Egyptian Blue – An Efficient Infrared Emitting Blue Pigment

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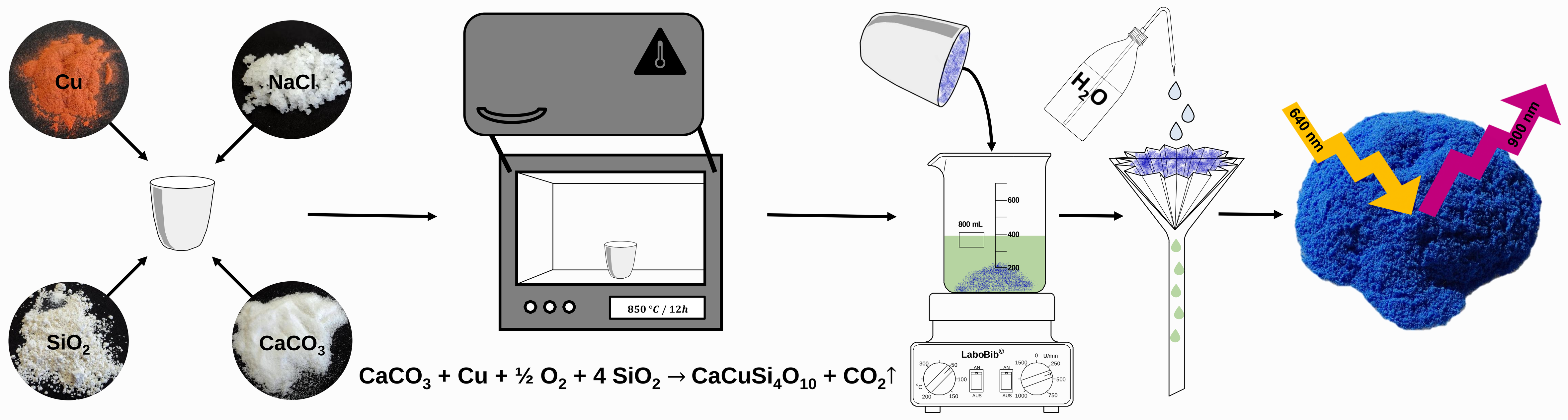
Background

The inorganic pigment Egyptian Blue belongs to the group of layer silicates, whereby its strong blue body color stems from Cu^{2+} with the configuration [Ar]$3d^9$ as part of the mineral phase called cuprorivaite ($CaCuSi_4O_{10}$). As it is very rarely found in nature, it is mostly offered as an artificial pigment and as such it is one of the oldest artificially manufactured pigments. The oldest documents concerning the pigment goes back to the ancient Egypt's. [1] Beyond $CaCuSi_4O_{10}$ also $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$ (Han Blue) are well known blue pigments. Recent studies have shown that all of these blue pigments show broad band emission in the near infrared range (NIR). This finding turns these pigments into rather interesting converter materials for fluorescent light sources, e.g. LEDs, for safety technology and biomedical imaging purposes. [2]

Synthesis

1. Grind the starting materials homogeneously, together with 5 mass-% of NaCl for the sake of fluxing.
2. Place the reaction mixture in a porcelain crucible.
3. Sinter the reaction mixture two times at 850 °C for 8 hours with an intermediate grinding step.
4. Wash product after sintering with hot HCl to get rid of residues (HCl : H_2O = 70 : 30).
5. Wash product with H_2O acid free and finally dry.



Characterization

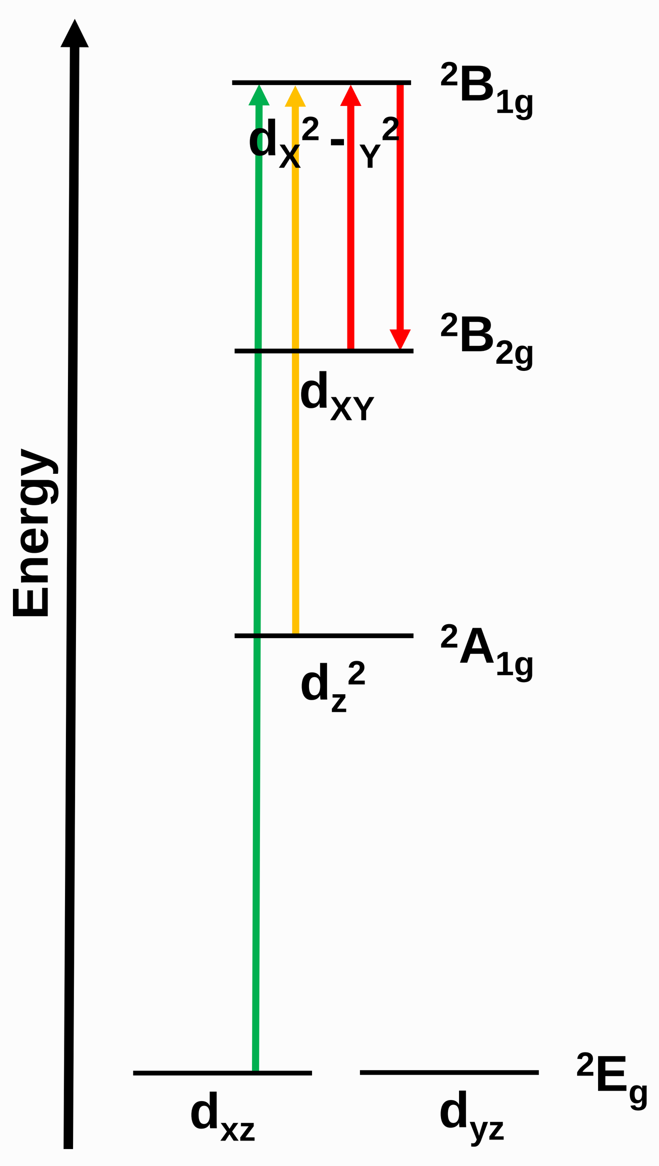


Fig. 4 Cu^{2+} crystal field terms in square planar coordination

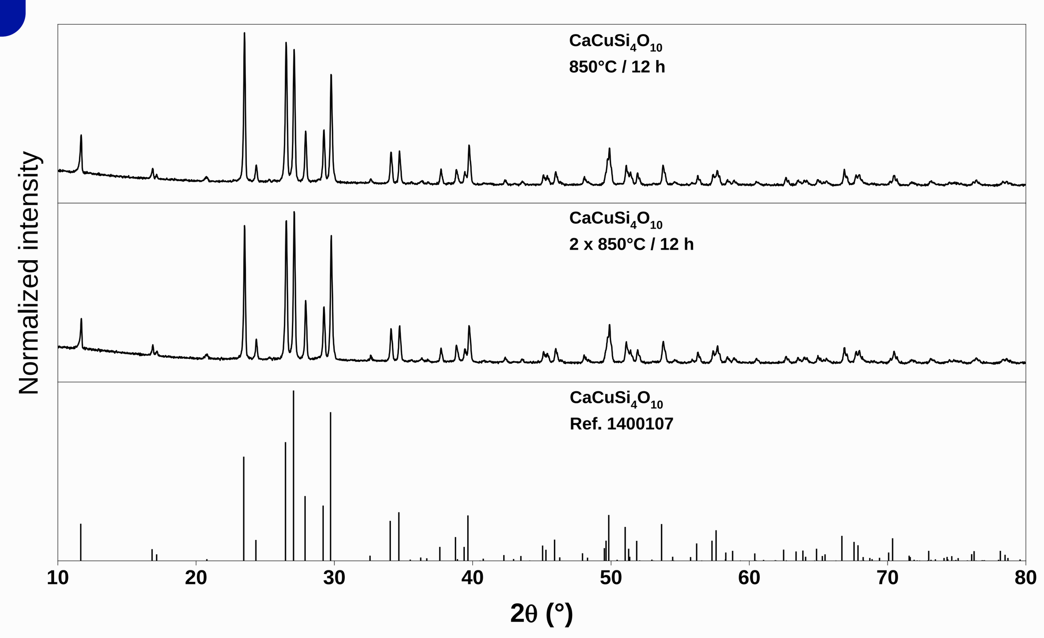


Fig. 1 XRD powder pattern of $CaCuSi_4O_{10}$ after first and second sinter step

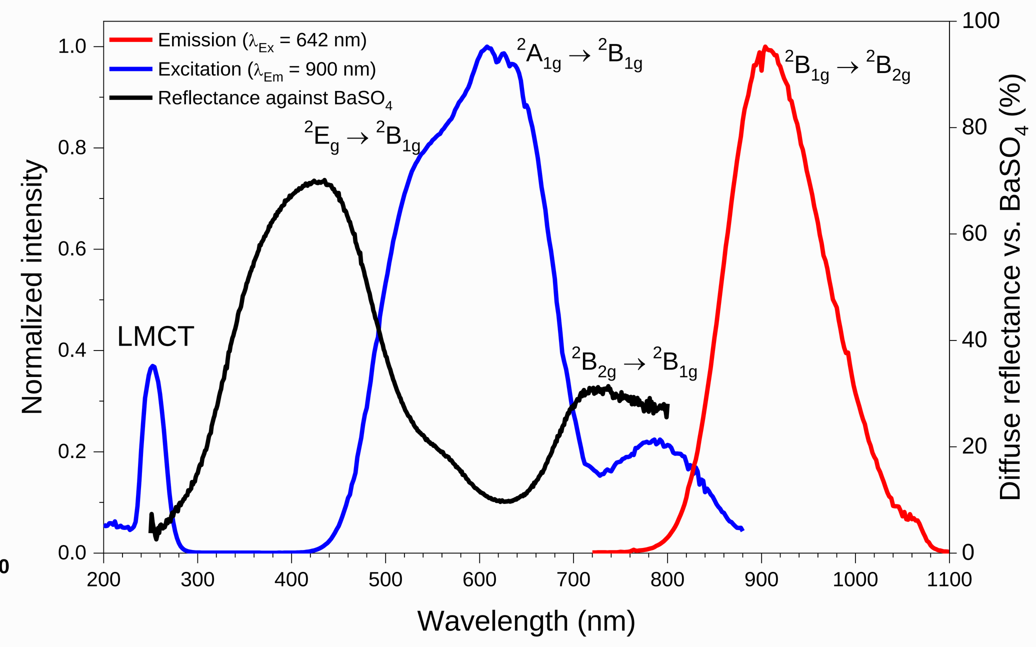


Fig. 2 Excitation, emission and reflection spectra of $CaCuSi_4O_{10}$

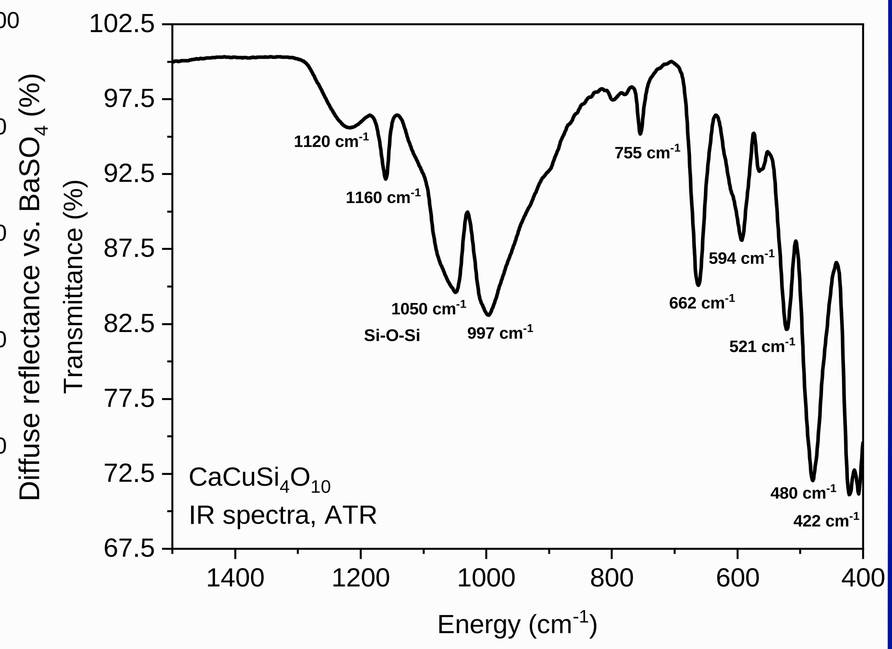


Fig. 3 IR spectra of $CaCuSi_4O_{10}$

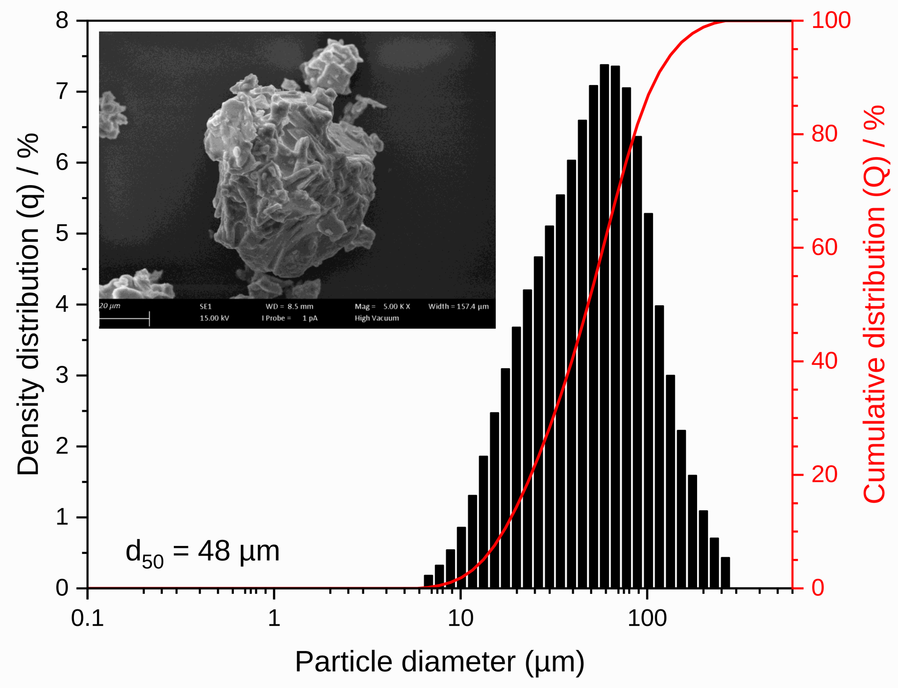


Fig. 5 Particle size distribution and SEM image of a synthesized $CaCuSi_4O_{10}$ pigment sample

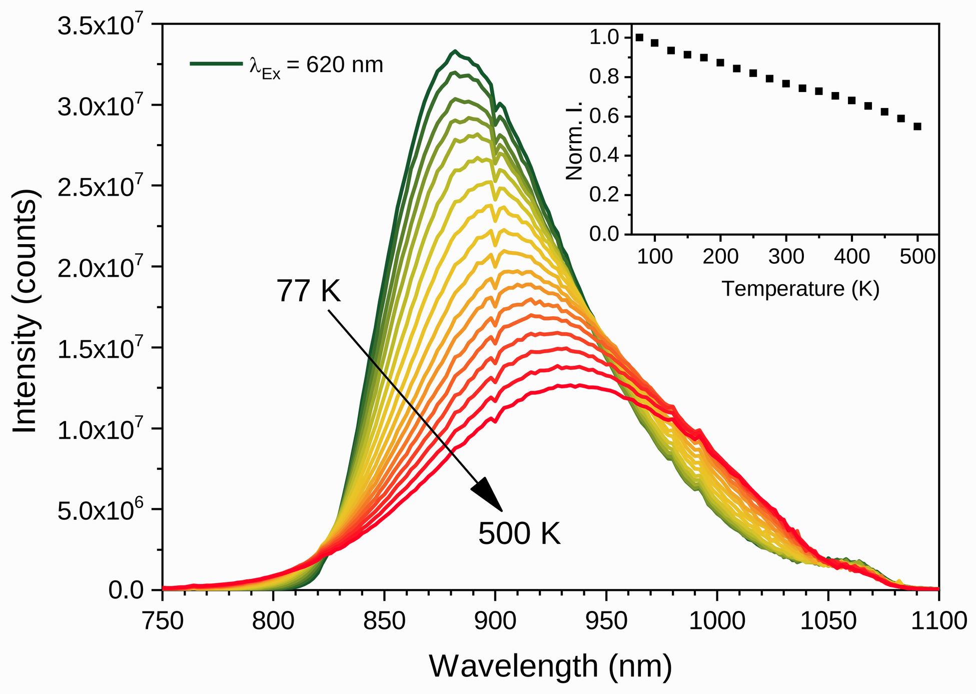


Fig. 6 Temperature dependent emission spectra and emission integrals

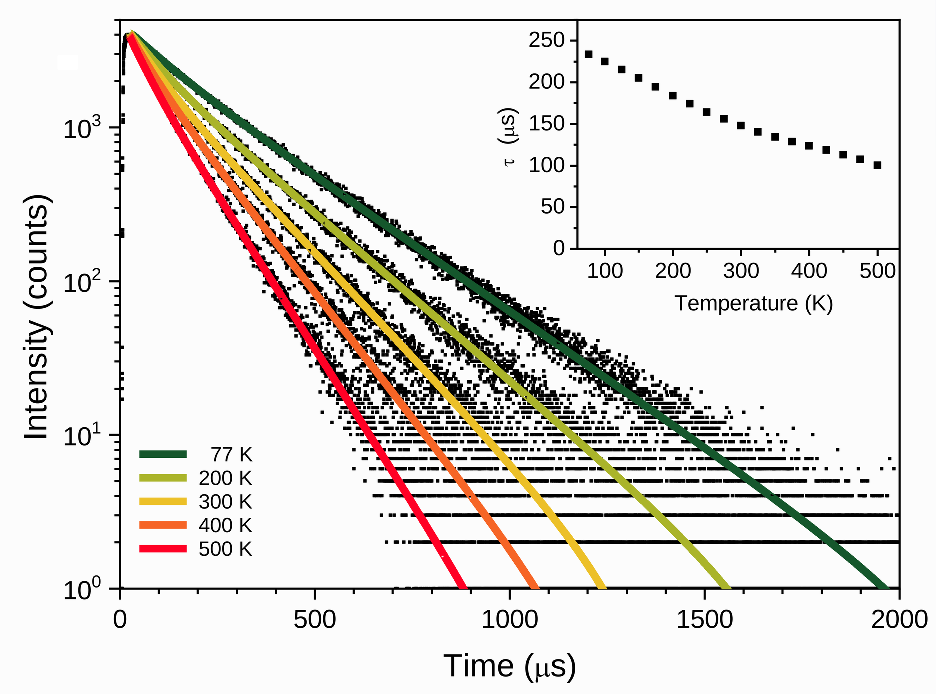


Fig. 7 Temperature dependent decay time of the Cu^{2+} emission in $CaCuSi_4O_{10}$

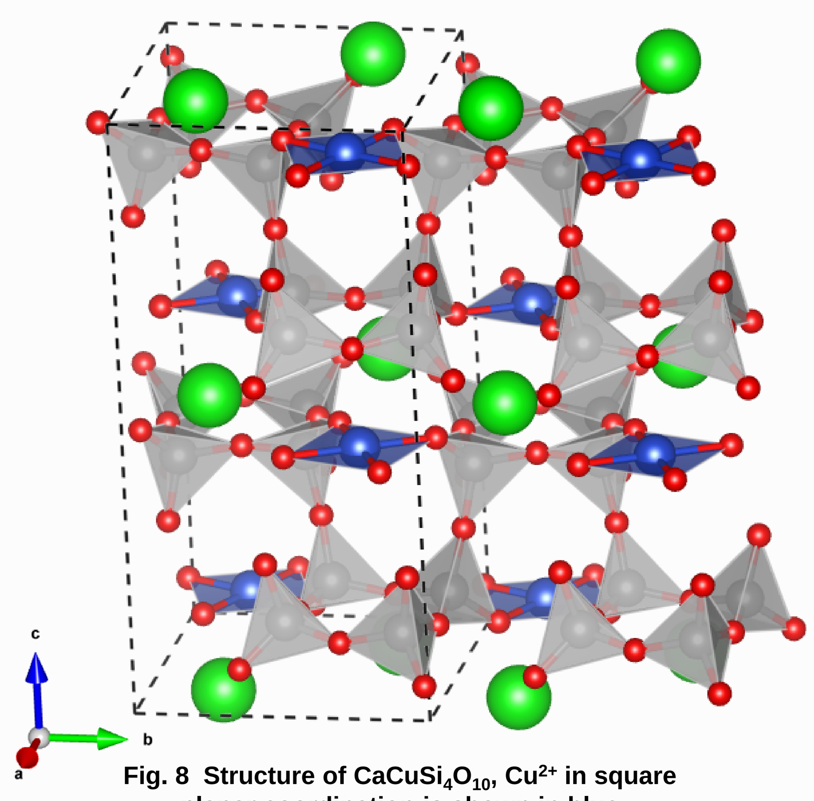


Fig. 8 Structure of $CaCuSi_4O_{10}$, Cu^{2+} in square planar coordination is shown in blue

Results

Single-phase $CaCuSi_4O_{10}$ was synthesized via a solid state synthesis at 850 °C / 12 h using NaCl as a flux. It turned out that the applied educts have tremendous influence on the resulting samples. Using metallic copper blended with quartz and lime powder and NaCl as flux was key to obtain high quality $CaCuSi_4O_{10}$. The crystallinity could be further improved by a second heating step with previous grinding. The particle size distribution was determined to be monomodal with a d_{50} of 48 µm. The synthesized blue pigment showed strong absorption in the region from 500 to 700 nm as well as a broad emission around 900 nm upon excitation at 640 nm. Temperature dependent spectroscopy reveal a broadening of the emission band as well as a decrease of the decay time with increasing temperature. Up to a temperature of 500 K the emission integral decreased by about 50 %. Future work will focus on the modification of IR emission by substitution of the host lattice.

References

[1] A. Lucas, J. Harris, Ancient Egyptian Materials and Industries, Dover Publications, 2012, 4th edition

[2] P. Berdahl, S. Boocock, G. Chan, S. Chen, R. Levinson, M. Zalich, High quantum yield of the Egyptian blue family of infrared phosphors ($MCuSi_4O_{10}$, M = Ca, Sr, Ba), Journal of Applied Physics 123, 2018, 193103

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