CHEMISTRY OF MATERIALS
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α-SrNCN:Eu^{2+} — A Novel Efficient Orange-Emitting Phosphor

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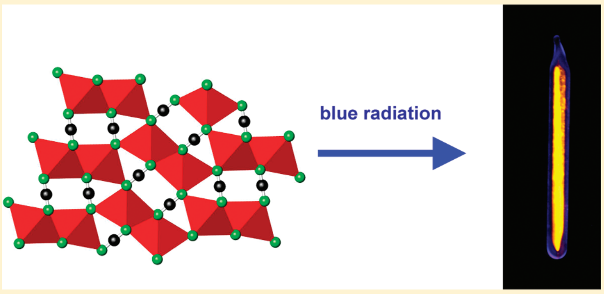
ABSTRACT: Yellow Eu^{2+}-doped strontium carbodiimide, SrNCN:Eu^{2+}, adopting the α-SrNCN structure type was obtained by the reaction of SrI_2, EuI_2, CsN_3 and CsCN in arc-welded Ta ampules. The product was characterized by high-resolution X-ray powder diffraction and infrared spectroscopy. Even at room temperature α-SrNCN:Eu^{2+} shows a strong orange emission peaking at 603 nm which is excitable by energies below 25 000 cm^{-1}. The little change of the optical properties with increasing temperature is rather unexpected and leads to the assumption that this material is a promising candidate for future phosphor converted LEDs as well as a key compound for the understanding of the influence of the host lattice on the luminescence properties of Eu^{2+}-doped materials.



KEYWORDS: strontium carbodiimide, Eu^{2+}, luminescence, phosphor, LED

INTRODUCTION

As a fundamental class of compounds in the fields of synthetic solid-state (and also molecular) chemistry, cyanamides and carbodiimides have gained increasing attention within the past decade. Because of their 2-fold anionic charge, both cyanamide and carbodiimide structural units allow the realization of nitrogen-based pseudo-oxide chemistry since NCN^{2-} is able to replace O^{2-} in a wide variety of novel materials. A number of alkali metal,[1] alkaline-earth metal,[2] main-group metal,[3,4] divalent transition-metal,[5−8] trivalent rare-earth metal,[9,10] and also trivalent transition-metal cyanamides/carbodiimides[11] were obtained following different synthetic routes. The only carbodiimide containing divalent lanthanide ions was reported by DiSalvo et al.,[12] who found that EuNCN is isostructural to the already known α-SrNCN.[13]

In general, this class of compounds reveals remarkably high thermal and chemical resistivity which makes them excellent candidates for luminescent material hosts. The luminescence of europium has been intensively studied during the last decades, and several applications have been reported. Currently, concerted efforts are in progress for the development of new phosphors for LED applications because of the advantages of LED technology.[14] In view of the luminescent species, Eu^{2+} ions, in particular, possess exceptional properties because of their low-lying excited $5d^1 4f^6$ states. In general, the spectra of Eu^{2+}-doped compounds are characterized by parity-allowed transitions $4f^7 \leftrightarrow 4f^6 5d^1$. The energetic position of the excited $4f^6 5d^1$ state and, thus, the emission of Eu^{2+}-doped compounds is influenced to a great extent by covalency, the size of the cation, and the strength of the crystal field,[15] so that tailoring of the luminescence properties is chemically possible by the choice of a suitable host lattice.

Compared to oxide host lattices doped with Eu^{2+} ions the number of compounds with nitrogen coordination used as host lattices is quite limited despite the fact that these systems are known to be excellent phosphors and are already used for commercial LED applications.[16] Some examples are $SrYSi_4N_7$:Eu^{2+},[17] MSi$_2$O$_2$N$_2$:Eu^{2+} (M = Ca, Sr, Ba),[18] $SrAlSi_4N_7$:Eu^{2+},[19] MAl$_{2-x}$Si$_x$O$_{4-x}$N$_x$:Eu^{2+} (M = Ca, Sr, Ba),[20] $M_2Si_5N_8$:Eu^{2+} (M = Ca, Sr, Ba),[21] $M_3Si_6O_{12}N_2$:Eu^{2+} (M = Ba, Sr),[22] and finally MAlSiN$_3$:Eu^{2+} (M = Ca, Sr).[23] From a chemical point of view pseudohalides such as M(SCN)$_2$:Eu^{2+} (M = Sr, Ba)[24,25] and Sr(OCN)$_2$:Eu^{2+} or even Eu(OCN)$_2$[26] are more comparable to the present carbodiimide because of the complex anions spreading negative charge over a larger space. In these cases, the cations are coordinated by both, nitrogen and chalcogen atoms. The materials emit intense green light with a high efficiency but with the drawbacks of poor thermal stability, and even worse, total luminescence quenching of the emission at room temperature.

In this paper, we present the metastable α-polymorph of strontium carbodiimide as a novel pseudochalkogenide host lattice for divalent europium ions. Because of the high thermal inertness and cationic nitrogen coordination of M^{2+}, this compound looks like a promising candidate for future applications. Furthermore, Sr-based compounds are ideal host lattices for divalent rare-earth-ions, simply because Sr^{2+} is spectroscopically inactive, and Sr^{2+} and Eu^{2+} have comparable ionic radii and identical charge. As a synthetic challenge, however, the preparation of phase-pure samples is required. Inspired by the reaction of EuN, BN, and NaN$_3$ to form Eu$_3$(NBN)$_2$,[27] and the synthesis of In$_{2.24}$(NCN)$_3$ from InBr and NaCN,[4] we developed a new flux route based on the metal halide, alkaline cyanide, and alkaline azide, which act as precursors for the synthesis of structurally rather complex rare-earth and alkaline-earth cyanamides and

Received: August 9, 2010
Revised: January 22, 2011
Published: March 10, 2011

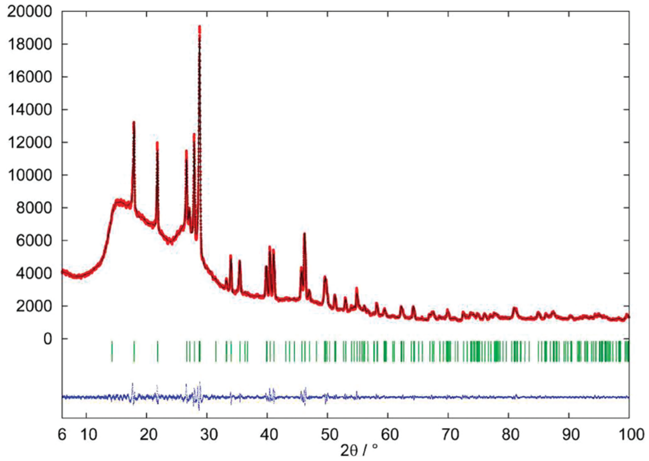


Figure 1. Rietveld refinement of the diffraction pattern of SrNCN:Eu^{2+}. The rather unusual background in the 10−35° range is an artifact going back to the setup of the evacuated flatsample holder because its windows had to be sealed with a Kapton foil.

Table 1. Crystallographic Rietveld Refinement Data^{a} of α-SrNCN:Eu^{2+}

compd	α-SrNCN
pattern 2θ (deg)	6−100
space group, No., Z	*Pnma*, 62, 4
lattice parameter a (Å)	12.422(2)
b (Å)	3.966(1)
c (Å)	5.392(1)
V (Å^3)	265.6
calcd density (g cm^{-3})	3.19
no. of reflns	170
no. of refined params	19
R_{Bragg}	9.92
R_{p}	2.58

atom	site	x	y	z	B_{iso} (Å^2)
Sr	4c	0.1301(1)	1/4	0.1121(1)	0.9(1)
C	4c	0.3765	1/4	0.1160	1(1)
N1	4c	0.3250(4)	1/4	0.915(1)	2(1)
N2	4c	0.432(1)	1/4	0.304(1)	2(1)

[a] Because of the background, the carbon position was not refined but taken from ref 27.

carbodiimides.[28−32] In other words, both EuNCN as well as α-SrNCN may be synthesized by the same type of reaction,[32] which is a major requirement for a successful doping strategy.

SYNTHESIS

All chemical manipulations of educts and products were, unless otherwise noted, performed in a glovebox under a clean argon atmosphere. SrI_2 (99.99%) and CsN_3 (99.99%) were purchased from Aldrich. EuI_2 was prepared as given in ref 33 by first dissolving ammonium iodide (99.9%, Aldrich) in liquid ammonia (5.0, Linde) at 195 K. Then, half an equivalent of europium was added and the solution was allowed to stir for 30 min. By removing the cooling bath, the ammonia was evaporated and the remaining yellow product was heated up to 473 K under vacuum to remove any leftover ammonia traces. The product EuI_2 was checked by X-ray diffraction, and it perfectly corresponds to the published data.[34] CsCN was prepared as described in the literature[35] as well.

For finally making SrNCN:Eu^{2+}, the starting materials SrI_2, EuI_2, CsCN and CsN_3 were then mixed in a molar ratio of $1-x$:x:1:1, with a total mass around 400 mg and $x \leq 0.01$, and the solid mixture was then arc-welded into a clean tantalum container. The reaction[32] follows the simple equation

$$(1-x)\ \mathrm{SrI_2} + x\mathrm{EuI_2} + \mathrm{CsCN} + \mathrm{CsN_3} \rightarrow$$
$$\mathrm{SrNCN} : \mathrm{Eu^{2+}} + 2\mathrm{CsI} + \mathrm{N_2}$$

Note that the tantalum container is desirable because most rare-earth elements react with glass or ceramic containers to form very stable trivalent oxides, silicides, borides, carbides, nitrides, etc. Because Ta is sensitive to oxidation at reaction temperature, the metal container was fused into an evacuated silica tube. The tube was placed upright into a tube furnace and heated to 1073 K within 24 h. After a reaction time of one day the furnace was cooled by 17 K/h. The resulting raw product was a bright yellow powder.

The side-phase CsI was removed in a subsequent step. To do so, the raw product was ground with 2 equiv. of purified and dried CsBr and heated under vacuo at 923 K for 12 h in a semiopen tantalum container placed in a silica tube. The CsBr·CsI mixture then evaporates and reappears at the cold part of the tube. The final product was a yellow powder.

CHARACTERIZATION

X-ray studies. X-ray analysis was performed using a Huber G 670 Guinier powder diffractometer with strictly monochromatized Cu−Kα_1 radiation. The results ensure the phase purity of the samples (Figure 1). All measurements were performed in an evacuated flat-sample holder to prevent the product from being contaminated by oxygen and air moisture. The Rietveld refinement was done with the programs FullProf and WinPlotr.[36,37]

The results of the Rietveld refinement are listed in Table 1 above. The europium atom was not refined because of the totally insignificant difference in scattering contributions.

As already mentioned, α-SrNCN and EuNCN adopt the same crystal structure, so it is not at all surprising that the doping product also crystallizes in the α-SrNCN structure.[38] The compound forms layers parallel to the *ac* plane containing both M^{2+} cations and NCN^{2-} anions (Figure 2). Four carbodiimide units lie parallel to each other while two others are flipped, and this results in a discontinued line of edge-sharing octahedra in which one metal atom (site symmetry *.m.*) is coordinated by six nitrogen atoms; the bond distances are given in Table 2. After two octahedra, the next two are connected by corner sharing. The nitrogen atoms are coordinated by distorted tetrahedra of three metal atoms and one carbon atom, the latter being coordinated by one nitrogen atom to the left and to the right.

Because of the fact that α-SrNCN is a metastable compound below ca. 920 K,[32] there may be traces of the more stable ground-state polymorph β-SrNCN in the sample, especially because both polymorphs differ by only a few kJ/mol in energy.[32] We note, however, that traces of β-SrNCN were not observable even in high-resolution X-ray powder diffraction such that they must be extremely small; nonetheless, they can be observed in the luminescence spectra (see below).

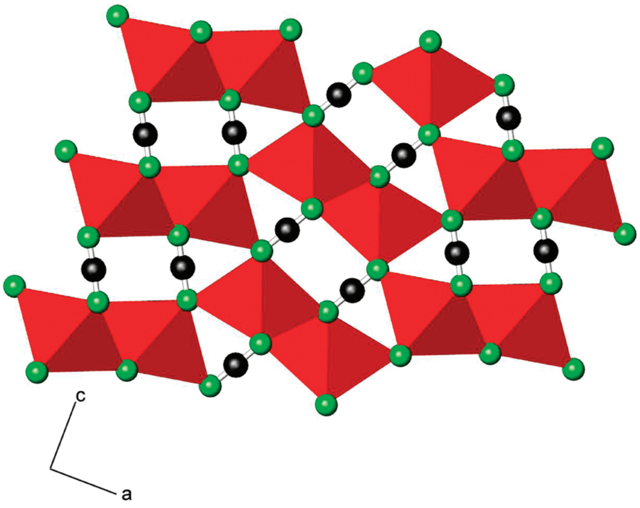


Figure 2. Polyhedral representation of the crystal structure of α-SrNCN in which carbodiimide units (N in green, C in black) coordinate strontium atoms to result in edge- and corner-sharing octahedra (in red).

Infrared Spectroscopy. Infrared spectra were recorded at room temperature using a Fourier transform Avatar 360 ESP spectrometer (Nicolet) in the range 4000−400 cm^{-1}. To do so, the samples were dispersed in strictly anhydrous KBr and pressed into pellets (Ø 1.3 cm). The spectra were corrected for the presence of KBr. The obtained spectra showed the nonsymmetric stretch (ν_{as}) at 1988 cm^{-1} and the deformation vibrations at 676 and 663 cm^{-1}, thereby corroborating the symmetric carbodiimide structural motif with two C═N double bonds between carbon and nitrogen.[38]

Luminescence Spectroscopy. Photoluminescence measurements were performed with the aid of a Fluorolog3 spectrofluorometer Fl3−22 (Horiba Jobin Yvon) equipped with double Czerny−Turner monochromators, a 450 W xenon lamp and a R928P photomultiplier with a photon counting system. Cooling down to 10 K was achieved by a closed cycle He cryostat (Janis Research). All emission spectra were corrected for the photomultiplier sensitivity and all excitation spectra for the intensity of the excitation source. To avoid any contamination of water on the sample's surfaces, we carried out the measurements in silica ampules with extreme purity which show no luminescence of the ampules itself. Reflection spectra were recorded on a Cary 5000 UV−vis−NIR spectrophotometer (Varian), which were corrected for both the lamp intensity and the photomultiplier sensitivity.

■ RESULTS AND DISCUSSION

The synthesis of europium-doped strontium carbodiimide, SrNCN:Eu^{2+}, was successfully accomplished by the solid-state reaction of SrI_2, EuI_2, CsCN, and CsN_3. The crystal structure and purity of the α polymorph were checked by X-ray diffraction and infrared spectroscopy (Figure 3), and the results closely resemble those already found for the pure strontium compound. In particular, the average M−N bond distance arrives at 2.634(6) Å, to be compared with d(Sr−N) = 2.644(4) Å from α-SrNCN.[32]

Luminescence Properties. Under photoexcitation SrNCN:Eu^{2+} exhibits a strong orange luminescence even at room temperature. The corresponding emission spectrum at 10 K excited at 427 nm (23405 cm^{-1}) is depicted in Figure 4, the room-temperature spectrum (not shown) is very similar both in shape and intensity. A broad band is detected with a maximum at 602 nm (16610 cm^{-1}, room temperature: λ_{max} = 603 nm, ν_{max} = 16575 cm^{-1}), this band can be assigned to the europium $5d^14f^6 \rightarrow 4f^7$ transition. The full-width at half-maximum (fwhm) of the band is about 3800 cm^{-1}. The emission curve shows a little shoulder at 19200 cm^{-1} but this finding cannot be caused by different cationic sites because, in contrast to β-SrNCN,[30,32] which has two inequivalent Sr sites, there is just one in α-SrNCN. On the other hand it may safely be assumed that the metastability of α-SrNCN causes a very small contamination of β-SrNCN in our samples which could not be detected by X-ray crystallography. Luminescence measurements of undoped α-SrNCN reveal that this shoulder is not due to defects or impurities of the host lattice because no emission in the visible range can be detected in this case.

Table 2. Refined Metal−Nitrogen Bond Distances in the MN_6 Octahedron of SrNCN:Eu^{2+}

bond	distance (Å)
Sr−N1	2.504(6)
Sr−N1 (2×)	2.628(5)
Sr−N2	2.645(6)
Sr−N2 (2×)	2.699(4)

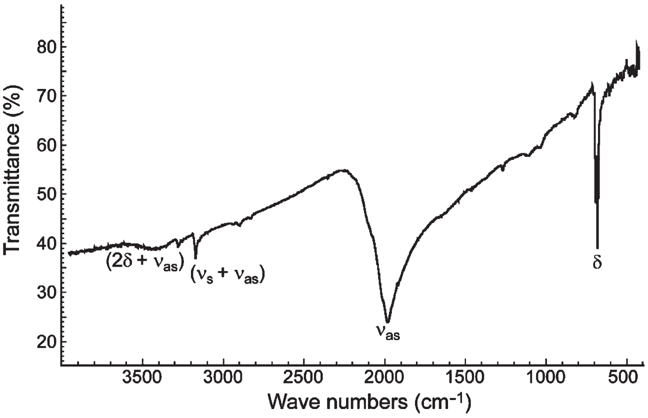


Figure 3. Infrared spectrum of α-SrNCN:Eu^{2+}.

Because of the pseudo-octahedral symmetry of the cationic site, the excitation spectrum consists of only two bands peaking at about 25500 and 38 000 cm^{-1}, whereas the lowest one starts at 18 000 cm^{-1}. Note that the orange emission can be excited around 22 200 cm^{-1} (450 nm) which is the wavelength commonly used in white light LEDs. As expected, single $4f^6(^7F_J)5d^1$ states are not resolved, which would be the condition for the exact determination of the position of the lowest state, $4f^6(^7F_0)5d^1$. According to Dorenbos,[39] it can be estimated at about 20% of the excitation maximum to 22 000 cm^{-1}, and this, in turn, leads to a Stokes shift of about 5400 cm^{-1}. Although the reflection spectra (Figure 5), of undoped α-SrNCN resulted in a band gap of 36630 cm^{-1} (4.54 eV), those of Eu^{2+}-doped samples show an identical shape but with some additional Eu $4f^7 \rightarrow 4f^65d^1$ bands, which are similar to the bands observed in the excitation spectra (Figure 4).

The comparison with Eu^{2+}-doped similar host lattices is very instructive to get some fundamental information about the structure−property relationship. While pseudohalide host lattices such as $Sr(OCN)_2$[26] and $Sr(SCN)_2$[24] cause a deep green

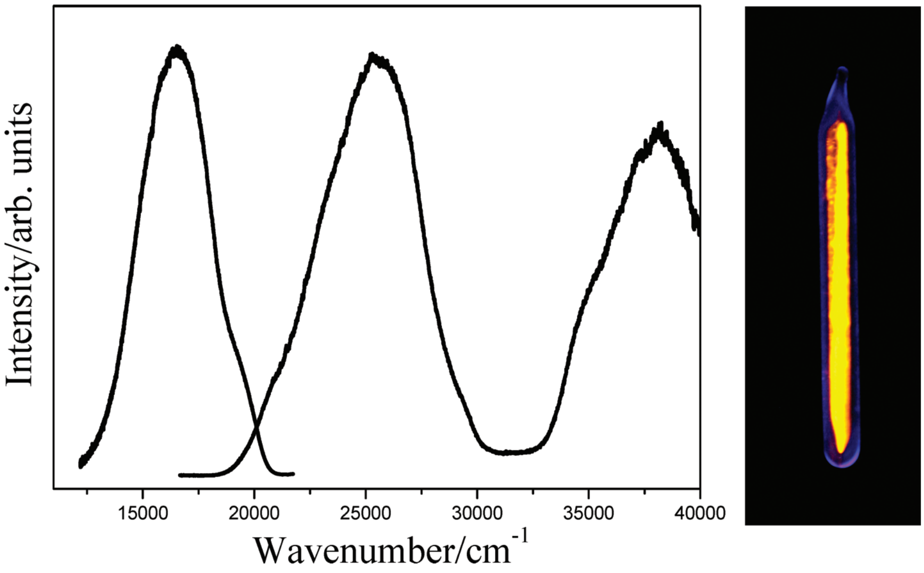


Figure 4. Emission (left) and excitation (right) spectra of α-SrNCN:Eu^{2+} at 10 K; λ_{ex} = 427 nm (23405 cm^{-1}), λ_{em} = 700 nm (14285 cm^{-1}).

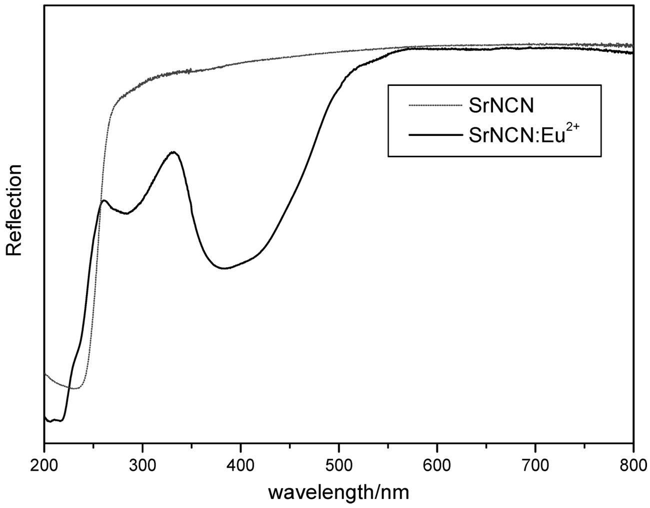


Figure 5. Reflection spectra of α-SrNCN and α-SrNCN:Eu^{2+}.

emission at low temperature, an orange emission even at room as well as low temperatures is observed in the present case of a pseudochalcogenic host lattice. The reason of this red shift can be explained by several factors. First of all the slightly shorter Sr—N average distance of 2.634 Å in SrNCN — for comparison, one finds Sr—N= 2 × 2.688 Å and 2 × 2.715 Å within Sr(SCN)$_2$[40] — causes a larger splitting of the excited 5d states, and, thus, an emission at lower energy. Moreover, the fwhm of 3800 cm^{-1} and the Stokes shift (SS) of 5400 cm^{-1} of SrNCN:Eu^{2+} are amazingly large compared to those of the aforementioned systems (Sr(OCN)$_2$:Eu^{2+}: fwhm = 2115 cm^{-1}, SS = 1870 cm^{-1},[26] Sr(SCN)$_2$:Eu^{2+}: fwhm = 1548 cm^{-1}, SS = 2535 cm^{-1}[24]) and also in comparison to numerous Eu^{2+}-doped host lattices.[41] This calls for a large increase in the Eu—N distance Δr in the excited $4f^6 5d^1$ state compared to the $4f^7$ ground state in this case (Figure 6), thereby also leading to a decrease of the emission energy. It must therefore be assumed that SrNCN is a rather "soft" host lattice which allows a rather large increase of Δr. The reason of this observation is not clear but it may go back to the fact that the carbodiimide unit allows more configurational freedom (N—C≡N^{2-} and N═C═N^{2-}) than the other species. Nonetheless, this finding may be of general interest for the development of low-energy-emitting phosphors, which are so important for applications for phosphor-converted LEDs.

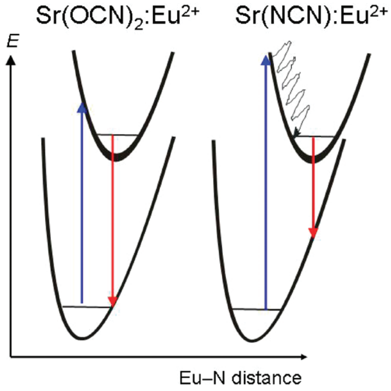


Figure 6. Sketch representing the consequences of a changed internuclear distance on the luminescence properties; left: small fwhm, small Stokes shift; right: large fwhm, large Stokes shift.

The most remarkable observation, however, is the low-temperature quenching of the emission for SrNCN:Eu^{2+} going together with the remarkably low shift of the emission band by temperature. Whereas for Sr(OCN)$_2$:Eu^{2+} (T_{quench} = 160 K[26]), Eu(OCN)$_2$ (T_{quench} = 140 K[26]), and Sr(SCN)$_2$:Eu^{2+} (T_{quench} = 220 K[24]). the emission intensity is fully quenched at room temperature, the emission intensity of SrNCN:Eu^{2+} at 10 K corresponds to 85% of the room temperature emission! In fact, the higher intensity at room temperature can only be a consequence of a stronger absorption of excitation radiation due to a shift of the excitation band with temperature. The large decrease in emission intensity for the pseudohalide host lattices was explained by the fact that the lowest exited Eu 5d state is located at slightly lower energy than the conduction band of the host lattice.[24] Although at low temperature, emission is observed from the lowest 5d states, at higher temperatures, higher 5d states located in the conduction band are occupied leading to excitonic nonradiative relaxation. In the present case, this situation is not observed, because the center of gravity of the electronic Eu^{2+} states must be located at lower energy in the band gap. The observation of the large Stokes Shift is, however, not consist with the absent temperature quenching because radiation-less relaxation from the excited state to the ground state via their crossing point (Figure 6) is often observed for large increases in the internuclear distance.

Due to the small shift of the luminescence properties with temperature as well as the temperature stability of the host lattice, low thermal quenching and the position of the excitation and emission bands this material is a promising candidate for future phosphor converted LEDs. In fact, LEDs operate at temperatures of about 150 °C, so luminescence spectroscopy at these temperature would be useful. Unfortunately, we are currently not able to perform this measurement, but low quenching behavior at 150 °C can be expected because of our results.

In general, the location of the electronic states of doped ions relative to the band gap energies of the host lattice is a very important point to avoid thermal quenching which is one of the key strategies for the development of high-efficiency LED phosphors. Moreover the shift of the emission band at increasing temperature leading to color coordinates shift of high efficient LEDs is also an unsolved problem. Unfortunately, these circumstances in relation to the structures are rather unexplored. In our opinion, the present work is therefore important to get some knowledge of the quenching and color shift behavior of phosphors with temperature and, thus, for the development of future promising luminescent materials. Quantum-chemical studies targeted on the unexpected optical properties of SrNCN:Eu^{2+} are in progress.

CONCLUSIONS

In this paper, we reported the luminescence properties of Eu^{2+}-doped strontium carbodiimide, SrNCN:Eu^{2+}, for the first time. A strong orange emission peaking at 602 nm at 10 K which is excitable with blue radiation is observed. Amazingly, the emission efficiency and maximum at room temperature is nearly the same as at low temperatures. These properties showing the high potential of this material for future LED-phosphors as well as suitable to get some information about the structure−property relationship of Eu^{2+}-containing luminescent materials.

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ACKNOWLEDGMENT

It is a pleasure to thank Deutsche Forschungsgemeinschaft for financial support.

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■ NOTE ADDED IN PROOF

Recently, a paper on the luminescence properties of $SrCN_2:Eu^{2+}$ has come to our attention (S. Yuan, Y. Yang, F. Chevire, F. Tessier, X. Zhang, G. Chen, *J. Am. Ceram. Soc.* **2010**, *93*, 3052) which describes total quenching of the emission at room temperature, in total contrast to our results. The reason for the different behavior is likely to go back to alternative preparations: Yuan et al. used europium(III) oxide for doping, and the subsequent reduction to Eu(II) generates defects that cause quenching of the emission. In our case, the direct doping with europium(II) iodide does not introduce defects such that strong emission results even at room temperature. In addition, the quality of the excitation spectra improves. Clearly, suitable preparation methods are of paramount importance for the development of materials with optimum properties.