Title	Ammonolysis-free synthesis of La2O2CN2 by cyanamidation of La(OH)3 using urea, and its photoluminescence properties
Author(s)	Okada, Ryoki; Kawanishi, Kodai; Katagiri, Kiyofumi; Inumaru, Kei
Citation	Ceramics International , 45 (7) : 9325 - 9329
Issue Date	2019-05
DOI	10.1016/j.ceramint.2019.01.262
Self DOI	
URL	https://ir.lib.hiroshima-u.ac.jp/00049716
Right	© 2019. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/ This is not the published version. Please cite only the published version. この論文は出版社版ではありません。引用の際には出版社版をご確認、ご利用ください。
Relation	

Ammonolysis-free synthesis of $La_2O_2CN_2$ by cyanamidation of $La(OH)_3$ using urea, and its photoluminescence properties

Ryoki Okada, Kodai Kawanishi, Kiyofumi Katagiri*, Kei Inumaru

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan.

* Corresponding author.

E-mail address: kktgr@hiroshima-u.ac.jp (K. Katagiri).

ABSTRACT

A facile method was successfully developed to prepare lanthanum oxycyanamide, $La_2O_2CN_2$. Urea was selected as a cyanamidation agent, instead of gaseous NH_3 with graphite containers, to achieve a safe and simple synthetic strategy. Through the optimization of reaction conditions, including content of urea and heat-treatment temperature, single-phase $La_2O_2CN_2$ could be obtained without any impurities. We also prepared a $La_2O_2CN_2:Eu^{3+}$ phosphor. The Eu^{3+}-doped $La_2O_2CN_2$ matrix showed a red emission. Furthermore, in comparison with $La_2O_3:Eu^{3+}$, the photoluminescence excitation bands corresponding to the Eu^{3+}–ligand charge transfer region were broadened. These results suggested that $La_2O_2CN_2$ prepared via the urea route will offer superb application prospects for photoluminescence materials such as white light-emitting diodes.

Keywords:

Oxycyanamide

Carbodiimide

Mixed anion compound

Phosphor

Urea

1. Introduction

Mixed-anion compounds are solid-state inorganic materials containing more than one anionic species in a single phase, such as oxynitrides, oxysulfides, and oxyfluorides [1]. Incorporating different kinds of anions can give rise to unique physical and chemical properties. During the past two decades, rare earth (RE) mixed-anion compounds have emerged as a rapidly growing family of functional materials, finding use in, for example, display devices [2,3], (photo)catalysts [4,5], X-ray scintillators [5], and white light-emitting diodes (LEDs) [6]. Among these materials, RE_2O_2X (where X is a divalent anion such as S^{2-}, Se^{2-}, Te^{2-}, CO_3^{2-}, CN_2^{2-}, and SO_4^{2-}) is a novel class of luminescent matrices that has shown considerable promise in recent years [7,8]. The photoluminescence properties of RE_2O_2S:$Eu^{3+}$and $RE_2O_2CN_2$:Eu^{3+} are quite similar because the structures of RE_2O_2S and $RE_2O_2CN_2$ are closely related, both consisting of a network of alternating layers of $RE_2O_2^{2+}$ and their interleaving anions [9,10]. Therefore, metal oxycyanamides can be considered as efficient host candidates for RE^{3+} activator ions such as Eu^{3+}. It has been reported that $La_2O_2CN_2$ is an excellent matrix for RE^{3+} [11]. $La_2O_2CN_2$ is most commonly prepared by ammonolysis of La_2O_3 precursors. Gaseous NH_3 is employed as a nitrogen source, with the aid of a graphite container serving as a carbon source, to prepare $La_2O_2CN_2$ [12]. Normally, such cyanamidation is carried out at temperatures between 700 and 900 °C and requires a long duration to complete the diffusion of nitrogen and carbon atoms. However, the use of gaseous NH_3 at such high temperatures incurs a relatively high risk and makes scaled-up synthesis difficult, and is thus a major drawback of this method [13]. Therefore, the development of ammonolysis-free preparation procedures of metal oxycyanamides, including $La_2O_2CN_2$, is a current research goal.

In this communication, we have demonstrated a facile preparation of $La_2O_2CN_2$ that addresses the obstacles associated with their conventional preparation route. We chose urea as a nitrogen source instead of gaseous NH_3. Urea is cheap, non-toxic, and non-corrosive, and is easily handled because it is solid at ambient temperature [14]. In addition, urea acts as a carbon as well as a nitrogen source. This enables us to use conventional calcination containers, such as alumina crucibles, instead of graphite boats. Here, we have optimized the conditions for transformation of $La(OH)_3$ to $La_2O_2CN_2$, including the mixing ratio of urea and heat-treatment temperature. In addition, we have also attempted preparation of $La_2O_2CN_2:Eu^{3+}$ and investigated its photoluminescence properties.

2. Materials and methods

2.1. Materials

Lanthanum nitrate hexahydrate ($La(NO_3)_3·6H_2O$; ≥99.0%) was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Urea ($CO(NH_2)_2$; 99%), ammonia solution (NH_3, 28% (w/w)), and ethanol (C_2H_5OH; ≥99.5%) were obtained from Nacalai Tesque, Inc. (Kyoto, Japan). Lanthanum hydroxide ($La(OH)_3$; 99.9%) was purchased from Strem Chemicals, Inc. (Newburyport, MA, USA). Europium nitrate *n*-hydrate ($Eu(NO_3)_3·nH_2O$) was obtained from FUJIFILM Wako Pure Chemical Co. (Osaka, Japan). All reagents were used as received without further purification. The water used in all experiments was deionized with a Milli-Q system (Merck Millipore, Billerica, MA, USA).

2.2. Preparation of $La_2O_2CN_2$

$La(OH)_3$ was mixed with urea using an agate mortar and pestle. The molar ratio of urea to $La(OH)_3$ ([urea] / [$La(OH)_3$] = R) was varied from 2.0 to 5.0. The mixture was heated under a nitrogen stream (300 mL min^{-1}) in a horizontal tube furnace using an alumina crucible boat. The temperature of the furnace was raised to the final temperature at a heating rate of 15 °C min^{-1}. The final heat-treatment temperature was varied from 600 to 1000 °C. The heat-treatment duration at the final temperature was fixed to 2 h.

2.3. Preparation of $La_2O_2CN_2:Eu^{3+}$

Firstly, $La(OH)_3:Eu^{3+}$ was prepared by the hydrothermal method. $La(NO_3)_3\cdot 6H_2O$ (5.70 mmol) was dissolved in deionized water. The pH of the solution was adjusted to 9 by adding aqueous NH_3 (28% (w/w)) solution. Then, $Eu(NO_3)_3\cdot nH_2O$ (0.300 mmol) was added to this solution. After stirring for 1 h, the mixture was transferred to a Teflon vessel. The vessel was sealed in a stainless-steel autoclave and heated at 200 °C for 24 h. After heating, the obtained product was washed with ethanol twice and dried overnight in an oven at 50 °C. Next, $La_2O_2CN_2:Eu^{3+}$ was prepared using $La(OH)_3:Eu^{3+}$ in the same manner as $La_2O_2CN_2$. The heat-treatment was carried out at 800 °C for 2 h.

2.4. Preparation of $La_2O_3:Eu^{3+}$

$La_2O_3:Eu^{3+}$ was prepared for comparison of its luminescence properties with those of $La_2O_2CN_2:Eu^{3+}$. $La_2O_3:Eu^{3+}$ was prepared from $La(OH)_3:Eu^{3+}$ by heat-treatment using a muffle furnace (in air). The heat-treatment temperature and duration were 800 °C and 2 h, respectively.

2.5. Characterizations

The phase compositions of the obtained samples were determined by powder X-ray diffraction (XRD) (D8 Advance, Bruker AXS, Germany) using Cu-Kα radiation. The emission and excitation spectra of the Eu^{3+}-doped samples were obtained by a fluorescent spectrophotometer (FP-8600, JASCO, Japan).

3. Results and discussion

3.1. Optimization of preparation conditions of $La_2O_2CN_2$ using urea

Initially, the mixing molar ratio of $La(OH)_3$ and urea ([urea] / $[La(OH)_3]$ = R) was optimized. The XRD patterns of the products obtained from mixtures of $La(OH)_3$ and urea with various mixing ratios (R = 2.0, 2.5, 3.0, and 5.0) after calcination at 800 °C for 2 h are presented in Fig. 1 within the 2θ range of 20° to 70°. Diffraction peaks indexed to the tetragonal phase of $La_2O_2CN_2$ (space group: *I*4/*mmm*) can be found in all the patterns. In this crystalline structure, the linear anion $[N\text{-}C\text{-}N]^{2-}$ sandwiches between two $La_2O_2^{2+}$ layers in parallel and each La^{3+} ion is coordinated with four O and four N atoms in the tetragonal lattice [8]. In the case of the lowest urea-to-$La(OH)_3$ ratio (R = 2.0), diffraction peaks assignable to the La_2O_3 phase co-existed with those of $La_2O_2CN_2$. This indicates that a deficiency of urea causes the formation of La_2O_3 as a by-product. In contrast, a number of unknown diffraction peaks were observed in the patterns of products prepared at higher urea-to-$La(OH)_3$ ratios ($R \geq 3.0$) in addition to the peaks of $La_2O_2CN_2$. Therefore, excess urea also causes the formation of by-products during the calcination process. Both the diffraction peaks of La_2O_3 and the unknown peaks were completely absent from the pattern of the product prepared at $R = 2.5$. Under this condition, single-phase $La_2O_2CN_2$ could be obtained. Judging from these results, the optimal mixing ratio to obtain $La_2O_2CN_2$ is R = 2.5, and this ratio was used in subsequent experiments.

The influence of the reaction temperature on the formation of $La_2O_2CN_2$ was investigated. Fig. 2 displays the XRD patterns of the products obtained from mixtures of $La(OH)_3$ and urea (R = 2.5) after calcination at various temperatures (600, 700, 800, 900, and 1000 °C). The calcination duration was fixed to 2 h. Even in the case of the sample prepared at 600 °C, diffraction peaks assignable to $La_2O_2CN_2$ were found. This indicates that the cyanamidation reaction from $La(OH)_3$ to $La_2O_2CN_2$ could be initiated below 600 °C. However, the formation of a by-product, $La_2O_2CO_3$, was also evident from this pattern. There are several reports that $La_2O_2CO_3$ can be prepared by calcination of hydrothermally prepared $La(OH)_3$ in air [15–17]. In most of those studies, $La(OH)_3$, which has a high capacity for adsorbing CO_2 and H_2O, was transformed to $La_2O_2CO_3$ by calcination at 400–500 °C in air containing CO_2. Thermal decomposition of urea can be written as follows [18,19]:

$$H_2NCONH_2 \longrightarrow NH_3 + HCNO \quad (140°C) \qquad (1)$$

$$H_2NCONH_2 \longrightarrow H_2O + H_2CN_2 \quad (140\ °C) \qquad (2)$$

The HCNO formed by the reaction of eq. (1) reacts with H_2O on the surface of metal oxides and hydroxides, producing another NH_3 molecule and CO_2 [20]. This suggests that CO_2 molecules were present during the calcination process herein, even though the calcination was carried out under a nitrogen stream. Therefore, $La_2O_2CO_3$ was generated as a by-product when the calcination was carried out at 600 °C. The peak intensity of $La_2O_2CO_3$ decreased with increasing calcination temperature and these peaks completely disappeared for the sample prepared at 800 °C. However, diffraction peaks attributable to a La_2O_3 phase were found in addition to those of $La_2O_2CN_2$ for the sample prepared at 1000 °C. Therefore, we determined that the optimal calcination temperature was 800–900 °C and used this range in subsequent experiments. Recently, we have reported the preparation of GaN:ZnO solid solution from Zn–Ga layered double hydroxide using urea as a nitriding agent [21]. By investigations using the X-ray absorption and infrared spectroscopies, we have discovered that C and N components in urea are converted to $[NCN]^{2-}$ species after decomposition around 150 °C (the reaction is known as eq. (2)) and $ZnCN_2$-like species generate as intermediates. Therefore, it seems that $[NCN]^{2-}$ species formed by the decomposition of urea concern the formation of $La_2O_2CN_2$ in the current process. The detailed cyanamidation mechanism is currently being investigated by our research group.

3.2. Preparation and photoluminescence properties of $La_2O_2CN_2:Eu^{3+}$

Metal oxycyanamide compounds, including $La_2O_2CN_2$, are considered to be promising host candidates for lanthanide activator ions such as Eu^{3+} [11]. Here, we focus on the photoluminescence properties of $La_2O_2CN_2:Eu^{3+}$ prepared from the corresponding precursor, $La(OH)_3:Eu^{3+}$. Firstly, $La(OH)_3:Eu^{3+}$ was prepared by the hydrothermal method using a mixture of $La(NO_3)_3$ and $Eu(NO_3)_3$. Fig. 3a presents the XRD pattern of the samples hydrothermally prepared using the mixture of $La(NO_3)_3$ and $Eu(NO_3)_3$ at 200 °C for 24 h. All of the diffraction peaks can be assigned to those of pure $La(OH)_3$ [22]. No other diffraction peaks arising from impurities can be detected at the studied doping concentrations. Meanwhile, the positions of the observed peaks shifted to higher 2θ angles than those of pure $La(OH)_3$. These results suggest that the Eu^{3+} ions completely inserted into the $La(OH)_3$ lattice in place of the La^{3+} ions, with the Eu^{3+} ions having a smaller ionic radius. In addition, the sample exhibits red fluorescence under short-wave UV light (λ_{ex} = 254 nm) (figure not shown). This result further supports that Eu^{3+} was doped into the structure of $La(OH)_3$. Next, the transformation of $La(OH)_3:Eu^{3+}$ to $La_2O_2CN_2:Eu^{3+}$ was performed by cyanamidation using urea. For comparison, the transformation of $La(OH)_3:Eu^{3+}$ to $La_2O_3:Eu^{3+}$ was also carried out by calcination in the absence of urea. The XRD patterns of the samples after calcination of $La(OH)_3:Eu^{3+}$ at 800 °C for 2 h with and without urea are displayed as (b) and (c) in Fig. 3, respectively. All the diffraction peaks of the samples were readily assigned to the pure hexagonal phase of La_2O_3 [22] when the $La(OH)_3:Eu^{3+}$ was calcined alone (without urea) at 800 °C for 2 h, as shown in Fig. 3b. Only slight peak shifts and no other impurity phases were detected, indicating the high purity and crystallinity of the $La_2O_3:Eu^{3+}$ product obtained. On the other hand, for the product of calcination of the mixture of $La(OH)_3:Eu^{3+}$ and urea ([urea] / $[La(OH)_3:Eu^{3+}]$ = 2.5), the characteristic diffraction peaks can be readily ascribed to the tetragonal phase of $La_2O_2CN_2$ (Fig. 3c). Only negligible impurity phase can be detected. Doping Eu^{3+} does not result in any phase transformation and only has a minor influence on the crystalline structure of the obtained $La_2O_2CN_2:Eu^{3+}$ sample. Fig. 4 shows the emission and excitation spectra of the $La_2O_2CN_2:Eu^{3+}$ samples. For comparison, the emission and excitation spectra of the $La_2O_3:Eu^{3+}$ samples are also given in Fig. 4. As displayed in Fig. 4a, the excitation of Eu^{3+} ions in the $La_2O_2CN_2$ and La_2O_3 hosts at 284 nm induced emission spectra containing the characteristic transitions of Eu^{3+}, corresponding to its $4f^6$ configuration undergoing the ^5D_j (j = 0, 1, and 2) → ^7F_j (j = 0, 1, 2, and 4) transitions

[8]. In the spectrum for $La_2O_2CN_2:Eu^{3+}$, the strongest peak is split into two peaks at 613 and 621 nm, as a result of the forced electric dipole transition ($^5D_0 \rightarrow {}^7F_2$), indicating that the Eu^{3+} ions are incorporated at sites with no inversion center low symmetry [23]. This transition is very sensitive to the chemical surroundings and crystalline structures. The dominant emission of $La_2O_3:Eu^{3+}$ is observed at 626 nm, and also corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions. The predominant emission bands at 613 and 621 nm in the spectrum for $La_2O_2CN_2:Eu^{3+}$ confirm the formation of the oxycyanamide host [23]. It is notable that the emission peak at 579 nm, which corresponds to the $^5D_0 \rightarrow {}^7F_0$ transition in the spectrum of $La_2O_2CN_2:Eu^{3+}$, is rather intense, because the transition from $J = 0$ to $J = 0$ is strictly forbidden, as the total orbital momentum does not change [24]. The emission bands at 586 and 594 nm arise from the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition and the peak at 706 nm corresponds to the $^5D_0 \rightarrow {}^7F_4$ transition [23,24]. As shown in Fig. 4b, when monitoring the emission of Eu^{3+} ions in the $La_2O_2CN_2$ (λ_{em} = 621 nm) and La_2O_3 (λ_{em} = 626 nm) hosts, the excitation spectra of both the $La_2O_2CN_2:Eu^{3+}$ and $La_2O_3:Eu^{3+}$ samples exhibit broad and intense bands with a maximum located around 280–290 nm. These bands are ascribed to the ligand-to-metal charge transfer band (CTB) between Eu^{3+} ions and anions (O^{2-} and/or CN_2^{2-}) [24]. The broad band in the spectrum of $La_2O_3:Eu^{3+}$ located from 250 to 330 nm is ascribed to the Eu^{3+}–O^{2-} CTB. It is noteworthy that the CTB in the spectrum of $La_2O_2CN_2:Eu^{3+}$extends to ca. 370 nm. This contribution of longer wavelengths to the broad band of $La_2O_2CN_2:Eu^{3+}$ can be attributed to the Eu^{3+}–CN_2^{2-} CTB. These results indicate that metal oxycyanamide hosts extend the excitation wavelength of CTBs, compared with metal oxide hosts, through the presence of mixed-anion ligands.

4. Conclusions

In summary, $La_2O_2CN_2$ has been successfully prepared via the cyanamidation of $La(OH)_3$ using urea. The previously reported processes for preparation of $La_2O_2CN_2$ required high-temperature calcination using harmful gaseous NH_3 with the aid of a graphite container as a carbon source. The preparation developed in this work is much simpler and safer because urea acts as both a nitrogen and a carbon source and has low toxicity. Following the optimization of reaction conditions including heat-treatment temperature and ratio of urea to $La(OH)_3$, single-phase $La_2O_2CN_2$ without impurities was efficiently obtained by calcination at 800–900 °C for 2 h using a mixture of $La(OH)_3$ and urea (R = 2.5). We have also prepared $La_2O_2CN_2:Eu^{3+}$, for potential application as a phosphor, using $La(OH)_3:Eu^{3+}$ and urea as starting materials. $La_2O_2CN_2:Eu^{3+}$ exhibits a characteristic red emission with strong peaks at 613 and 621 nm arising from the forced electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) under excitation of the CTB. The CTB of the excitation spectrum of $La_2O_2CN_2:Eu^{3+}$ is broader than that of $La_2O_3:Eu^{3+}$, because a Eu^{3+}–CN_2^{2-} CTB exists in addition to that of Eu^{3+}–O^{2-}. This indicates that $La_2O_2CN_2:Eu^{3+}$ is efficiently excitable at the near-ultraviolet wavelength region and can be expected to be a versatile candidate as a red phosphor for white LEDs. Therefore, metal oxycyanamides should be recognized as a promising family of mixed-anion compounds, in addition to metal oxynitrides and metal oxysulfides. Because of the safety, low cost, and simplicity of this process, we believe that cyanamidation using urea will open up opportunities for facile synthesis of various metal oxycyanamide phosphors.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers JP17H05483 and JP17H03392. This work was partly supported by the Center for Functional Nano Oxide at Hiroshima University. We thank Leo Holroyd, Ph.D., from Edanz Group (www.edanzediting.com/ac) for editing a draft of this manuscript.

References

[1] H. Kageyama, K. Hayashi, K. Maeda, J.P. Attfield, Z. Hiroi, J.M. Rondinelli, K. R. Poeppelmeier, Expanding frontiers in materials chemistry and physics with multiple anions, Nat. Commun. 9 (2018) 772, https:// doi.org/10.1038/s41467-018-02838-4.

[2] W.-T. Chen, H.-S. Sheu, R.-S. Liu, J. P. Attfield, Cation-size-mismatch tuning of photoluminescence in oxynitride phosphor, J. Am. Chem. Soc. 134 (19) (2012) 8022–8025, https://doi.org/10.1021/ja301593z.

[3] S. Park, T. Vogt, Luminescent phosphors, based on rare earth substituted oxyfluorides in the $A(1)_{3-x}$ $A(2)_{x}MO_{4}F$ family with A(1)/A(2)=Sr, Ca, Ba and M=Al, Ga, J. Lumin. 129 (2009) 952–957, https://doi.org/10.1016/j.jlumin.2009.04.005.

[4] Y. Kobayashi, Y. Tang, T. Kageyama, H Yamashita, N. Masuda, S. Hosokawa, H. Kageyama, Titanium-based hydrides as heterogeneous catalysts for ammonia synthesis, J. Am. Chem. Soc. 139 (50) (2017) 18240–18246, https://doi.org/10.1021/jacs.7b08891.

[5] A. Fuertes, Metal oxynitrides as emerging materials with photocatalytic and electronic properties. Mater. Horiz. 2 (2015) 453–461, https://doi.org/10.1039/c5mh00046g.

[6] R.-J. Xie, N. Hirosaki, M. Mitomo, Oxynitride/nitride phosphors for white light-emitting diodes (LEDs), J Electroceram 21 (2008) 370–373, https://doi.org/10.1007/s10832-007-9202-7.

[7] S. Yuan, L. Wang, Y. Yang, F. Chevíré, F. Tessier, G. Chen, Novel color-tunable $Gd_2O_2CN_2$:Tb^{3+}, Eu^{3+} phosphors: Characterization and photoluminescence properties, Ceram. Int. 42 (2016) 12508–12511, https://doi.org/10.1016/j.ceramint.2016.04.059.

[8] H. Bai, Y. Song, D. Li, Q. Ma, X. Dong, W. Yu, Y. Yang, H. Yu, J. Wang, G. Liu, Emerging $La_2O_2CN_2$ matrix with controllable 3D morphology for photoluminescence applications, CrystEngComm 19 (2017) 6498–6505, https://doi.org/10.1039/c7ce01418j.

[9] T. Takeda, N. Hatta, S. Kikkawa, Gel nitridation preparation and luminescence property of Eu-doped $RE_2O_2CN_2$ (RE = La and Gd) phosphors, Chem. Lett. 35 (9) (2006) 988–989, https://doi.org/10.1246/cl.2006.988.

[10] S. Xu, X. Wang, X. Dong, W. Yu, J. Wang, G. Liu, Novel construction technique, structure and photocatalysis of $Y_2O_2CN_2$ nanofibers and nanobelts, RSC Adv. 6 (2016) 43322–43329, https://doi.org/10.1039/c5ra23192b.

[11] E. Säilynoja, M. Lastusaari, J. Hölsä, P. Porcher, Luminescence of a novel rare earth oxycompound, $La_2O_2CN_2$:Eu^{3+}, J. Lumin. 72–74 (1997) 201–203, https://doi.org/10.1016/S0022-2313(96)00377-8.

[12] Y. Hashimoto, M. Takahashi, S. Kikkawa, F. Kanamaru, Synthesis and crystal structure of a new compound, lanthanum dioxymonocyanamide ($La_2O_2CN_2$), J. Solid State Chem. 114 (1995) 592–594, https://doi.org/10.1006/jssc.1995.1090.

[13] M. Hara, G. Hitoki, T. Takata, J. N. Kondo, H. Kobayashi, K. Domen, TaON and

Ta_3N_5 as new visible light driven photocatalysts, Catal. Today 78 (2003) 555–560, https://doi.org/10.1016/s0920-5861(02)00354-1.

[14] K. E. Knol, E. A. Bramer, M. Valk, Reduction of nitrogen oxides by injection of urea in the freeboard of a pilot scale fluidized bed combustor, Fuel 68 (1989) 1565–1569, https://doi.org/10.1016/0016-2361(89)90295-0.

[15] X. E. Verykios, Catalytic dry reforming of natural gas for the production of chemicals and hydrogen, Int. J. Hydrog. Energy 28 (2003) 1045–1063, https://doi.org/10.1016/S0360-3199(02)00215-X.

[16] Q. Mu, Y. Wang, Synthesis, characterization, shape-preserved transformation, and optical properties of $La(OH)_3$, $La_2O_2CO_3$, and La_2O_3 nanorods, J. Alloys Compd. 509 (2011) 396–401, https://doi.org/10.1016/j.jallcom.2010.09.041.

[17] Y.-H. Hou, W.-C. Han, W.-S. Xia, H.-L. Wan, Structure sensitivity of $La_2O_2CO_3$ catalysts in the oxidative coupling of methane, ACS Catal. 5 (2015) 1663−1674, https://doi.org/10.1021/cs501733r.

[18] S. Podsiadło, Stages of the synthesis of gallium nitride with the use of urea, Thermochim. Acta 256 (2) (1995) 367–373, https://doi.org/10.1016/0040-6031(94)02026-K.

[19] M. Koebel, E. O. Strutz, Thermal and hydrolytic decomposition of urea for automotive selective catalytic reduction systems: thermochemical and practical aspects, Ind. Eng. Chem. Res. 42 (10) (2003) 2093–2100, https://doi.org/10.1021/ie020950o.

[20] S. D. Yim, S. J. Kim, J. H. Baik, I.-S. Nam, Y. S. Mok, J.-H. Lee, B. K. Cho, S. H. Oh, Decomposition of urea into NH_3 for the SCR process, Ind. Eng. Chem. Res. 43 (16) (2004) 4856–4863, https://doi.org/10.1021/ie034052j.

[21] K. Katagiri, Y. Hayashi, R. Yoshiyuki, K. Inumaru, T. Uchiyama, N. Nagata, Y. Uchimoto, A. Miyoshi, K. Maeda, Mechanistic insight on the formation of GaN:ZnO solid solution from Zn–Ga layered double hydroxide using urea as the nitriding agent, Inorg. Chem. 57 (21) (2018) 13953–13962, https://doi.org/10.1021/acs.inorgchem.8b02498.

[22] S. K. Hussain, G. Nagaraju, E. Pavitra, G. S. R. Raju, J. S. Yu, $La(OH)_3:Eu^{3+}$ and $La_2O_3:Eu^{3+}$ nanorod bundles: growth mechanism and luminescence properties, CrystEngComm 17 (2015) 9431–9442, https://doi.org/10.1039/c5ce01688f.

[23] L. Wang, S. Yuan, Y. Yang, F. Chevire, F. Tessier, G. Chen, Luminescent properties of novel red-emitting phosphor: $Gd_2O_2CN_2:Eu^{3+}$, Opt. Mater. Exp. 5 (11) (2015) 2616–2624, https://doi.org/10.1364/ome.5.002616.

[24] M. Kubus, D. Enseling, T. Jüstel, H.-J. Meyer, A Luminescent material: $La_3Cl(CN_2)O_3$ doped with Eu^{3+} or Tb^{3+} ions, . Eur. J. Inorg. Chem. 2013 (18) (2013) 3195–3199, https://doi.org/10.1002/ejic.201300224.

Figure captions:

Fig. 1. XRD patterns of products obtained from mixtures of $La(OH)_3$ and urea with various mixing ratios (R = (a) 2.0, (b) 2.5, (c) 3.0, and (d) 5.0) after calcination at 800 °C for 2 h.

Fig. 2. XRD patterns of products obtained from mixtures of $La(OH)_3$ and urea ($R = 2.5$) after calcination at (a) 600, (b) 700, (c) 800, (d) 900, and (e) 1000 °C for 2 h.

Fig. 3. XRD patterns of products obtained via (a) hydrothermal treatment at 200 °C for 24 h of a mixture of $La(NO_3)_3 \cdot 6H_2O$ and $Eu(NO_3)_3 \cdot nH_2O$, (b) calcination of (a) alone at 800 °C for 2 h, and (c) calcination of a mixture of (a) and urea ([urea] / [(a)] = 2.5) at 800 °C for 2 h.

Fig. 4. (a) Emission and (b) excitation spectra of $La_2O_2CN_2:Eu^{3+}$ and $La_2O_3:Eu^{3+}$. The excitation wavelength is 284 nm (a). The emission wavelengths for $La_2O_2CN_2:Eu^{3+}$ and $La_2O_3:Eu^{3+}$ are 621 and 626 nm, respectively (b).