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Syntheses and Crystal Structures of Trigonal Rare-Earth Dioxymonocyanamides, $Ln_2O_2CN_2$ (Ln = Ce, Pr, Nd, Sm, Eu, Gd)

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New compounds, trigonal rare-earth dioxymonocyanamides $Ln_2O_2CN_2$, were synthesized by heating Ln_2O_3 (Ln = Nd, Sm, Eu, Gd), $Ce_2(CO_3)_3 \cdot 8H_2O$, or Pr_6O_{11} in the presence of carbon under flowing ammonia gas. The crystal structures of $Ln_2O_2CN_2$ were refined by the Rietveld method using X-ray diffraction data. The $Ln_2O_2CN_2$ compounds crystallize in the trigonal space group $P\bar{3}m1$, with a and c parameters varying from 3.9442 to 3.7812 Å and from 8.3609 to 8.2311 Å, respectively, as Ln atoms change from Ce to Gd. A choice of the space group was done assuming that the structure of $Ln_2O_2CN_2$ is like that of Ln_2O_2S. In this paper, structural parameters for both $Ce_2O_2CN_2$ and $Gd_2O_2CN_2$ are not reported because the parameters for the atoms did not converge to reasonable values. These compounds have the layer structures which consist of the $Ln_2O_2^{2+}$ layers with the interlayer CN_2^{2-} ions. The $Ln_2O_2^{2+}$ layers are piled perpendicular to the c axis and the linear cyanamide ions, $^-N{=}C{=}N^-$, are inserted parallel to the c axis.

INTRODUCTION

Some kinds of the rare-earth compounds have a feature characterized by the layer structure. For example, $LnOX$(X = halogen), Ln_2O_2Y(Y = chalcogen), and $Ln_2O_2CO_3$ belong to this kind of the compounds. These compounds consist of the $Ln_2O_2^{2+}$ layers and the interlayer anions. They crystallize in the trigonal (or hexagonal) and/or the tetragonal form depending on the interlayer anions. Only CO_3^{2-} has been known as the polyatomic interlayer anion. In our study, a series of compounds, $Ln_2O_2CN_2$ which contain other polyatomic anion have been synthesized. These compounds have the tetragonal and the trigonal structure depending on the Ln^{3+} ionic radii (1). The synthesis and the crystal structure refined by the Rietveld method of $La_2O_2CN_2$ which crystallizes in the tetragonal structure have been already reported (2). In this paper, the syntheses and the crystal structures of the trigonal $Ln_2O_2CN_2$ are reported.

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EXPERIMENTAL

The trigonal $Ln_2O_2CN_2$ were prepared by heating Pr_6O_{11} or Ln_2O_3 (Ln = Nd, Sm, Gd) at 1223 K for 12 h in a graphite boat under flowing ammonia gas. The reaction condition is the same as that for the preparation of $La_2O_2CN_2$ (tetragonal) (2). In the case of Ln = Ce, $Ce_2(CO_3)_3 \cdot 8H_2O$ was heated at 1273 K. For Ln = Eu, Eu_2O_3 was calcined at 1023 K because the sample melted above 1023 K. Chemical compositions of the products were determined by CHN analyses and weight changes upon oxidizing the products to the corresponding oxides. Densities of the products were measured using pycnometery. IR spectra were recorded on a Hitachi spectrophotometer using the KBr method. Powder X-ray diffraction data were collected using a Rigaku RAD-RB diffractometer fitted with a graphite-monochromator employing Cu$K\alpha_1$ radiation. All powder X-ray diffraction data were refined by the Rietveld method using RIETAN (5, 6). The diffraction data were collected in steps of 0.02° over a range of 20°–100° in 2θ. Thermal analysis data were obtained on a Rigaku TAS-100 using a heating rate of 10 K/min in the temperature region between the room temperature and 1473 K.

RESULTS AND DISCUSSION

The result of the CHN analysis of the product produced from Nd_2O_3 indicated that the amounts of C, H, and N were 3.3, 0.0, and 7.6 wt%, respectively. After heating the sample above 1323 K in air, it decomposed into Nd_2O_3 with a weight loss of 6.6%. The chemical formula of the product was determined to be $Nd_2O_2CN_2$. Values of C, N, and O contents calculated as $Nd_2O_2CN_2$ are consistent with those obtained by the chemical and the thermal analysis. The same procedures were carried out for other products, and the chemical formula $Ln_2O_2CN_2$ was obtained for all compounds (see Table 1). The N atoms in $Ln_2O_2CN_2$ came from NH_3 gas and the C atoms from the graphite boat. It is thought that the C atoms in the graphite boat react with NH_3 gas, vaporize, and then react with the rare-earth

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TABLE 1
Comparison between the Experimental and the Calculated Values of C, N, and O in $Ln_2O_2CN_2$

	C (wt%)	N (wt%)	O (wt%)	Weight loss (%)
		Ce		
Experimental	3.5[a]	7.8[a]	9.2[b]	2.3
Calculated	3.4	8.0	9.1	2.3
		Pr		
Experimental	3.4[a]	7.8[a]	9.0[b]	3.6
Calculated	3.4	7.9	9.0	3.8
		Nd		
Experimental	3.3[a]	7.6[a]	9.0[b]	6.6
Calculated	3.3	7.8	8.9	6.7
		Sm		
Experimental	3.2[a]	7.4[a]	8.6[b]	6.3
Calculated	3.2	7.5	8.6	6.4
		Eu		
Experimental	3.2[a]	7.5[a]	7.8[b]	5.7
Calculated	3.2	7.4	8.5	6.4
		Gd		
Experimental	3.2[a]	7.3[a]	7.9[b]	5.9
Calculated	3.1	7.2	8.3	6.2

[a] The values were obtained by CHN analysis.
[b] Oxygen contents were determined by weight losses on oxidation of the samples to the corresponding oxides and CHN analysis data.

oxides or carbonate because the graphite boat corrodes by heating under flowing ammonia gas. At first, the syntheses were carried out by using only the graphite boat as the carbon source. However, the sample had to be heated twice in order to obtain a single phase. The active charcoal in an alumina boat was placed at the upper end of the stream of the ammonia gas, since it was assumed that a larger quantity of carbon would cause the staring material to readily produce the desired products in one heating. The single phases were obtained by heating once at the above mentioned temperature for Ln = Ce to Eu. However, Gd_2O_3 had to be heated twice even though this reaction system was used.

Figure 1 shows the IR spectra of $Ln_2O_2CN_2$. All IR spectra of $Ln_2O_2CN_2$ show two absorption peaks in the vicinity of 670 and 1950 cm^{-1}. These absorption peaks were assigned to the ν_2 and ν_3 modes of the CN_2^{2-} ion which were comparable to the IR spectrum of $La_2O_2CN_2$ (2). The IR spectra of $Ln_2O_2CN_2$ indicate that the trigonal $Ln_2O_2CN_2$ also contain CN_2^{2-} ions.

When CeO_2 was used as a starting material, the product was a mixture of $Ce_2O_2CN_2$, CeO_2, Ce_2O_3, and Ce_2ON_2. The stable oxide for Ce is CeO_2 in which Ce is tetravalent. To synthesize $Ce_2O_2CN_2$ from CeO_2, Ce^{4+} has to be reduced to Ce^{3+} but it does not occur fully under the reaction condition used for this study. Therefore $Ce_2(CO_3)_3 \cdot 8H_2O$ containing Ce^{3+} was chosen as a starting material. In the case of Pr_6O_{11} with a mixed valence state of Pr^{3+} and Pr^{4+}, the conversion from Pr_6O_{11} to $Pr_2O_2CN_2$ occurred smoothly.

The powder X-ray diffraction patterns of $Ln_2O_2CN_2$ could not be identified by using JCPDS data (7). All the diffraction peaks of each sample were indexed using the trigonal cell with the a and c parameters listed in Table 3 for Ln = Pr, Nd, Sm, and Eu, which were obtained by the Rietveld refinement which is mentioned later. The cell parameters for Ln = Ce and Gd were obtained by least square; a = 3.9441(7), c = 8.361(2) Å for Ln = Ce, and a = 3.7813(2), c = 8.2323(5) Å for Ln = Gd. The CELL package of programs (8) were used for indexing. The observed d values are in good agreement with those calculated as shown in Table 2. $Nd_2O_2CN_2$ is presented, and the others may be obtained from the authors. The observed density of $Nd_2O_2CN_2$ is 5.55 g/cm^3, which is in good agreement with the calculated value of 5.52 g/cm^3 at Z = 1.

The powder X-ray diffraction patterns exhibit no system-

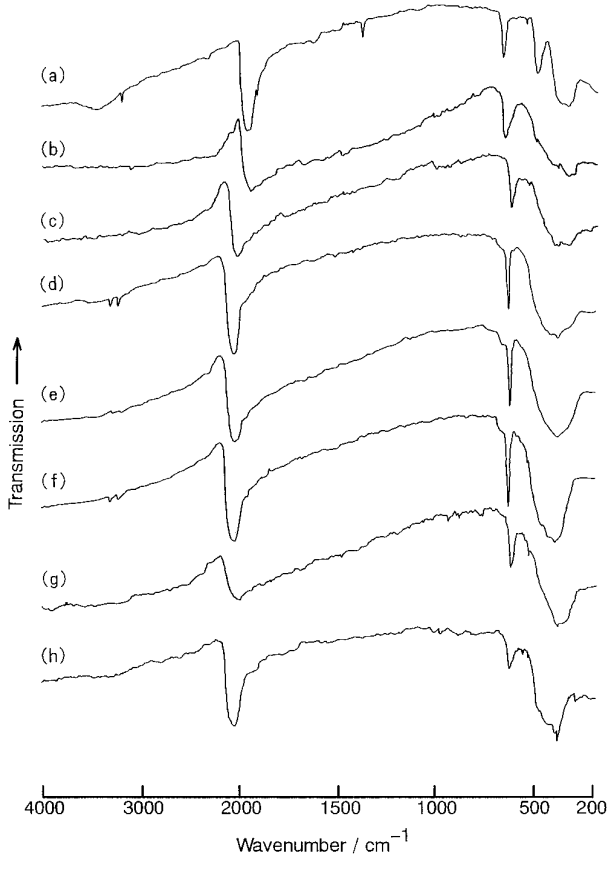

FIG. 1. Infrared spectra of $Ln_2O_2CN_2$, (a)La, (b)Ce (tetragonal), (c)Ce (trigonal), (d)Pr, (e)Nd, (f)Sm, (g)Eu, (h)Gd.

TABLE 2
Powder X-Ray Diffraction Data for $Nd_2O_2CN_2$

h k l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}/I_0	I_{cal}/I_0
0 0 1	8.333	8.311	28	—
0 0 2	4.158	4.155	19	19
1 0 0	3.364	3.364	17	16
1 0 1	3.118	3.118	100	98
0 0 3	2.770	2.770	17	17
1 0 2	2.614	2.614	38	39
1 0 3	2.138	2.138	22	22
0 0 4	2.077	2.078	1	1
1 1 0	1.9415	1.9420	30	29
1 1 1	1.8907	1.8911	7	7
1 0 4	1.7670	1.7676	23	23
1 1 2	1.7593	1.7593	11	11
2 0 0	1.6815	1.6818	3	2
0 0 5	1.6614	1.6621	2	2
2 0 1	1.6479	1.6484	15	15
1 1 3	1.5896	1.5902	19	19
2 0 2	1.5585	1.5590	9	8
1 0 5	1.4895	1.4901	6	6
2 0 3	1.4370	1.4376	5	5
1 1 4	1.4181	1.4187	1	1
0 0 6	1.3845	1.3851	1	2
2 0 4	1.3066	1.3072	8	8
1 0 6	1.2802	1.2808	4	4
2 1 0	1.2709	1.2713	2	2
1 1 5	1.2622	1.2628	5	5
2 1 1	1.2563	1.2567	12	12
2 1 2	1.2153	1.2157	8	7
0 0 7		1.1872		<1
	1.1818		3	
2 0 5		1.1822		3
2 1 3	1.1551	1.1555	5	5
1 1 6	1.1272	1.1277	5	5
3 0 0	1.1207	1.1212	4	4
1 0 7	1.1182	1.1195	6	5
3 0 1	1.1107	1.1111	1	1
2 1 4		1.0844		9
	1.0840		11	
3 0 2		1.0825		2
2 0 6	1.0688	1.0692	2	2
3 0 3		1.0393		5
	1.0390		6	
0 0 8		1.0388		1
1 1 7	1.0129	1.0129	<1	<1
2 1 5	1.0095	1.0098	4	4

atic extinctions. Therefore the space group of these compounds could be any of the following hexagonal groups, $P\bar{6}$, $P6/m$, $P622$, $P6mm$, $P\bar{6}m2$, $P\bar{6}2m$, $P6/mmm$, or in one of the following trigonal groups, $P3$, $P\bar{3}$, $P312$, $P321$, $P3m1$, $P31m$, $P\bar{3}1m$, $P\bar{3}m1$. Assuming that the crystal structure of the trigonal $Ln_2O_2CN_2$ is similar to that of Ln_2O_2S with a trigonal symmetry which consists of the $Ln_2O_2^{2+}$ layers and S^{2-}'s located between the layers, where the refinement of the structure was carried out by the Rietveld method. In the structural model which consists of the $Ln_2O_2^{2+}$ layers with the interlayer CN_2^{2-} ions, the refinement of the atomic coordinates and the isotropic thermal factors led to the lowest R factor when $P\bar{3}m1$ was adopted. The structures were therefore refined with space group $P\bar{3}m1$ with the structure model Ln at $2d$ ($\frac{1}{3}$, $\frac{2}{3}$, z_1) with $z_1 \approx 0.18$, O at $2d$ ($\frac{1}{3}$, $\frac{2}{3}$, z_2) with $z_2 \approx 0.89$, C at $1b$ (0, 0, $\frac{1}{2}$), and N at $2c$ (0, 0, z_3) with $z_3 \approx 0.35$. No preferred orientations were corrected. Figure 2 illustrates the profile fit and the difference pattern for $Nd_2O_2CN_2$. The solid line is calculated intensities, plus dots overlying the line are observed intensities, and Δy_i is the difference between the observed and the calculated intensities. Figure 2 shows that the calculated pattern fits the observed pattern very well. Tables 3 and 4 list the results of the Rietveld refinement and Table 5 presents interatomic distances. The definitions of the R factors in Table 3 can be seen in Ref. (9). The thermal parameters for the atoms in $Ce_2O_2CN_2$ did not converge to the reasonable values which can be attributed to poor crystal growth of $Ce_2O_2CN_2$. As for Ln = Gd, the C–N distance obtained by the Rietveld refinement was 1.40 Å, which deviates significantly from 1.26–1.30 Å obtained for Ln = Pr, Nd, Sm, and Eu. If this value is correct, the wavenumbers of the ν_2 and ν_3 modes of the CN_2^{2-} ion in the IR spectrum for $Gd_2O_2CN_2$ would differ greatly from those of other $Ln_2O_2CN_2$, but such a change is not observed in Fig. 1. It is guessed that $Ce_2O_2CN_2$ and $Gd_2O_2CN_2$ have the same structure as the others. A neutron diffraction study is now being carried out in order to determine the positions of the C and the N atoms. Therefore in this paper, the results of the Rietveld refinement for Ln = Ce and Gd are excluded.

Several inorganic cyanamides have been reported, such as Na_2CN_2 (10), $PbCN_2$ (11), and $CaCN_2$ (12). There are two types of the CN_2^{2-} ions; one has two equivalent double bonds, C=N, and the other has C—N and C≡N bonds which have different distances between the C and the N atoms. In $CaCN_2$, both C—N distances are 1.25 Å, indicat-

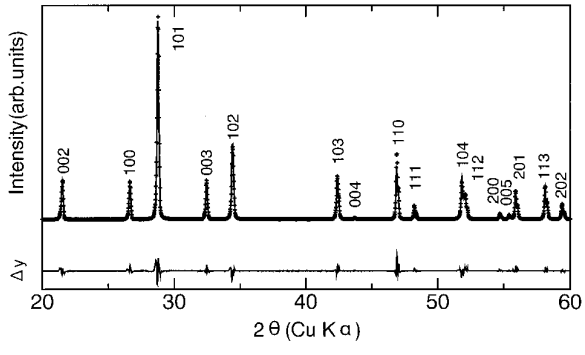

FIG. 2. Observed (+++) and calculated (−) powder X-ray diffraction pattern of $Nd_2O_2CN_2$. The difference profile appears below at the same scale.

TABLE 3
Results of the Rietveld Refinement for the Trigonal $Ln_2O_2CN_2$

	Pr	Nd	Sm	Eu
Cell dimension (Å)	a = 3.9139(10) c = 8.3324(15)	a = 3.8840(7) c = 8.3106(12)	a = 3.8276(9) c = 8.2666(15)	a = 3.8049(6) c = 8.2515(9)
Volume (Å)	110.5	108.6	104.9	103.5
Calculated density (g/cm^3)	5.32	5.51	5.90	6.04
R_{wp}	0.135	0.142	0.156	0.159
R_p	0.097	0.102	0.115	0.111
R_B	0.020	0.024	0.027	0.038
R_F	0.011	0.013	0.016	0.024
$S = R_{wp}/R_e$	2.18	2.24	2.44	2.36

Note. Space group is $P\bar{3}m1$, and Z is 1. $R_{wp} = [\Sigma w_i(y_i(\text{obs}) - y_i(\text{calc}))^2/(\Sigma w_i y_i(\text{obs})^2)]^{1/2}$. $R_p = (\Sigma|y_i(\text{obs}) - y_i(\text{calc})|)/\Sigma y_i(\text{obs})$. $R_B = (\Sigma|I_K(\text{'obs'}) - I_K(\text{calc})|)/\Sigma I_K(\text{'obs'})$. $R_F = (\Sigma|I_K(\text{'obs'})^{1/2} - I_K(\text{calc})^{1/2})|/\Sigma I_K(\text{'obs'})^{1/2}$. $R_e = [(N - P)/\Sigma w_i y_i(\text{obs})]^{1/2}$ (Ref. 9).

ing that there are two double bonds in the symmetrical $^-N{=}C{=}N^-$ ion. In $H_2N{-}C{\equiv}N$, the bond distance of one C—N bond is 1.31 Å and another is 1.15 Å. Similarly $PbCN_2$ has two different C—N bonds, i.e., 1.25 and 1.17 Å. In both cases of $CaCN_2$ and $H_2N{-}C{\equiv}N$, the N—C—N group is linear, while as for $PbCN_2$, the N—C—N angle is 177° 30′, which deviates slightly from linearity. In $Ln_2O_2CN_2$, the CN_2^{2-} ion has two equivalent double bonds and is linear. The value of C=N distances in $Ln_2O_2CN_2$ are 1.26–1.30 Å, which are similar to the C—N distance in $CaCN_2$, 1.25 Å (12). Our results also support the existence of cyanamide ions in $Ln_2O_2CN_2$.

Figure 3 illustrates the crystal structure of the trigonal $Ln_2O_2CN_2$. The structures of the $Ln_2O_2^{2+}$ layers in the trigonal $Ln_2O_2CN_2$ are similar to those of the trigonal or the hexagonal Ln_2O_2X (X = S (13, 14), Se (15), CO_3 (16)). In $Ln_2O_2CN_2$, Ln^{3+}'s are slightly stuck out of the O^{2-} plane toward the outside from the central plane of the $Ln_2O_2^{2+}$ layers. The $Ln_2O_2^{2+}$ layers are laid perpendicular to the c axis and the linear CN_2^{2-} ions are inserted parallel to the

TABLE 4
Structural Parameters for the Trigonal $Ln_2O_2CN_2$ in $P\bar{3}m1$
(T = Room temperature)

Atom	Site	g	x	y	z	B(Å^2)
			Pr			
Pr	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.1819(9)	0.4(1)
O	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.892(6)	0.9(14)
C	1b	1.0	0	0	$\frac{1}{2}$	2.3(44)
N	2c	1.0	0	0	0.346(9)	1.6(16)
			Nd			
Nd	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.1811(8)	0.4(1)
O	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.893(6)	1.0(13)
C	1b	1.0	0	0	$\frac{1}{2}$	3.8(49)
N	2c	1.0	0	0	0.349(9)	1.3(16)
			Sm			
Sm	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.180(1)	0.4(2)
O	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.882(7)	1.2(15)
C	1b	1.0	0	0	$\frac{1}{2}$	3.5(52)
N	2c	1.0	0	0	0.345(10)	0.8(17)
			Eu			
Eu	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.180(1)	0.3(2)
O	2d	1.0	$\frac{1}{3}$	$\frac{2}{3}$	0.887(6)	0.2(13)
C	1b	1.0	0	0	$\frac{1}{2}$	0.7(37)
N	2c	1.0	0	0	0.342(12)	1.8(19)

TABLE 5
Interatomic Distances in the Trigonal $Ln_2O_2CN_2$ in Å

	Pr	Nd	Sm	Eu
Ln–O	2.34(1)	2.32(1)	2.27(1)	2.26(1)
Ln–N	2.64(4)	2.64(4)	2.59(4)	2.57(5)
C–N	1.28(8)	1.26(7)	1.29(9)	1.30(10)

c axis. The coordination number of Ln^{3+} is 7. The orientation of the linear $^-N{=}C{=}N^-$ ion does not deviate from the parallel to the *c* axis. N atom would have a larger thermal parameter in the position used in this analysis if the $^-N{=}C{=}N^-$ chain was inclined at some degrees. Ln^{3+} is surrounded by four oxygen and three nitrogen atoms. Ln^{3+} exists on the plane formed by three oxygen atoms, another oxygen atom locates under or over Ln^{3+}, and three nitrogen atoms form a plane parallel to the plane formed by Ln^{3+} and three oxygen atoms. On the other hand, in the tetragonal $Ln_2O_2CN_2$, the Rietveld analysis of the powder X-ray diffraction pattern revealed that the $Ln_2O_2^{2+}$ layers are perpendicular to the *c* axis, and the CN_2^{2-} ions are perpendicular to the *c* axis, i.e., parallel to the $Ln_2O_2^{2+}$ layers. The coordination number of Ln^{3+} is 8. The Ln^{3+} is surrounded by four oxygen atoms on the same plane and statistically four nitrogen atoms which are located on the same plane against the $Ln_2O_2^{2+}$ layers (2).

The ν_2 (bending) and ν_3 (antisymmetric stretch) modes of $^-N{=}C{=}N^-$ in IR spectra shift in the trigonal structure when compared to the tetragonal structure (Fig. 1b and 1c). In the trigonal structure, the ν_2 mode shifts to lower wavenumber and the ν_3 mode shifts to higher wavenumber when compared to the tetragonal phase. The differences in the wavenumbers of the ν_2 and the ν_3 modes between the tetragonal and the trigonal structures are 25 and 100 cm^{-3}, respectively. The shift of the ν_2 mode indicates that the bending of the $^-N{=}C{=}N^-$ ion in the trigonal structure occurs more easily than in the tetragonal structure. It is thought that the ν_3 mode is influenced by Ln^{3+}'s bond to N atoms. One N atom is surrounded by four Ln^{3+}'s in the tetragonal phase (2) and three in the trigonal phase. Therefore, the Coulomb force between the rare-earth and nitrogen atoms in the trigonal structure is less than that in the tetragonal structure, so the interaction between C and N is stronger and the ν_3 mode shifts to higher wavenumber in the trigonal structure.

Figure 4 shows the TG-DTA curve for $Nd_2O_2CN_2$. The measurement was carried out in air. The weight of sample begins to increase at about 923 K accompanied by an exothermic DTA peak. The curve shows a maximum weight gain at about 973 K and afterward shows a large decrease in weight. The weight of sample becomes constant at about 1323 K. The sample heated at about 1323 K was found to be Nd_2O_3 by X-ray diffraction. At the temperature where the weight of the sample is at a maximum, it was found by X-ray diffraction that the hexagonal $Nd_2O_2CO_3$ was produced. The results of the TG-DTA measurement and X-ray diffraction indicates that the interlayer anion CN_2^{2-} is oxidized to CO_3^{2-} by heating in air. The exothermic

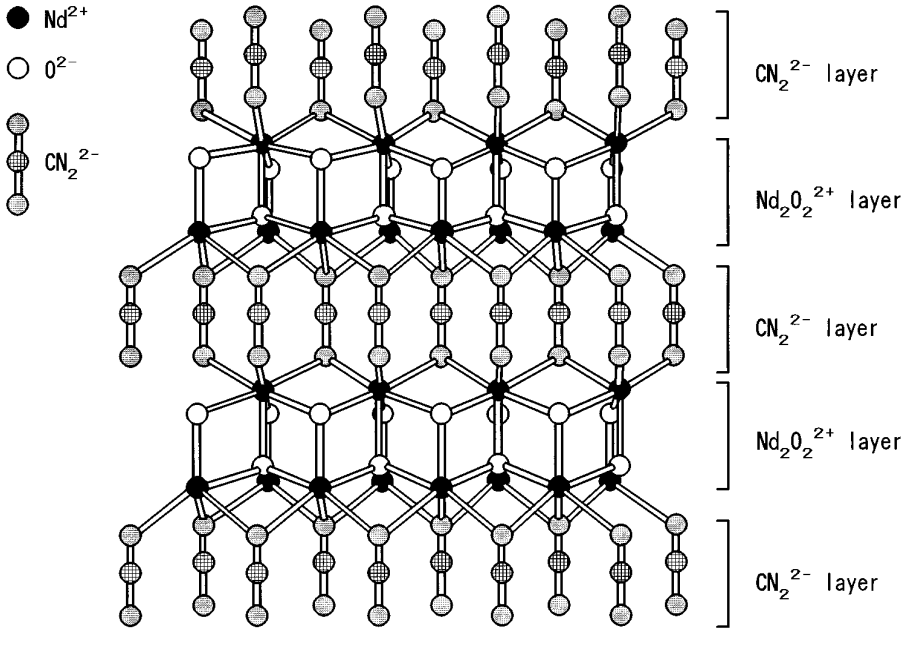

FIG. 3. Crystal structure of $Nd_2O_2CN_2$.

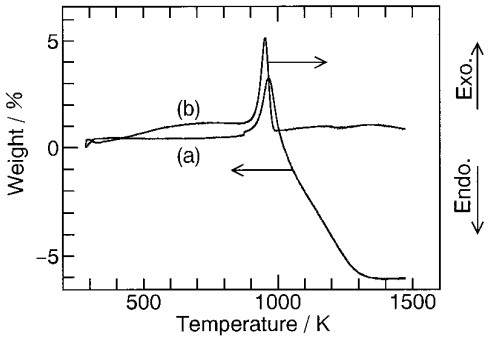

FIG. 4. (a)TG and (b)DTA curve for $Nd_2O_2CN_2$.

DTA peak at about 973 K is due to the oxidation of CN_2^{2-} to CO_3^{2-}. In addition to Ln= Nd, other $Ln_2O_2CN_2$ showed similar TG-DTA curves. The temperatures where the oxidations begin are 603, 803, 923, 943, 993, and 993 K for Ce, Pr, Nd, Sm, Eu, and Gd, respectively. The temperature increases remarkably with decreasing ionic radii of Ln^{3+}. Ln_2O_2S also become $Ln_2O_2SO_4$ by heating in air. In this case, the interlayer anion S^{2-} is oxidized to SO_4^{2-} and the crystal structures change from the trigonal (Ln_2O_2S) to the orthorhombic ($Ln_2O_2SO_4$) structure (17).

Supplementary materials have been deposited and may also be obtained from the authors.

CONCLUSION

The crystal structures of the trigonal $Ln_2O_2CN_2$ were analyzed by the Rietveld refinement of the powder X-ray diffraction pattern. The trigonal $Ln_2O_2CN_2$ crystallize in the space group $P\bar{3}m1$ ($Z = 1$). It was found that these compounds consist of the $Ln_2O_2^{2+}$ layers with the interlayer CN_2^{2-} ions. The IR spectra of the trigonal and the tetragonal $Ln_2O_2CN_2$ indicate that the coordination of Ln^{3+} atoms around nitrogen atoms are different in each structure type. Because of the layer structure, the interlayer CN_2^{2-} ion is oxidized to CO_3^{2-} by heating in air. The structures of the trigonal $Ln_2O_2CN_2$ are closely related to those of the trigonal Ln_2O_2X (X = S, Se) and the hexagonal Ln_2O_2X ($X = CO_3$) which consist of the $Ln_2O_2^{2+}$ layers and the interlayer anions.

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