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Heavy-Metal-Free Solution-Processed Nanoparticle-Based Photodetectors: Doping of Intrinsic Vacancies Enables Engineering of Sensitivity and Speed

Jiang Tang,† Gerasimos Konstantatos,‡ Sean Hinds,‡ Stefan Myrskog,‡ Andras G. Pattantyus-Abraham,‡ Jason Clifford,‡ and Edward H. Sargent‡,*

†Department of Materials Science and Engineering, 184 College Street, Toronto, Ontario M5S 3E4, and ‡Department of Electrical and Computer Engineering, University of Toronto, 10 King’s College Road, Toronto, Ontario M5S 3G4, Canada

Digital imaging relies on arrays of individually read photodetectors. High signal-to-noise imaging at low light, combined with operation at video frame rates, requires sensitivity and speed simultaneously. In conventional photodiodes, in which the current collected is limited to one electron per photon incident, external quantum efficiency (EQE) is used as a proxy for sensitivity. Temporal response may be quantified through the longest time constant in a device’s rise or fall in response to changes in illumination. EQEs approaching 100% (unity gain) are desired; while temporal responses faster than 100 ms are desired for video frame-rate lag-free imaging.

There is a growing interest1–6 in integrating photosensitive layers on top of an electronic read-out circuit instead of relying on silicon’s own sensitivity.7 Whereas photodiodes are restricted to unity EQE, photoconductive photodetectors provide gains of 10-fold and above, thus providing many electrons for each photon incident. In conventional silicon CMOS imaging, photodiodes are buried beneath multiple micrometers of dielectric and metal interconnect, and they typically occupy less than half of the pixel area owing to sharing of silicon area with read-out circuitry. In contrast, top-surface photodetectors offer 100% fill factor.8 Silicon’s bandgap limits its applications to the visible and near-infrared, whereas the use of alternative top-surface photodetector materials makes possible imaging from the UV through to the short-wavelength infrared.1

ABSTRACT Photodetection in semiconductors enables digital imaging, spectroscopy, and optical communications. Integration of solution-processed light-sensing materials with a range of substrates offers access to new spectral regimes, the prospect of enhanced sensitivity, and compatibility with flexible electronics. Photoconductive photodetectors based on solution-cast nanocrystals have shown tremendous progress in recent years; however, high-performance reports to date have employed Pb- and Cd-containing materials. Here we report a high-sensitivity (photon-to-electron gain >40), high-speed (video-frame-rate-compatible) photoconductive photodetector based on In$_2$S$_3$. Only by decreasing the energetic depth of hole traps associated with intrinsic vacancies in beta-phase In$_2$S$_3$ were we able to achieve this needed combination of sensitivity and speed. Our incorporation of Cu$^+$ cations into beta-In$_2$S$_3$’s spinel vacancies that led to acceptable temporal response in the devices showcases the practicality of incorporating dopants into nanoparticles. The devices are stable in air and under heating to 215 °C, advantages rooted in the reliance on the stable inclusion of dopants into available sites instead of surface oxide species.

KEYWORDS: indium sulfide · doping · intrinsic vacancy · solution-processed · photoconductive · photodetector

Promising recent reports of low-lag top-surface photoconductive photodetectors having the combination of good gain (>3) and acceptable temporal response (<100 ms)$^{10}$ have employed PbS colloidal quantum dots. More broadly, many recent advances in colloidal quantum dot electronics$^{11,12}$ and optoelectronics$^{13–15}$ have relied on the use of heavy-metal cations such as Cd and Pb that raise concerns regarding toxicity and regulatory acceptance.

Here we report Pb- and Cd-free photoconductive photodetectors. Our materials are based instead on indium sulfide (In$_2$S$_3$), a III–VI$_2$ semiconductor having a band gap of 2.03 eV.

As we report in detail below, employing this much less familiar colloidal nanoparticle materials system raised significant

See the accompanying Perspective by Noone and Ginger on p 261.

*Address correspondence to ted.sargent@utoronto.ca.

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challenges in making a photoconductive photodetector having attractive performance. Specifically, long-lived trap states, traceable to cationic vacancies associated with unoccupied indium tetrahedral positions in In$_2$S$_3$’s defect spinel structure (beta phase), produced unacceptably long temporal responses in our first generation of devices.

In response we searched for a means of filling these vacant sites using metal ions. We found that the use of Cu cations allowed us to engineer the trap state lifetime to enable a desirable gain without the deleterious effects of excess lag. We note that these findings on doping overcome a longstanding problem in the colloidal nanocrystal field: self-purification, a consequence of the fact that the impurity solubility in small nanocrystals is much lower than in bulk materials. We hypothesized that we could overcome such difficulties in achieving stable net doping by working with a material having intrinsic vacancies that would readily incorporate impurities if the size of impurity ion was compatible with the volume of vacancy; and if the affinity of the impurity ion was properly chosen.

As a consequence, we report herein a sensitive (R/H11010 A/W) and fast (τ ~ 0.1 s) solution-processed visible photodetector based on Cu$^+$/H11010-doped In$_2$S$_3$ nanocrystals. We initially produced visible photodetectors, based on In$_2$S$_3$ nanocrystals, having high responsivity but slow temporal response. Then we developed a one-pot postdoping strategy to introduce Cu$^+$ into In$_2$S$_3$ nanocrystals in solution. Careful characterization of these materials confirmed the success of Cu$^+$ doping. An optimal level of Cu$^+$ doping greatly improved photodetector speed with little sacrifice of responsivity. These devices hold promise for high-sensitivity, video-frame-rate visible photodetector applications.

RESULTS

We first synthesized undoped In$_2$S$_3$ nanocrystals and characterized the performance of devices made from such materials. In$_2$S$_3$ nanocrystals were synthesized by heating InCl$_3$ and sulfur powder in oleylamine at 215 °C using a previously reported protocol. As shown in Figure 1A, monodisperse In$_2$S$_3$ nanocrystals were produced. The crystalline plates exhibit 6-fold symmetry with dimensions in the plane on the order of 30 nm. After synthesis and isolation, solution ligand exchange was employed to replace long oleylamine (2.4 nm) with short butylamine (0.6 nm) with the goal of increasing charge carrier mobility by reducing interparticle spacing. We used Fourier transform infrared spectroscopy (FTIR) to evaluate the effectiveness of this ligand exchange strategy. FTIR peaks (Figure 1b) of particular interest are the asymmetric and symmetric C/H11022 H stretching vibration of a CH$_2$ group at 2930 and 2857 cm$^{-1}$. Complete replacement of oleylamine by butylamine would produce a 4.5-fold decrease in the absorbance of these peaks. The observed 30% drop indicates partial replacement.

The ligand exchange procedure resulted in denser film (Figure S1) and improved carrier transport as evidenced by a 5 orders-of-magnitude increase in dark conductivity. Photoresponse was observed from the exchanged film, and thermal annealing further increased photoresponse. Figure 1 panels C and D show device response following 10 min annealing in a vacuum oven. The device showed responsivity of 200 A/W, corresponding to a gain of greater than 500 electrons per incident photon. However, the temporal response of the device, seen in Figure 1D, exhibited time...
constants in the order of seconds. Such speed is unacceptable for conventional imaging application because lag, or ghosting, will be perceptible in the image.

Motivated by previous reports of surface modification of nanoparticle-based films improving temporal response through the passivation of deep traps, we investigated a variety of surface modifications. We attempted treatment with ethanethiol, ethanedithiol, formic acid, and methanol, and we also explored the use of annealing in different atmospheres (N₂, air, and vacuum) and at a number of temperatures (100–300 °C) (Figure S2). We additionally explored a variety of synthetic procedures such as the introduction of oleic acid (Figure S3) or TOP during the synthesis, use of different sulfur and indium sources, variations in In to S precursor ratios (Figure S4), and changes to growth temperature. Finally, we also explored a variety of handling procedures including isolation in ambient and different durations for the butylamine ligand exchange (Figure S5). Notably, all of these variants to the process failed to improve the temporal response of the photoconductive photodetectors while maintaining high responsivity (>1 A/W).

We tentatively concluded that manipulations to nanoparticle surfaces were not effective in improving temporal response. Physically, this could be explained if the deep trap states in these materials found their origins in the bulk, rather than the surface, properties of the crystals. In₂S₃ is a body-centered tetragonal compound with ordered vacancies. Indium atoms occupied all 24 octahedral sites and 8 tetrahedral sites in the unit cell, leaving 4 tetrahedral sites empty. We posited that these vacancies inside—rather than on the surface of—the particle could be responsible for long-lived trapping, and would be unmodified by surface treatments alone.

In an effort to fill vacancies with metal ligands that would remove, or, more desirably, render more shallow the trap state energy, we investigated the incorporation of CuCl₂, Cu(CH₃COO), CdCl₂, SnCl₂, GaCl₃, FeCl₃, or Se into synthesis (Figure S6). Only the introduction of CuCl₂ and Cu(CH₃COO) improved temporal response (Figure S7). CuCl₂ is stable in air and produces better performance with high reproducibility, therefore we focus our investigation on the CuCl₂ doping results.

The most effective experimental protocol was one-pot postdoping which we now summarize. First, In₂S₃ is synthesized before doping and no isolation or purification is carried out. The resultant In₂S₃ nanoplates are doped by introducing CuCl₂ dissolved in oleylamine into the In₂S₃ solution vessel. The solution color changes from bright yellow to pink to red to dark red as more CuCl₂ is introduced. Drop-by-drop addition of CuCl₂ solution was found to produce the best results; we propose that maintaining a low copper concentration in the solution facilitates the gradual incorporation of copper ions into In₂S₃ nanoplates and avoids nucleation of a new phase. As shown in Figure 2A,B, when less than 3 mg of CuCl₂ was added during this process, the size and morphology of In₂S₃ nanoplates were maintained. Figure 2D showed HRTEM image of copper-doped In₂S₃ nanoplate. Careful examination of several nanoplates showed continuous lattice fringes and no observation of second phase. When 12 mg CuCl₂ was applied in synthesis, an additional phase appeared on the edge of In₂S₃ nanoplates, as marked by white stars in Figure 2C. In this overdoping case, the integrity of In₂S₃ hexagonal nanoplates was partly destroyed, and they were converted into nanoplates with irregular shapes and saw-toothed edges. Excessive levels of Cu²⁺ result in competition with In³⁺ for S, resulting in formation of copper sulfide, similar to the cation exchange observed in the Ag₂S–CdS system.
We carried out several experiments to ascertain whether copper was truly being incorporated into In$_2$S$_3$. We sought first to confirm the presence of copper in our sample: after 3 days of butylamine ligand exchange, a process that should remove dopant not incorporated into the bulk but instead loosely bound to the surface,$^{23,24}$ we carried out ICP-AES measurements. As summarized in Table 1, copper was detected in all samples, including ligand-exchanged materials, into which CuCl$_2$ had been added postsynthesis. In addition, the composition calculated from ICP results agreed very well with the value expected from added precursors, indicating nearly complete incorporation of copper into final products. We note sulfur content lies below its stoichiometric value in all samples, consistent with the n-type nature of our materials further discussed below.$^{20,25}$

We then carried out powder XRD to investigate which crystalline phases were present in our synthetic products. As shown in Figure 3A, the XRD pattern of copper-doped sample showed characteristic peaks of tetragonal In$_2$S$_3$ (JCPDS 25-0390). We found evidence of no phase other than β-In$_2$S$_3$. The strong broad peak at 20° was also observed in InCl$_3$ and oleylamine mixture without any treatment: we associate this peak with the In$^{3+}$-oleylamine complex. Careful examination of the XRD patterns revealed no additional peaks associated with copper compounds such as CuO or Cu$_2$S. This finding, that a single phase was present, agreed with STEM observations discussed above that all nanoplates had the same contrast, as shown in Figure 2A and Figure 2B.

Taken together, these findings—that Cu is present in the samples (ICP-AES), but does not form a second phase (XRD and STEM)—suggest that the Cu is indeed incorporated into the In$_2$S$_3$ lattice.

We sought to investigate the state in which Cu dopants are in the lattice using electron paramagnetic resonance (EPR) investigation. EPR characterization of all our samples with 35 GHz Q-band at 77 K revealed no signal, indicating that Cu$^{2+}$ is not present in our samples.$^{26}$ We conclude that copper exists as Cu$^+$ in our samples, a finding that is supported by XPS data shown in Figure 3B. The binding energy of Cu 2p$_{3/2}$ is 932.7 eV in our sample, characteristic of monovalent copper.$^{27}$ We believe Cu$^{2+}$ is reduced by oleylamine to Cu$^+$ during the doping process. Oleylamine is widely used to reduce sulfur or selenium in sulfide$^{28}$ and selenide$^{29}$ Cu$^{2+}$ to Cu$^+$ in chalcopyrite nanocrystal$^{30}$ synthesis, and Reihaneh Malakooti et al. proposed the amine group could be oxidized into a nitroso group.$^{31}$ However, the detailed reaction pathway is not clear yet.

![Figure 3. (A) XRD patterns of undoped In$_2$S$_3$ nanoplates (red), copper-doped In$_2$S$_3$ nanoplates (black), and InCl$_3$ and oleylamine mixture (yellow); (B) XPS spectrum of copper in copper-doped In$_2$S$_3$; (C) absorption spectra of undoped and doped In$_2$S$_3$ nanoplates in toluene solution.](image-url)
As further evidence of Cu\(^+\) incorporation, we note that the absorption spectrum of these materials shows a 50 nm shift in its onset following doping. Since quantum confinement is not at play in this material, this red shift is most likely a consequence of a bulk bandgap change instead of a surface effect. Co\(^2+\) doping in In\(_2\)S\(_3\) has previously been reported to reduce the band gap of bulk In\(_2\)S\(_3\) thin film from 1.98 to approximately 1.86 eV.\(^{32}\) A similar shift appears to be at work in our Cu\(^+\)-doped In\(_2\)S\(_3\) nanoparticles.

In summary, these data indicate that our In\(_2\)S\(_3\) nanoparticles are doped with Cu\(^+\) at concentrations ranging from 0.4% to 0.9% (for 1.1 mg and 2.7 mg CuCl\(_2\) in synthesis, respectively). Previous studies showed that for 2% Co\(^2+\) and 4% Cu\(^+\) doped In\(_2\)S\(_3\) thin film,\(^{33,34}\) the dopants located in the T\(_d\) symmetry site of the In\(_2\)S\(_3\) host lattice, therefore we believe Cu\(^+\) ions also fill into the intrinsic tetragonal vacancies in our In\(_2\)S\(_3\) nanoparticles. Diffuse reflectance measurements of Cu\(^+\)-In\(_2\)S\(_3\) materials could further clarify the details of Cu\(^+\) incorporation.\(^{34}\)

We report in detail on the device performance of Cu\(^+\)-In\(_2\)S\(_3\) nanoplate photodetectors in Figure 4. All measurements were carried out in air and the applied field is 2 V/\(\mu\)m. As shown in Figure 4A, 0.4% Cu\(^+\)-doped In\(_2\)S\(_3\) device showed high responsivity (47.8 A/W) but slow temporal response (>1 s), similar to the undoped In\(_2\)S\(_3\) device. In contrast, 0.9% Cu\(^+\)-doped In\(_2\)S\(_3\) showed dramatically improved performance: responsivity as high as 15 A/W, gain as high as 39, and temporal response (defined as time spent in 90% photocurrent decay) below 0.1 s were achieved simultaneously. Further increase of Cu\(^+\) doping to 3.8% maintained fast response; however, it also was accompanied with decreased responsivity and undesired drift. All device performance is summarized in Table 2 for clear comparison.

We further characterized our best 0.9% Cu\(^+\)-doped In\(_2\)S\(_3\) device. Figure 5A shows typical \(I−V\) characteristics in the dark and under 7.4 W/cm\(^2\) illumination (\(\lambda = 470\) nm). The gold electrode (\(E_F = 5.1\) eV) and Cu\(^+\)-In\(_2\)S\(_3\) film form a nonohmic contact as seen in the nonlinear \(I−V\) near the origin. This is consistent with a large work function difference between Au (\(5.2\) eV) and n-type In\(_2\)S\(_3\) (\(E_c = −3.8\) eV and a Fermi energy a few tenths of an eV deeper in view of significant but nondegenerate doping).

The dependence of photocurrent on incident optical power, shown in Figure 5B, exhibits a power dependence of \(0.88\), that is, \(I_p \propto P^{0.88}\), suggestive of a sensitized photoconductor with a multiplicity of trap states.

We report the spectral responsivity of Cu\(^+\)-In\(_2\)S\(_3\) in Figure 5C. The 50 nm red-shift of photoresponse onset for Cu\(^+\)-In\(_2\)S\(_3\) device compared with undoped In\(_2\)S\(_3\) closely follows the absorption spectral shift in solution seen in Figure 3C. The correspondence between optical absorbance and photodetector responsivity spectral shifts are also consistent with the successful incorporation of Cu\(^+\) into the nanocrystals.

We also carried out photocurrent decay fitting to compare time constant of photoresponse in In\(_2\)S\(_3\) and Cu\(^+\)-In\(_2\)S\(_3\) photodetector. As shown in Figure 5D, the In\(_2\)S\(_3\) photodetector showed two time constants of 0.96 and 11.0 s. In contrast, the Cu\(^+\)-In\(_2\)S\(_3\) photodetector revealed a fast component with time constant of \(\sim 39\) ms and a slower one of \(\sim 256\) ms. This observation sug-

<table>
<thead>
<tr>
<th>Cu(^+) content (atom %)</th>
<th>(I_d) (nA)</th>
<th>(I_l) (nA)</th>
<th>(R) (A/W)</th>
<th>temporal response</th>
<th>gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4%</td>
<td>35.4</td>
<td>79.7</td>
<td>47.8</td>
<td>&gt;1 s</td>
<td>126.0</td>
</tr>
<tr>
<td>0.9%</td>
<td>23.8</td>
<td>24.7</td>
<td>14.8</td>
<td>~0.1 s</td>
<td>39.0</td>
</tr>
<tr>
<td>3.8%</td>
<td>12.8</td>
<td>0.8</td>
<td>0.5</td>
<td>~0.1 s</td>
<td>1.3</td>
</tr>
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gested that Cu\textsuperscript{+} doping indeed improved device temporal response.

For photodetector application, responsivity and noise current should be jointly taken into account to yield specific (or normalized) detectivity $D^*$ in unit of jones (cm Hz\textsuperscript{1/2} W\textsuperscript{-1}). $D^*$ is given as $(\Delta f)^{1/2} R/\text{in}$, where $A$ is the effective area of the detector in cm\textsuperscript{2}, $\Delta f$ is the electrical bandwidth in Hz, and $R$ the responsivity in A/W measured under the same conditions as the noise current $i_n$ in A. The measured dark current noise of our device at 10 Hz is $\sim 0.18$ pA/Hz\textsuperscript{1/2} resulting the $D^*$ of 2.8 $\times$ 10\textsuperscript{-11} jones.

**DISCUSSION**

We now discuss the flow of current and the origins of photoconductive gain in the devices reported herein. In\textsubscript{2}S\textsubscript{3} is reported to be n-type material\textsuperscript{20} our observed sulfur deficiency in all samples is consistent with this n-type behavior. Thus we present the photoconductive operation of these devices with reference to electron flow. Upon illumination, electron—hole pairs are created, and holes are rapidly captured to traps associated with the valence band. This trapping process extends the lifetime $\tau$ of both carrier types, and photo-generated electrons are thus able to flow for this lifetime. If the carrier lifetime exceeds the time for electrons to transit the device $\tau$, photoelectrons can be extracted and re-injected within their lifetime: gain, defined as the ratio of extracted electrons to incident photons, or equivalently the ratio of carrier lifetime to transit time, may result. Our observed lifetime of 0.1 s combined with observed gain of 39 leads to our estimation of the transit time for electrons across the 5 um gap as 2.6 ms. From knowledge of the applied field, we are able to provide a lower-bound estimate of the electron mobility to be 9.6 $\times$ 10\textsuperscript{-4} cm\textsuperscript{2}/Vs. This lower-bound is obtained by assuming that the field is constant across the device.

In the In\textsubscript{2}S\textsubscript{3} device, deep hole traps result in high gain and slow response. Cu\textsuperscript{+} doping narrows the band gap of In\textsubscript{2}S\textsubscript{3} and decreases the distance between valence band edge and traps depth. Traps are shallower in Cu\textsuperscript{+}-In\textsubscript{2}S\textsubscript{3} and consequently produce devices with lower gain and higher speed. Even if the 0.2 eV band-gap contraction were evenly split between the bands, as much as an exp($-0.1/kT$) $\approx$ 50-fold decrease in carrier lifetime can be accounted for through this effect (please refer to Supporting Information for details).

**CONCLUSION**

In summary, we reported the first solution-processed visible photodetector with high sensitivity and fast temporal response from Cu\textsuperscript{+}-doped In\textsubscript{2}S\textsubscript{3} nanomaterials. This is the first demonstration of an In\textsubscript{2}S\textsubscript{3} visible-wavelength photodetector. The undoped In\textsubscript{2}S\textsubscript{3} device showed hundreds of A/W for responsivity but slow response. By taking advantage of their intrinsic vacancies, we successfully doped In\textsubscript{2}S\textsubscript{3} with Cu\textsuperscript{+} in solution and significantly improved device speed to response time of around 0.1 s. Low toxicity, solution-processed capability, high responsivity, and reasonable speed make our Cu\textsuperscript{+}-In\textsubscript{2}S\textsubscript{3} photodetector a strong candidate for many potential applications.
METHODS

InS\textsubscript{3} and Cu\textsuperscript{+}−InS\textsubscript{3} Nanoplates Synthesis. All chemicals used were purchased from Sigma-Aldrich. Oleylamine was pumped with a Schlenk line at 80 °C for 1 day, butylamine was distilled before use. All other materials were used without further purification. Synthesis was conducted under inert atmosphere using a Schlenk line and isolated in a glovebox. Synthesis of In\textsubscript{3}S\textsubscript{5} nanoflakes is described elsewhere.\textsuperscript{19} For Cu\textsuperscript{+}−InS\textsubscript{3} nanoplates, we first mixed 1 mmol InCl\textsubscript{3}, 1.5 mmol sulfur powder, and 10 mL of oleylamine and pumped at 120 °C for 1 h to produce a clear brown solution. Afterward N\textsubscript{2} was introduced into the reacting vessel and heated the solution to 215 °C and incubated for 1 h to produce In\textsubscript{3}S\textsubscript{5} nanoplates. Then a given amount of CuCl\textsubscript{2} dissolved in 5 mL oleylamine was injected into the flask drop by drop with syringe. This injection process lasted for 40 min and the solution color changed from yellow to red. After injection, the solution was maintained at 215 °C for another 40 min. After cooling naturally to room temperature, the flask was sealed and transferred into glovebox for isolation. The raw solution was washed first by toluene and precipitated by methanol, and repeated this process twice. Finally the precipitates were collected and dried for ligand exchange.

Ligand Exchange, Device Fabrication, and Treatment. Butylamine ligand exchange and device produce were done at inert atmosphere in a glovebox. Typically we dispersed all sediments collected during ligand exchange into 10 mL of distilled butylamine and stored them undisturbed for 2 days. Afterward In\textsubscript{3}S\textsubscript{5} nanomaterials were precipitated by methanol and redispersed in 5 mL of toluene to produce concentrated solution. Photodetector was fabricated by dropping 10 μL of such solution onto precleaned interdigitated gold electrodes and dried naturally. When the device was ready, we transferred it into vacuum oven (preheated to 200 °C) and sealed under vacuum for 10 min. Device was measured in air.

Characterization. Visible−near-NIR absorption spectra of the nanomaterials in toluene were recorded at room temperature using a Cary 500 UV−vis−near-NIR spectrophotometer. FTIR spectra were obtained using a Bruker Tensor 27 infrared spectrometer. Fluorescence lifetime measurements were taken with an Agilent 8614B nanosecond photoluminescence spectrophotometer. All the spectra were measured using a Stanford Research SRS830 lock-in amplifier. The devices were biased using alkaline batteries at 10 V and testing was carried out in an electrically shielded and optically sealed probe station on a floating table to minimize vibrational noise. Knowing device area, responsivity, and the noise current normalized to the measurement bandwidth, we were able to obtain the D\textsuperscript{*} normalized detectivity value of our device as reported in the text.

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Supporting Information Available: SEM characterization of In\textsubscript{2}S\textsubscript{3} films, details of many “failed” examples of trap manipulation as well as theoretical calculation of change of trap activation energy after Cu\textsuperscript{+}−doping. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


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21. Mixed InCl$_3$, CuCl$_2$, and sulfur powder at the beginning and then cooked also produced copper-doped In$_3$S$_3$ but with large size and morphology distribution. Direct injection of CuCl$_2$ solution into the reaction vessel rendered a sudden burst of copper concentration in solution, leading to porous copper-doped In$_3$S$_3$ nanoparticles.


