Journal of Materials Chemistry

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COMMUNICATION

Ultra-broad near-infrared photoluminescence from crystalline (K-crypt)₂Bi₂ containing [Bi₂]²⁻ dimers†

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For the first time, we report that a single crystal of (K-crypt)₂Bi₂ containing [Bi₂]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 [Bi₂]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.[1–5] 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_5^{3+} and Bi_8^{2+} exhibit extremely broad near-infrared (NIR) photoluminescence,[4a–c] 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.[5a] 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)₂Bi₂ which contains [Bi₂]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 [Bi₂]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)₂Bi₂ crystal was first synthesized and structurally characterized by Xu *et al.* using the precursor of K₃Bi₂.[3a] 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 K₅Bi₄ 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)₂Bi₂ crystallize cleanly. Representative crystals of the different morphologies were indexed by single-crystal X-ray

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† Electronic supplementary information (ESI) available: Detailed procedure for obtaining high-quality (K-crypt)₂Bi₂ single crystals and the PL behavior under 514.5 nm excitation. See DOI: 10.1039/c2jm34101h

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J. Mater. Chem., 2012, **22**, 20175–20178 | 20175

diffraction, and all of them displayed the same unit cell as the that of the previously reported (K-crypt)$_2$Bi$_2$, thus confirming the structure of exactly the same compound.[3a] The high-quality single crystals obtained without impurities paves the way for the following spectroscopy evaluation. The naked [Bi$_2$]$^{2-}$ dianion is oriented along the 3-fold axis of the rhombohedral structure and its charge is balanced by two [K-crypt]$^+$ cations (Fig. 1). Due to the air and moisture-sensitivity of the compound, its UV-vis-NIR absorption spectrum was measured on crystals enclosed between two 1 mm thick pure silica pieces (V-570 spectroscope equipped with an integrating sphere, JASCO, Japan). Steady-state PL measurements were carried out at room temperature with 641 nm excitation light from a laser diode. The signal was analyzed by a single grating monochromator and detected by a liquid-nitrogen-cooled InGaAs detector.

The UV-vis-NIR diffuse reflectance spectrum demonstrates peculiar absorption bands at 471, 593, 705, 990, 1090, and 1273 nm (Fig. 2). It has been shown before that [Bi$_2$]$^{2-}$, in an ethylenediamine solution, shows two broad peaks at 435 and 605 nm without observable NIR bands.[3c] One possible rationale for this difference might be that the bond length of [Bi$_2$]$^{2-}$ in the solid state is somewhat different from that in solution since the polarization of the valence electron density distribution in the dianion by the surrounding cations in the solid state will effectively reduce the intra-molecular electrostatic repulsion and hence shorten the Bi–Bi bond length.[3c] It is also noted that the absorption in the NIR region is much weaker than that in the visible range, suggesting that the electronic transition probabilities in the NIR and visible ranges are different.

Next, we studied the PL properties of crystalline (K-crypt)$_2$Bi$_2$. As shown in Fig. 3, the emission spectrum generated with 641 nm excitation light has a very broad emission range, spanning 975 to 1400 nm. The FWHM of the spectrum is 212 nm and the emission peak is at around 1190 nm. Furthermore, it is found that the spectrum does not show the Gaussian profile, but rather two notable shoulders at *ca.* 1050 and 1330 nm are present. We further analyzed the emission spectrum by Gaussian decomposition, resulting in three decomposed curves peaking at 1047, 1190 and 1331 nm with FWHMs of 99, 146, and 56 nm, respectively. It is necessary to point out that these three emission energies are lower than the corresponding absorption energies at 990, 1090, and 1273 nm, respectively (Fig. 2). The difference between the positions of the band maxima of the absorption and emission spectra of the same electronic transition is due to the loss of excitation energy by thermalization of the excess vibrational energy. In general, there are two possibilities for the emissions under 641 nm excitation: they are either single- or multiple-photon processes. In the latter case, the active center will sequentially absorb at least two photons to emit one photon. In order to ascertain the process that contributes to the observed emission, we plotted the log–log dependence of the NIR emission intensity at the peak
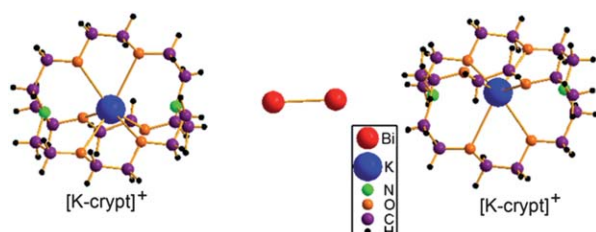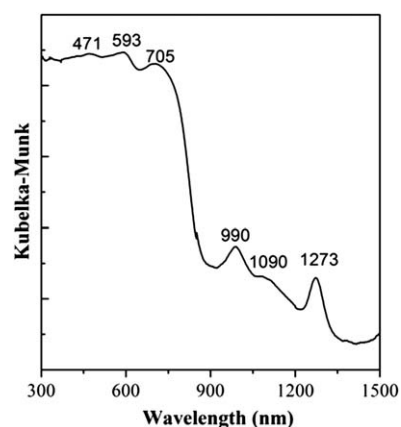

Fig. 2 The UV-vis-NIR diffuse reflectance spectrum of crystalline (K-crypt)$_2$Bi$_2$.

wavelength as a function of the excitation power. As displayed in Fig. 4, the slope is unity, thus evidence that the emission is a single-photon process. It is noteworthy that the sample shows similar emission behaviors under the excitation of 514.5 nm (ESI, Fig. S1†), further indicating that the PL stems from the same type of active center.

It is well known that relativistic effects could give rise to a very strong spin–orbit coupling and exert a profound influence on the chemical bonding of compounds involving bismuth.[3c,5a,7,8] This makes it rather difficult to accurately determine the excitation energies of bismuth related species. For instance, Dai *et al.* first calculated the theoretical excitation energies of [Bi$_2$]$^{2-}$ with d(Bi–Bi) = 2.8377 Å in (K-crypt)$_2$Bi$_2$ using the Beijing density function program and revealed that the anion should have at least four excitation bands located at around 1380, 1062, 562, and 399 nm.[3c] In a more recent work, Sokolov *et al.* calculated the excitation energies using the Gamess (US) quantum-chemical code.[8] The authors showed that several transitions from the $^3\Pi_{2g}$ ground state to the $^3\Sigma$ excited states are allowed and correspond to absorption bands near 880, 715, 470 nm, and below 400 nm. Moreover, it was shown that NIR luminescence bands with wavelengths in the range 1420–1520, 1275–1375, and 1000–1060 nm should also occur due to spin–forbidden
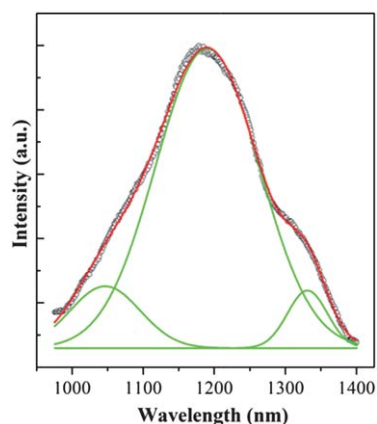

Fig. 1 Part of the structure of (K-crypt)$_2$Bi$_2$.

Fig. 3 The PL spectrum of (K-crypt)$_2$Bi$_2$ crystals under 641 nm excitation light. The black, red and green curves are experimental, fitted, and three decomposed Gaussian peaks, respectively.
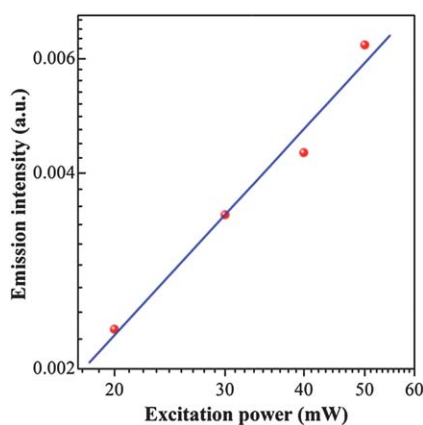
Fig. 4 Log–log dependence of the emission intensity at the peak wavelength on the excitation power of the 641 nm diode laser.

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.[8] 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 observed photophysical behavior can be given as follows. The $[Bi_2]^{2-}$ 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.
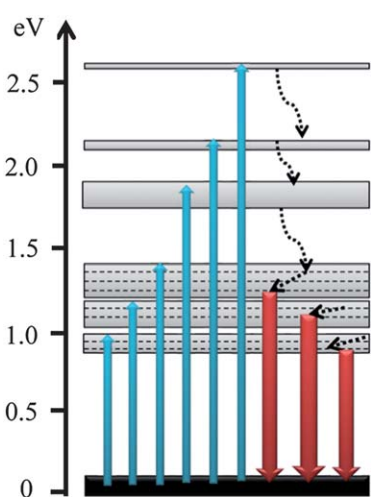

Fig. 5 Simplified energy-level diagram of the $[Bi_2]^{2-}$ emitter based on the observed absorption spectrum from Fig. 2. The blue and red arrows represent the excitation and emission bands, respectively. The black dotted arrows label the nonradiative relaxations. The dotted horizontal lines represent the vibrational sublevels corresponding to the lowest three excited levels.

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 $[Bi_2]^{2-}$. 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[4,5,8–14] as well as encourage efforts for the design of photonic materials with such emitters.

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