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Published in:
Journal of Alloys and Compounds

DOI:
10.1016/j.jallcom.2017.11.092

Published: 05/03/2018

Please cite the original version:
Solution synthesis of CuSbS$_2$ nanocrystals: a new approach to control shape and size

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Abstract

Chalcostibite copper antimony sulfide (CuSbS$_2$) micro- and nanoparticles with a different shape and size have been prepared by a new approach to hot injection route. In this method, sulfur in oleylamine (OLA) is employed as a sulfonating agent providing a simple route to control the shape and size of the particles, which enables the optimization of CuSbS$_2$ for a variety of applications. The sulfur to metallic precursor ratio appears to be one of the most effective parameters along with the temperature and time for controlling the size and morphology of the particles. The growth mechanism study shows in addition to the CuSbS$_2$ phase the presence of not previously observed intermediate phases (stibnite (Sb$_2$S$_3$) and famatinite (Cu$_3$SbS$_4$)) at the initial stage of the reaction. By increasing the ratio of sulfur to copper and antimony, wider and thinner CuSbS$_2$ particles are obtained. The particles have nanoplate and nanosheet morphology with a good shape and size uniformity. Coalescence of very thin nanosheets occurs with increasing reaction time eventually leading to formation of thicker particles which can be called nanobricks. Band gap determinations demonstrate that the obtained CuSbS$_2$ particles have both direct (1.51-1.57 eV) and indirect (1.44-1.51 eV) bandgaps. Transmission Electron Microscopy (TEM) studies revealed that the preferred growth directions are along the basis axes of the unit cell ([100] and [010]). Optical and structural properties of the obtained CuSbS$_2$ particles are indicative for their great potential in different generations of solar cells and supercapacitor applications.

Keywords: Copper antimony sulfide, crystal structure, growing mechanism, morphology.
1. Introduction

Semiconductor nanocrystals have attracted considerable attention owing to their wide range of applications in photodetectors [1-3], light emitting diodes [4, 5], biology [6] supercapacitors [7, 8], and solar cells [9-11]. Different kinds of semiconductors have been developed for each purpose [12]. Interesting candidates among those specifically aimed for solar cell applications are ternary and quaternary copper-based chalcogenide semiconductors, because they have high absorption coefficients and appropriate band gaps for light absorption. Within ternary chalcogenide semiconductors chalcostibite (CuSbS$_2$) is an emerging one due to its suitable bandgap. It is relatively less explored in comparison with CuInS$_2$ [13, 14], Cu(InGa)Se$_2$ [15], and Cu$_2$ZnSnS$_4$ [16, 17] and has been demonstrated as a promising alternative, because all elemental components of CuSbS$_2$ are earth abundant and economical, as the price of antimony is much lower than that of indium [18]. First-principle calculations using density functional theory have indicated CuSbS$_2$ as a new promising candidate for a p-type absorber material [19]. The results of the calculations suggest that CuSbS$_2$ has a strong light absorption coefficient ($\alpha > 1 \times 10^4$ cm$^{-1}$), and suitable electrical properties, both of which are essential for solar cell application [20, 21]. CuSbS$_2$ crystallizes in an orthorhombic crystal system with a Pnma space group [22]. It is chemically quite similar to CuInS$_2$ but structurally very different due to its low valence state of antimony [23]. Theoretical simulations predict that CuSbS$_2$ has an indirect band gap, but experimental investigations show that the material has a direct band gap. However, many key parameters of CuSbS$_2$, such as the conduction band and valence band positions have not been fully investigated [21, 24]. Studies of this material as a potential absorber for sustainable and scalable thin film solar cells have been conducted, but still more research and investigation needs to be done in order to fully characterize the properties of these materials [25-28].
In recent years, characterization of CuSbS$_2$ thin films deposited by sputtering [29], thermal evaporation [30, 31], and chemical bath deposition [32] have been published, but there are only a few studies on the synthesis of CuSbS$_2$ in powder form. In the synthesis of ternary materials, controlling the reaction condition, which is directly related to the synthesis method is essential. Many efforts have been focused on the nanoparticle formation mechanism, and many reliable and reproducible synthesis approaches have been developed [33, 34]. Solvothermal, hydrothermal and hot injection methods have already been reported for the formation of CuSbS$_2$ nanocrystals [7, 22, 26, 35]. As simultaneous nucleation and growth leads to poor size distribution, separating nucleation and growth stages is desirable. To separate these two stages, injection of precursors into solvents at a high temperature, followed by a reduction of the reaction temperature may be employed [36]. In hot injection method nucleation occurs at high temperature at the injection of the reactant. This instantaneous nucleation results in narrow size distribution and good control of particle size [33].

To date, the influence of sulfur precursor ratio and temperature on controlling the shape, size, and crystal structure of CuSbS$_2$ have not been investigated. These characteristics are important for final application. In this paper, we report a systematic study of synthesis procedure via hot injection route for obtaining of CuSbS$_2$ powders with controlled size and shape only by using one kind of sulfonating agent.

2. Experimental

2.1. Synthesis of CuSbS$_2$ powder

The CuSbS$_2$ samples were synthesized using a hot injection method. Typically, CuCl (1 mmol) and SbCl$_3$ (1 mmol) were dissolved in OLA and backfilled with nitrogen for 15 min, and
then heated to 120 °C until a clear yellow solution was reached. The temperature was increased to
the target temperature in N₂ atmosphere, and then OLA containing sulfur was injected into the
mixture. This mixture was maintained at the target temperature (either 240 °C or 260°C) for 5 min.
The molar ratios of copper (Cu), antimony (Sb), and sulfur (S) precursors were adjusted to 1:1:2,
1:1:2.5, 1:1:3, 1:1:3.5, and 1:1:4 (later referred to ratios of 2, 2.5, 3, 3.5 and 4). After completion
of the reaction, the solution was cooled down to 60 °C and the product was washed several times
using a mixture of n-hexane and ethanol. Finally, the precipitate was dried at 60 °C for further
characterizations.

2.2. Measurements and characterization

The crystal structure and phase purity of CuSbS₂ were analyzed by X-ray diffraction (XRD)
with PANalytical X’pert Powder Pro diffractometer using Cu-Kα radiation (1.5406 Å) at a voltage
setting of 45 kV and a current setting of 40 mA. The morphology and elemental compositions of
the powders obtained was studied by Scanning Electron Microscopy (SEM; TESCAN Mira 3)
equipped with energy dispersive X-ray spectroscopy (EDX). The average particle size was
analyzed from SEM images by using 100 particles of each sample. TEM (Tecnai G2 F20) was
used to investigate particle morphology and crystal structure at an operating voltage of 200 kV.
The UV-vis-NIR diffuse reflectance spectrum was recorded using a Perkin Elmer Lambda 950 for
band gap calculation.

3. Results and Discussion

3.1. Sulfur precursor ratio and temperature study

3.1. 1. XRD Analyses

XRD patterns of the synthesized powders obtained with different sulfur ratios at 240 °C are
portrayed in Fig. 1. All the diffraction peaks from the powders obtained at sulfur ratios of 2, 2.5, or 3 can be indexed to the orthorhombic CuSbS$_2$ (ICSD No. 98-017-1051, space group $Pnma$; $a = 6.018\text{Å}; b = 3.7958\text{Å}; c = 14.495\text{Å}$). However, the peaks related to ratios of 2.5 and 3 are more intense and sharper than those with the ratio of 2. Wider peaks at the ratio of 2 suggest smaller particle size. The growth of CuSbS$_2$ particles at ratios of 2.5 and 3 has resulted from raising the amount of injected sulfur above the stoichiometric composition. By increasing the sulfur ratio further to 3.5 while keeping other reaction conditions constant, a Sb$_2$S$_3$ phase appeared (ICSD No. 98-009-5556). Observation of Sb$_2$S$_3$ phase suggested that it was formed primarily at 240 °C after the injection of the sulfur source, and CuSbS$_2$ phase formation was through the reaction between initially formed Sb$_2$S$_3$ nanocrystals and copper in the reaction solution. Increasing the ratio to 4 caused not only the appearance of Sb$_2$S$_3$, but also a famatinite Cu$_3$SbS$_4$ phase (ICSD No. 98-000-2857). It indicates that controlling the sulfur ratio at this temperature is necessary to avoid formation of these phases, but it is still possible to obtain pure stoichiometric CuSbS$_2$ at sulphur ratios of up to 3.

XRD patterns of samples synthesized at 260 °C are depicted in Fig. 2. The pattern of the sample with the stoichiometric sulfur ratio of 2 illustrates that an antimony (Sb) phase existed beside the CuSbS$_2$ phase and it disappeared only with the increasing of sulfur to ratio of 2.5. Moreover, at this ratio the XRD pattern shows intense preferred orientation in the powders and the intensity of {104} and {013} reflections are dramatically enhanced. This observation confirms that for the completion of the reaction and for the formation of CuSbS$_2$, sulfur content greater than stoichiometric is needed. The XRD pattern for a sample with a ratio of 3 was similar to that of 2.5. Enhancement of the sulfur ratio to 3.5 and 4 led to the appearance of a small peak, obviously related to a sulfur phase. In addition, absence of Cu$_3$SbS$_4$ indicates that at this temperature
variation in sulfur content will not lead to formation of this phase and thus the temperature plays more important role in its formation. In summary, the phase stability and purity of CuSbS$_2$ appears to be strongly affected by the synthesis conditions including the precursors’ ratio and reaction temperature. The ratios of 2.5 and 3 of sulfur precursor provide good results at both temperatures. The values of lattice parameters are summarized in Table 1.

3.1.2. Morphological observations

Figs. 3a-e depict SEM images of the powders synthesized at 240 °C for 5 min. As can be seen, the shape and size of the particles was a variable of the ratio of sulfur addition to copper and antimony content. This observation suggests that the shape and size of CuSbS$_2$ powders can be controlled by the variation of only the amount of sulfur added to the process without having the phase alterations contrary to the report by Ramasamy et.al. [37] who changed solvent from OLA to a mixture of 1-dodecanethiol and t-dodecanethiol to obtain nanosheet morphology. The results of particle size measurements are summarized in Table 2. These results demonstrate a trend toward increasing length and width and decreasing thickness of the particles with the addition of excess of sulfur. At the same time, the ratio between the length and width changes dramatically, i.e., particles evolve from nearly square to a long rectangular shape. Powders synthesized at the ratios of 2 and 2.5 (Figs. 3a and b) consisted of a few to multiple layers of nanoplatelets with the length around 200-300 nm and 0.6 - 1 μm respectively. At the ratio of 3 (Fig. 3c) nanosheets were obtained with the length around 1–2 μm. The thickness of the nanoplatelets was found to be ~ 25-50 nm.
for a ratio of 2, 5-20 nm for a ratio of 2.5 and 1-5 nm for nanosheets at a ratio of 3. The small particle size at the ratio of 2 is in accordance with the peak shape in the XRD pattern. On the other hand, uniform growth of particles achieved at the ratio of 3 suggested that a sufficient amount of sulfur was provided at this ratio and control of the shape uniformity is attainable at a constant temperature. As the ratio of sulfur source to Cu and Sb exceeds 3.5, the change in the appearance of the particles is evident. Both XRD and SEM results indicate that a small amount of rod-like Sb$_2$S$_3$ phase is present besides the CuSbS$_2$ phase. At the ratio of 4 (two times excess the stoichiometric quantity), absence of plate-like particles is clear. With the scrutiny of XRD patterns and SEM images at the ratio of 3.5 and 4 (Figs. 3d and e, respectively), it can be argued that aggregations of small particles in Fig. 3e are Cu$_3$SbS$_4$ phase, and the rod-like particles are Sb$_2$S$_3$ phase.

(Figure 3)

Figs. 4a-e shows that the trend of alteration of the particle shape and growth was repeated at 260 °C except that the particles are smaller at the same precursor ratio when compared with the samples obtained at 240 °C. This is probably due to the higher temperature of injection that causes more nuclei to form and consequently results in smaller size particles [28]. As the temperature increases, the nucleation rate and thus particle concentration increases and the time required to reach the same size increases. It is distinctive to observe in Fig. 4a that the reaction at the ratio of 2 and at 260 °C is imperfect, as was perceived previously from the XRD pattern as well. The length of the particles ranges between 250 to 350 nm and 300 to 600 nm for powders obtained at the ratio of 2.5 and 3, with a thickness of 25-50 nm and 10-50 nm, respectively. Very small particles on the surfaces of nanoplatelets for the ratio of 3.5 and 4 illustrates that probably there are some unreacted precursors in agreement with XRD patterns.
3.1.3. Optical properties

Band gap calculation of CuSbS₂ nanocrystals was carried out using UV-Vis-NIR diffuse reflectance data ( Insets of Figs. 5a-d) and Tauc equation in the form of \((h\nu F(R))^{1/n}\), where \(h\), \(\nu\), and \(F(R)\) represent Plank’s constant, frequency and Kubelka-Munk function, respectively. For direct allowed transition \(n=1/2\), and for indirect allowed transition \(n=2\). Figs. 5a-d and Figs. 6a-d portray the calculations of the band gaps of the CuSbS₂ samples for direct and indirect bandgap at the ratio of 2.5 and 3 for both temperatures, respectively. The band gap values range from 1.51 to 1.57 eV for direct and from 1.44 to 1.51 eV for indirect values. Comparison of the indirect and direct values demonstrates a small difference, in which indirect band gaps are smaller than direct ones. A schematic diagram of the energy band structure of CuSbS₂ is shown in the insets of Figs. 6a-d. These results are in agreement with earlier studies [38, 39] confirming that CuSbS₂ has both indirect and direct band gaps. Nevertheless, other observations exist as well. Ramasamy et al. [37] reported direct and indirect values with a difference of 0.3 eV while Chen et al. reported CuSbS₂ as a material with an indirect band gap [40]. The differences between the results are due to differences in structure and morphology of each study.

3.2. Formation and initial growth of CuSbS₂

Because both Sb₂S₃ and Cu₃SbS₄ peaks were recognized in the synthesis at 240 °C by XRD,
sampling during the synthesis procedure was carried out to understand growth mechanism at this temperature. Fig. 7 displays XRD patterns at the ratio of 3 at 240 and 260 °C at the initial stage of the growth (after injection and reaching once again the target temperature (zeroth min)). From the XRD pattern, it can be concluded that intermediate Sb$_2$S$_3$ and Cu$_3$SbS$_4$ phases are absent at a higher temperature (260 °C). Selected area electron diffraction (SAED) pattern and TEM images of zeroth min sample (Fig. 8a and b) and 2 min after that (Fig. 8d and e) confirm XRD results and show that nanosheets are CuSbS$_2$ (based on the analysis of the SAED pattern) and small particles on top of the surfaces are Cu$_3$SbS$_4$ (based on the analysis of diffraction rings). The SAED pattern of the zeroth min sample suggest that the directions along the length and width are close to [010] and [100], respectively. According to the stereographic projection depicted in Fig. 8 c the observed zone axis [103] is only about 8 degrees apart from the [001]. It is quite likely that the sheet is not exactly perpendicular to the beam due to the small nanoparticles on its surface. Similar case is also evident for the sample collected after 2 min reaction time [Fig. 8b]. The length of the sheet is parallel to [010] direction and the width is parallel to [100]. The zone axis [112] is deviated about 13 degrees from the [001] axis (Fig. 8f). The EDX mapping images from zeroth min sample in Fig. 9 clearly indicate that the rods consist of Sb and S atoms and according to XRD and SAED pattern of this sample (Fig. 7), rods are likely to be Sb$_2$S$_3$ phase. SEM images of samples collected from the reaction solution at 240 ºC and at the ratio of 3 at different times of growing procedure are in Figs. 10a-f. Immediately after injection (Fig. 10a), an agglomeration of nanoparticles that ascertained nucleation formation is observable. Fig. 10b demonstrates the presence of a mixture of CuSbS$_2$ nanosheets, rod shaped Sb$_2$S$_3$ particles and round Cu$_3$SbS$_4$ nanoparticles for zeroth min sample. It should be noted that time interval between injection and reaching once again the target temperature was around 2.5 min. This is the period when conversion to CuSbS$_2$, Cu$_3$SbS$_4$, and
Sb$_2$S$_3$ phases occurred. After 2 min (Fig. 10c) since the temperature was stabilized nanosheets were grown, but Sb$_2$S$_3$ phase still existed. The difference in the reactivity of precursors probably results in these separate phases. Nevertheless, when time passes Cu$_3$SbS$_4$ nanoparticles and Sb$_2$S$_3$ rods dissolve to the leached precursor solution and redeposit to grow the existing CuSbS$_2$ nanosheets (Figs. 10d-f). This investigation showed that famatinite to chalcostibite phase transformation is possible and revealed how CuSbS$_2$ phase is formed from precursors. Schematic illustration of growth mechanism is presented in Fig. 11.

(Figure 7)

(Figure 8)

(Figure 9)

(Figure 10)

(Figure 11)

3.3. Further growth of CuSbS$_2$

In order to investigate the effect of reaction time on the growth procedure, powders at the ratio of 3 were synthesized at 240 °C and the reaction was continued for 20 min. Fig. 12a and the inset depicts the fact that nanosheets become thicker with reaction time. It is inferred that coalescence of very thin nanosheets form thicker plate-like particles which can be called nanobricks having thickness ranging from 100 to 150 nm, average length of 1.3 μm and average width of 0.8 μm. The XRD pattern in Fig. 12c shows pure orthorhombic CuSbS$_2$ phase. Estimated direct and indirect band gaps for this sample (Fig. 12b and inset) suggests decreasing of the band gap in comparison
with the nanosheets. Figs. 13 (a-d) show SAED pattern, TEM, fast Fourier transform (FFT), and HRTEM images from a single particle that confirm the single-crystal nature of the CuSbS$_2$ particles. Accordingly, the SAED patterns from the top and bottom side of the particle (inset of Fig. 13b) were similar. It should be noted that the SAED pattern and the HRTEM were taken after an alpha tilt of -14.6 degrees (Fig. 13e). After tilting the sample back to the original perpendicular position (Fig. 13f), it can be concluded that the normal of the plate is [001] and the length and width of the plate are along the [010] and [100] axes, respectively. Crystallographic orientations of the particle are illustrated in Fig. 13g. This analysis confirms the suggestion of Ramasamy et al. [37].

(Figure 12)

(Figure 13)

4. Conclusions

High-quality CuSbS$_2$ nanocrystals have been successfully synthesized by a hot injection route with a different shape of nanoplatelets, nanosheets, and nanobricks depending on the ratio of sulfur and metallic precursors, temperature and reaction time and only by utilizing one type of sulfonating agent. The size of CuSbS$_2$ nanocrystals can be varied from 250 nm to 2 μm in length, 200–700 nm in width and 1–150 nm in thickness. At a sulfur ratio of 4 a Cu$_3$SbS$_4$ phase appeared at 240 °C. However, this phase was avoided at 260 °C at the same ratio of precursors. Moreover, the average size of powders obtained at higher temperature (260 °C) was smaller due to formation of more nuclei. Band gap calculations based on UV-Vis-NIR diffuse reflectance data confirmed that differences between indirect and direct values are smaller than 0.1 eV and synthesized CuSbS$_2$ has both indirect and direct bandgaps. A Sb$_2$S$_3$ intermediate phase was identified at the initial stage of
the reaction. An increase in reaction time showed coalescence of CuSbS$_2$ nanosheets resulting in nanobricks having band gap of 1.46 eV in comparison to 1.52 eV of the nanosheets. Growth directions were studied carefully for nanosheets at the initial stage of the synthesis and nanobricks obtained after 20 min which indicated growth directions are along the basis axes of the unit cell. Structural and optical properties of obtained CuSbS$_2$ suggest that it can be used for several applications such as supercapacitors and in particular for solar cells.

5. Acknowledgement

The authors would like to acknowledge Nanomicroscopy Center (Aalto-NMC) of Aalto University. One of the authors (SM) acknowledges the Ministry of Science, Research and Technology of the Islamic Republic of Iran for the scholarship.

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Figure captions

Figure 1. XRD patterns of powders synthesized at 260 °C with different sulfur ratios.

Figure 2. XRD patterns of powders synthesized at 260 °C with different sulfur ratios.

Figure 3. SEM images of powders obtained at 240 °C with different ratios of sulfur: 2 (a), 2.5 (b), 3 (c), 3.5 (d), and 4 (e).

Figure 4. SEM images of samples obtained at 260 °C with different ratios of sulfur: 2 (a), 2.5 (b), 3 (c), 3.5 (d), and 4 (e).

Figure 5. Diffuse reflectance spectra (insets) and direct band gap estimation of CuSbS$_2$ nanocrystals prepared at different ratio and temperature; 240 °C and ratio of 2.5 (a), 240 °C and ratio of 3 (b), 260 °C and ratio of 2.5 (c), 260 °C and ratio of 3 (d).

Figure 6. Indirect band gap calculation and schematic diagram of energy band structure (inset) and CuSbS$_2$ nanocrystals at different ratios and temperatures; 240 °C and ratio of 2.5 (a), 240 °C and ratio of 3 (b), 260 °C and ratio of 2.5 (c) and 260 °C and ratio of 3 (d).

Figure 7. XRD patterns from the initial stage of growth (zeroth min) for samples prepared at temperatures of 240 °C and 260 °C and at the ratio of 3.

Figure 8. SAED patterns (a, d), TEM images (b, e), and stereoprojection graphics (c, f) of samples collected at zeroth min and after 2 min of reaction, respectively.

Figure 9. EDX mapping of sample collected at zeroth min of reaction.

Figure 10. Time-dependent SEM images of samples collected from the reaction solution at 240
°C and at the ratio of 3; Immediately after injection (a), zeroth min (b), after 2 min (c), 3 min (d), 4 min (e), and 5 min (f).

Figure 11. Schematic illustration of growth mechanism at 240 °C and at a ratio of 3.

Figure 12. SEM images (a and inset), direct and indirect (b and inset) band gaps calculation, and XRD pattern (c) for sample grown at 240 °C and at a ratio of 3 for 20 min.

Figure 13. SAED (a), TEM (b), FFT (c), HRTEM (d) images, stereoprojection graphics (e, f), and schematic representation of growth directions (g) of nanobricks grown at 240 °C for 20 min.
Table 1. Summary of powder X-ray diffraction measurements for samples.

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<th>Sample</th>
<th>Cu:Sb:S</th>
<th>Reaction temperature (T) (°C)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
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<td>1:1:2.5</td>
<td>240</td>
<td>6.024</td>
<td>3.800</td>
<td>14.506</td>
</tr>
<tr>
<td>C</td>
<td>1:1:3</td>
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<td>6.024</td>
<td>3.800</td>
<td>14.504</td>
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<tr>
<td>D</td>
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<td>260</td>
<td>6.024</td>
<td>3.800</td>
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<tr>
<td>E</td>
<td>1:1:3</td>
<td>260</td>
<td>6.023</td>
<td>3.798</td>
<td>14.503</td>
</tr>
</tbody>
</table>

Table 2. Summary of the calculation for average particle size after 5 min reaction time

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<th>(T) (°C)</th>
<th>Average length (nm)</th>
<th>Average width (nm)</th>
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<td>240</td>
<td>260</td>
<td>215</td>
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<tr>
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<td>240</td>
<td>970</td>
<td>730</td>
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<tr>
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<td>670</td>
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<td>1:1:2.5</td>
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