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Syntheses of Rare Earth Dioxymonocyanamides ($Ln_2O_2CN_2$, Ln=La, Ce, Pr, Nd, Sm, Eu, Gd)

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A series of new compounds were prepared by heating Ln_2O_3 (Ln=La, Nd, Sm, Eu, Gd), Pr_6O_{11}, or $Ce_2(CO_3)_3 \cdot 8H_2O$ in the presence of carbon under an ammonia atmosphere. Thermogravimetric and CHN analyses revealed that these compounds are of rare earth dioxymonocyanamides ($Ln_2O_2CN_2$). They are classified into two structure types depending on Ln^{3+} ionic radii, viz., type I (tetragonal) for Ln=La, Ce and type II (trigonal) for Ln=Ce, Pr, Nd, Sm, Eu, Gd. $Ce_2O_2CN_2$ takes both structure types depending upon preparative temperature.

There are some compounds involving rare earth metal ions, anions, and polyatomic anions, e.g., $LaONO_3$,[1-3] $La_2O_2(SO_4)$,[4] $CeFCO_3$,[5] $Nd_2O(SO_4)_2$[6] and so on. We have recently synthesized a new compound consisting of rare earth metal ions, oxide ions, and polyatomic anions, which was prepared by heating La_2O_3 in the presence of carbon under an ammonia atmosphere.[7] The chemical composition was determined to be $La_2O_2CN_2$ by CHN elemental analysis and thermogravimetry in air. The compound was identified to have a tetragonal unit cell with a=0.4096 and c=1.2334 nm by the x-ray diffraction analysis. There is a possibility to form a series of compounds with chemical formula $Ln_2O_2CN_2$ because the valency state of most rare earth metal ions are usually trivalent and their chemical properties are similar to that of La. This paper concerned with the preparation of new compounds, rare earth dioxymonocyanamides, $Ln_2O_2CN_2$ (Ln=La, Ce, Pr, Nd, Sm, Eu, Gd).

Ln_2O_3 (Ln=La, Nd, Sm, Gd) or Pr_6O_{11} was heated in graphite boats at 1223 K for 12h in flowing ammonia gas. When CeO_2 was used as a starting material, the product was a mixture of CeO_2, Ce_2O_3, and Ce_2ON_2 and was deflagrated on opening furnace. The desired compound was only obtained using $Ce_2(CO_3)_3 \cdot 8H_2O$ as a starting material. In the case of Ln=Eu, Eu_2O_3 was calcined at 1073 K because Eu_2O_3 melted at 1073 K. Chemical compositions of the products were determined by both CHN and TG analyses on oxidizing the samples to oxides. Powder x-ray diffraction data were collected using a Rigaku Rint 1000 diffractometer fitted with a graphite-monochromator and Cu-$K\alpha$ radiation. Densities of the products were measured using a pycnometer. Infra-red spectra were recorded on a Hitachi spectrophotometer using samples in spectroscopically pure KBr pellets.

The chemical formula of the compounds was determined by the same way as that of $La_2O_2CN_2$. The chemical formula of all the product was estimated to be $Ln_2O_2CN_2$ from both results of CHN and TG analyses. For Ln=Nd, the experimental values of C, N, and O contents and the theoretical ones calculated as $Nd_2O_2CN_2$ are shown in Table 1 as the typical example.

It was found by the x-ray diffractometry that there are two types of crystal structures, i.e., type I for La or Ce and type II for Ce, Pr, Nd, Sm, Eu, Gd. In the case of Ln=Ce, the both structures were

Table 1. Comparison between the experimental and calculated values of C, N, and O in $Nd_2O_2CN_2$

	C / wt%	N / wt%	O / wt%	Weight loss / %
Expd.	3.3[a)]	7.6[a)]	9.0[b)]	6.6
Calcd.	3.3	7.8	8.9	6.7

a) The values were obtained by CHN analysis.

b) Oxygen content was determined by weight loss on oxidation of the sample to Nd_2O_3 and CHN analysis data.

obtained depending upon firing temperature. When $Ce_2(CO_3)_3 \cdot 8H_2O$ was heated at about 1223 K, the compound with structure type Ⅰ was produced, and when heated at about 1273 K, that with structure type Ⅱ was produced. The powder x-ray diffraction patterns of the products for Ln=La and Ln=Nd are shown in Fig. 1 as the typical examples for the structure type Ⅰ and type Ⅱ, respectively. These products could not be identified by using JCPDS data.[8)] All the diffraction peaks of structure type Ⅰ could be indexed as a tetragonal cell, and those of structure type Ⅱ could be indexed as a trigonal cell. Programs CELL[9)] series were available for indexing. It depends on Ln^{3+} ionic radii which structure type of Ⅰ or Ⅱ is yielded, and the ionic radius of trivalent cerium ion seems to be just one on the boundary between two types. The observed density of $Nd_2O_2CN_2$ was 5.55 g/cm^3, which was in good agreement with the calculated one, 5.52 g/cm^3 at Z=1. The observed density of $La_2O_2CN_2$ was 5.44 g/cm^3 and calculated one was 5.62 g/cm^3 at Z=2.[7)] It was found by neutron diffractometry that the coodination numbers of type Ⅰ and type Ⅱ are 8 and 7, respectively. The details of the structure analyses will be mentioned elsewhere. Relation between Ln^{3+} effective ionic radii (R^e) and lattice constants or cell volumes per a formula unit are shown in Fig. 2. The values of Ln^{3+} effective ionic radii for type Ⅰ and type Ⅱ were adopted those of

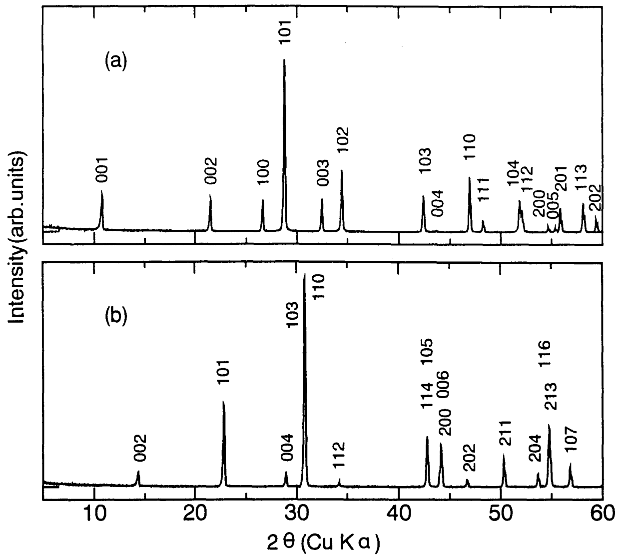

Fig. 1. Powder x-ray diffraction patterns of $Ln_2O_2CN_2$, (a) Ln=Nd, (b) Ln=La.

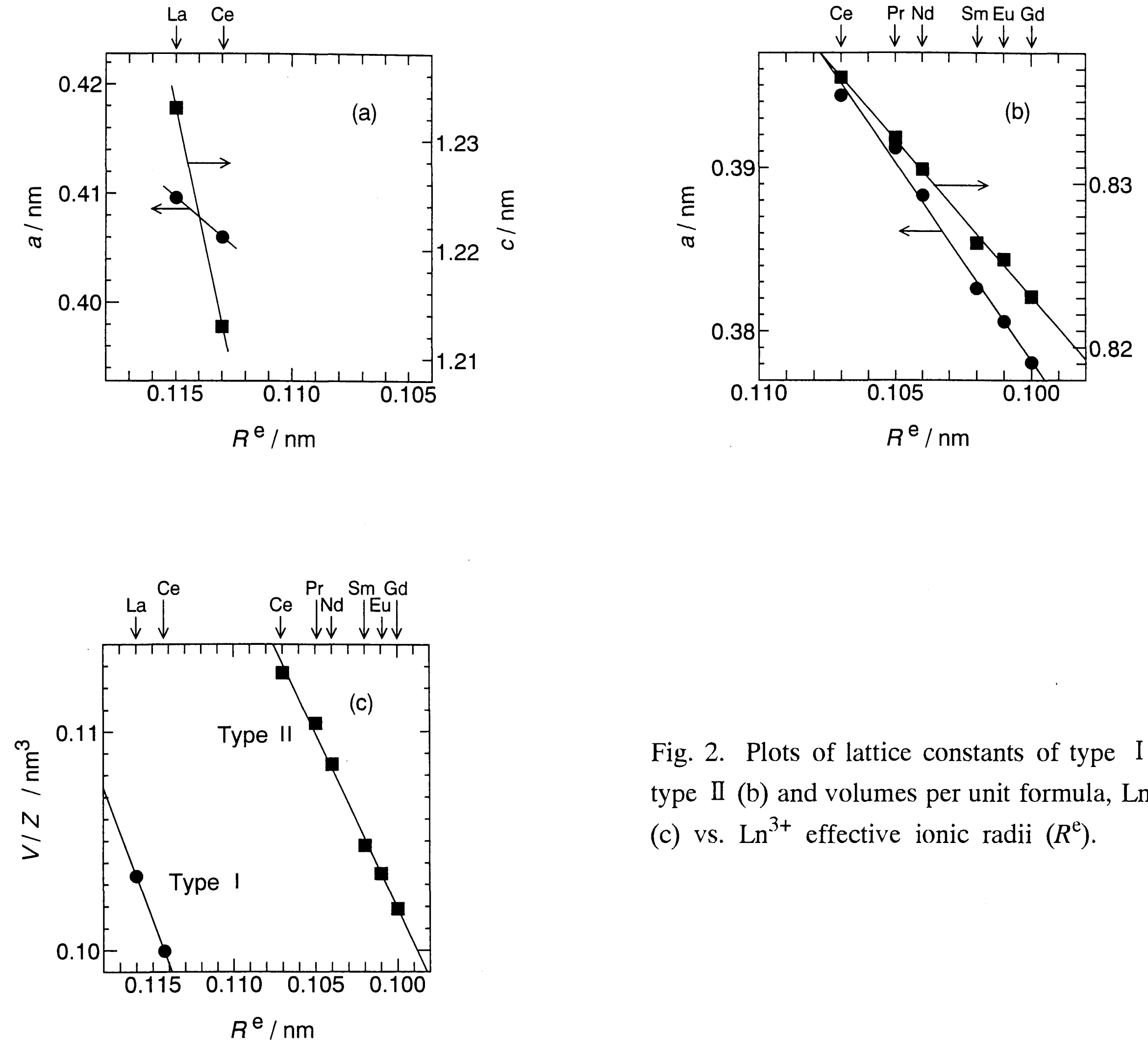

Fig. 2. Plots of lattice constants of type I (a) and type II (b) and volumes per unit formula, $Ln_2O_2CN_2$ (c) vs. Ln^{3+} effective ionic radii (R^e).

coordination number 8 and 7,[10] respectively. It is found that the lattice constants and the cell volumes of type I and type II compounds monotonously decrease with decreasing of Ln^{3+} effective ionic radii. Figure 2(c) also shows that type I compounds are packed more loosely than type II compounds. This is due to the difference of coordination numbers between type I and type II structure. X-ray study revealed that all the products did not decompose at room temperature in air and even in water.

Figure 3 shows the ir spectra of $La_2O_2CN_2$ and $Nd_2O_2CN_2$. Ir spectra for $Nd_2O_2CN_2$ and $La_2O_2CN_2$ have the intense peaks at 2050 and 1950 cm^{-1}, respectively. We reported in the previous study that the noticeable peak at 1950 cm^{-1} in the spectrum of $La_2O_2CN_2$ was assigned to ν_3 mode of CN_2^{2-} according to the results of XPS and ir spectrum. Therefore, the spectrum in Fig. 3 (b) shows that compounds of type II also contain CN_2^{2-} ions.

From above-mentioned observations, it was found that a series of rare earth dioxymonocyanamides was represented as the chemical formula of $Ln_2O_2CN_2$.

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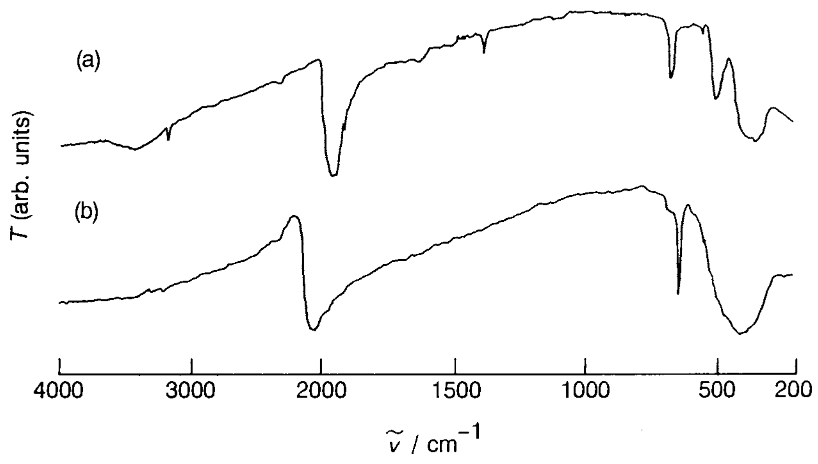

Fig. 3. Infra-red spectra of $Ln_2O_2CN_2$, (a) Ln=La, (b) Ln=Nd.

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