

One-step synthesis of cubic gauche polymeric nitrogen with high yield just by heating

Liangfei Wu(吴良飞), Yuxuan Xu(徐宇轩), Guo Chen(陈果), Junfeng Ding(丁俊峰), Ming Li(李明), Zhi Zeng(曾雉), and Xianlong Wang(王贤龙)

Citation: Chin. Phys. B, 2024, 33 (**12**): 126802. DOI: 10.1088/1674-1056/ad9569

Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Large-scale synthesis of polyynes with commercial laser marking technology

Liang Fang(房良), Yanping Xie(解燕平), Shujie Sun(孙书杰), and Wei Zi(訾威)

Chin. Phys. B, 2022, 31 (**12**): 126803. DOI: 10.1088/1674-1056/ac7cd1

Synthesis of black phosphorus structured polymeric nitrogen

Ying Liu(刘影)†, Haipeng Su(苏海鹏), Caoping Niu(牛草萍), Xianlong Wang(王贤龙), Junran Zhang(张俊然), Zhongxue Ge(葛忠学), and Yanchun Li(李延春)

Chin. Phys. B, 2020, 29 (**10**): 106201. DOI: 10.1088/1674-1056/aba9bd

Effect of ultrathin GeO_x interfacial layer formed by thermal oxidation on Al_2O_3 capped Ge

Han Le (韩乐), Wang Sheng-Kai (王盛凯), Zhang Xiong (张雄), Xue Bai-Qing (薛百清), Wu Wang-Ran (吴汪然), Zhao Yi (赵毅), Liu Hong-Gang (刘洪刚)

Chin. Phys. B, 2014, 23 (**4**): 046804. DOI: 10.1088/1674-1056/23/4/046804

RAPID COMMUNICATION

One-step synthesis of cubic gauche polymeric nitrogen with high yield just by heating

Liangfei Wu(吴良飞)[1,†], Yuxuan Xu(徐宇轩)[1,2,†], Guo Chen(陈果)[1,2], Junfeng Ding(丁俊峰)[1,2], Ming Li(李明)[1,2,‡], Zhi Zeng(曾雉)[1,2], and Xianlong Wang(王贤龙)[1,2,§]

[1] *Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei* 230031, *China*
[2] *University of Science and Technology of China, Hefei* 230026, *China*

(Received 17 November 2024; revised manuscript received 20 November 2024; accepted manuscript online 21 November 2024)

A high-efficient one-step synthesis of cubic gauche polymeric nitrogen was developed just by thermal treatment of KN_3 powders. Raman and infrared spectra confirm the formation of cubic gauche polymeric nitrogen. Further thermogravimetric differential scanning calorimeter measurements show that the content of cubic gauche polymeric nitrogen is as high as 1.5 wt% with high thermal stability, which is the highest content value reported so far.

Keywords: cg-N, thermal treatment, polymeric nitrogen, high-energy-density materials, KN_3

PACS: 68.35.bt **DOI:** 10.1088/1674-1056/ad9569

1. Introduction

Polymeric nitrogen is characterized by its N–N single or N=N double bonds, when these bonds transform into N≡N triple bonds in nitrogen gas, the process releases a vast amount of energy. The most attractive polymeric nitrogen is the cubic gauche polymeric nitrogen (cg-N), which consists of only N–N single bonds with similar crystal structure of diamond.[1–4] After cg-N was successfully synthesized at 110 GPa, LP-N, HLP-N, and BP-N were discovered successively under pressures of 126 GPa, 244 GPa, and 146 GPa, respectively.[5–10] However, the extreme high-temperature and high-pressure conditions required for these syntheses have significantly hindered their practical applications.

In recent years, researchers have begun exploring more moderate synthesis methods, particularly the preparation of cg-N under ambient conditions using plasma-enhanced chemical vapor deposition (PECVD) technology.[11–16] Since 2020, we have started to work in this field.[17] Most recently, we reported that KN_3, as a precursor, is more favorable than NaN_3 for the synthesis of cg-N, and free-standing cg-N was successfully synthesized at ambient conditions, which shows high thermal stability up to 760 K, and related explosion parameters were reported for the first time.[16] In this work, we report a one-step synthesis of cg-N just by thermal treatment, which is the simplest way to date, and the highest cg-N content is realized.

2. Results and discussion

The detailed synthesis process and measurement results are shown below. A certain amount of ordered KN_3 powder was put into the porcelain boat and then heated at temperatures between 150 °C and 300 °C for 0.5–3 h in vacuum or protection gas. Flow rates of 20 sccm (standard cubic centimeters per minute) were maintained for each gas and the heating rate was fixed at 10 °C/min. The raw KN_3 was white powder (Fig. 1(a)) and the color was changed into green after thermal treatment (Fig. 1(b)). Moreover, we also compressed KN_3 powder into a white pellet (Fig. 1(c)) and then the same thermal treatment process was applied. As shown in Fig. 1(d), it could be seen that the surface and interior of the pellet turned green after thermal treatment, indicating that the thermal treatment can efficiently induce bulk reaction with high yield, whereas plasma is confined to the surface of the sample.

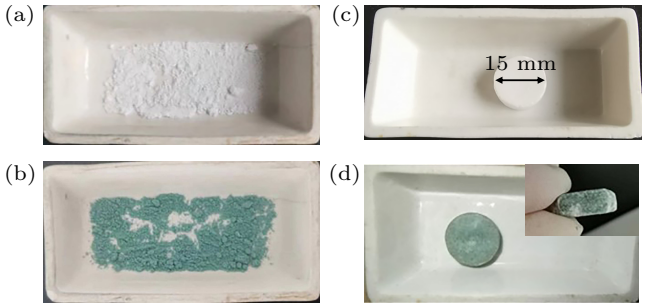


Fig. 1. KN_3 powder (a) before and (b) after thermal treatment. KN_3 pellet (c) before and (d) after thermal treatment (Inset: the cross-sectional view of the pellet sample).

The as-synthesized sample was characterized by FTIR spectra and the result is displayed in Fig. 2(a). The characteristic peaks of KN_3 are observed at 640 cm^{-1} for the bending ν_2 mode and the absorption at 2100 cm^{-1} is related to the antisymmetric stretching ν_3 mode of azide ions. A low-intensity

†These authors contributed equally to this work.
‡Corresponding author. E-mail: liming@issp.ac.cn
§Corresponding author. E-mail: xlwang@theory.issp.ac.cn

© 2024 Chinese Physical Society and IOP Publishing Ltd

vibrational peak located at 883 cm^{-1} of the as-synthesized sample can be assigned to the T(TO) symmetry vibration of cg-N at room temperature and ambient pressure. This is in agreement with the results of infrared spectra measured by Benchafia *et al.*[11] using PECVD process involving NaN_3, and is also consistent with the experimental results of our earlier research.[16]

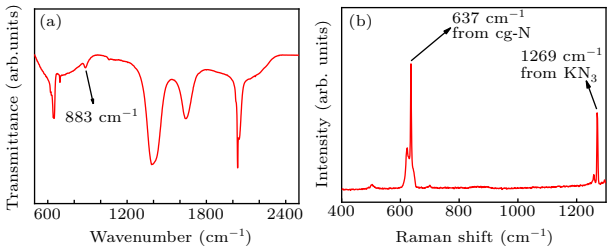


Fig. 2. (a) FTIR and (b) Raman spectra of KN_3 after the thermal treatment.

Figure 2(b) shows the Raman spectra of the as-synthesized sample. The characteristic peak at 1269 cm^{-1} corresponds to the $2\nu_2$ mode of the azide ion. Specifically, a peak located at 637 cm^{-1} could also be observed. This is in agreement with the results measured by Benchafia *et al.*[11] and with Caracas' density-functional theory calculations of the peak positions and intensities of Raman-activated modes at zero pressure for the cg-N phase,[18] as well as the experimental results of our previous work.[16] The results above suggest the successful synthesis of cg-N from KN_3 using one-step heating process.

Thermogravimetric differential scanning calorimeter (TG-DSC) analysis of the KN_3 after thermal treatment was carried out in a flowing N_2 atmosphere (Fig. 3). The DSC curve shows KN_3 undergoes a phase transition from the solid state to the liquid state in the temperature range from 325 °C to 350 °C and the complete decomposition temperature of KN_3 is above 500 °C, while a minor endothermic DSC peak at 448 °C is owing to the decomposition of cg-N. These results are consistent with the experimental results of our previous work by using PECVD process.[16]

Importantly, a clear weight loss of ∼ 1.5 wt% at 448 °C in the TG curve (see inset in Fig. 3(b)) is attributed to the decomposition of cg-N, indicating that the cg-N content in this one-step synthesis is ∼ 1.5 wt%, which is two times higher than that of our previous work by using PECVD process.[16] This is the highest content reported so far, suggesting that our one-step method is high-efficient to obtain cg-N.

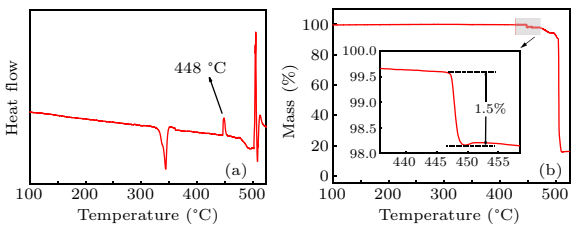


Fig. 3. The (a) DSC and (b) TG curves of KN_3 after the thermal treatment.

Since we observed the transformation from KN_3 into cg-N in PECVD,[16] we started to understand the reaction mechanism. First of all, we should answer the question whether potassium exists after the formation of cg-N. Therefore, a small amount of deionized water was added into the tube containing raw KN_3 powder (Fig. 4(a)). As shown in Fig. 4(b), the raw KN_3 powder dissolved immediately and no bubble appeared. However, a large number of bubbles were generated in the case of KN_3 containing cg-N (Fig. 4(d)). The gas chromatographic analysis demonstrated the presence of H_2, N_2 and O_2 (Fig. 4(e)). In this case, H_2 can only be generated from the reaction between metal potassium and water. Thus, it can be speculated that metal potassium is precipitated from the KN_3 during the reaction process. It is noted that N_2 and O_2 may derive from the air, therefore determining whether the reaction product of cg-N with water contains N_2 is difficult at present and further investigation is needed.

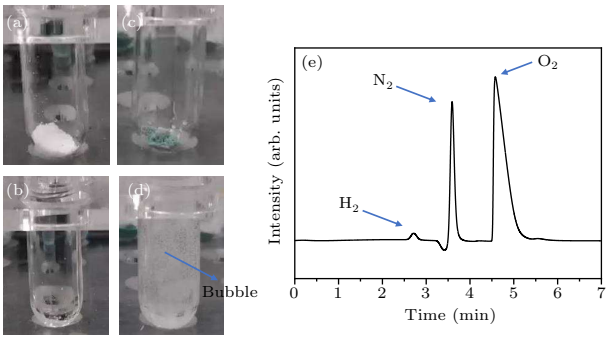


Fig. 4. The digital images of KN_3 powders (a) before and (b) after adding deionized water. The digital images of thermally treated KN_3 (c) before and (d) after adding deionized water (the related video is available online). (e) The gas chromatographic analysis of the bubbles.

3. Conclusion

In summary, we developed the simplest way to synthesize cg-N with high yield via a one-step scheme to date. The highest content of cg-N was obtained so far under ambient conditions. The same thermal treatment process was also applied to NaN_3 and the cg-N was successfully synthesized, however, the conversion efficiency was lower than that of KN_3. We are trying to apply this one-step routine to other azides. Our results will promote the applications of polymeric nitrogen.

Note

Just before submitting this manuscript, we notice the work on thermal-chemical route with multi-steps to synthesize cg-N.[19] In that work, a solution of azides is prepared first, and then pretreatment under vacuum conditions is used, finally, the obtained precursor is heated at high temperature. Here, we used one-step method through heating the primary material under vacuum condition or protection gas environments to get the cg-N.

Acknowledgment

Project supported by the CASHIPS Director's Fund (Grant Nos. YZJJ202207-CX, YZJJ202308-TS, and YZJJ-GGZX-2022-01).

References

[1] Mailhiot C, Yang L H and McMahan A K 1992 *Phys. Rev. B* **46** 14419
[2] Yakub L N 2016 *Low Temp. Phys.* **42** 1
[3] Zhang G, Liu X, Xue Y and Huang J 2014 *Chin. J. Energ. Mater.* **22** 422
[4] Zarko V E 2010 *Combust. Explos. Shock Waves* **46** 121
[5] Eremets M I, Gavriliuk A G, Trojan I A, Dzivenko D A and Boehler R 2004 *Nat. Mater.* **3** 558
[6] Tomasino D, Kim M, Smith J and Yoo C S 2014 *Phys. Rev. Lett.* **113** 205502
[7] Laniel D, Geneste G, Weck G, Mezouar M and Loubeyre P 2019 *Phys. Rev. Lett.* **122** 066001
[8] Liu Y, Su H, Niu C, Wang X, Zhang J, Ge Z and Li Y 2020 *Chin. Phys. B* **29** 106201
[9] Laniel D, Winkler B, Fedotenko T, Pakhomova A, Chariton S, Milman V, Prakapenka V, Dubrovinsky L and Dubrovinskaia N 2020 *Phys. Rev. Lett.* **124** 216001
[10] Ji C, Adebayo A, Yang L X, *et al.* 2020 *Sci. Adv.* **6** eaba9206
[11] Benchafia E M, Yao Z, Yuan G, Chou T, Piao H, Wang X and Iqbal Z 2017 *Nat. Commun.* **8** 930
[12] Benchafia E M, Yu C, Sosnowski M, Ravindra N M and Iqbal Z 2014 *JOM* **66** 608
[13] Alzaim S, Wu Z, Benchafia E M, Young J and Wang X 2021 *Phys. Chem. Chem. Phys.* **23** 15713
[14] Zhuang H, Alzaim S, Li S, Benchafia E M, Young J, Ravindra N M, Iqbal Z and Wang X 2022 *Chem. Mater.* **34** 4712
[15] Zhuang H, Huo S, Alzaim S, Iqbal Z, Ravindra N M and Wang X 2023 *Catal. Today* **409** 149
[16] Xu Y, Chen G, Du F, *et al.* 2024 *Sci. Adv.* **10** eadq5299
[17] Chen G, Niu C, Xia W, Zhang J, Zeng Z and Wang X 2023 *Chin. Phys. Lett.* **40** 086102
[18] Caracas R 2007 *J. Chem. Phys.* **127** 144510
[19] Chen R T, Zhang J, Wang Z L, *et al.* 2024 *Sci. Bull.*