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Rare Earth Carbodiimide Silicates: $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$

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Dedicated to Professor Rüdiger Kniep on the occasion of His 75th Birthday

Keywords: Rare earth; Carbodiimide; Silicate; Metathesis; Structure elucidation, X-ray diffraction

Abstract. Rare earth carbodiimide silicates $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ with RE = Y, La, and Pr where synthesized via solid state metathesis reactions of RECl_3 , $\text{Li}_2(\text{CN}_2)$, and SiO_2 or Li_2SiO_4 , respectively, in silica tubes at 550 °C. All three compounds crystallize with different structures, although all of them represent distorted derivatives of the sodium chloride type structure. The structure of $\text{Y}_2(\text{CN}_2)(\text{SiO}_4)$ was refined monoclinically ($C2/m$, $Z = 2$, $a = 1301.382(5)$ pm, $b = 377.630(1)$ pm, $c = 527.656(2)$ pm, $\beta = 93.9816(2)^\circ$) from X-ray powder data. The crystal structure of $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$ was refined in a different monoclinic space group ($P2_1/c$, $Z = 4$, $a = 660.3(1)$ pm, $b = 1282.01(2)$ pm, $c = 656.2(1)$ pm, $\beta = 105.23(2)^\circ$), and the structure of $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$ was refined triclinically ($P\bar{1}$, $Z = 2$, $a = 646.7(2)$ pm, $b = 669.2(2)$ pm, $c = 671.8(2)$ pm, $\alpha = 86.18(3)^\circ$, $\beta = 73.22(3)^\circ$, $\gamma = 74.08(3)^\circ$) from X-ray single crystal data.

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Introduction

A great deal of rare earth carbodiimide compounds was synthesized following solid state metathesis (SSM) reactions between rare earth trihalides and lithium carbodiimide. On heating these mixtures, metathesis reactions reveal their characteristics, with a soft ignition coming about when heating up reaction mixtures into a temperature region within 450 to 550 °C. The series of quasi-binary carbodiimide $\text{RE}_2(\text{CN}_2)_3$ compounds [1,2] with trivalent rare earth ions ($\text{RE} = \text{Y} - \text{Lu}$, except Pm , La) are fundamental examples of rare earth carbodiimide chemistry. But there are also multinary carbodiimide (or in some cases cyanamide) compounds represented by the formulas $\text{REX}(\text{CN}_2)$ ($\text{X} = \text{Cl}$, F) [3,4], $\text{RE}_2\text{X}(\text{CN}_2)\text{N}$ ($\text{X} = \text{Cl}$, Br , I) [5,6], $\text{LiRE}_2\text{X}_3(\text{CN}_2)_2$ ($\text{X} = \text{F}$) [4], as well as very recently discovered compounds $\text{LiRE}(\text{CN}_2)_2$ ($\text{RE} = \text{La}$, Ce) and $\text{Ce}_3(\text{CN}_2)_3\text{N}$ [7]. All these compounds being obtained from SSM reactions, departing from different stoichiometries of REX_3 and $\text{Li}_2(\text{CN}_2)$ mixtures, account for the rapid growth of this new family of rare earth carbodiimide compounds, and the thereon resting development of tetracyanamidosilicates [8].

An extension of this preparative concept to higher complexity comes about when another reaction partner is being introduced into a given SSM reaction. The introduction of oxide into a SSM reaction was previously explored with various oxygen sources in order to develop a high yield synthesis of $\text{Y}_2\text{O}_2(\text{CN}_2):\text{Eu}$ [9]. During reactions performed in silica tubes an unknown side phase appeared which later turned out to be $\text{Y}_2(\text{CN}_2)(\text{SiO}_4)$, which was the starting point of this work.

Mixed anion compounds like $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ are known for various examples of rare earth orthosilicates containing yet another anion. The doubly charged carbodiimide ion and its assignment as a pseudo-chalcogenide [9, 10, 11] leads to compounds having the general formula $\text{RE}_2\text{Ch}(\text{SiO}_4)$ being known for $\text{Ch} = \text{O}$ [12], S [13], Se [14] and Te [15]. From a structural point of view, the compounds RE_2O_3 , $\text{RE}_2\text{O}_2\text{S}$ and $\text{RE}_2\text{O}_2(\text{CN}_2)$ have been shown to crystallize in closely related structures [9].

The luminescence behaviour of lanthanide-doped carbodiimide oxide compounds having the general formula $\text{RE}_2\text{O}_2(\text{CN}_2):\text{Ln}$ [16,17,18] provides an interesting potential of carbodiimide compounds. Moreover, the luminescence behaviour of $\text{Y}_2\text{O}_2(\text{CN}_2):\text{Eu}$ appears to be similar with that of the well-known red light emitter $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ [9]. In addition, the rare earth silicates $\text{Y}_3\text{SiO}_5:\text{Ln}$ ($\text{Ln} = \text{Ce}$ or Tb) are phosphors of current interest, being used in field emission displays (FEDs) [19].

In this work we present the novel $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ compounds, originally obtained from a reaction of rare earth carbodiimide with silica glass, and we describe the selective SSM preparations of these compounds, including their crystal structures.

Experimental Section

Synthesis of $\text{Li}_4(\text{SiO}_4)$

Lithium orthosilicate was prepared by solid state reaction on heating amorphous silica (Ventron, 99.9%, -325 mesh) and lithium carbonate (Li_2CO_3 , Alfa, ultra pure). Amorphous silica and Li_2CO_3 were carefully mixed in an agate mortar in 1:2 molar ratio and heated at 800 °C for 4 h in air [20].

Lithium orthosilicate obtained from the reaction was X-ray pure.

Synthesis of $\text{RE}_2(\text{SiO}_4)(\text{CN}_2)$

Method 1: Reaction mixtures were prepared in an argon filled glove box starting from carefully homogenized mixtures of RECl_3 (ABCR 99.9 %), $\text{Li}_2(\text{CN}_2)$ (prepared as previously reported [7]) and SiO_2 (Ventron, 99.9%, $\approx$ 325 mesh). Reaction mixtures of 61.3 mg LaCl_3 , 61.8 mg PrCl_3 and 48.8 mg YCl_3 , respectively, were loaded with 54 mg Li_2CN_2 , 15 mg SiO_2 and 20 mg KCl (Merck, p.a.) being carefully mixed and ground in a agate mortar. Each mixture was placed into a dry silica ampoule. Ampoules were evacuated, sealed under vacuum and heated up to 550 °C (5 °C/min), held at this temperature for 3 days, and then cooled down to room temperature. The reaction products were washed with water several times, rinsed with ethanol, and dried at 85 °C in air. Results of powder XRD measurement revealed that the title compounds were the main crystalline products with estimated yields >90 %.

Method 2: Reaction mixtures were prepared in an argon filled glove box starting from carefully homogenized mixtures of RECl_3 , $\text{Li}_2(\text{CN}_2)$ and Li_4SiO_4 being carefully mixed and ground in a agate mortar. Each mixture was placed into a dry silica ampoule. Ampoules were evacuated, sealed under vacuum and heated up to 550 °C (5 °C/min), held at this temperature for 3 days, and then cooled down to room temperature. The reaction products were washed with water several times, rinsed with ethanol, and dried at 85 °C in air. Results of powder XRD measurement revealed reflections of the title compounds as the only crystalline products with estimated yields >95 %.

Powder X-Ray Diffraction

The powder XRD patterns of all reaction products were collected with a Stadi-P (Stoe, Darmstadt) powder diffractometer using $\text{Cu-K}_{\alpha 1}$ ($\lambda = 154.06$ pm) radiation (germanium monochromator). Most samples occurred to be X-ray pure, except for some samples being prepared following method 1 which were slightly contaminated with Li_2SiO_3 .

The patterns were indexed by using the program system WinXPow [21]. The structure of $\text{Y}_2(\text{CN}_2)(\text{SiO}_4)$ was indexed monoclinically with $a = 1303.3(3)$ pm, $b = 377.6(6)$ pm, $c = 527.8(1)$ pm, $\beta = 93.96(1)^\circ$ and $V = 259.2(2) \text{ \AA}^3$ based on 28 single indexed lines, $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$ was indexed monoclinically with $a = 666.1(2)$ pm, $b = 1282.0(3)$ pm, $c = 651.8(2)$ pm, $\beta = 105.13(1)^\circ$ and $V = 537.4(3) \text{ \AA}^3$ based on 37 single indexed lines, and $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$ was indexed

1 triclinically with $a = 646.5(3)$ pm, $b = 670.0(5)$ pm, $c = 671.5(4)$ pm, $\alpha = 86.09(3)^\circ$, $\beta = 73.29(2)$
2 $^\circ$, $\gamma = 74.09(3)^\circ$ and $V = 267.9(3) \text{ \AA}^3$ based on 22 single indexed lines.

3 The crystal structure $\text{Y}_2(\text{CN}_2)(\text{SiO}_4)$ was solved and refined in the monoclinic space group $C2/m$
4 from powder XRD data ($a = 1301.38(7)$ pm, $b = 377.63(2)$ pm, $c = 527.66(3)$ pm and $\beta =$
5 $93.982(4)^\circ$, $Z = 2$) using the program packages EXPO [22] and Fullprof [23] based on 258
6 independent reflections and 40 refined parameters, yielding $R_{\text{Bragg}} = 6.42$.
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8 Positions of $(\text{CN}_2)^{2-}$ and $(\text{SiO}_4)^{4-}$ were refined in a disordered fashion on similar positions. No
9 sign of a superstructure could be detected. Atom positions are listed in Table 2 and selected
10 bond lengths are given in Table 3.
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15 **Single-Crystal X-Ray Diffraction**

16 Colorless transparent crystals of $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$ and light green crystals of $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$ were
17 selected from the reaction product and mounted on the tip of a glass fiber for a crystal structure
18 determination. Intensity data were collected on a Stoe IPDS diffractometer using $\text{Mo-K}\alpha$
19 radiation. The data sets were corrected for Lorentz and polarization effects. Absorption
20 corrections were carried out using crystal-shape optimization (X-Shape, X-RED). The program
21 package SHELX97 [24] was used for crystal structure solutions and anisotropic refinements of
22 all atoms. Some selected crystallographic data and some details of the structure refinements are
23 listed in Table 1. Atomic positions and equivalent isotropic displacement parameters are given in
24 Table 2, and a summary of selected bond lengths is given in Table 3.
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33 Further details of the crystal-structure investigation may be obtained from the
34 Fachinformationszentrum Karlsruhe, D-73644 Eggenstein-Leopoldshafen, Germany (fax:
35 (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-
36 420943 for $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$ and CSD-420944 for $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$.
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41 **Results and Discussion**

42 Solid state metathesis reactions were used for the synthesis of three selected examples of
43 hitherto unknown new rare earth carbodiimide silicates. Powders of $\text{Y}_2(\text{CN}_2)(\text{SiO}_4)$ were
44 originally obtained as a side phase from reactions of YCl_3 and $\text{Li}_2(\text{CN}_2)$ with the wall of the silica
45 container. This reaction was successfully reproduced in our synthesis described as method 1 in
46 the experimental section by using small sized SiO_2 as a reactant. Subsequent reactions
47 described in method 2 are straight forward SSM reactions to combine a rare earth element (as
48 RECl_3) simultaneously with carbodiimide (as $\text{Li}_2(\text{CN}_2)$) and orthosilicate (as $\text{Li}_4(\text{SiO}_4)$) ions. Since
49 $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ compounds behave stable in air and in water, the coproduced LiCl can be easily
50 removed from the reaction products. The use of KCl in the reaction mixture was intended to
51 allow better crystal growth, due to the formation of a LiCl/KCl flux in course of the reaction. The
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example of our $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ synthesis provides a general concept for SSM reactions to obtain mixed anion compounds.

The three compounds $\text{Y}_2(\text{CN}_2)(\text{SiO}_4)$, $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$, and $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$ crystallize with three different crystal structures, all being related to the motif of the arrangement of ions in the NaCl type structure, where the centers of gravities of $(\text{CN}_2)^{2-}$ and $(\text{SiO}_4)^{4-}$ ions occupy anion positions in an alternating fashion. However, the structure refined for $\text{Y}_2(\text{CN}_2)(\text{SiO}_4)$ revealed disordering of these anions, resulting in a picture in which anions superimpose each other at the same lattice voids. Although the refinement from powder data may reveal an intrinsically higher degree of uncertainty of a given structure refinement, no evidence for the presence of a superstructure was detectable from powder X-ray patterns. With respect to the difficulty related with this structure, we will only discuss the structures of $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$ and $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$ in more detail, with their structures being projected in Figures 1 and 2, in which the NaCl type related unit sections are emphasized as dotted lines. The alternating arrangements the two types of anions in the structures introduce a layered nature, being characterized by alternating $[\text{RE}(\text{CN}_2)]^+$ and $[\text{RE}(\text{SiO}_4)]^-$ sequences (with $\text{RE} = \text{La}, \text{Pr}$). As a consequence, the crystal structures of $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ contain two crystallographically distinct RE ions displayed in Figures 3 and 4. La1 is surrounded by four carbodiimide (La1–N: 265 – 284 pm) and three silicate ions (La1–O: 242 – 283 pm) and La2 by two carbodiimide (La2–N: 265 – 269 pm) and four silicate ions (La2–O: 238 – 288 pm), whereas silicate groups connect via one or two oxygen atoms with one and the same lanthanum atom. The coordination environment of Pr1 involves two carbodiimide (Pr1–N: 252 – 257 pm) and four silicate ions (Pr1–O: 228 – 275 pm) and Pr2 is surrounded by three carbodiimide (Pr2–N: 253 – 270 pm) and three silicate ions (Pr2–O: 244 – 264 pm).

Each of the presented $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ structure contains one distinguishable $[\text{NCN}]^{2-}$ ion, having N–C–N bond angles of 177(1) ° with C–N bond length of 121(2), 126(2) pm for $\text{RE} = \text{La}$, and N–C–N bond angles of 176.4(8) ° with C–N bond length of 125(1), 122(4) pm for $\text{RE} = \text{Pr}$. In spite of their significant deviations from ideal $D_{\infty h}$ symmetry, the $[\text{N}=\text{C}=\text{N}]^{2-}$ ions are considered as carbodiimide ions (rather than cyanamide) for reasons discussed previously [7].

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Table 1. Single crystal data on structure refinements on RE₂(CN₂)(SiO₄) with RE = La, Pr. P $\bar{1}$

Empirical formula	La ₂ (CN ₂)(SiO ₄)	Pr ₂ (CN ₂)(SiO ₄)
Formula weight / g/mol	409.94	413.94
Temperature / K	293(2)	293(2)
Wavelength / Å	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group (No.)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> $\bar{1}$
Unit cell dimensions / pm or °	<i>a</i> = 660.3(1) <i>b</i> = 1282.0(2), β = 105.23(2) <i>c</i> = 656.2(1)	<i>a</i> = 646.7(2), α = 86.18(3) <i>b</i> = 669.2(2), β = 73.22(3) <i>c</i> = 671.8(2), γ = 74.08(3)
Volume / 10 ⁶ pm ³	535.9(2)	267.7(1)
Z	4	2
Density (calculated) / g/cm ³	5.081	5.136
Absorption coefficient / mm ⁻¹	15.891	18.150
F(000)	720	368
Crystal size / mm ³	0.14 x 0.13 x 0.04	0.12 x 0.10 x 0.06
Theta range for data collection / °	3.18 to 24.71	3.17 to 25.04
Index ranges	-7 ≤ <i>h</i> ≤ 7, -15 ≤ <i>k</i> ≤ 15, -7 ≤ <i>l</i> ≤ 7	-7 ≤ <i>h</i> ≤ 7, -7 ≤ <i>k</i> ≤ 7, -7 ≤ <i>l</i> ≤ 7
Reflections collected	5318	2710
Independent reflections	939 [R(int) = 0.0883]	884 [R(int) = 0.0271]
Completeness to theta	100.0 %	93.3 %
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	939 / 0 / 92	884 / 0 / 91
Goodness-of-fit on F ²	1.114	1.293
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0375 wR2 = 0.1057	R1 = 0.0244 wR2 = 0.0665
R indices (all data)	R1 = 0.0379 wR2 = 0.1064	R1 = 0.0257 wR2 = 0.0670
Largest diff. peak and hole / e/10 ⁶ pm ³	2.127 and -2.910	1.047 and -2.726

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (10^4 pm^2) for $\text{RE}_2(\text{CN}_2)(\text{SiO}_4)$ (RE = La, Pr). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Isotropic displacement parameters U_{iso} (10^4 pm^2) are given for RE = Y.

$\text{La}_2(\text{CN}_2)(\text{SiO}_4)$

Atom	x	y	z	U_{eq}
La1	0.4131(1)	0.09933(6)	0.2186(1)	0.0144(3)
La2	0.0294(1)	-0.1454(1)	0.3295(1)	0.0151(3)
Si	0.0924(6)	-0.0995(3)	0.8115(6)	0.0150(8)
O1	0.105(2)	0.0532(8)	0.370(1)	0.017(2)
O2	0.253(2)	-0.0075(8)	-0.085(2)	0.024(2)
O3	-0.026(2)	-0.1656(7)	-0.042(2)	0.016(2)
O4	0.222(2)	-0.1802(8)	0.705(2)	0.015(2)
C	-0.474(2)	-0.152(1)	0.272(2)	0.017(3)
N1	-0.574(2)	-0.0974(9)	0.360(2)	0.024(3)
N2	-0.372(2)	-0.2047(9)	0.172(2)	0.019(3)

$\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$

Atom	x	y	z	U_{eq}
Pr1	0.06189(5)	0.23652(5)	0.33127(5)	0.0068(2)
Pr2	0.45537(5)	0.31934(6)	-0.21243(5)	0.0084(2)
Si	-0.0428(3)	0.2955(3)	-0.1844(3)	0.0072(4)
O1	0.1118(8)	-0.1304(8)	0.3035(7)	0.010(1)
O2	-0.1359(7)	0.6117(7)	0.3701(7)	0.0089(9)
O3	0.0896(8)	0.2237(8)	-0.0145(7)	0.011(1)
O4	0.2758(8)	0.5199(8)	0.1105(7)	0.011(1)
C	0.563(1)	0.178(1)	0.303(1)	0.010(2)
N1	0.478(1)	0.070(1)	0.236(1)	0.019(2)
N2	0.6401(9)	0.299(1)	0.3758(9)	0.011(1)

Y₂(CN₂)(SiO₄)

Atom	x	y	z	U _{iso}	Occ.
Y	0.1291(1)	0	0.3749(3)	0.0063(5)	1
Si	0.0930(6)	1/2	0.819(2)	0.003(3)	0.5
O1	0.116(2)	1/2	0.108(5)	0.023(4)	0.5
O2	0.203(2)	1/2	0.656(5)	0.016(4)	0.5
O3	0.0352(6)	0.136(2)	0.730(1)	0.013(3)	0.5
C	0.155(2)	1/2	0.865(6)	0.02(1)	0.5
N1	0.152(2)	1/2	0.090(5)	0.023(4)	0.5
N2	0.177(2)	1/2	0.643(6)	0.016(4)	0.5

Table 3. Selected bond lengths (pm) and angles (°) for RE₂(CN₂)(SiO₄) compounds.

La ₂ (CN ₂)(SiO ₄)			Pr ₂ (CN ₂)(SiO ₄)			Y ₂ (CN ₂)(SiO ₄)		
La1-O1	256(1)		Pr1-O1	253.0(5) 240.0(5)		Y-O1	235(2)	2 x
La1-O2	242(1) 283(1)		Pr1-O2	247.8(5) 252.5(5)		Y-O2	255(2) 221(3)	2 x
La1-O3	265(1)		Pr1-O3	228.3(5)		Y-O3	236.4(8) 223.1(8)	2 x 2 x
La1-O4	255(1)		Pr1-O4	275.5(5)				
La1-N1	268(1) 269(1)		Pr1-N1	251.8(6)		Y-N1	244(2)	2 x
La1-N2	265(1) 284(1)		Pr1-N2	257.4(6)		Y-N2	254(2) 241(2)	2 x
La2-O1	260(1) 264(1)		Pr2-O1	264.2(5)				
La2-O2	288(1)		Pr2-O2	250.6(5)				
La2-O3	238(1) 262.3(9)		Pr2-O3	258.3(5)				
La2-O4	250(1) 280(1)		Pr2-O4	243.6(5) 254.2(5)				
La2-N1	265(1)		Pr2-N1	252.7(7)				
La2-N2	269(1)		Pr2-N2	267.4(6) 269.7(6)				
Si-O1	162.9(9)		Si-O1	162.9(5)		Si-O1	154(3)	
Si-O2	161(1)		Si-O2	165.4(5)		Si-O2	172(3)	
Si-O3	163(1)		Si-O3	159.2(5)		Si-O3	162.0(9)	2 x
Si-O4	162(1)		Si-O4	163.4(5)				
C-N1	121(2)		C-N1	120(1)		C-N1	119(4)	
C-N2	126(2)		C-N2	125(1)		C-N2	122(4)	
N1-C-N2	177(2)		N1-C-N2	176.4(8)		N1-C-N2	169(5)	

References

- [1] M. Neukirch, S. Tragl, H.-J. Meyer, *Inorg. Chem.* **2006**, 45, 8188.
- [2] J. Glaser, L. Unverfehrt, H. Bettentrup, G. Heymann, H. Huppertz, T. Jüstel, H.-J. Meyer, *Inorg. Chem.* **2008**, 47, 10455.
- [3] R. Srinivasan, J. Glaser, S. Tragl, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2005**, 631, 479.
- [4] L. Unverfehrt, J. Glaser, M. Ströbele, S. Tragl, K. Gibson, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2009**, 635, 479.
- [5] R. Srinivasan, M. Ströbele, H.-J. Meyer, *Inorg. Chem.* **2003**, 42, 3406.
- [6] R. Srinivasan, Dissertation, Univ. Tübingen, 2004.
- [7] L. Unverfehrt, M. Ströbele, J. Glaser, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2009**, 635, 1947.
- [8] J. Glaser, S. Tragl, H.-J. Meyer, *Angew. Chem.* **2008**, 120, 7658; *Angew. Chem. Int. Ed. Engl.* **2008**, 47, 7547.
- [9] J. Sindlinger, J. Glaser, H. Bettentrup, T. Jüstel, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2007**, 633, 1686.
- [10] X. Liu, M. Krott, P. Müller, C. Hu, H. Lueken, R. Dronskowski, *Inorg. Chem.* **2005**, 44, 3001.
- [11] X. Liu, M. Krott, L. Stork, M. Speldrich, H. Lueken, R. Dronskowski, *Chem. Eur. J.* **2009**, 15, 1558.
- [12] H. Müller-Bunz, T. Schleid, *Z. Anorg. Allg. Chem.* **1999**, 625, 613; I. Hartenbach, S.F. Meier, J. Wontcheu, T. Schleid, *Z. Anorg. Allg. Chem.* **2002**, 628, 2907.
- [13] I. Hartenbach, P. Lauxmann, T. Schleid, *Z. Anorg. Allg. Chem.* **2004**, 630, 1408.
- [14] M. Gruppe, W. Urland, *Z. Naturforsch.* **1989**, 45b, 456.
- [15] H. Person, M. Grupe, W. Urland, *Z. Anorg. Allg. Chem.* **2000**, 626, 280.
- [16] E. Säilynoja, M. Lastusaari, J. Hölsä, P. Porcher, *J. Lumin.* **1997**, 210, 72.
- [17] J. Hölsä, R.-J. Lamminmäki, M. Lastusaari, E. Säilynoja, P. Porcher, *Spectrochim. Acta A* **1998**, 54, 2065.
- [18] M. Takahashi, Y. Hashimoto, S. Kikkawa, H. Kobayashi, *Zairyo* **2000**, 49, 1230.
- [19] T. Jüstel, H. Nikol, C. Ronda, *Angew. Chem. Int. Ed.* **1998**, 37, 3097.
- [20] T. Tang, Z. Zhang, J.-B. Meng, D.-L. Luo, *Fus. Eng. Des.* **2009**, article in press.
- [21] *WinXPow, Version 1.10: Diffractometer Software*, Stoe & Cie GmbH, Darmstadt, Germany, 2001.
- [22] A. Altomare, M.C. Burla, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori: "Extra: a Program for extracting Structure-Factor Amplitudes from Powder Diffraction Data", *J. Appl. Cryst.* **1995**, 28, 842; A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli: "SIRPOW.92 - a program for automatic solution of crystal structures by direct methods optimized for powder data", *J. Appl. Cryst.* **1994**, 27, 435.

[23] J. Rodriguez-Carvajal, T. Roisnel, *FullProf and WinPLOTR, Windows Applications for Powder Diffraction Patterns Analysis*, France, 2006. T. Roisnel and J. Rodríguez-Carvajal, *WinPLOTR: a Windows tool for powder diffraction patterns analysis*, *Materials Science Forum*, *Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7)*, **2000**, 118, Ed. R. Delhez and E.J. Mittenmeijer.

[24] G.M. Sheldrick, *SHELX-97: Program Package for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, 1997.

Figure Captions

Figure 1. Crystal structure of $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$. The NaCl type related unit cell is indicated by the dotted line, with La1 at the corner.

Figure 2. Crystal structure of $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$. The NaCl type related unit cell is indicated by the dotted line, with Pr2 at the corner.

Figure 3. Coordination environment of lanthanum ions in the structure of $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$.

Figure 4. Coordination environment of praseodymium ions in the structure of $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$.

Figure 1. Crystal structure of $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$. The NaCl type related unit cell is indicated by the dotted line, with La1 at the corner.

Figure 2. Crystal structure of $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$. The NaCl type related unit cell is indicated by the dotted line, with Pr2 at the corner.

Figure 3. Coordination environment of lanthanum ions in the structure of $\text{La}_2(\text{CN}_2)(\text{SiO}_4)$.

Figure 4. Coordination environment of praseodymium ions in the structure of $\text{Pr}_2(\text{CN}_2)(\text{SiO}_4)$.