

# Intrinsic Optical Properties and Divergent Doping Effects of Manganese(II) on Luminescence for Tin(II) Phosphite Grown from a Deep-Eutectic Solvent

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## S Supporting Information

**ABSTRACT:** This is the first study on the ionothermal synthesis, intrinsic photoluminescence (PL), and dopant effects for tin(II) phosphite, a stereochemically active  $5s^2$  lone-pair-electron-containing compound, the fundamental properties of which have rarely been explored before. In a new deep-eutectic solvent, single-phased products of  $\text{SnHPO}_3$  (**1**) and  $\text{Sn}_{1-x}\text{Mn}_x\text{HPO}_3$  (**2**) have been achieved in high yield. The crystalline powder of **1** is non-enantiomorphic, with an intense second-harmonic generation comparable to that of potassium dihydrogen phosphate. Under UV excitation, it unexpectedly emits white PL, an important intrinsic property never discovered in tin(II) oxyalts. Electron paramagnetic resonance hyperfine splitting characteristic of manganese has been detected on **2** and a three-pulse electron-spin-echo envelope modulation technique implemented to locate its corresponding location in the inorganic host. On the basis of temperature-dependent PL and lifetime measurements, the incorporated  $\text{Mn}^{2+}$  uncommonly acts as a sensitizer in enhancing white emission until extremely low temperatures, in which it would resume its normal role as an activator to give out characteristic orange light.

For the past 2 decades, researches on inorganic open-framework materials from silicates to germanates to phosphates have shown a profound versatility of structural topologies and a wide range of potential applications.<sup>1</sup> In particular, many unique structures with record-breaking large pores or channels have been synthesized in phosphorus-based metal oxides (MPOs).<sup>2,3</sup> They led to the discovery of a remarkable intrinsic photoluminescence (PL) property, i.e., emission of green, yellow, or white fluorescence without the presence of doped metal activators in the host lattice.<sup>4–6</sup> Nanoporous MPO solids with this new optical property have created a new class of color-conversion phosphors for light-emitting diodes for applications in modern optoelectronics. However, in comparison with contemporary lanthanide-doped inorganic phosphors, the new activator-free MPO-type lacks explicitness in the emission mechanism and thermal stability in structure. Therefore, after the yellowish-green phosphor of organic–inorganic hybrid metal phosphite of NTHU-7,<sup>6</sup> we have started out to search in pure inorganics for potential intrinsic optical properties, especially white-light phosphors. They are of great importance in modern solid-state lighting and displays.<sup>7</sup>

It has been noted that metal ions with a  $ns^2$  configuration form a fundamental class of luminescence materials, including  $5s^2$   $\text{Sn}^{2+}$  and  $\text{Sb}^{3+}$  and  $6s^2$   $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$  ions. The nonbonded and stereochemically active  $5s$  lone-pair electrons on tin(II) can also lead to noncentrosymmetric coordination that may bring about nonlinear optical (NLO) activity. Aiming at the features of  $ns^2$  metal for new properties and functions, we chose divalent tin to explore its phosphite phases with ionothermal synthesis<sup>8</sup> where a deep-eutectic solvent (DES)<sup>9,10</sup> was involved. To achieve better solubility and reactivity, pyrazole and choline chloride were combined to create a new DES for ionothermal reactions (see the Supporting Information), from which a pure phase of  $\text{SnHPO}_3$  (**1**) in high yield with good-quality crystals was prepared. Compared to other divalent metal phosphites such as zinc,<sup>11</sup> only a limited number of structures have been characterized in the system of  $\text{Sn}^{\text{II}}/\text{P}/\text{O}$ , where no substantial synthesis and optical properties were ever documented except solid-state NMR studies.<sup>12,13</sup>

In this work, an optimal reaction condition for preparing the fundamental tin(II) phosphite compound has been established and its intrinsic optical property explored. The nonenantiomorphic crystals of **1** were measured with a strong second-harmonic-generation (SHG) signal and observed with a broad band of white PL emission under long UV (365 nm) excitation. The unusual intrinsic luminescence behavior of **1** has never been discovered in oxyalts of tin(II) before. Moreover, doping of the  $\text{Mn}^{2+}$  ion, whose ionic radii and coordination geometry are very distinct from those of  $\text{Sn}^{2+}$ , has been successfully achieved to significantly improve the internal quantum efficiency of white-light emission. Temperature-dependent PL and lifetime measurements have been conducted on crystalline powdered samples to investigate the role played by the Mn dopant ion. Moreover, electron paramagnetic resonance (EPR) with a three-pulse electron-spin-echo envelope modulation (ESEEM) technique has also been used to confirm the presence and location of the  $\text{Mn}^{2+}$  ion in the tin(II) phosphite lattice.

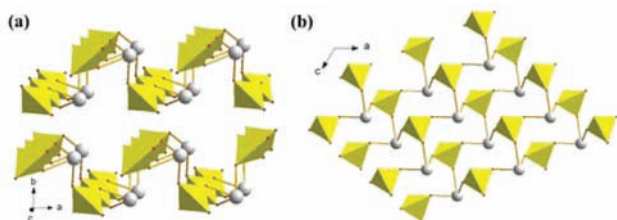
DESs based on choline chloride and urea (or urea derivatives) or oxalic acid are widely applied for systems like gallium(III)<sup>6</sup> or zinc(II)<sup>14</sup> but not for tin(II) yet. On the basis of plausible symmetry, we switched to a less symmetrical molecular component of pyrazole to form a new DES not

Received: November 10, 2011

Published: January 30, 2012

exercised before. With a molar ratio of 1:1, the eutectic point of the two high-melting solids of pyrazole and choline chloride could be lowered to 25 °C. This DES presumably can provide a favorable environment for the formation of noncentrosymmetric tin(II) products. Under ionothermal conditions, the reaction mixture was sufficiently authenticated to produce a homogeneous phase of transparent platelike crystals of **1** in 70% yield (based on tin). The as-synthesized crystals were all in good quality, and thus the structure was redetermined<sup>12</sup> (Table S1 in the Supporting Information and CCDC 859528) to locate phosphite hydrogen atoms. Such information was previously missing but is important for verifying the integrity of the structure and further studying properties such as ESEEM analysis<sup>15</sup> for a doped Mn ion.

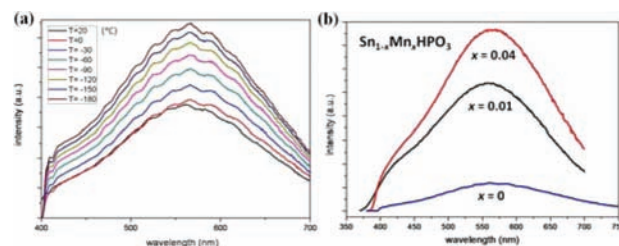
The layered topology of **1** consisted of trigonal pyramids of SnO<sub>3</sub> and pseudotetrahedra of HPO<sub>3</sub> to form six-ring nets similar to graphite sheets except that those of **1** are puckered (Figure 1). Although the coordination numbers for low-



**Figure 1.** Structure plots for **1** (or **2**): (a) two adjacent layers related by the *c*-glide plane; (b) section of the neutral layer showing three-coordinated Sn<sup>2+</sup> ions (gray balls).

oxidation tin may range from 2 to 6, three-coordination is relatively rare and the SnO<sub>3</sub> unit was scarcely encountered in inorganic structures before. The average Sn<sup>2+</sup>–O bond length of 2.153 Å observed in **1** is 0.02 Å shorter than those previously determined and longer than that of Sn<sup>4+</sup>–O (2.054 Å), indicating the ionic radii of the divalent tin ion is, on average, 0.1 Å longer than that of the tetravalent tin ion. As depicted in Figure 1, the 5s<sup>2</sup> lone pairs on tin centers are envisaged to orient directly toward the interlayer space to avoid repulsion. Therefore, the neutral layers, which are stacking along the *b* axis related by *c*-glide symmetry planes, should be connected through dipole–dipole interactions (between the lone-pair electrons) and positively charged phosphite hydrogen atoms. A preliminary result from high-pressure experiments on **1** suggested that it would undergo its first phase transition at 1.5 GPa and another one at 2.3 GPa.

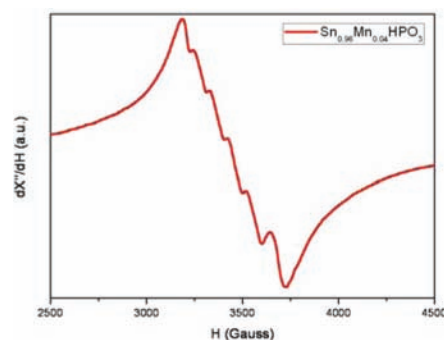
Redetermined for **1** is the standard space group *Cc*, indicating that it is nonenantiomorphic but presumably optically active.<sup>16</sup> The results from SHG measurements on **1** revealed that the intensity was comparable to that of the well-known NLO material potassium dihydrogen phosphate (KDP; Figure S2 in the Supporting Information). Moreover, intrinsic white-light PL emission from crystals of **1** was observed when they were exposed to long UV light. The PL spectra (Figure 2) show a broad band centering at ~560 nm and spreading across the entire visible region. The resultant emission was a nearly perfect white light because the Commission internationale de l'éclairage (CIE) coordinates were calculated to be (0.30, 0.36). While the Sn<sup>2+</sup> ion has been a common dopant in luminescence materials and used to be excited by short UV (245 nm), compound **1** is rare as a pure tin(II) compound with distinctive



**Figure 2.** PL emission spectra showing (a) emission curves of **1** with fine structures that became more evident with decreasing temperatures and (b) the intensities of white emission largely enhanced by a doped Mn<sup>2+</sup> ion at a rate proportionate to the dopant concentration in **2**.

fluorescence and is excitable by much longer wavelengths. Of particular note is that the emission curves for **1** exhibit fine features, which becomes more evident with decreasing temperatures (Figure 2). The 5s<sup>2</sup> lone-pair electrons are known to be sensitive to site symmetry, spin–orbital interaction, or the Jahn–Teller (JT) effect.<sup>7</sup> Here it is assumed that the JT effect has caused splitting of the excited states, which are further coupled with vibrational modes to give the observed fluctuation in the emission intensity.

The achievement of optimal synthesis conditions and the discovery of remarkable white-light emission in **1** have led us to investigate further the PL to make it a potential phosphor material. Attempts to introduce any of the activator elements like the current practice failed except the Mn<sup>2+</sup> ion, which was unexpectedly found to be incorporated into **1** to give the doped phase Sn<sub>1-x</sub>Mn<sub>x</sub>HPO<sub>3</sub> (**2**; *x* = 0.04).<sup>17</sup> The maximum concentration of manganese was 4% in millimoles, as confirmed by inductively coupled plasma atomic emission spectrometry (ICP-AES) data. X-band EPR spectral measurements were performed on a powdered sample of **2**, which gave a typical signal of <sup>55</sup>Mn<sup>II</sup> centered at *g* ~ 1.9 with six major hyperfine splittings (Figure 3). The manganese-doped crystals grow

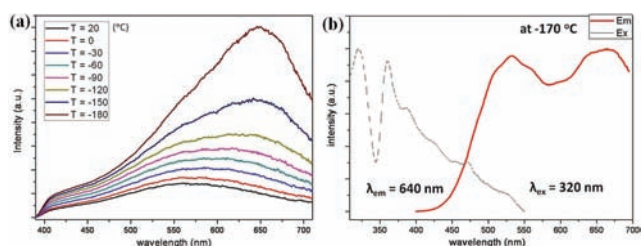


**Figure 3.** EPR signal measured on **2** showing the hyperfine splitting characteristic of a doped Mn<sup>2+</sup> ion.

larger in size with a disposition to be twinned. Nonetheless, single-crystal structure analysis was performed on a decent crystal of **2**, with a result indicating that the doped Mn<sup>2+</sup> was to be on the same site as tin.<sup>18</sup> A three-pulse ESEEM technique was also employed to probe into the information beyond the first coordination sphere around Mn<sup>2+</sup>. The results clearly confirmed that the doped Mn<sup>2+</sup> ion should be residing on the tin site (see the Supporting Information for detailed analysis). The presence of manganese has promoted the intensity of white emission (Figure 2b). Even with a concentration as small as 4% of Mn<sup>2+</sup>, the internal quantum yield for white emission

was observed to have improved to 10%. Manganese did not act as an activator because no characteristic band of manganese was observed. At this point, the role of the  $\text{Mn}^{2+}$  ion was conjectured to act abnormally as a sensitizer. More evidence for this remarkable behavior was obtained from lifetime measurements: the decay time for **1** was 0.68 ms, but it was shortened to 0.39 ms for **2**, indicating the presence of sensitizer ( $\text{Mn}^{2+}$  ion)-facilitated energy transfer within the lattice.

The temperature-dependent PL study on the sample of **2** indicated that the  $\text{Mn}^{2+}$  ion played no single role but a dual role as both a sensitizer and an activator. As shown in Figure 4a, the



**Figure 4.** PL emission spectra for **2**: (a) broad band red-shifted with decreasing in temperature until the orange band of  $\text{Mn}^{2+}$  stood out ( $\lambda_{\text{ex}} = 350$  nm); (b) characteristic  $\text{Mn}^{2+}$  excitation curves (dashed line) and dual emissions observed clearly with  $\lambda_{\text{ex}} = 320$  nm.

broad emission band started to red-shift with a substantial increase in the intensity with decreasing temperature. A much stronger emission band with the peak centering at 640 nm characteristic of  $\text{Mn}^{2+}$  appeared manifestly at temperatures below  $-150$  °C. The resultant emissions displayed pale-yellow light with calculated CIE coordinates (0.46, 0.41). Figure 4b depicts an excitation spectrum monitored at 640 nm, suggesting that the absorption bands should correspond to the  $\text{Mn}^{2+}$  ion.<sup>19</sup> When a sample of **2** was excited by 320 nm (a stronger absorbing wavelength) again, two emission bands started emerging below 150 °C (Figures 4b and S5 in the Supporting Information), implying there were two activators,  $\text{Sn}^{2+}$  and  $\text{Mn}^{2+}$ . Apparently, both metal ions would become less vibrated at lower temperatures, under the conditions of which, as a sensitizer,  $\text{Mn}^{2+}$  would transfer only partial energy absorbed to  $\text{Sn}^{2+}$ , with the rest directly emitting by itself as an activator.

In conclusion, we have designed a new DES for the ionothermal synthesis of a pure phase product of tin(II) phosphite, which exhibits intrinsic white-light emission not previously discovered. Moreover, an unanticipated doping of the  $\text{Mn}^{2+}$  ion has been successfully achieved, largely enhancing the quantum efficiency of white luminescence. As indicated in a series of temperature-dependent PL and lifetime measurements, it is unprecedented to find divalent manganese acting abnormally as a sensitizer in moderate conditions and yet it plays dual roles as both a sensitizer and an activator in extreme conditions. In addition to single-crystal X-ray diffraction, the ESEEM technique has been successfully extended to determine the exact location of the doped activator ion in an inorganic oxide lattice, a piece of information unavailable in previous studies. The ESEEM technique, in this way, can function as a powerful tool to better understand the environment of activator/sensitizer in all kinds of luminescent materials. The temperature-dependent luminescence of **2** can serve as a potential sensor in extreme low temperatures. More research on low-oxidation tin phosphite or phosphate materials is in progress.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Crystallographic information files (CIF), tables of crystal data and selected bond lengths, ORTEP figure of **1**, ICP-AES data, IR spectrum, SHG signal, and details of EPR and ESEEM experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) See the Supporting Information for details of EPR experiments and ESEEM analysis.
- (16) *International Tables for Crystallography*, Table 10.5.1.
- (17) The value of  $x$  in  $\text{Sn}_{1-x}\text{Mn}_x\text{HPO}_3$  can vary from 0.01 to 0.04. All measurements, except single-crystal analysis, were conducted on the bulk sample with  $x = 0.04$ .
- (18) The best-quality crystals of **2** were those with a manganese content of less than 4%. Crystal data:  $\text{Sn}_{0.97}\text{Mn}_{0.03}\text{PO}_3\text{H}$  (CCDC 859529),  $M_r = 196.76$ , monoclinic; space group  $Cc$  (No. 9),  $a = 7.0555(7)$  Å,  $b = 12.242(1)$  Å,  $c = 4.6683(4)$  Å;  $V = 343.85(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{cal}} = 3.801$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 7.591$  mm<sup>-1</sup>. A total of 2016 reflections were measured on a CCD diffractometer system at 296 K, which gave 838 independent reflections with  $R_{\text{int}} = 0.0103$ . Final refinement converged at  $R1 = 0.0102$  and  $wR2 = 0.0264$ . Manganese was detected virtually at the same site of tin. Later the ESEEM study also supported this result.
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