BRIEF COMMUNICATION

Synthesis and Crystal Structure of a New Compound, Lanthanum Dioxymonocyanamide ($La_2O_2CN_2$)

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A new compound was prepared by heating La_2O_3 in the presence of carbon under an ammonia atmosphere. The chemical formula of the compound was determined to be $La_2O_2CN_2$ both from results of CHN analysis and weight change upon oxidation of the compound to La_2O_3. The existence of CN_2^{2-} ions was confirmed by IR and X-ray photoelectron spectroscopy. The structure is tetragonal with cell constants $a = 4.0964(2)$ Å, $c = 12.333(1)$ Å, and $Z = 2$. X-ray Rietveld analysis revealed that the compound has a layered-type structure with space group, $I4/mmm$. © 1995 Academic Press, Inc.

INTRODUCTION

There is a large group of compounds of composition Ln_2O_2X with $X =$ S (1), Se (2), Te (3), and so on. Their structure is closely related to that of the high-temperature form of La_2O_3 in which the third O takes a position between the $La_2O_2^{2+}$ layers (1). In addition, $La_2O_2CO_3$ (4) also takes a similar structure to Ln_2O_2X in which CO_3^{2-} ions are located between the $La_2O_2^{2+}$ layers. In these compounds, the $La_2O_2^{2+}$ layers are perpendicular to the c-axis, and anions are held between these layers. The crystal structure is tetragonal in the case of $X =$ Se, Te, and CO_3. Regardless of the kind of anions, their a-parameters are about 4 Å because of rigidity of the $La_2O_2^{2+}$ layers, but the c-parameters vary remarkably depending on the size of anions which are located at the interlayers.

Recently, we synthesized a new compound, $La_2O_2CN_2$ with a layered structure which is related to the La_2O_2X structure. This paper is concerned with the preparation and characterization of $La_2O_2CN_2$.

EXPERIMENTAL

La_2O_3 was heated in a graphite boat at 1223 K for 12 hr under flowing ammonia gas. Powder X-ray diffraction data were collected using a Rigaku RINT 1000 diffracto-meter fitted with a graphite monochromator operating $CuK\alpha$ radiation. Chemical composition of the product was determined by both CHN analysis and weight change upon oxidizing the sample to La_2O_3. The density of the product was measured using a pycnometer. The XPS measurements were performed using a VG Microlab Mark 3 spectrometer with $MgK\alpha$ X-rays. Binding energy, E_B, was calibrated by referring to the E_B of the C1s peak of graphite as 284.3 eV (5). Infrared spectra were recorded on a Hitachi spectrophotometer using samples of spectroscopically pure KBr pellets.

RESULTS AND DISCUSSION

The powder X-ray diffraction pattern of the product is shown in Fig. 1. The product could not be identified by using JCPDS data (6). All the diffraction peaks could be indexed using a tetragonal cell with $a = 4.0964(2)$ Å and $c = 12.333(1)$ Å. The observed d-values are in good agreement with the calculated values, as shown in Table 1. The powder X-ray diffraction pattern exhibits a systematic extinction rule as follows: $hkl, h + k + l = 2n; hk0, h + k = 2n; 0kl, k + l = 2n; hhl, l = 2n; 00l, l = 2n;$ and $h00, h = 2n$. Therefore the space group of this compound is $I4, I\bar{4}, I4/m, I422, I4mm, I\bar{4}m2, I\bar{4}2m,$ and $I4/mmm$. The result of the CHN analysis indicated that the amounts of C, H, and N in the product were 3.5, 0.0, and 8.0 wt%, respectively. After heating the sample above 1100 K in air, it converted to La_2O_3 with an accompanying the weight loss of 6.9%. The chemical formula of the product was evaluated to be $La_2O_2CN_2$ from those results. The theoretical values of the C, N, and O contents calculated as $La_2O_2CN_2$ are consistent with the observed values obtained by the chemical and thermal analyses as shown in Table 2. The observed density of $La_2O_2CN_2$ was 5.44 g/cm³, which was in good agreement with calculated value, 5.62 g/cm³, using $Z = 2$. The density of $La_2O_2CN_2$ is smaller than those of La metal (6.17 g/cm³), LaN (6.822

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TABLE 1
Powder X-Ray Diffraction Data

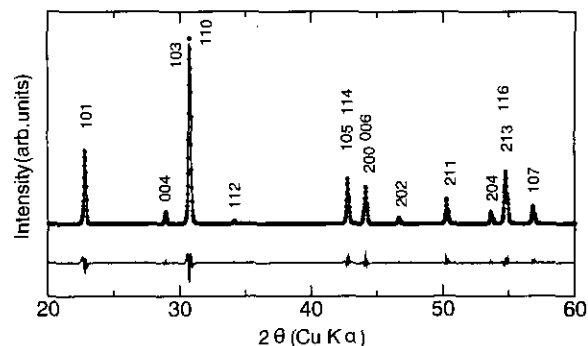| h	k	l	d_{obs} (Å)	d_{calc} (Å)	I/I_0
0	0	2	6.169	6.167	9
1	0	1	3.889	3.888	42
0	0	4	3.084	3.083	9
1	0	3	2.901	2.902	100
1	1	0		2.897	
1	1	2	2.622	2.622	2
1	0	5	2.111	2.113	25
1	1	4		2.111	
0	0	6	2.056	2.056	8
2	0	0	2.049	2.048	20
2	0	2	1.9438	1.9438	3
2	1	1	1.8122	1.8121	13
2	0	4	1.7059	1.7061	6
1	1	6	1.6762	1.6763	18
2	1	3	1.6734	1.6733	26
1	0	7	1.6185	1.6185	10
0	0	8	1.5417	1.5416	1
2	0	6	1.4506	1.4509	5
2	2	0	1.4483	1.4483	6
2	2	2	1.4100	1.4099	1
1	1	8	1.3573	1.3609	2
3	0	1		1.3572	
2	2	4	1.3109	1.3109	3
1	0	9	1.2995	1.2995	3
3	0	3	1.2959	1.2959	10
3	1	0		1.2954	
2	1	7	1.2700	1.2699	7
3	1	2		1.2677	
0	0	10	1.2333	1.2333	2
2	0	8	1.2317	1.2317	1
3	0	5	1.1943	1.1946	5
3	1	4		1.1943	
2	2	6	1.1841	1.1839	2
1	1	10	1.1347	1.1347	3
3	2	1	1.1316	1.1313	3
2	1	9	1.0974	1.0973	3
3	1	6	1.0955	1.0959	7
3	2	3		1.0951	
1	0	11	1.0815	1.0814	2
3	0	7	1.0793	1.0793	3
2	0	10	1.0567	1.0565	2
2	2	8		1.0556	
0	0	12	1.0278	1.0278	<1
4	0	0	1.0243	1.0241	2
4	0	2	1.0104	1.0103	<1

FIG. 1. Observed (· · ·) and calculated (—) powder X-ray diffraction patterns of $La_2O_2CN_2$. The difference profile appears below at the same scale.

and ν_3 modes for either cyanamide (CN_2^{2-}) or cyanato (NCO^-) groups. Other peaks have not been assigned as yet. It was quite difficult to determine whether the compound contains cyanamide or cyanate ions because both species exhibit similar IR spectra.

XPS was measured on the $La_2O_2CN_2$ tablet sintered at 1273 K under flowing ammonia gas. Three E_B peaks at 530.4, 398.6, and 286.2 eV were assigned to O1s, N1s, and C1s peaks, respectively. The observed E_B of oxygen in $La_2O_2CN_2$ is similar to those of oxygen ions in metal oxides, such as Sb_2O_3 (O1s = 529.8 ev), Eu_2O_3 (O1s = 531.2 ev) and so on (9), indicating that oxygen in $La_2O_2CN_2$ exists as O^{2-} ions. The E_B of C1s in $La_2O_2CN_2$ is similar to those of C1s in CN^- ions (C1s = 285.4–285.5 ev) (10) but different from those of C1s in RCO_2^- ions (C1s = 288.3–288.5 eV) (11). Furthermore the E_B of N1s in $La_2O_2CN_2$ is also similar to those of N1s in CN^- ions (N1s = 399.5–399.9 eV). Therefore it is appropriate to consider that a covalent bond is formed between C and N in $La_2O_2CN_2$.

The results of both XPS and IR spectra suggest that the compound includes CN_2^{2-} ions.

There are many compounds expressed as La_2O_2X such as La_2O_2Se, La_2O_2Te, $La_2O_2CO_3$, and so on. The crystal structure of these compounds are tetragonal, and consists of the $La_2O_2^{2+}$ layers and the anions located between them.

g/cm³), and La_2O_3 (6.573 g/cm³), indicating that the new compound packed rather loosely.

Figure 2 shows the IR spectra of $La_2O_2CN_2$ and La_2O_3. The IR spectrum of $La_2O_2CN_2$ and that of La_2O_3 scarcely resemble each other. The IR spectrum of $La_2O_2CN_2$ has a characteristic peak at 1950 cm⁻¹. On the basis of comparison of the IR spectra of $La_2O_2CN_2$ and the inorganic compounds containing NCO^- (7) and CN_2^{2-} (8), the observed peaks at 670 and 1950 cm⁻¹ are assigned to the ν_2

TABLE 2

Comparison between Experimental and Calculated Values of C, N, and O Content and Weight Loss in Conversion from $La_2CN_2O_2$ to La_2O_3

	C (wt%)	N (wt%)	O (wt%)	Weight loss (%)
Experimental	3.5	8.0	—	6.9
Calculated	3.4	8.0	9.1	6.9

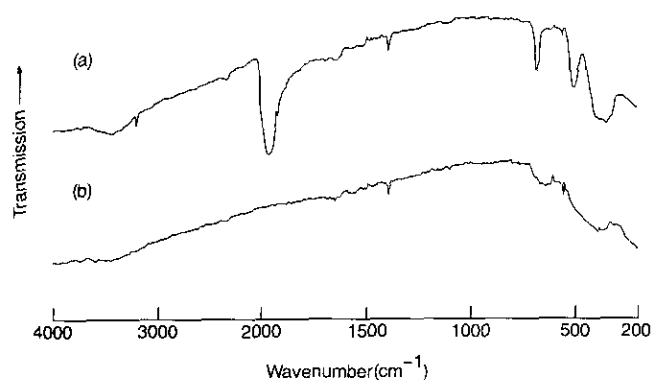**FIG. 2.** Infrared spectra of (a) $La_2O_2CN_2$ and (b) La_2O_3.

These compounds have almost the same a-parameters, but the c-parameters vary depending on the size of the anions at the interlayer. The values of the a-parameters of $La_2O_2CN_2$ with a tetragonal lattice are also very close to those of La_2O_2X. It was assumed that the crystal structure of $La_2O_2CN_2$ consists of $La_2O_2^{2+}$ layers and CN_2^{2-} ions at the interlayer positions. In this model, the structure analysis of $La_2O_2CN_2$ was conducted by Rietveld refinement using the program RIETAN (12). The refinement of the atomic coordinates and the isotropic thermal factors led to the lowest R factor when $I4/mmm$ was adopted. The result is shown in Fig. 1, where the observed X-ray diffraction pattern is in good agreement with the calculated one. Table 3 shows the crystallographic data, and Table 4 lists the final structural parameters of $La_2O_2CN_2$. The nitrogen atoms occupying the $8j$ sites ($x = 0.20(2)$, $y = 0.5$, and $z = 0$) in $I4/mmm$ with an occupancy of 0.5, indicating that the linear chain $N{=}C{=}N$ takes two statistically different orientations at an angle of $90°$ to each other. It is certain that the $La_2O_2^{2+}$ layers stack along

TABLE 3
Crystallographic Data

Crystal system	Tetragonal
Space group	$I4/mmm$
Cell dimension (Å)	$a = 4.0964(2)$
	$c = 12.333(1)$
Volume (Å³)	207.0
Z	2
R_p	0.105
R_{wp}	0.151

TABLE 4
Final Structural Parameters

Atom	Wycoff position	x	y	z	B_{eq} (Å²)	Occupancy
La	$4e$	0	0	0.1502(6)	0.27	1
O	$4d$	0	0.5	0.25	0.45	1
C	$2b$	0	0	0.5	0.62	1
N	$8j$	0.20(2)	0.5	0	1.06	0.5

the c-axis, but the precise positions of C and N are still uncertain. The neutron diffraction analysis of $La_2O_2CN_2$ is being carried out to solve the latter problem and the results of the analysis will be reported elsewhere.

As for other rare earths, the compounds having the same chemical formula as $Ln_2O_2CN_2$ were obtained, but they took different structures from that of $La_2O_2CN_2$. The details of the structure of $Ln_2O_2CN_2$ will be mentioned elsewhere.

ACKNOWLEDGMENTS

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