Preparation and Properties of Perovskite-Type Oxides from Three-Dimensional Heterometal Assemblies, $\{\text{Ln}[\text{Cr}(\text{ox})_3] \cdot 10\text{H}_2\text{O}\}_x$ (Ln=La, Pr or Nd)

Masatomi SAKAMOTO, Kimihiro MATSUKI, Rie OHSUMI, Yusuke NAKAYAMA, Yoshihiko SADAOKA, Susumu NAKAYAMA*, Naohide MATSUMOTO** and Hisashi ŌKAWA**

Department of Applied Chemistry, Faculty of Engineering, Ehime University, 3, Bunkyo-cho, Matsuyama-shi 790

*New Materials Research Center, Shinagawa Refractories Co., Ltd., 707, Inbe, Bizen-shi 705

**Department of Chemistry, Faculty of Science, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka-shi 812

三次元ヘテロ金属集合体, $\{\text{Ln}[\text{Cr}(\text{ox})_3] \cdot 10\text{H}_2\text{O}\}_x$ (Ln=La, Pr or Nd),
を出発原料とするペロブスカイト型酸化物の調製とその性質

坂本政臣・松木公博・大角利枝・中山祐輔・定岡芳彦・中山 享*・松本尚英**・大川尚士**

愛媛大学工学部応用化学科, 790 松山市文京町 3

*品川白煉瓦(株)新材料研究センター, 705 備前市伊部 707

**九州大学理学部化学科, 812 福岡市東区箱崎 6-10-1

[Received May 11, 1992; Accepted July 8, 1992]

Three kinds of heterometal assemblies, $\{\text{Ln}[\text{Cr}(\text{ox})_3] \cdot 10\text{H}_2\text{O}\}_x$ (Ln=La, Pr or Nd), were prepared by the reaction of $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ with $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in water. These compounds were regarded to have the oxalato-bridged three-dimensional lattice. The thermal decomposition behavior of these assemblies was investigated in an air stream. The behavior was similar to each other. The mixed oxides, LnCrO_4 , and the perovskite-type oxides, LnCrO_3 , were found to form in the temperature range of 823 to 973 K and above 1023 K, respectively. Specific surface areas of LaCrO_3 , PrCrO_3 , and NdCrO_3 obtained by calcining the corresponding complex assemblies at 1073 K were 1.82, 1.85, and 1.91 $\text{m}^2 \cdot \text{g}^{-1}$, respectively. The effective magnetic moment per LaCr unit of LaCrO_3 increased from 1.98 μ_B at 296 K to 2.79 μ_B at 285 K, and then the moment decreased below 285 K because of the phase transition. PrCrO_3 and NdCrO_3 showed ferrimagnetic behavior. That is, the magnetic moments per LnCr units of PrCrO_3 and NdCrO_3 increased drastically below 240 and 225 K, respectively, also due to the phase transition. The moments of PrCrO_3 and NdCrO_3 were 9.79 μ_B at 219 K and 18.98 μ_B at 223 K, respectively, which were much larger than those expected from the respective total spin states, $S_T=5/2$ for PrCrO_3 and $S_T=3$ for NdCrO_3 .

Key-words: Lanthanoid(III) tris(oxalato)chromate(III), Pyrolysis, Perovskite, Microstructure, Specific surface area, Magnetic property

1. Introduction

The perovskite-type oxides have been, in general, prepared by calcining after mechanically mixing the oxides or carbonates of metal components. However, the high calcining temperatures above 1000°C are required for such conventional methods. Furthermore, there is an inevitable problem that the preparation of homogeneous materials is rather difficult. In order to remove these disadvantages, some techniques have been proposed. Among of

them, Yamazoe et al.^{1,2)} reported that the perovskite was obtained in the temperature range of 550° to 650°C when an amorphous complex-precursor, which were prepared by mixing the metal nitrates and citric acid in water, was decomposed.

Recently we investigated the thermal decomposition behaviors of double complex $[\text{Co}(\text{NH}_3)_6][\text{La}(\text{CO}_3)_3 \cdot \text{H}_2\text{O}]$ ³⁾ and $[\text{La}[\text{Cr}(\text{CH}_2(\text{COO})_2)_3] \cdot 6\text{H}_2\text{O}]$ ⁴⁾ and found that the perovskite formed in the range of 600° to 800°C for both complexes. Such methods are considered to be useful for the preparation of a homogeneous mixed oxide in an atomic level.

In the present work heterometal complexes, $\text{Ln}[\text{Cr}(\text{ox})_3] \cdot 10\text{H}_2\text{O}$ (abbreviated as La-Cr, Pr-Cr, and Nd-Cr for Ln=La, Pr or Nd, respectively), have been prepared and characterized. Although Roy and Nag⁵⁾ synthesized the same complexes from an aqueous nitric acid solution and reported the formation of perovskites, their cryomagnetic properties as well as microstructures were not investigated. According to the present work, the complexes were found to be easily synthesized from neutral aqueous solution. The magnetic properties, specific surface areas, and microstructures of perovskites obtained will also be discussed, together with the thermal decomposition behaviors of complexes.

2. Experimental

2.1 Preparation of complexes

To an aqueous solution (200 cm^3) of $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ ⁶⁾ (40 mmol) was added an aqueous solution (80 cm^3) of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (40 mmol) under stirring at room temperature. Greenish precipitates were immediately formed. After the mixture was further stirred for 1 h, the precipitates were collected by suction filtration, washed with water, ethanol and then diethyl ether, and dried in the open air. Yields were 94, 83, and 66% for the La-Cr, Pr-Cr and Nd-

Cr complexes, respectively.

2.2 Measurements

Elemental analyses of carbon and hydrogen were carried out at the Advanced Instrumentation Center for Chemical Analysis, Ehime University or the Service Center of Elemental Analysis, Kyushu University. Metal contents were determined by EDTA titration method after the mixed oxides obtained by the ignition of complexes at about 850°C in air were dissolved in dilute nitric acid. Thermal gravimetric analyses were carried out with a Cahn 2000 Recording Electrobalance. Each sample was heated at a rate of 4°C · min⁻¹ in a constant flow (50 cm³ · min⁻¹) of dried air. Powder X-ray diffraction spectra were recorded with a Rigaku Denki D-3F Diffractometer, using Cu K α radiation. Infrared spectra and reflectance spectra were measured with a JASCO IR-G Spectrometer and an Otsuka Electronics MCPD 1000 Spectrophotometer, respectively. Magnetic susceptibilities were determined in the temperature range of 80 to 300 K by the Faraday method. The apparatus was calibrated by the use of [Ni(en)₃]S₂O₃ (en=ethylenediamine). The susceptibilities were corrected by the use of Pascal's constants.⁷⁾ Effective magnetic moments were calculated by the equation, $\mu_{\text{eff}}=2.828 (\chi_{\text{M}}T)^{-1/2}$, where μ_{eff} and χ_{M} are values per LnCr unit (Ln=La, Pr or Nd). Scanning electron micrographs (SEM) were taken using a Nihon Denshi JSM-6400. Specific surface areas were determined in an atmosphere of nitrogen by the BET method.

3. Results and discussion

3.1 Characterization of {Ln[Cr(ox)₃]·10H₂O}_x

Analytical results summarized in Table 1 demonstrate the compositions of all of the complexes to be Ln[Cr(ox)₃]·10H₂O. Figure 1 shows the electronic spectra of K₃[Cr(ox)₃]·3H₂O and La[Cr(ox)₃]·10H₂O in the d-d band region. The spectra of Pr- and Nd-complexes were similar to the La-complex. The bands characteristic of [Cr(ox)₃]³⁻ around 420 and 570 nm suggest that the structure of the chromo-

Fig. 1. Electronic spectra of K₃[Cr(ox)₃]·3H₂O (—) and {La[Cr(ox)₃]·10H₂O}_x (·····) in solid state.

phore, [Cr(ox)₃]³⁻, is maintained also in the complexes, La-Cr, Pr-Cr and Nd-Cr.⁸⁾ In the IR spectra of these complexes the antisymmetric and symmetric $\nu(\text{CO})$ vibrations are observed at 1645 and 1435 cm⁻¹, respectively, whereas in K₃[Cr(ox)₃]·3H₂O the respective vibrations are observed around 1680 and at 1380 cm⁻¹ (Fig. 2). From these observations it is presumed that the three-dimensional networks should be constructed by Ln(III)-ox-Cr(III) linkages as reported for {NBu₄[CuCr(ox)₃]}_x.⁹⁾ Some of the ten water molecules may coordinate to lanthanoid ions since the coordination numbers of lanthanoid ions are, in general, larger than six, and the other water molecules may be incorporated into the crystal lattice, though the detailed structure is unclear at present.

3.2 Thermal decomposition

The thermal decomposition behaviors of La-Cr, Pr-Cr and Nd-Cr were investigated in order to prepare the perovskites, LnCrO₃. The behaviors were essentially similar to each other. The TG curve for La-Cr is shown in Fig. 3. The decomposition begins at about 323 K to give the first plateau in the temperature range of 473 to 573 K. The weight loss percentage in this plateau range is about 28%, indicating

Table 1. Analytical results.

Complex	Found(%) (Calcd(%))				Weight loss(%)	
	C	H	Ln	Cr	at 873 K	at 1273 K
La-Cr	11.54 (11.35)	2.98 (3.17)	20.89 (21.87)	9.02 (8.19)	59.50 (59.87) ^{a)}	62.19 (62.38) ^{b)}
Pr-Cr	11.38 (11.31)	2.80 (3.16)	21.50 (22.12)	8.54 (8.16)	59.80 (59.68) ^{a)}	62.45 (62.19) ^{b)}
Nd-Cr	11.41 (11.25)	2.73 (3.15)	22.76 (22.52)	8.20 (8.12)	59.21 (59.37) ^{a)}	61.61 (61.87) ^{b)}

The values for C, H, Ln, and Cr in parentheses are those calculated for {Ln[Cr(ox)₃]·10H₂O}_x.

a) The values calculated assuming the formation of LnCrO₄.

b) The values calculated assuming the formation of LnCrO₃.

Fig. 2. The IR spectra of $K_3[Cr(ox)_3] \cdot 3H_2O$ (a) and $\{Ln[Cr(ox)_3] \cdot 10H_2O\}_x$ ((b) for $Ln=La$, (c) for $Ln=Pr$, and (d) for $Ln=Nd$).

Fig. 3. The TG curve of $\{La[Cr(ox)_3] \cdot 10H_2O\}_x$ in an air stream.

the formation of anhydrate, $\{La[Cr(ox)_3]\}_x$. The abrupt weight loss is observed at about 573 K to give the second plateau, and then the third plateau appears in the range of 803 to 973 K after the weight loss at about 773 K. The weight loss percentage (about 59.5%) in the third plateau range is in agreement with that calculated by assuming the formation of $LaCrO_4$ (Table 1). Finally, the weight loss corresponding to a release of one oxygen atom from $LaCrO_4$ occurs at about 973 K and the last plateau is observed above 1023 K. The weight loss percentage (62.2%) in the last plateau range agrees very well with that calculated by assuming the formation of $LaCrO_3$ (Table 1). The weight loss percentages observed at 873 and 1273 K for Pr–Cr and Nd–Cr are also summarized in Table 1, together with those calculated.

The decomposition products were characterized by measuring the powder X-ray diffraction spectra of the products formed at 673, 873, 1023, 1073 and 1273 K. The spectra obtained for La–Cr, Pr–Cr, and Nd–Cr were similar to each other. From Fig. 4,

which shows the spectra for La–Cr, the perovskite is found to form above 1023 K.^{5),10)} Crystal system and space group were rhombic and $Pbnm$, respectively, for all of the perovskites obtained at 1273 K, and the lattice constants (Å) were estimated as follows: $a=5.477$, $b=5.502$, $c=7.741$ for $LaCrO_3$, $a=5.434$, $b=5.470$, $c=7.695$ for $PrCrO_3$, and $a=5.434$, $b=5.468$, $c=7.691$ for $NdCrO_3$.

3.3 Surface area and microstructure

The SEM photographs of the starting oxalato-complexes, $\{Ln[Cr(ox)_3] \cdot 10H_2O\}_x$, and the perovskites obtained by calcining at 1073 K are shown in Fig. 5. It is apparently observed that each chunk, the size of which is in the range of a few μm to about ten μm of

Fig. 4. Power X-ray diffraction spectra of thermal decomposition products of $\{La[Cr(ox)_3] \cdot 10H_2O\}_x$.

Fig. 5. The SEM photographs of $\{Ln[Cr(ox)_3] \cdot 10H_2O\}_x$ ([1] for $Ln=La$, [2] for $Ln=Pr$, and [3] for $Ln=Nd$) and $LnCrO_3$ prepared by calcining at 1073 K.

Table 2. Specific surface areas ($\text{m}^2 \cdot \text{g}^{-1}$).

La-Cr	Pr-Cr	Nd-Cr	LaCrO ₃	PrCrO ₃	NdCrO ₃
1.33	1.29	0.83	1.82	1.85	1.91

Surface areas of perovskites were determined for samples obtained by calcining at 1073 K.

the starting complexes is decomposed to give many fine grains, while the original chunk-shape is essentially maintained with the contraction in size. The specific surface areas of perovskites are a little larger, compared with those of the corresponding starting complexes (Table 2). This seems to be related to the smaller grain size of perovskites as seen in Fig. 5.

3.4 Magnetic properties of perovskites

The magnetic behaviors of perovskites obtained at 1273 K are shown in Fig. 6 in the forms of plots of χ_M vs. T and μ_{eff} vs. T , where χ_M and μ_{eff} stand for the magnetic susceptibility and effective magnetic moment per LnCr (Ln=La, Pr or Nd) unit, respectively. The magnetic moment per LaCr of LaCrO₃ at room temperature is $1.98 \mu_B$, which is smaller than the spin-only value ($3.87 \mu_B$). The discontinuous point appears at about 285 K which agrees with the phase-transition temperature, 282 K,¹¹⁾ reported previously for LaCrO₃. The magnetic moments per PrCr of PrCrO₃ decrease from $4.18 \mu_B$ at room temperature, which is smaller than the spin-only value ($4.80 \mu_B$), to $4.05 \mu_B$ at 240 K as the temperature is lowered. Then the moment increases abruptly below 240 K, which is also in agreement with the phase-transition temperature (239 K).¹¹⁾ For NdCrO₃ the moment at room temperature is $4.27 \mu_B$ (calculated spin-only value = $5.48 \mu_B$) and the abrupt increase of moment is also observed below 225 K (phase-transition temperature reported = 224 K).¹¹⁾ The magnetic moments per LnCr (Ln=Pr or Nd) below the respective phase-transition temperature are unusually large, compared with the respective spin-only

values. Furthermore, the plots of $1/\chi_M$ vs. T for PrCrO₃ and NdCrO₃ were found to obey the Curie-Weiss law in the paramagnetic region (above phase-transition temperature) and the negative Weiss constants were estimated for both perovskites. These results suggest that the antiferromagnetic interaction between paramagnetic Pr(III) or Nd(III) and Cr(III) ions is built up over the three-dimensional space to exhibit a ferrimagnetism.

4. Conclusions

The formation processes of perovskite-type oxides, LnCrO₃, were studied by following the thermal decomposition behaviors of $\{\text{Ln}[\text{Cr}(\text{ox})_3] \cdot 10\text{H}_2\text{O}\}_x$ (Ln=La, Pr and Nd), which have the three-dimensional network structures constructed by Ln(III)-ox-Cr(III) linkages and hence are very useful for the preparation of perovskites highly ordered in an atomic level. The perovskites obtained were characterized by SEM photographs, measurements of specific surface areas, and investigating the temperature dependences of magnetic susceptibilities. The results are summarized as follows:

(1) Perovskites were completely formed at about 1023 K, which is lower than temperatures of the conventional ceramic technique.

(2) Specific surface areas of the perovskites were $1.8\text{--}2.0 \text{ m}^2 \cdot \text{g}^{-1}$, which are slightly larger than those ($0.8\text{--}1.4 \text{ m}^2 \cdot \text{g}^{-1}$) of the starting complexes, $\{\text{Ln}[\text{Cr}(\text{ox})_3] \cdot 10\text{H}_2\text{O}\}_x$. This difference is reasonably interpreted by SEM photographs. That is, chunks of starting complexes were decomposed to many fine grains.

(3) Cryomagnetic investigations revealed that the phase-transition temperatures of LaCrO₃, PrCrO₃ and NdCrO₃ prepared by the present method are about 285, 240 and 225 K, respectively, which are in good agreement with those of the corresponding perovskites reported so far.

(4) PrCrO₃ and NdCrO₃ showed ferrimagnet-like behaviors below their phase-transition temperatures. These behaviors are due to the building-up of antiferromagnetic interactions between Pr(III) or Nd(III) and Cr(III) ions over the three-dimensional space.

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Fig. 6. Temperature dependences of χ_M (○) and μ_{eff} (●) for LnCrO₃ obtained by calcining $\{\text{Ln}[\text{Cr}(\text{ox})_3] \cdot 10\text{H}_2\text{O}\}_x$ at 1273 K for 2 h.

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