Atomic structures of luminescent centers in size-mismatch systems

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After the success of blue-light emission in GaN and related materials, it has been realized that hexagonal-, cubic-BN (*h*- or *c*-BN) and wurtzite-AlN (*w*-AlN), having a much wider energy band-gap, would have high potential for shorter wavelength optoelectronic applications. Rare-earth doped these nitrides are also highly desirable for high-efficiency electroluminescent applications. However, it has long eluded us because it is difficult to control impurity levels and rare-earth dopants have no solubility due to the large size-mismatch. In the present study, we use a reactive flux method under high pressure and high temperature, and we obtained sub-millimeter c-BN:Ce [1] and *w*-AlN:Ce [2,3] single crystals with blue- and pink-colored luminescence. Combining atomic-resolution scanning transmission electron microscopy (STEM) and systematic first-principles calculations, we show the direct determination of the atomic structures of luminescent centers in *c*-BN:Ce and *w*-AlN:Ce, and we revealed how these nitrides can accept a dopant with a large size mismatch.

Figure 1 shows a typical ADF STEM image obtained from *c*-BN:Ce viewed along the [110] direction. One can recognize the location of single Ce dopants as brighter contrast, and the Ce single dopants are randomly distributed in *c*-BN. The high-magnification ADF STEM image is shown in Figure 2. The sub-angstrom BN dumbbell is clearly resolved, and moreover the B and N atomic columns can be distinguishable, *i.e.*, N atomic column at left-hand has brighter Z-contrast. Interestingly, the cationic Ce dopants are located at not cationic B-site but anionic N-site. Systematic first-principles calculations revealed that the most energetically stable atomic configuration is the Ce dopant is located at the N atomic site surrounded by four B vacancies, which is consistent with the present experimental result. Our finding indicates that even dopant atoms with large size mismatch can be stably incorporate into host crystal through the formation of vacancy-related complex point defect structures. This new strategy will be useful for the exploring new physical properties or applications.

References
[1] R. Ishikawa et al., Phys. Rev. Letts, 110 (2013) 065504.
[2] R. Ishikawa et al., Sci. Rep. 4 (2014) 3778.
[3] R. Ishikawa et al., Microsc. Microanal. (2014) in press.

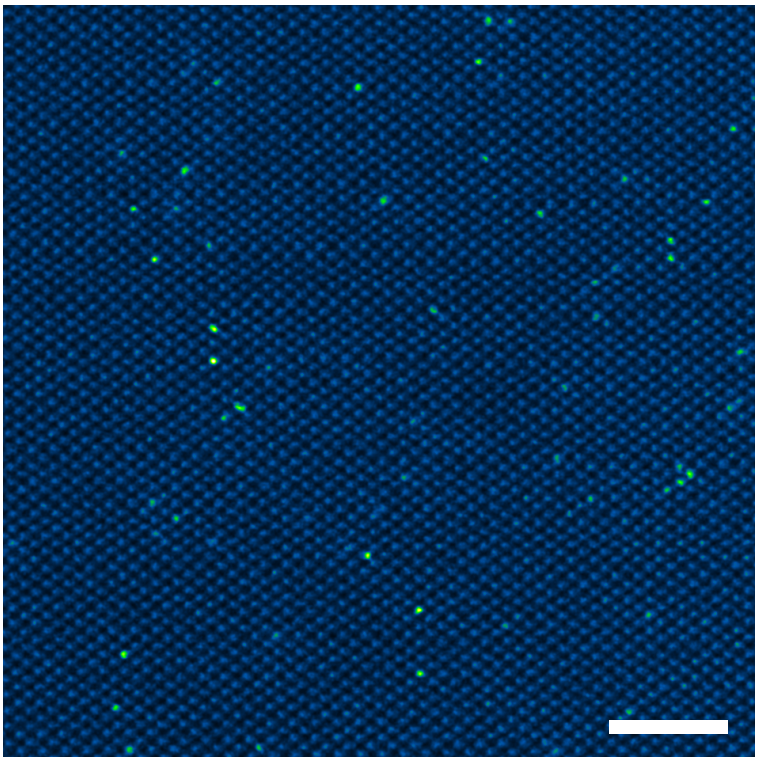

FIG. 1. Low-magnification ADF STEM image of c-BN:Ce viewed along the [110] direction. The scale bar is 5 nm.

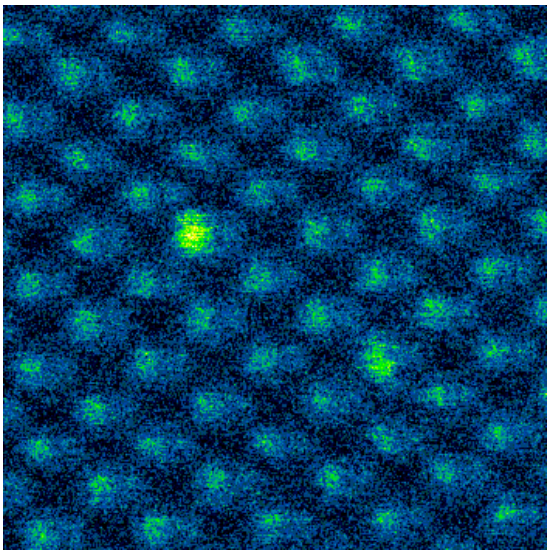

FIG. 2 Atomic-resolution ADF STEM image of *c*-BN:Ce.