Ultra-broad near-infrared photoluminescence from crystalline (K-crypt)$_2$Bi$_2$ containing [Bi$_2$]$^{2-}$ dimers

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Received 25th June 2012, Accepted 16th August 2012
DOI: 10.1039/c2jm34101h

For the first time, we report that a single crystal of (K-crypt)$_2$Bi$_2$ containing [Bi$_2$]$^{2-}$ displays ultra-broad near-infrared photoluminescence (PL) peaking at around 1190 nm and having a full width at the half maximum of 212 nm, stemming from the inherent electronic transitions of [Bi$_2$]$^{2-}$. The results not only add to the number of charged Bi species with luminescence, but also deepen the understanding of Bi-related near-infrared emission behavior and lead to the reconsideration of the fundamentally important issue of Bi-related PL mechanisms in some material systems such as bulk glasses, fibers, and conventional optical crystals.

The heavier p-block elements could form fascinating structures such as anionic and cationic polyhedra.$^{1-4}$ Bismuth, which has been called 'the wonder metal', is one of the most thoroughly investigated members of these elements.$^{1-4}$ So far, a broad range of compounds containing bismuth polycations or polyanions have been successfully synthesized.$^{1-4}$ In contrast to this rapid advance in the synthesis of novel bismuth structures, their optical properties, especially their photoluminescence (PL), have not attracted the attention they deserve. Recently, Sun et al. found that molecular crystals containing bismuth polycations such as Bi$_4^{3+}$ and Bi$_8^{2+}$ exhibit extremely broad near-infrared (NIR) photoluminescence.$^{4e,5}$ suggesting that such systems with bismuth polycations have great potential for photonic applications.$^4$ Interestingly, very recently it was found that substructures of Bi$^+$ stabilized by zeolite Y frameworks also demonstrate peculiar NIR emission bands because of their intrinsic electronic transitions.$^5$ Insights obtained from the determination of the Bi distribution in these porous structures by high-resolution synchrotron powder X-ray diffraction coupled with detailed PL evaluation and quantum chemistry calculation of the Bi$^+$ substructures have inspired great interest in the exploration of more generic evolution rules of the Bi oxidation states. This has raised new possibilities for the design and synthesis of novel photonic materials using charged elemental clusters as the optically active centers.$^{5e}$ However, all aforementioned Bi species were positively charged.$^{4,5}$ As far as we are aware, until recently the PL properties of Bi polyanions had not been demonstrated experimentally, although a number of crystalline compounds containing such peculiar structural units have already been reported.$^3$ It is noteworthy that many of these compounds with Bi polyanions absorb light in the visible range of the electromagnetic spectrum since they are colored, thus giving promise for unique optical properties. It is reasonable, therefore, to anticipate that some of the polyanions may turn out to be novel optical emitters, perhaps in important spectral ranges such as biological and/or telecommunication optical windows, due to their inherent electronic transitions.

In this communication, for the first time, we report that a single crystal of (K-crypt)$_2$Bi$_2$ which contains [Bi$_2$]$^{2-}$ polyanions displays an ultra-broad NIR emission at around 1190 nm with a full width at the half maximum (FWHM) of 212 nm. The single crystal was characterized by single-crystal X-ray diffraction (XRD), diffuse reflectance spectroscopy, and PL measurements. Our results revealed that [Bi$_2$]$^{2-}$ is a NIR emitter resulting from the characteristic electronic transitions from the excited levels to the ground level. The experimental results reported here require the reconsideration of the fundamentally important issue on Bi-related PL mechanisms in some material systems such as bulk glasses, fibers, and conventional optical crystals.

The (K-crypt)$_2$Bi$_2$ crystal was first synthesized and structurally characterized by Xu et al. using the precursor of K$_3$Bi$_2$. Here, we used an alternate approach to obtain high-quality single crystals (see details in ESI†). In brief, an ethylenediamine solution of 2,2,2-crypt is pipetted onto a powdered precursor of K$_3$Bi$_2$ and then stirred for 15 minutes while forming a bright green-blue solution.$^6$ After filtering, the filtrate is carefully layered with three parts of toluene followed by two parts hexane. After several days, dark red-brown plates, cubes, and blocks of (K-crypt)$_2$Bi$_2$ crystallize cleanly. Representative crystals of the different morphologies were indexed by single-crystal X-ray
shoulders at

1050 and 1330 nm are present. We further analyzed

calculation of the absorption energies at 990, 1090, and 1273 nm, respectively. It is necessary to point
out that these three emission energies are lower than the corre-
transitions from the three $^1\Sigma$ singlet excited states to the $^3\Pi$ ground state and/or to one of the first two excited $^3\Pi$ states. These calculated emission characteristics are similar to the experimentally determined PL spectrum (Fig. 3). Despite this similarity, however, it is clear that at present the theoretical results are only approximate and do not completely agree with the experimental facts.

A better, although only qualitative, explanation of the observation of photophysical behavior can be given as follows. The $[\text{Bi}_2]^{2-}$ anion absorbs photons with energies in the NIR and visible ranges as shown in Fig. 5. After irradiation with high-energy photons, the electrons in the upper excited levels tend to nonradiatively relax to the first three excited levels from where the electrons relax to the lowest vibrational sublevels, thus resulting in Stokes NIR emissions. That is, the NIR PL is attributable to the radiative electronic transitions from the first three excited levels to the ground level based on a one-photon process. The overlapping of the three emission bands leads to the observed ultra-broad PL band ranging from 975 to 1400 nm.

In summary, we have demonstrated here that crystalline (K-crypt)$_2$Bi$_2$ emits an ultra-broad NIR band, stemming from the inherent electronic transitions of $[\text{Bi}_2]^{2-}$. This represents the first experimental observation of NIR emission from negatively charged bismuth species. These results not only add to the number of charged Bi species with luminescence, but also deepen the understanding of Bi-related NIR emission behavior as well as encourage efforts for the design of photonic materials with such emitters.

H. Sun gratefully acknowledges the funding support from Hokkaido University and NIMS, Japan. T. Yonezawa is grateful for the partial financial support through a Grant-in-Aid for Scientific Research (B) (21310072) from JSPS and a Grant-in-Aid for Scientific Research in Priority Area (Strong Photon–Molecule Coupling Fields for Chemical Reactions (470, 21020010)) from MEXT, Japan. S. C. Sevov thanks the US National Science Foundation (CHE-0742365) for the financial support of this research. H. Sun greatly thanks the support from Dr Z. H. Bai in Kobe University for the PL measurement.

Notes and references
6 Crypt is short for 4,7,13,16,21,24-hexaaza-1,10-diazacycloc[8,8.8]hexacosane.


