Electronic Supplementary Material (ESI) for RSC Advances.

Y doping effect on high-pressure behavior in Ag_2S nanocrystals

Pan Wang[a,b], Rui Zhao[c], Lixin Wu[b] and Mingzhe Zhang*[a]

[a]State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

[b]State Key Laboratory of Supemolecular Structure and Materials, Jilin University, Changchun 130012, China

[c]College of Computer, Jilin Normal University, Siping 136000, China

*Corresponding Author, E-mail: zhangmz@jlu.edu.cn

1. XPS analysis of monoclinic Ag_2S:Y nanocrystals

For Y doped Ag_2S nanocrystals, it is obviously seen that no other impurities are detectable in the full X-ray photoelectron spectroscopy (XPS) spectra of Fig. S1c. There is some overlap in Figure S1a, due to the close binding energies of Y and S elements. The S $2p_{3/2}$ and S $2p_{1/2}$ peaks (Fig. S1a) at 161.6 and 162.7 eV manifest that the S is in S^{2-} state.[1] The peak (Fig. S1a) of Y $3d_{5/2}$ at 158.5 eV manifests that Y is in Y^{3+} state,[2] excluding the possibility of Y metal clusters. The Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks (Fig. S1b) at 368.8 and 374.7 eV suggest that Ag is in Ag^+ state, in agreement with the reported value of Ag_2S.[3] As we can see from Table S1 of XPS analysis, Y content is about 0.41 atom% in the monoclinic Ag_2S:Y samples.

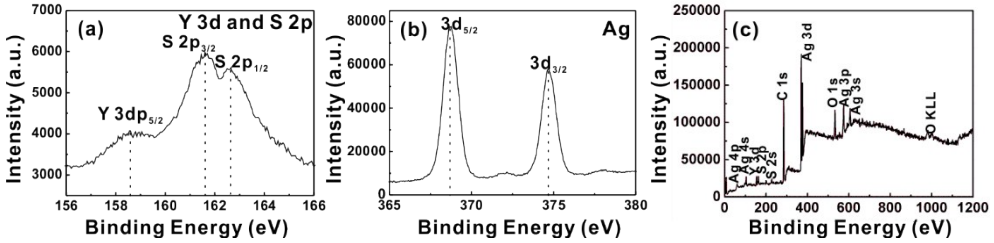

Fig. S1 XPS spectra of (a-c) the monoclinic Ag_2S:Y nanocrystals at ambient conditions. (a)

Binding energy of Y 3d and S 2p regions; (b) binding energies of Ag 3d regions; (c) full scan spectra, respectively.

Table S1. Element content percentage of the monoclinic Ag_2S:Y nanocrystals at ambient conditions.

Element	Weight (%)	Atom (%)
S	12.36	32.15
Y	0.43	0.41
Ag	87.21	67.44
Total	100.00	100.00

2. Representative Rietveld refinement results

Representative Rietveld refinement results from Materials Studio and POWDERCELL softwares of the pure Ag_2S and Ag_2S:Y samples are displayed in Table S2 and S3, respectively. For Ag_2S:Y samples, representative Rietveld refinement figures at several pressure points are shown in Fig. S2 to display the goodness of the Rietveld refinements.

Table S2. Representative Rietveld refinement results of the pure Ag_2S nanocrystals from Materials Studio and POWDERCELL softwares.

Phase	Pressure (GPa)	Space group	Cell parameter				Position parameter				Refinement agreement	
			a (Å)	b (Å)	c (Å)	β (°)	Atom	x	y	z	R_p	R_{wp}
			uncertainty									
I	0	P21/n	4.220	6.916	7.853	99.651	S	0.354	0.254	0.121	0.076	0.093
			0.001	0.002	0.003	0.023	Ag1	0.771	0.010	0.318		
							Ag2	0.288	0.311	0.444		
I	0.93	P21/n	4.176	6.780	7.843	99.585	S	0.351	0.221	0.139	0.092	0.135
			0.001	0.001	0.002	0.019	Ag1	0.751	0.029	0.324		
							Ag2	0.258	0.299	0.457		
I	6.83	P21/n	4.097	6.481	7.672	98.550	S	0.315	0.213	0.134	0.087	0.128
			0.001	0.001	0.003	0.025	Ag1	0.739	0.009	0.870		
							Ag2	0.241	0.326	0.442		

II	6.83	$P2_12_12_1$	6.625 0.002	4.170 0.001	7.220 0.001	-	S Ag1 Ag2	0.236 0.014 0.135	0.157 0.253 0.431	0.159 0.394 0.830	0.087	0.128
II	9.30	$P2_12_12_1$	6.589 0.002	4.187 0.003	7.138 0.001	- -	S Ag1 Ag2	0.236 0.014 0.142	0.133 0.249 0.400	0.154 0.422 0.812	0.079	0.095
III	9.30	P21/n	4.191 0.001	5.830 0.003	7.982 0.001	94.819 0.034	S Ag1 Ag2	0.200 0.7160 0.232	0.249 .01520 0.299	0.094 .280 0.443	0.079	0.095
III	18.20	P21/n	4.135 0.002	5.672 0.003	7.931 0.001	93.580 0.026	S Ag1 Ag2	0.205 0.734 0.238	0.258 0.016 0.310	0.090 0.264 0.436	0.067	0.078

Table S3. Representative Rietveld refinement results of the Ag_2S:Y nanocrystals from Materials Studio and POWDERCELL softwares.

Phase	Pressure (GPa)	Space group	Cell parameter				Position parameter				Refinement agreement	
			a (Å)	b (Å)	c (Å)	β (°)	Atom	x	y	z	R_p	R_{wp}
			uncertainty									
I	0	P21/n	4.213 0.001	6.904 0.001	7.839 0.001	99.639 0.014	S Ag1 Ag2	0.363 0.767 0.289	0.254 0.012 0.315	0.121 0.317 0.434	0.071	0.090
I	1.23	P21/n	4.188 0.001	6.820 0.001	7.872 0.001	99.548 0.010	S Ag1 Ag2	0.337 0.745 0.268	0.232 0.030 0.331	0.138 0.311 0.448	0.055	0.121
I	5.90	P21/n	4.158 0.002	6.562 0.002	7.719 0.001	99.125 0.015	S Ag1 Ag2	0.318 0.735 0.235	0.202 0.026 0.318	0.127 0.298 0.473	0.087	0.105
II	5.90	$P2_12_12_1$	6.525 0.001	4.220 0.001	7.318 0.002	- -	S Ag1 Ag2	0.246 0.013 0.139	0.133 0.277 0.455	0.159 0.408 0.844	0.087	0.105

II	9.00	$P2_12_12_1$	6.612 0.001	4.106 0.003	7.263 0.001	-	S Ag1 Ag2	0.251 0.024 0.158	0.109 0.225 0.425	0.143 0.432 0.823	0.071	0.092
III	9.00	P21/n	4.241 0.001	5.827 0.001	7.883 0.001	94.989 0.015	S Ag1 Ag2	0.224 0.728 0.256	0.232 0.006 0.316	0.095 0.290 0.451	0.071	0.092
III	17.08	P21/n	4.114 0.004	5.718 0.000	7.965 0.004	93.012 0.037	S Ag1 Ag2	0.223 0.736 0.255	0.268 0.033 0.298	0.105 0.287 0.429	0.050	0.074

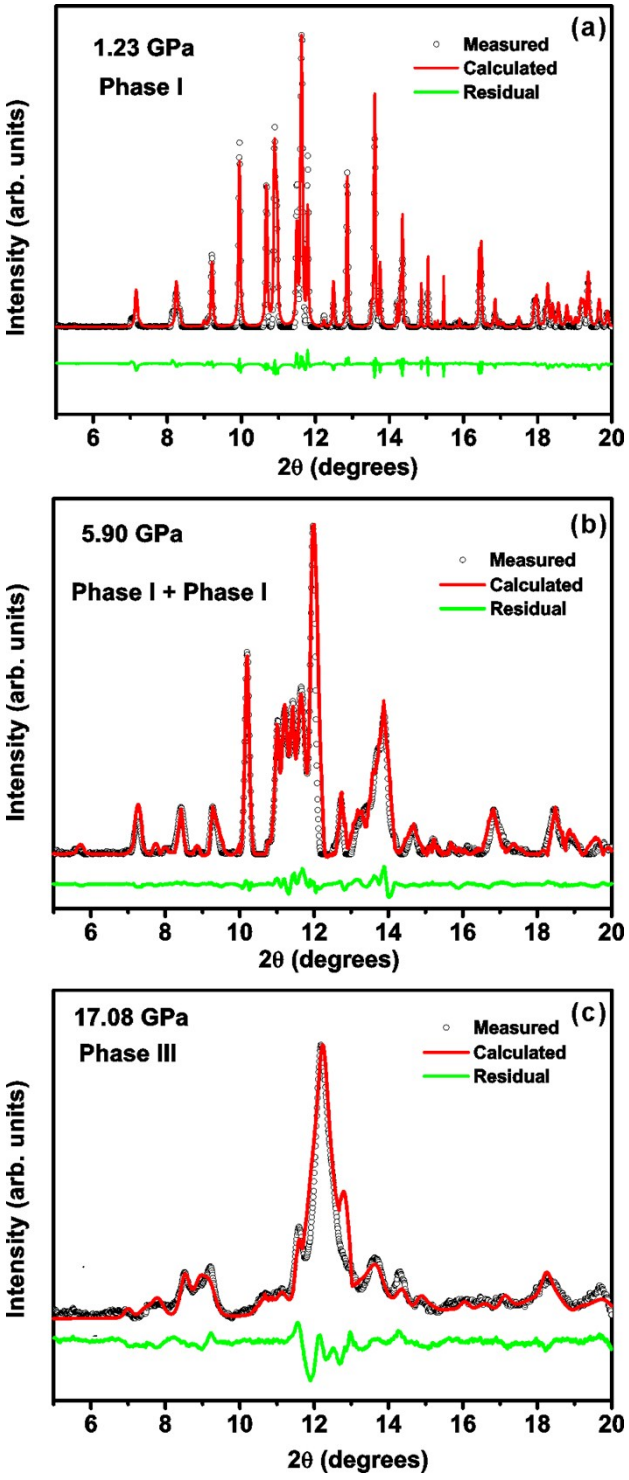

Fig. S2 Rietveld refinements at (a) 1.23 GPa, phase I, (b) 5.90 GPa, phase I + phase II, (c) 17.08 GPa, phase III for Ag_2S:Y samples.

3. The evolution of normalized cell parameters for three phases

The evolution of normalized cell parameters (Fig. S3) for the three phases of the pure Ag_2S sample are investigated to reveal the phase transformation route. During the initial compression,

the contraction of the lattice parameters is rather anisotropic and the b axis is the most compressible of the lattice constants, as indicated in the obtained evolution for the normalized cell parameters of the phase I (Fig. S3a). In phase II, it can be seen that a and b axes are less compressible in Fig. S3b. As can be seen in Fig. S3c, in phase III, the b axis is the most compressible of the lattice constants and the c axis is almost incompressible.

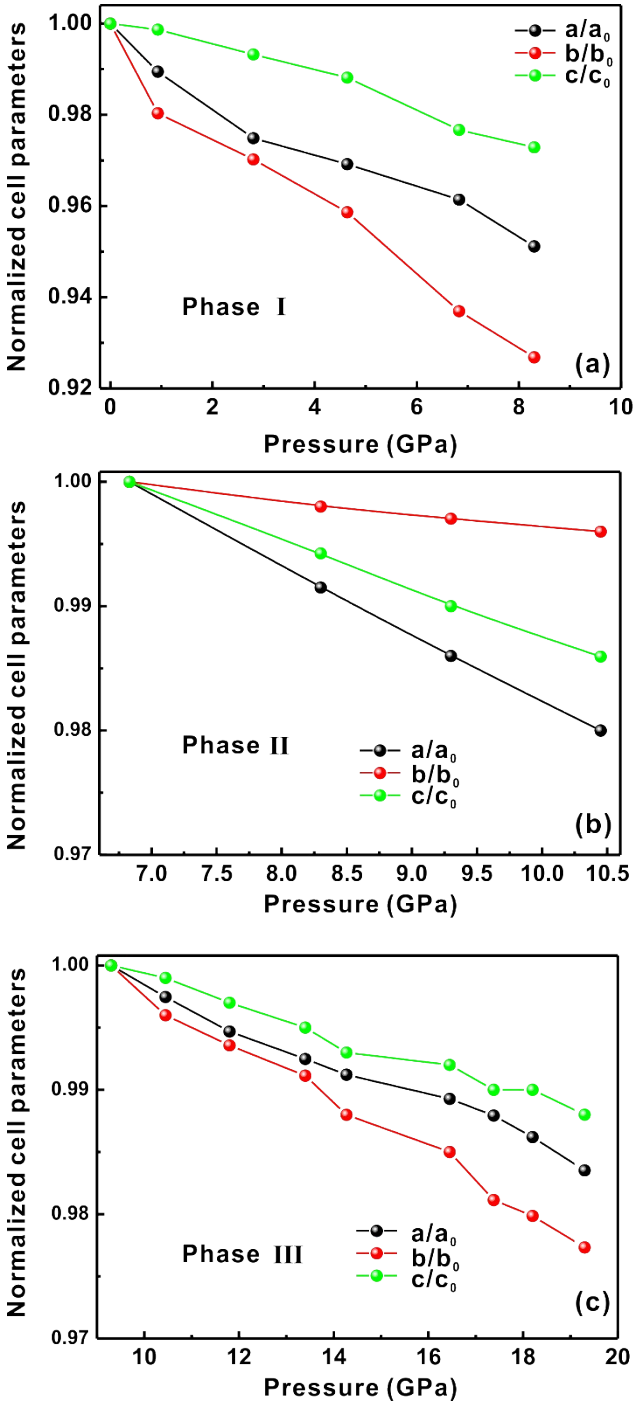

Fig. S3 Normalized cell parameters a/a_0, b/b_0, c/c_0 as a function of pressure for (a) phase I, (b) phase II, and (c) phase III of the pure Ag_2S nanocrystals.

References

1. X. Yang, H. T. Xue, J. Xu, X. Huang, J. Zhang, Y.-B. Tang, T.-W. Ng, H.-L. Kwong, X.-M. Meng and C.-S. Lee, *ACS Appl Mater Interfaces*, 2014, **6**, 9078-9084.
2. I. Gonzalo-Juan, J. A. Escribano, Y. Castro, A. J. Sanchez-Herencia, J. L. G. Fierro and B. Ferrari, *Green Chem.*, 2014, **16**, 3286-3296.
3. W. Jiang, Z. M. Wu, X. N. Yue, S. J. Yuan, H. F. Lu and B. Liang, *RSC Adv.*, 2015, **5**, 24064-24071.