

## **High-frequency electron spin resonance study of a single crystal of Egyptian blue at 4.2 K**

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### **Experimental section**

#### *Materials:*

Egyptian Blue (EB) pigment was purchased from Kremer Pigmente (art. #10060, particle size < 120  $\mu$ ). Single crystals of EB were grown by heating the commercial powder at 1223 K in air for 8 h followed by slow cooling to rt (0.2 K $\cdot$ min<sup>-1</sup>).

#### *Characterization*

Experimental data set was collected on a Bruker D8 VENTURE diffractometer using graphite monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at  $T = 100$  K. Absorption corrections based on measurements of equivalent reflections were applied (SADABS).<sup>S1</sup> The structure was solved by direct methods and refined by full matrix least-squares on  $F^2$  with anisotropic thermal parameters for all atoms using SHELXTL software.<sup>S2</sup> Crystallographic details are presented in Table S1 and S2. CCDC 2474502 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre / FIZ Karlsruhe via <https://www.ccdc.cam.ac.uk>.

Powder X-ray diffraction data were collected on a Haoyuan DX2700 diffractometer (CuK $\alpha$ ,  $\lambda = 1.5418$  Å, Ni-filter, reflection geometry,  $2\theta$  from 8 to 80°) equipped with a scintillator detector. The PXRD pattern was analyzed using JANA2006.<sup>S3</sup> The diffractogram was fully indexed with no visible impurity phases (Figure S1); the refined cell dimensions are well consistent with those determined by SCXRD (Table S3).

Table S1. X-ray crystallography details for Egyptian Blue.

	Egyptian Blue
Radiation	MoK $\alpha$
CCDC	2474502
Empirical formula	CaCuSi <sub>4</sub> O <sub>10</sub>
M <sub>w</sub>	375.98
Temperature (K)	100
Cryst. system	tetragonal
Space group	<i>P4/ncc</i>
<i>a</i> (Å)	7.3072(5)
<i>c</i> (Å)	15.1197(15)
<i>V</i> (Å <sup>3</sup> )	807.32(14)
<i>Z</i>	4
$\rho_{\text{cald}}$ (g·cm <sup>-3</sup> )	3.093
Abs coeff (mm <sup>-1</sup> )	3.981
<i>F</i> (000)	740.0
$\theta$ range (deg)	2.69 < $\theta$ < 30.50
no. of collected/unique rflns	10256/627
Completeness to $\theta$ (%)	100.0
no. of data/restraints/params	627/0/38
Goodness of fit on <i>F</i> <sup>2</sup>	1.100
Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	R <sub>1</sub> = 0.0308, wR <sub>2</sub> = 0.0790
<i>R</i> indices (all data)	R <sub>1</sub> = 0.0374, wR <sub>2</sub> = 0.0825
Largest diff peak/hole (e/Å <sup>3</sup> )	0.55 / -0.69

Table S2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for EB.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.

Atom	x	y	z	$U_{\text{eq}}$
Cu1	0.2500	0.2500	0.58144(4)	9.24(18)
Ca1	0.2500	0.7500	0.5000	10.4(2)
Si1	0.50265(10)	0.57294(10)	0.64701(5)	9.12(19)
O1	0.35290(3)	0.49310(3)	0.58183(13)	11.6(4)
O2	0.46190(3)	0.53810(3)	0.7500	16.7(6)
O3	0.70740(3)	0.49780(3)	0.62596(13)	12.8(4)

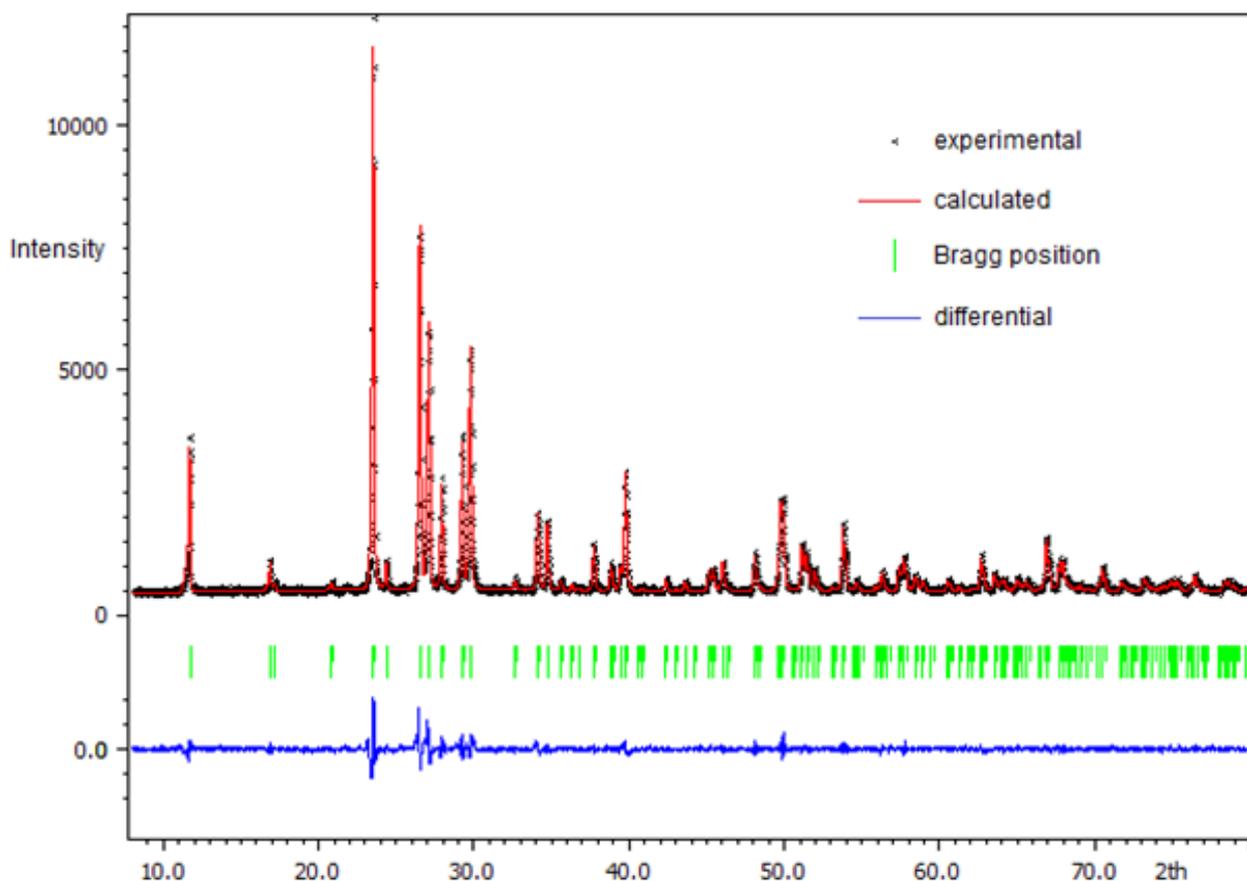


Figure S1. Powder X-ray diffraction pattern for Egyptian Blue ( $T = 298\text{K}$ ). Red line – the calculated fit superimposed with the experimental curve (black points), green bars – Bragg reflections, blue line – the difference curve.

Table S3. PXRD refinement parameters for Egyptian Blue.

Rp	4.54	
wRp	5.99	
GOF	1.57	
2Theta zeropoint	-0.020(3)	
	Refined cell parameters (T = 298K)	Single crystal data (T = 100K)
Space group	<i>P4/ncc</i>	<i>P4/ncc</i>
<i>a</i> , Å	7.3051(7)	7.3072(5)
<i>c</i> , Å	15.1281(17)	15.1197(15)
<i>V</i> , Å <sup>3</sup>	807.3(1)	807.32(14)

The IR spectrum was recorded in 4000-400 cm<sup>-1</sup> range in the attenuated total internal reflection mode (ATR-IR) using Bruker ALPHA spectrometer equipped with a diamond tool. The spectrum was measured at RT 24 times with a resolution of 4 cm<sup>-1</sup> followed by the averaging procedure. The spectrum is shown on Fig. S2.

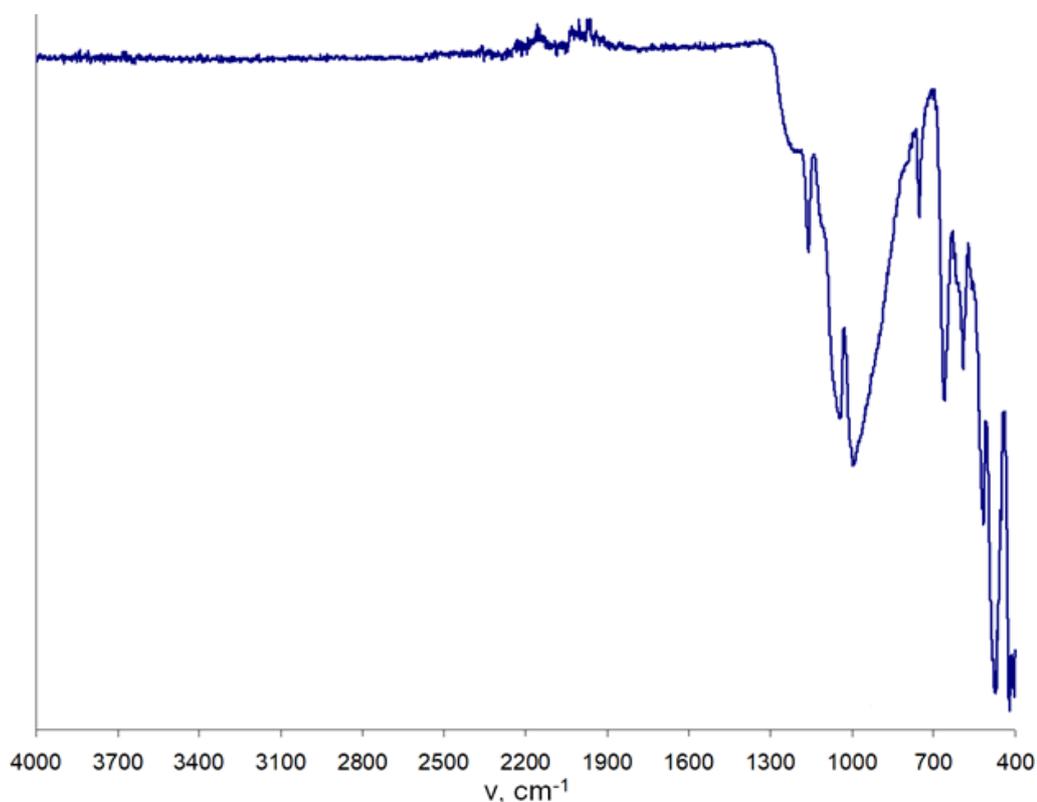


Figure S2. ATR-IR spectrum of EB pigment.

The bands in the spectrum mostly agree with the reported data,<sup>S4-S6</sup> except for the absence of a broad band of stretching vibrations of water molecules reported in.<sup>S5</sup> Thus, unlike the respective

sample, one studied herein does not contain water. The bands in 1250-990  $\text{cm}^{-1}$  and 800-590  $\text{cm}^{-1}$  ranges respectively correspond to antisymmetric and symmetric Si-O-Si stretching vibrations.<sup>S4-S6</sup> The poorly resolved band at c.a. 560  $\text{cm}^{-1}$  and clear cut one at 518  $\text{cm}^{-1}$  respectively correspond to symmetric and antisymmetric vibrations of  $\text{CuO}_4$  tetrahedra.<sup>S6</sup> Noteworthy, considerably higher intensity of the band at 518  $\text{cm}^{-1}$  apparently originates from its complex origin, namely the additional contribution of Si-O-Si bending vibrations.<sup>S4</sup> These vibrations also result in the bands at 477 and 470  $\text{cm}^{-1}$ .<sup>S4</sup> The bands at 420 and 412  $\text{cm}^{-1}$  may be ascribed to, respectively, bending O-Si-O<sup>S6</sup> and stretching Si-O-Cu vibrations.<sup>S5</sup> The band at 405  $\text{cm}^{-1}$  corresponds to Cu-O stretching vibrations.<sup>S5</sup>

## References

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