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Local structure and chemistry of C-doped ZnO@C core-shell nanostructures with room-temperature ferromagnetism

Duc-The Ngo,^{a,*} Le Thanh Cuong,^b Nguyen Huu Cuong,^b Cao Thai Son,^b Pham Thanh Huy,^b
and Nguyen Duc Dung,^{b,**}

^a Electron Microscopy Centre, School of Materials, University of Manchester, Oxford Road,
Manchester M13 9PL, United Kingdom

^b Advanced Institute of Science and Technology (AIST), Hanoi University of Science and
Technology, No.1 Dai Co Viet, Hanoi, Viet Nam

* Corresponding author: duc-the.ngo@manchester.ac.uk (Duc-The Ngo)

** Corresponding author: dung.nguyenduc@hust.edu.vn (Nguyen Duc Dung)

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Abstract

We present a superior approach to study quantitatively fine structure of C-doped ZnO nanostructure using transmission electron microscopy (TEM) from which the role of carbon in ZnO crystal to form ferromagnetism is revealed at the first time. Electron diffraction in TEM shows Wurtzite structure in the nanoparticles with lattice parameters ($a = 0.327 \pm 0.03$ nm, and $c = 0.529 \pm 0.04$ nm) slightly different from the original structure. Interestingly, the Zn-C bonding with a bonding length of 2.58 Å is experimentally determined using atomic pair distribution function (PDF) calculated from electron diffraction data. Together with other

1 bonding, such as C-C, Zn-O obtained from the PDF, this demonstrates migration of C atoms
2 into ZnO crystal to substitute O vacancies. This is furthermore visualized by high-resolution
3 TEM image, and strongly supports the proposal of origin of ferromagnetism in the C-doped
4 ZnO nanoparticles where the s - p and p - p hybridizations formed by $C2p$ - $Zn4s$, and $O2p$ -
5 $C2p$ orbitals are believed to cause ferromagnetism.

6

1. Introduction

Dilute magnetic semiconductors (DMSs), such as Mn-doped ZnO,^[1] Co-doped ZnO,^[2] GaMnAs,^[3] Cr-doped AlN,^[4] etc. are desired candidates for spintronic applications. DMSs are commonly synthesized by doping non-magnetic semiconductor with several atomic per cent of transition metal (TM) elements to create ferromagnetism.^{[5] [6]} Creating ferromagnetism in zinc oxide (ZnO), a well-known II-VI semiconductor, has attracted much attention due to its abundance, low environment impact, wide bandgap (3.3 eV) and high exciton binding energy.^[7] Room temperature ferromagnetism in ZnO has been observed by doping the material with 3d metals, such as, Fe, Co, Mn,^[2] and Cu.^[8] However, 3d TM doping of ZnO also produced unwanted second phase precipitation, which may result in unpredicted properties and limits the practical applications of such materials.^[9]

A number of theoretical studies have proposed the use of non-TM doping elements to create magnetism in ZnO, without the problem of second phase precipitation.^[9–13] These papers predict that elements like carbon, could be substituted at an anion site to develop a spin polarised solution in ZnO.^[9] Experimental demonstration of ferromagnetism above room temperature has already been demonstrated for doping by carbon,^[14–16] boron,^[17,18] and potassium,^[19]. C-doped ZnO nanostructures are particularly attractive because of this dopant is cheap, safe and abundant.^{[20][14–16]} It has been demonstrated that carbon doping could result in a new energy state in the band gap as well as oxygen vacancies in ZnO lattice that might be responsible for the visible photoactivity of C-doped ZnO.^[21] These make C-doped ZnO nanostructures an excellent candidate for opto-spintronic applications.^[22]

In previous work,^[23] we demonstrated strong ferromagnetism above room temperature in sol-gel synthesized C-doped ZnO nanoparticles. Co-existence of different magnetic phases in the materials was experimentally demonstrated by means of magnetometric measurements. X-ray photoelectron spectroscopy (XPS) revealed the presence of Zn-C, O-C and C-C bonds at

the surface of C-doped ZnO nanoparticles but which could not be detected by refinement of X-ray diffraction data. This suggests that the C substitution in the ZnO structure only occurs on the surface of ZnO nanoparticles but no direct experimental evidence has confirmed this hypothesis. Here we present a deeper investigation to determine the local structure and chemistry of C-doped ZnO nanoparticles using transmission electron microscopy to better understand the origin of the observed room-temperature ferromagnetism. For the first time, we quantitatively demonstrate the existence of Zn-C, C-C bonding in the ZnO nanostructures, revealing the ability of C to substitute into O vacancies.

2. Experimental details

ZnO nanoparticles were prepared by sol-gel method from a solution of zinc acetate and diethanolamine (DEA) in isopropanol. Carbon doping was produced by thermal treatment at 450°C in Ar with C additive. Further details of materials preparation can be found in ref.^[23]

Morphology, structure and elemental chemistry of the materials were investigated using transmission electron microscopy (TEM) in a FEI Tecnai F30 equipped with a field emission gun (FEG) and high-angle annular dark field (HAADF) detector for scanning TEM (STEM) imaging, and a FEI Talos F200A AEM with Ultrahigh brightness SuperX FEG (200 kV). Chemical analysis was performed by an energy dispersive X-ray spectroscopy (EDS) in the TEM (the FEI Talos F200A) using SuperX silicon drift detectors (SSDs) built-in the pole piece of the objective lens for high-resolution and high-precision elemental mapping. Chemical analysis was also further conducted by energy-filtering TEM (EFTEM) in FEI Tecnai F30 using a post column Gatan Imaging Filter (GIF). Indexing of the selected area diffraction patterns was performed using the CrysTBox software.^[24] The magnetization of the materials was measured by MicroSense EZ9 vibrating sample magnetometer (VSM).

3. Results and discussion

Figure 1. Magnetization curve of the C-doped ZnO nanoparticles measured at room temperature $T = 300$ K. The inset shows temperature dependence of magnetisation of the sample measured in an applied field of 0.5 T.

Figure 1 presents a virgin magnetization (M - H) curve of the C-doped ZnO nanoparticles obtained at room temperature ($T = 300$ K). The sample shows ferromagnetic behaviour with two magnetization processes including magnetic moments rotation and magnetic metastable phase transition.^[23] The magnetization is observed to saturate when the applied magnetic field is larger than about 0.5 T. The saturation magnetization of the C-doped ZnO sample is about 5-6 times larger than in undoped ZnO nanoparticles reported previously.^[25] The thermomagnetic (M - T) curve shown inset in Fig. 1 demonstrates two phase transition Curie temperatures, T_C , in the at temperature ranges of 780-800 K and 860-880 K respectively. These likely correspond to two different ferromagnetic phases in the sample with different exchange energies. The presence of more than one ferromagnetic phases in these materials may explain why previous reports have found different values for the Curie points in similar materials.^[26,27] It could also be assumed that such two magnetic phases belong separately to the two types of ZnO nanocrystal morphology. As the discussion in previous work ref.^[23], the original mechanism of ferromagnetism of C-doped ZnO presumably comes from two causes: the defects of the ZnO crystalline structure and the substitution of C atoms at O sites in ZnO

Wurtzite crystalline structure to create Zn-C bonding. The studies of morphology, crystalline structure and the doping of C into ZnO crystalline lattices will provide more information on the mechanism of ferromagnetic properties in the ZnO material systems. Based on high resolution transmission electron microscopy (HRTEM, EFTEM) imaging as well as electron diffraction and energy dispersive X-ray spectroscopy (EDS) mapping, the studied results are discussed in detail in the following.

The bright-field (BF) TEM images of the C-doped ZnO nanoparticles (Figure 2a) shows that these have a spherical morphology with a diameter of 80-120 nm. Magnified BF TEM and high-resolution TEM (HRTEM) images [Fig. 2(b,c)] reveal a core-shell structure where a crystalline core is surrounded by an amorphous shell [Fig. 2(c)]. Analysis of selected area electron diffraction (SAED) patterns averaging over many nanoparticles [Fig. 2(d)] indicate a Wurtzite hexagonal crystal structure with lattice parameters $a = 0.327 \pm 0.03$ nm, and $c = 0.529 \pm 0.04$ nm. This gives a c/a ratio of 1.62, slightly lower than that in the original ZnO Wurtzite nanoparticles where $c/a \approx 1.60$. Lattice parameters obtained by analysing HRTEM images of the crystalline core in Fig. 2(c) are consistent with the SAED data.

Figure 2. TEM images of the C-doped ZnO nanoparticles: (a) low-magnification bright-field TEM image, (b) magnified BF TEM image from a small area in (a), (c) HRTEM image of an individual nanoparticle in (a), and (d) indexed SAED pattern.

In addition to SAED analysis, the crystal structure of the individual C-doped ZnO nanoparticle was also measured with high precision using convergent beam electron diffraction (CBED). Using a microprobe STEM alignment, a STEM-HAADF image of the nanoparticle cluster was firstly acquired [Fig. 3(a)] then the electron beam was focussed on an individual particle to generate the CBED pattern [Fig. 3(b)]. The pattern is a good fit to with the Wurtzite ZnO structure viewed along the $[\bar{1}21]$ crystal zone axis with the lattice parameters

determined as $a = 0.326 \pm 0.02$ nm, and $c = 0.530 \pm 0.02$ nm, in excellent agreement with our SAED measurements.. Furthermore, local lattice strain could be observed from the dark fringes in the CBED disks (Supporting Information, S1).^[28]

Figure 3. (a) STEM-HAADF image of C-doped ZnO nanoparticles, (b) a CBED pattern of the C-doped ZnO nanoparticle indicated by the white circle in (a). The electron beam was parallel to the $[121]$ zone axis of the ZnO crystal.

In order to probe the local disorder of the C-doped ZnO nanoparticles a pair distribution function (PDF) analysis was performed on the SAED data to quantify the bond lengths between atoms. To achieve this a total scattering intensity profile of the diffraction pattern was first obtained from the SAED image by rotationally averaging. The PDF can then be derived using SUEPDF software based on kinematical electron scattering theory as well as the total scattering methodology.^[29] The PDFs reconstructed after Fourier transformation are normalised with respect to number density, nanoparticle form factor and with the requirement of non-negativity of the probability density.^[29]

Figure 4. Electron diffraction PDF of C-doped ZnO nanoparticles (dark solid line plot) compared with PDF of original Wurtzite structure calculated from ZnO single crystal data.^[30]

Bond lengths in the material can be inferred from the position peaks in the PDF^[29,31] Fig. 4 illustrates the PDF for our C-doped ZnO nanoparticles compared with pure Wurtzite ZnO calculated from a ZnO single crystal model.^[30] The PDF of the C-doped ZnO nanoparticles shows peaks that can be associated with Zn-O bonding (@ 2.01 Å), and with Zn-Zn or O-O bonding (@ 3.22 Å) in the Wurtzite structure. A small increase is observed for the Zn-O bond length in our C-doped ZnO PDF (2.01 Å) compared to that of the single crystal Wurtzite ZnO structure (1.98 Å), most likely due to a slight difference in the lattice parameters of the two materials. This is consistent with previous reports where Zn-O bond lengths in ZnO nanoparticles varied from 1.96 Å to 2.06 Å depending on particle size and doping^[32].

Importantly the PDF of the C-doped ZnO, also shows new peaks at 1.42 Å and 2.58 Å. The peak at 1.42 Å is a good match to the C-C intraplanar bond length in graphene and is likely associated with carbon on the surface of the particle.^[33] However the peak at 2.58 Å is

believed to be due to the presence of Zn-C bonds in the material. An X-ray diffraction study by Ruccolo *et al.* indicated that Zn-C bond lengths vary between 2.17 and 2.68 Å depending on the compounds.^[34] Zhanpeisov *et al.* theoretically found a bond length of 2.381 Å for Zn-C bonding on the surface of ZnO adsorbed with carbon monoxide.^[35] In addition, Sharma and Singh theoretically predicted that when C atoms were doped into ZnO clusters, interstitial C atoms showed a preference to bond with Zn atoms with a bond length between 2.2-2.5 Å.^[36] The relatively high bond length found for Zn-C (within the predicted range) suggests that C atoms are substituting into O lattice sites in the ZnO Wurtzite crystal rather than being associated with the surface. This is in agreement with experimental results from XPS analysis reported by Pan *et al.*^[26]

According to Nayak and co-workers,^[13] although substitution of C for O is less energetically favourable than that for Zn, it could be stabilized under specific growth conditions (O *e.g.* poor and C rich growth condition) which are similar to those used to synthesis our nanoparticles. Furthermore, they predict that C substituted into O vacancies would be associated with a localized magnetic moment of 2 μ_B /atom (C).^[13] This is because when the carbon atom substitutes for the O site in the ZnO lattice, it has a zinc atom as the first nearest neighbour and an oxygen atom as the second nearest neighbour, and as a result, magnetism would result from ZnC, Zn₂C, Zn₂OC, and Zn₂C₂ clusters.^[10] It should be noted that the exchange energy is sensitive to the dimensionality of the clusters and it is believed to be highest for three-dimensional clusters. Sharma *et al.*^[36] found that the eigenvalues for 2*p* orbitals of C atoms and 4*s* orbitals of Zn atoms were relatively close to each other for spin up-states, whereas the spin down eigenvalue of the C atoms' 2*p* orbital was significantly higher than the Zn4*s*. The *s-p* hybridization formed by C2*p* and Zn4*s* orbitals, as well as the splitting of the up and down energy levels exists for all the C-doped ZnO systems result in the formation of a magnetic moment localized on the carbon atoms due to the doubly degenerate

pure p states.^[36] Experimental work based on XPS and Auger spectroscopy by Li et al.^[37] on C-doped ZnO films also supported the proposed s - p hybridization.

In addition, Pan *et al.*^[26] have predicted that substitution of C atoms at O sites in ZnO crystals created holes in the $O2p$ states coupling with the parent $C2p$ localized spins by a p - p interaction which was similar to p - d hybridization in TM-doped semiconductors or oxides. Such a p - p interaction resulted in the appearance of additional mixed band levels originating from the valence band. The $O2p$ – $C2p$ coupling was believed to push the minority p - p mixed state upward and the opposite spin state downward causing a reduction in the total energy of the system. The wave function of the $C2p$ states was found to extend spatially to neighbouring $O2p$ states, and couple to these. Therefore, holes reportedly aligned the spin of parent C atoms to cause an indirect ferromagnetic coupling of C atoms. Interestingly, the p - p interaction is relatively long range,^[38,39] which explains the strong ferromagnetism behaviour in ZnO induced even at low doping concentrations. An anomalous Hall effect measurement conducted on C-doped ZnO nanoneedles by Herng *et al.*^[14] experimentally supported this hypothesis by demonstrating the role of p -type conduction (localised holes) in the magnetotransport properties of the material. These theoretical calculations and our new experimental evidence of Zn-C bonding supports the proposed mechanism of ferromagnetism in non-TM doped ZnO nanostructures in which hybridization of p - p ($O2p$ - $C2p$ interaction) and s - p ($Zn4s$ - $C2p$) orbitals play a crucial role to produce long range ferromagnetic behaviour.

In fact, the Zn-C bonding was qualitatively confirmed in our previous study using XPS analysis which is sensitive to the surface effect but could not be detected by refinement of X-ray diffraction. It suggests that the C occupation in the ZnO structure only occurs on the surface of ZnO nanoparticles. This proposal could be clarified by elemental mapping using STEM-EDS presented in the following paragraph.

Figure 5. (a) STEM-HAADF image of a C-doped ZnO nanoparticle, (b,c,d) STEM-EDS elemental maps of Zn, O and C obtained from the area in (a), (e) a mixture map of Zn, O and C, and (f) a line profile shows how concentration of carbon varies through the edge of the crystalline core along the dark line on the HAADF image (a).

Fig. 5 presents a high-resolution elemental mapping of the C-doped ZnO nanoparticles using STEM-EDS performed on the FEI Talos F200A. The crystalline ZnO particle is observed in the HAADF image [Fig. 5(a)] as a bright-contrast particle on the dark background. Elemental maps of Zn, O and C are also constructed [Fig. 5(b,c,d)] from which a distribution of carbon through the edge of the crystalline core is plotted in Fig. 5(f). It could be seen that the concentration of carbon goes through a maximum peak within a thickness of 2-3 nm [Fig. 5(f)] to prove the above assumption that carbon doping only occurs in a certain depth on the surface of the ZnO crystal. Although this variation could be seen in the EDS line distribution such a variation is weak to observe on the elemental map. It could also somehow seen in the HRTEM image a thin crystalline layer (visible as lattice fringes in the HRTEM image -

Supporting information, S2) with brighter contrast arising from lower-weight atoms than the inner atomic column.

It is worth noting that this effect only occurs on the surface of the nanoparticles at a few-nanometre depth thus it could be hardly detectable using macroscopic measurements such as X-ray diffraction or magnetometric measurement. XPS is a surface-sensitive technique^[40] to detect this effect but quantitative measurement of bond length using XPS would be a challenge. Therefore, it is emphasized that extraction of chemical bond length by obtaining the PDF from TEM diffraction data could be considered a simple but superior quantitative approach.

Figure 6. EFTEM images of a C-doped ZnO nanoparticle: (a) BF-TEM image, (b-d) EFTEM elemental maps (Zn, O and C) from the particle in BF-TEM image.

EFTEM elemental mapping of a single nanoparticle reveals that the amorphous shell is enriched in carbon compared to the crystalline core, although small quantities of both Zn and O are found to be associated with the shell (Fig. 6). This compositional analysis is confirmed by STEM-EDS elemental mapping presented in Supporting Information (S3). We hypothesise that the Zn-O-C amorphous shell formed on the nanoparticle surface during high temperature heat treatment. The amorphous shell may play a role in the optical properties (*e.g.* photoluminescence)^[41] but, to the best of our knowledge, an amorphous surface structure such as this is not able to create the observed ferromagnetic behaviour we observe. Thus we predict that C atoms are able to diffuse into the crystalline core from the shell and substitute for the O to form C-doped ZnO. Therefore, further understanding the role of carbon would be needed

to tailor the materials structure and properties, and TEM characterisation, such as, electron energy loss spectroscopy (EELS),^[42,43] would be the state-of-the-art approach to fulfil this thirst.

4. Conclusions

In conclusion, we demonstrated a quantitative analysis of bonding in C-doped ZnO nanocrystals from TEM electron diffraction data in order to better understand the ferromagnetism above room temperature. For the first time, a bond length of 2.58 Å has been experimentally determined for Zn-C bonding indicating the presence of C atoms substituted for O vacancies in the ZnO lattice. This is expected to occur on the surface of the doped ZnO nanocrystals and is ascribed to the origin of room temperature ferromagnetism due to s-p hybridization formed by C p and Zn 4s orbitals, and *p-p* hybridization formed by O *p* and C *p* orbitals. A C-rich amorphous shell coating on ZnO has also been revealed using EFTEM and HRTEM imaging. We emphasize our approach to extract the bond length from TEM diffraction data is a simple technique which is particularly useful for nanoparticulate systems where XRD measurements fail and is highly complementary to XPS measurements of chemical state.

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References

- [1] P. Sharma, A. Gupta, K. V Rao, F. J. Owens, R. Sharma, R. Ahuja, J. M. O. Guillen, B. Johansson, G. a Gehring, *Nat. Mater.* **2003**, 2, 673.
- [2] K. Ueda, H. Tabata, T. Kawai, *Appl. Phys. Lett.* **2001**, 79, 988.
- [3] H. Ohno, *Science* (80-.). **1998**, 281, 951.
- [4] D. Kumar, J. Antifakos, M. G. Blamire, Z. H. Barber, *Appl. Phys. Lett.* **2004**, 84, 5004.
- [5] W. Prellier, A. Fouchet, B. Mercey, *J. Phys. Condens. Matter* **2003**, 15, 1583.
- [6] S. A. Chambers, B. Gallagher, *New J. Phys.* **2008**, 10, 55004.
- [7] T. Dietl, H. Ohno, *Rev. Mod. Phys.* **2014**, 86, 187.
- [8] D. B. Buchholz, R. P. H. Chang, J. Y. Song, J. B. Ketterson, *Appl. Phys. Lett.* **2005**, 87, 82504.
- [9] A. El-Amiri, H. Lassri, E. K. Hlil, M. Abid, *J. Magn. Magn. Mater.* **2015**, 374, 338.
- [10] B. J. Nagare, S. Chacko, D. G. Kanhere, *J. Phys. Chem. A* **2009**, 144, 2689.
- [11] H. Wu, A. Stroppa, S. Sakong, S. Picozzi, M. Scheffler, P. Kratzer, *Phys. Rev. Lett.* **2010**, 105, 2.
- [12] A. Pham, M. H. N. Assadi, Y. B. Zhang, a. B. Yu, S. Li, *J. Appl. Phys.* **2011**, 110, 123917.
- [13] S. K. Nayak, M. E. Gruner, S. Sakong, S. Sil, P. Kratzer, S. N. Behera, P. Entel, *Phys. Rev. B* **2012**, 86, 1.
- [14] T. S. Herng, S. P. Lau, C. S. Wei, L. Wang, B. C. Zhao, M. Tanemura, Y. Akaike, *Appl. Phys. Lett.* **2009**, 95, 2009.
- [15] H. Kwak, J. R. Chelikowsky, *Appl. Phys. Lett.* **2009**, 95, 263108.
- [16] X. Zhang, J. Qin, R. Hao, L. Wang, X. Shen, R. Yu, S. Limpanart, M. Ma, R. Liu, *J. Phys. Chem. C* **2015**, 119, 20544.
- [17] S. Yilmaz, J. Nisar, Y. Atasoy, E. McGlynn, R. Ahuja, M. Parlak, E. Bacaksiz, *Ceram. Int.* **2013**, 39, 4609.

- 1 [18] M. H. Farooq, X.-G. Xu, H.-L. Yang, C.-J. Ran, J. Miao, M. Z. Iqbal, Y. Jiang, *Rare*
2 *Met.* **2013**, 32, 264.
- 3 [19] R. Krithiga, S. Sankar, V. Arunkumar, *J. Supercond. Nov. Magn.* **2015**, 245.
- 4 [20] S. Cho, J.-W. Jang, J. S. Lee, K.-H. Lee, *CrystEngComm* **2010**, 12, 3929.
- 5 [21] A. S. Alshammari, L. Chi, X. Chen, A. Bagabas, D. Kramer, A. Alromaeh, Z. Jiang,
6 *RSC Adv.* **2015**, 5, 27690.
- 7 [22] Z. Dai, A. Nurbawono, A. Zhang, M. Zhou, Y. P. Feng, G. W. Ho, C. Zhang, *J. Chem.*
8 *Phys.* **2011**, 134, 104706.
- 9 [23] N. D. Dung, C. T. Son, P. V. Loc, N. H. Cuong, P. T. Kien, P. T. Huy, N. N. Ha, *J.*
10 *Alloys Compd.* **2016**, 668, 87.
- 11 [24] M. Klinger, A. Jager, *J. Appl. Crystallogr.* **2015**, 48, 2012.
- 12 [25] M. A. Garcia, J. M. Merino, E. F. Pinel, A. Quesada, J. De La Venta, M. L. R.
13 González, G. R. Castro, P. Crespo, J. Llopis, J. M. González-Calbet, A. Hernando,
14 *Nano Lett.* **2007**, 7, 1489.
- 15 [26] H. Pan, J. B. Yi, L. Shen, R. Q. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H.
16 Van, J. H. Yin, *Phys. Rev. Lett.* **2007**, 99, 127201.
- 17 [27] F. B. Zheng, C. W. Zhang, P. J. Wang, H. X. Luan, *J. Appl. Phys.* **2012**, 111, 44329.
- 18 [28] A. Béché, J. L. Rouvière, J. P. Barnes, D. Cooper, *Ultramicroscopy* **2013**, 131, 10.
- 19 [29] D. T. Tran, G. Svensson, C. W. Tai, *J. Appl. Crystallogr.* **2017**, 50, 304.
- 20 [30] H. Sawada, R. Wang, A. W. Sleight, *J. Solid State Chem.* **1996**, 122, 148.
- 21 [31] R. B. Neder, V. I. Korsunskiy, *J. Phys. Condens. Matter* **2005**, 17, S125.
- 22 [32] T. Liu, H. Xu, W. S. Chin, Z. Yong, A. T. S. Wee, *J. Phys. Chem. C* **2008**, 112, 3489.
- 23 [33] L. Brockway, L. Pauling, *J. Am. Chem. Soc.* **1937**, 59, 1223.
- 24 [34] S. Ruccolo, W. Sattler, Y. Rong, G. Parkin, *J. Am. Chem. Soc.* **2016**, 138, 14542.
- 25 [35] N. U. Zhanpeisov, G. M. Zhidomirov, M. Baerns, *J. Struct. Chem.* **1994**, 35, 9.
- 26 [36] H. Sharma, R. Singh, *J. Phys. Condens. Matter* **2011**, 23, 106004.

- [37] X. L. Li, J. F. Guo, Z. Y. Quan, X. H. Xu, G. A. Gehring, *IEEE Trans. Magn.* **2010**, *46*, 1382.
- [38] J. Lee, N. G. Subramaniam, I. A. Kowalik, J. Nisar, J. Lee, Y. Kwon, J. Lee, T. Kang, X. Peng, D. Arvanitis, R. Ahuja, *Sci. Rep.* **2015**, *5*, 17053.
- [39] G. Z. Xing, Y. H. Lu, Y. F. Tian, J. B. Yi, C. C. Lim, Y. F. Li, G. P. Li, D. D. Wang, B. Yao, J. Ding, Y. P. Feng, T. Wu, *AIP Adv.* **2011**, *1*, 22152.
- [40] D. R. Baer, D. J. Gaspar, P. Nachimuthu, S. D. Techane, D. G. Castner, *Anal. Bioanal. Chem.* **2010**, *396*, 983.
- [41] N. Tu, K. T. Nguyen, D. Q. Trung, N. T. Tuan, V. N. Do, P. T. Huy, *J. Lumin.* **2016**, *174*, 6.
- [42] B. D. Yuhas, D. O. Zitoun, P. J. Pauzauskie, R. He, P. Yang, *Angew. Chemie - Int. Ed.* **2006**, *45*, 420.
- [43] E. S. Cho, A. M. Ruminski, S. Aloni, Y.-S. Liu, J. Guo, J. J. Urban, *Nat. Commun.* **2016**, *7*, 10804.