J=7 Hz, CH$_3$), 4.36 (q, 2H, J=7 Hz, CH$_2$), 7.56 (t, 1H, J=8 Hz, aromatic H-5), 8.01 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.24 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.40 (t, 1H, J=2 Hz, aromatic H-2), 10.06 (s, 1H, CHO); mass (m/e) 179 (<1), 178 (M$^+$, 9), 177 (3), 150 (14), 149 (25), 133 (100), 105 (32), 77 (29), 51 (34), 50 (23); IR (ν_{CO}) 1721 and 1705 cm^{-1}.

^{n}Propyl 3-formylbenzoate. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 1.04 (t, 3H, J=7 Hz, CH$_3$), 1.81 (m, 2H, CH$_2$), 4.33 (t, 2H, J=6 Hz, CH$_2$), 7.65 (t, 1H, J=8 Hz, aromatic H-5), 8.13 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.34 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.55 (t, 1H, J=2 Hz, aromatic H-2), 10.15 (s, 1H, CHO); mass (m/e) 152 (6), 151 (82), 149 (29), 133 (100), 105 (29), 77 (21), 51 (19); IR (ν_{CO}) 1720 and 1699 cm^{-1}.

^{n}Butyl 3-formylbenzoate. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 0.98 (t, 3H, J=7 Hz, CH$_3$), 1.66 (m, 4H, (CH$_2$)$_2$), 4.36 (t, 2H, J=6 Hz, CH$_2$), 7.65 (t, 1H, J=8 Hz, aromatic H-5), 8.13 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.34 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.55 (t, 1H, J=2 Hz, aromatic H-2), 10.13 (s, 1H, CHO); mass (m/e) 164 (2), 161 (6), 152 (50), 151 (74), 149 (15), 133 (100), 105 (36), 77 (35), 56 (51), 51 (34); IR (ν_{CO}) 1722 and 1705 cm^{-1}.

Analytical data of 2-(3-carboalkoxyphenyl)-1,3-dioxolanes were as follows

2-(3-Carbomethoxyphenyl)-1,3-dioxolane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 3.93 (s, 3H, CH$_3$), 4.08 (s, 4H, (CH$_2$)$_2$), 5.87 (s, 1H, CH), 7.47 (t, 1H, J=8 Hz, aromatic H-5), 7.73 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.10 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.21 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 208 (M$^+$, 15), 207 (100), 193 (15), 177 (36), 163 (82), 149 (42), 136 (23), 135 (23), 133 (25), 119 (21), 105 (59), 77 (32), 73 (88), 45 (40); IR (ν_{CO}) 1717 cm^{-1}.

2-(3-Carboethoxyphenyl)-1,3-dioxolane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 1.36 (t, 3H, J=7 Hz, CH$_3$), 4.07 (s, 4H, (CH$_2$)$_2$), 4.40 (q, 2H, J=7 Hz, CH$_2$), 5.85 (s, 1H, CH), 7.45 (t, 1H, J=8 Hz, aromatic H-5), 7.70 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.10 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.20 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 223 (<1), 222 (M$^+$, 8), 221 (53), 193 (21), 177 (57), 149 (42), 105 (36), 77 (16), 73 (100), 45 (38); IR (ν_{CO}) 1717 cm^{-1}.

2-(3-Carbo-^{n}propoxyphenyl)-1,3-dioxolane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 1.00 (t, 3H, J=7 Hz, CH$_3$), 1.73 (m, 2H, CH$_2$), 4.10 (s, 4H, (CH$_2$)$_2$), 4.29 (q, 2H, J=6 Hz, CH$_2$), 5.86 (s, 1H, CH), 7.46 (t, 1H, J=8 Hz, aromatic H-5), 7.73 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.08 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.20 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 236 (M$^+$, 6), 233 (48), 193 (29), 191 (15), 177 (38), 149 (69), 105 (38), 77 (21), 73 (100), 45 (36); IR (ν_{CO}) 1717 cm^{-1}

2-(3-Carbo-^{n}butoxyphenyl)-1,3-dioxolane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 0.98 (t, 3H, J=7 Hz, CH$_3$), 1.50 (m, 4H, (CH$_2$)$_2$), 4.10 (s, 4H, (CH$_2$)$_2$), 4.26 (q, 2H, J=6 Hz, CH$_2$), 5.87 (s, 1H, CH), 7.48 (t, 1H, J=8 Hz, aromatic H-5), 7.74 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.13 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.20 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 250 (M$^+$, 8), 249 (46), 193 (32), 177, (32), 149 (67), 105 (32), 73 (100); IR (ν_{CO}) 1717 cm^{-1}

Analytical data of 2-(3-carboalkoxyphenyl)-1,3-dithianes were as follows

2-(3-Carbomethoxyphenyl)-1,3-dithiane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 2.06 (m, 2H, CH$_2$), 2.90 (m, 4H, (CH$_2$)$_2$), 3.93 (s, 3H, CH$_3$), 5.17 (s, 1H, CH), 7.42 (t, 1H, J=8 Hz, aromatic H-5), 7.67 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.00 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.13 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 255 (13), 254 (M$^+$, 100), 223 (23), 222 (51), 181 (17), 179 (42), 149 (63), 121 (42), 119 (19), 105 (38), 77 (32), 74 (46); IR (ν_{CO}) 1723 cm^{-1}

2-(3-Carboethoxyphenyl)-1,3-dithiane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 1.40 (t, 3H, J=7 Hz, CH$_3$), 2.06 (m, 2H, CH$_2$), 2.90 (m, 4H, (CH$_2$)$_2$), 4.36 (q, 2H, J=7 Hz, CH$_2$), 5.17 (s, 1H, CH), 7.43 (t, 1H, J=8 Hz, aromatic H-5), 7.73 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.03 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.15 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 270 (8), 269 (15), 268 (M$^+$, 100), 223 (34), 222 (59), 194 (69), 166 (44), 165 (36), 149 (87), 121 (65), 119 (36), 105 (46), 77 (51), 74 (61), 45 (97); IR (ν_{CO}) 1717 cm^{-1}

2-(3-Carbo-^{n}propoxyphenyl)-1,3-dithiane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 1.03 (t, 3H, J=7 Hz, CH$_3$), 1.60-2.20 (m, 4H, (CH$_2$)$_2$), 2.93 (m, 4H, (CH$_2$)$_2$), 4.24 (t, 2H, J=6 Hz, CH$_2$), 5.03 (s, 1H, CH), 7.43 (t, 1H, J=8 Hz, aromatic H-5), 7.73 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.03 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.15 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 284 (11), 283 (17), 282 (M$^+$, 100), 223 (34), 222 (51), 208 (34), 166 (80), 165 (34), 149 (53), 121 (42), 119 (27), 105 (38), 77 (29), 74 (48), 45 (53); IR (ν_{CO}) 1717 cm^{-1}

2-(3-Carbo-^{n}butoxyphenyl)-1,3-dithiane. Colorless oil; ^{1}H-NMR (CDCl$_3$) δ 1.02 (t, 3H, J=7 Hz, CH$_3$), 1.60-2.20 (m, 6H, (CH$_2$)$_3$), 2.93 (m, 4H, (CH$_2$)$_2$), 4.28 (t, 2H, J=6 Hz, CH$_2$), 5.03 (s, 1H, CH), 7.43 (t, 1H, J=8 Hz, aromatic H-5), 7.73 (dt, 1H, J=8 and 2 Hz, aromatic H-4), 8.03 (dt, 1H, J=8 and 2 Hz, aromatic H-6), 8.15 (t, 1H, J=2 Hz, aromatic H-2); mass (m/e) 297 (19), 296 (M$^+$, 100), 223 (11), 222 (38), 221 (82), 167 (34), 166 (96), 165 (39), 149 (62), 121 (52), 119 (36), 105 (62), 77 (36), 74 (65), 45 (65), 41 (78); IR (ν_{CO}) 1717 cm^{-1}

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A New Ordered Perovskite Oxide, $(CaCe)(CaNb)O_6$

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In the perovskite type oxides like $A_2(BB')O_6$ and $(AA')(BB')O_6$, 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.[1-4] 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[5] (6-coordination) and the cuboctahedral[6,7] (12-coordination) crystal-fields result in quite different magnetic behaviors. However, no systematic studies on the crystal-field effect for Ce^{3+} (f^1) ion in perovskite lattice have been performed as yet.

There are only a few compounds that contain cerium ion such as $Ba_2(CeM)O_6$, (M=Nb,[8], Ta,[9] Pa[10]), 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_2LnNbO_6 (Ln=lanthanide ions except for Ce^{3+}), our attention was paid to preparing the new perovskite, Ca_2CeNbO_6 (Ln=Ce^{3+}) and performing its structural and magnetic characterizations which will be the stepping-stones for understanding the magnetic properties of Ce^{3+} ions stabilized in the different crystal fields.

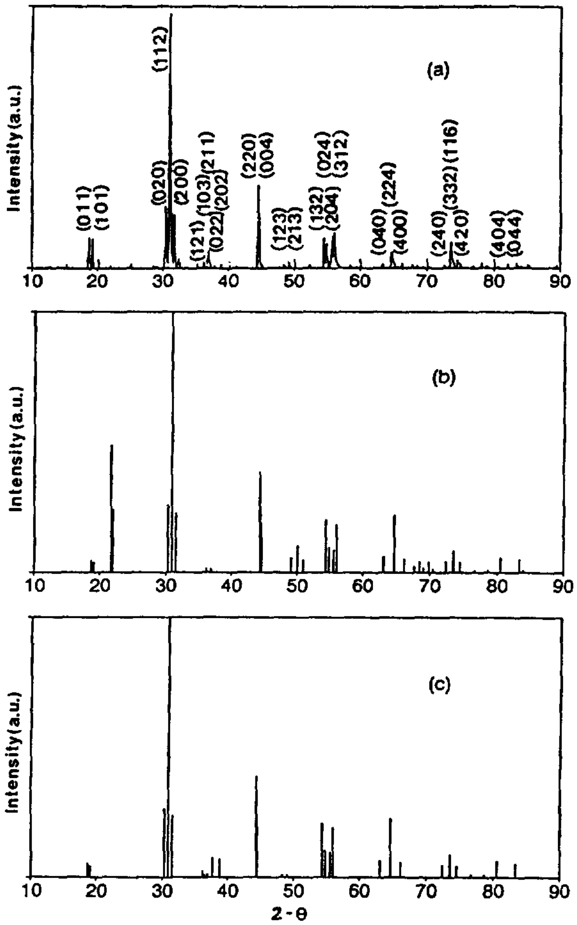

Figure 1. (a) The observed powder XRD pattern for (CaCe)(CaNb)O_6, and the calculated patterns based upon models that, (b) only calcium ions are distributed in A-site, and cerium and niobium ions are completely ordered in B-site, (c) calcium and cerium ions are randomly distributed in A-site and calcium and niobium ions are ordered in B-site.

The polycrystalline sample of Ca_2CeNbO_6 was prepared by two step solid state reactions under high temperature. At first, the stoichiometric mixture of high purity reactants of CeO_2, Nb_2O_5 and $CaCO_3$ was well ground in an agate mortar, pelleted and prefired at 900℃ for about 10 hours under the flowing hydrogen. Then the sample was finally fired at 1350℃ 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_2CeNbO_6 has a monoclinically distorted perovskite structure with lattice constants of $a_0=b_0=8.152$ Å, $c=8.139$ Å and $\gamma=87.7°$, 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 ($A_2^{2+}CeB^{5+}O_6$) where Ce^{3+} is the largest among lanthanides and even larger than Ca^{2+}, cerium ion could be stabilized in the A-site preferentially. Therefore two possible compounds, $Ca_2(CeNb)O_6$ and