Supplementary Materials: The State of Trace Elements (Cu, Ag, In) in Sphalerite Studied by X-ray Absorption Spectroscopy of Synthetic Minerals

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Table S1. Position of edge jump (e.j.) and white line (WL) of In *K*-edge, Cu K-edge, and Ag *K*-edge XANES spectra.

Sample, standard	Feature	Position, eV
In *K*-edge XANES		
3757	e.j.	27941.3
	WL	27948.6
4108	e.j.	27941.3
	WL	27948.2
4169	e.j.	27941.6
	WL	27948.5
4186	e.j.	27941.2
	WL	27948.5
4197	e.j.	27940.8
	WL	27948.6
$CuInS_2$	e.j.	27941.2
	WL	27948.7
$AgInS_2$	e.j.	27940.3
	WL	27948.6
In_2S_3	e.j.	27941.5
	WL	27946.8
In_2O_3	e.j.	27942.4
	WL	27949.0
Cu *K*-edge XANES		
4065	e.j.	8981.0
	WL	8986.4
4108	e.j.	8983.0
	WL	8986.2
4186	e.j.	8982.5
	WL	8985.8
Cu foil	e.j.	8979.0
	WL	8994.2
$CuInS_2$	e.j.	8983.0
	WL	8985.8
$CuFeS_2$	e.j.	8983.0
	WL	9000.2
Cu_2O	e.j.	8980.6
	WL	8995.6
CuO	e.j.	8983.8
	WL	8997.5
Cu_2S	e.j.	8980.7
	WL	8998.4
CuS	e.j.	8981.7

	WL	8986.3
$Cu_{2-x}S_2$	e.j.	8981.0
	WL	8985.6
Ag *K*-edge XANES		
4152	e.j.	25512.1
	WL	25525.2
4169	e.j.	25512.1
	WL	25526.1
4197	e.j.	25512.5
	WL	25533.1
Ag foil	e.j.	25514.0
	WL	25525.0
$AgInS_2$	e.j.	25511.6
	WL	25535.6
Ag_2S	e.j.	25514.7
	WL	25547.8

Table S2. Results of Linear Combination Fit (LCF) analysis of Ag *K*-edge XANES and EXAFS spectra performed using ATHENA program.

Sample ID	**LCF analysis (%)**								
	XANES						**EXAFS**		
	Fitting in μ(E)[1]			Fitting in derivative of $\mu(E)$[1]			Fitting in χ(k)[2]		
	Ag_{Ag}[3]	Ag_{Ag2S}[3]	Ag_{ss}[3]	Ag_{Ag}[3]	Ag_{Ag2S}[3]	Ag_{ss}[3]	Ag_{Ag}[3]	Ag_{Ag2S}[3]	Ag_{ss}[3]
	(Reduced χ^2, R-factor)			(Reduced χ^2, R-factor)			(Reduced χ^2, R-factor)		
4152 [4] 0.9 wt.% Ag	82 ± 1	18 ± 1	0	81 ± 2	19 ± 2	0	88±3	12 ± 3	0
	(<0.1; 0.001)			(<0.1; 0.008)			(<0.1; 0.178)		
4169 [4] 0.11wt.% Ag 0.09 wt.% In	68±3	0	32±3	65±2	0	35±2	69±2	0	31±2
	(<0.1; 0.001)			(<0.1; 0.003)			(<0.1; 0.163)		
4197 [4] 5.04 wt.% Ag 5.37 wt.% In	0	2±2	98±2	0	4±2	96±2	0	0	100±1
	(<0.1; 0.001)			(<0.1; 0.005)			(<0.1; 0.246)		

Uncertainties are calculated by ATHENA program; XANES – X-ray absorption near edge structure; EXAFS – Extended X-ray absorption fine structure; [1] Energy range 25,493-25,558 eV; [2] *k*-range 3-12 $Å^{-1}$; [3] $Ag_{Ag} = Ag^0$ inclusions, $Ag_{Ag2S} = Ag_2S$ inclusions, Ag_{ss} = Ag solid solution; [4] Concentrations of admixtures in starting materials

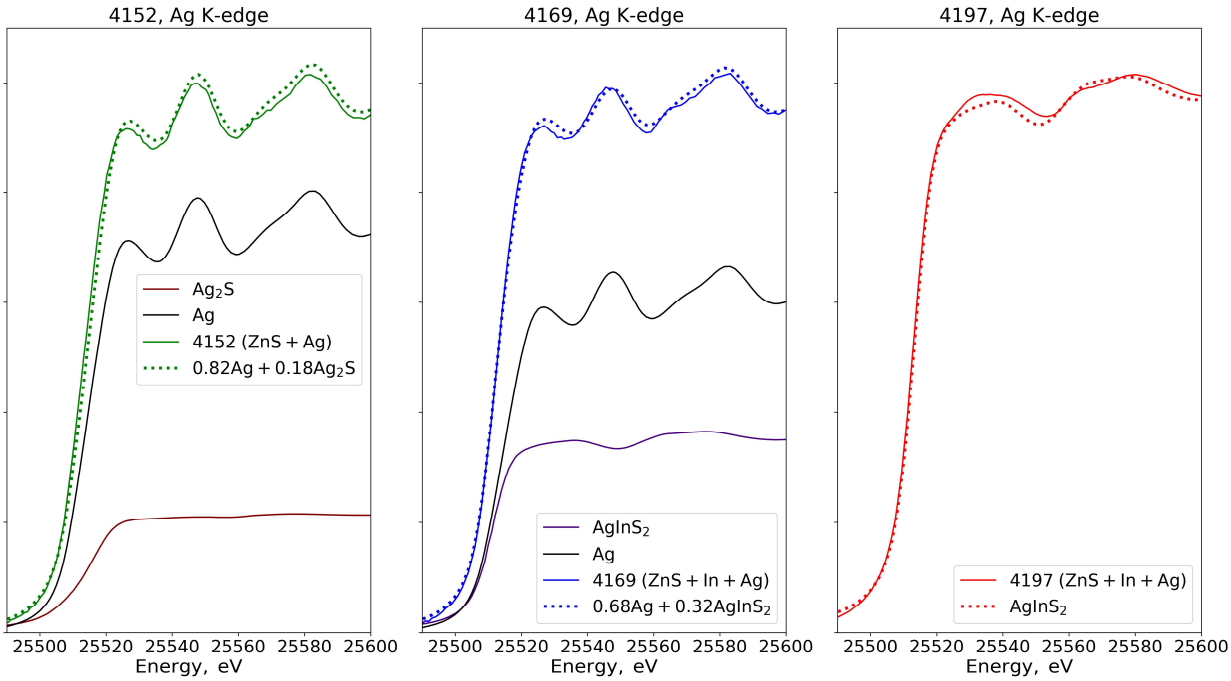

Figure S1. Results of Linear Combination Fit (LCF) analysis of Ag *K*-edge XANES and EXAFS spectra performed using ATHENA program.

Wavelet transform (WT) analysis of the experimental EXAFS spectra.

Wavelet transform of a given signal χ(k) is defined as:

$$W_f^{\psi}(a,k') = \frac{1}{\sqrt{a}} \int_{-\infty}^{+\infty} \chi(k) \psi\left(\frac{k-k'}{a}\right) dk \quad (1)$$

where the scalar product of the EXAFS signal, and the complex conjugate of the wavelet (ψ) is calculated as a function of *a* and *k'*; *a* is the parameter connected with *R* as $a = \frac{\eta}{2R}$ and *k'* conform to localization of wavelet function in *k* space. In this work we use the WT based on the Morlet wavelet functions:

$$\psi(k) = \frac{1}{\sqrt{2\pi}\sigma} e^{i\eta k} e^{-k^2/2\sigma^2} \quad (2)$$

where parameters σ and η correspond to width and frequency of the wavelet function, respectively. These parameters should be adjusted to get appropriate resolution in *k*- an *R*-space. For providing better quality of WT images we used modified WT functions (Timoshenko at al., 2009).

References

1. Timoshenko, J.; Kuzmin, A. Wavelet data analysis of EXAFS spectra (2009) *Comput. Phys. Commun* **180,** 920–925.

Table S3. Interatomic distances in sphalerite with and without dopants determined by DFT calculations. Literature data on interatomic distances for unrelaxed pure sphalerite structure are given at the bottom of the table. Data for the systems ZnS+Cu and Zn+Ag are obtained in the present study, all other data are adopted from Filimonova et al. (2019). The method of the calculations is given in Filimonova et al. (2019).

Bond		Coordination shels							
		Me-S		Me-Zn		Me1-Me2		Me-S	
		N	R,Å	N	R,Å	N	R,Å	N	R,Å
ZnS+In Me=In		4	2.50	12	3.93	-	-	12	4.53
ZnS+Cu Me=Cu		4	2.33	12	3.81	-	-	12	4.51
ZnS+Ag Me=Ag		4	2.50	12	3.86	-	-	12	4.51
ZnS+Cu+In (In and Au atoms are located in neighboring cites)	Me1=In	4	2.46, 2.50, 2.50, 2.51	12	3.85-3.97	1	3.87	12	4.50-4.54
	Me2=Cu	4	2.31, 2.32, 2.32, 2.34	12	3.82-3.92			12	4.45-4.55
ZnS+Cu+In (In and Au atoms are located far from each other)	Me1=In	4	2.49	12	3.93	1	12.78	12	4.53
	Me2=Cu	4	2.33	12	3.81			12	4.51
ZnS		4	2.36	12	3.86	-	-	12	4.51
ZnS, literature XRD data, Jamieson and Demarest (1980)		4	2.34	12	3.83	-	-	12	4.49

References

1. Filimonova, O.N.; Trigub, A.L.; Tonkacheev, D.E.; Nickolsky, M.S.; Kvashnina, K.O.; Chareev, D.A.; Chaplygin, I. V.; Kovalchuk, E. V.; Lafuerza, S.; Tagirov, B.R. (2019) Substitution mechanisms in In-, Au-, and Cu-bearing sphalerites studied by X-ray absorption spectroscopy of synthetic compounds and natural minerals. *Mineral. Mag.* **83,** 435–451. 10.1180/mgm.2019.10.
2. Jamieson, J.C. and Demarest, H.H., Jr. (1980) A note on the compression of cubic ZnS. *Journal of Physics and Chemistry of Solids* **41,** 963–964.