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COPPER – BASED SILICATES: SYNTHESIS AND OPTOELECTRONIC PROPERTIES

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INTRODUCTION & AIM

Copper silicates ($MCuSi_4O_{10}$, M=Ca, Sr, Ba) are a fascinating and versatile class of inorganic materials, known for their remarkable stability, intrinsic luminescent properties, and potential use in various technological sectors. Some of these materials have been known since antiquity, yet despite their promising optoelectronic characteristics and lower toxicity, in some cases even reaching biocompatibility, compared to other compounds with similar properties, they haven't yet been used for large-scale applications. Among them, Egyptian Blue ($CaCuSi_4O_{10}$), the oldest artificial pigment, stands out for its intense color and near-infrared luminescence, properties that make it an ideal candidate for advanced applications [1]. Han Blue ($BaCuSi_4O_{10}$) is also a synthetic pigment produced in ancient China, with a history as rich as that of its more famous relative. Visible examples of historical applications of these pigments are still evident today, observable on Egyptian artworks and the Terracotta Army [2].

METHOD

Here, we present our results on the preparation of nanocrystals of these three compounds, utilizing a two-step process: a bottom-up synthesis like the hydrothermal method coupled with a top-down methodology such as exfoliation. Few bottom-up syntheses are reported in the literature; most synthesis protocols are solid-state, leading to material only usable in bulk form. Our syntheses focused on studying the matrix effect of the precursors on the products, by varying the precursors' morphology, composition, and size to modulate the characteristics of the resulting products [3]. During the exfoliation process, solvents with varying polarities and the presence of surfactants were explored.

The hydrothermal syntheses were conducted at 250°C, under autogenous pressure, and for a duration varying from 2 to 4 days [4].

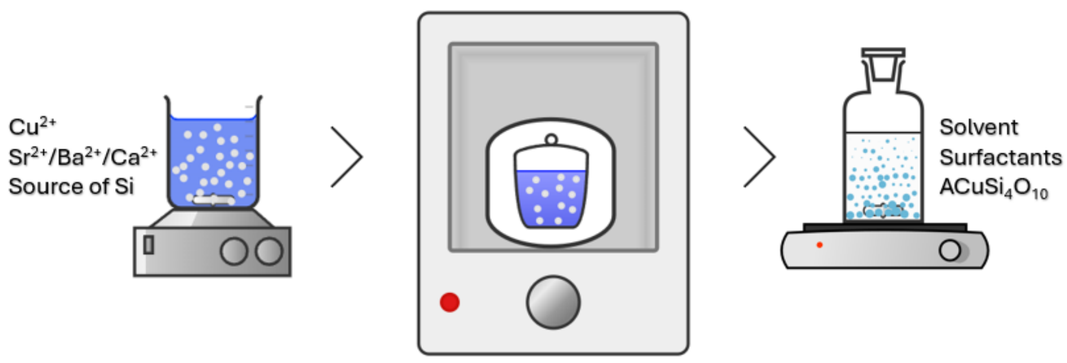
We used three different species as our Si source:

- Pre-formed $nanoSiO_2$
- Cu/SiO_2: a copper phyllosilicate known for its catalytic properties
- NaRUB18: a layered silicate

For the Cu, Sr, Ca, and Ba sources, we used inorganic salts like nitrates and chlorides. The solutions were brought to the desired pH using NH_3 (28%).

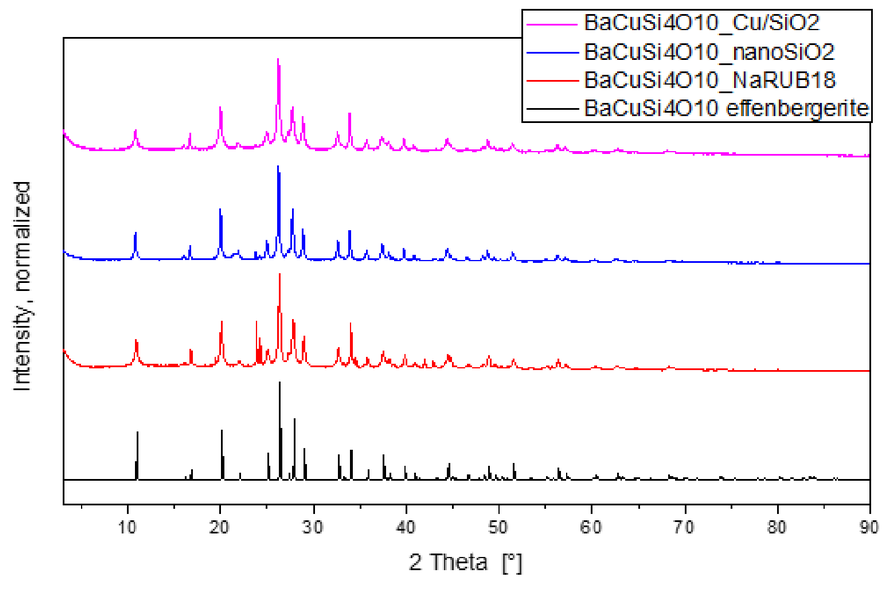
Exfoliation was performed via simple stirring in a solvent at 85°C for four weeks. The different conditions explored were:

- Aqueous solution of Cetyl Trimethyl Ammonium Bromide (CTAB)
- MilliQ water
- Ethylene glycol
- Dimethyl sulfoxide

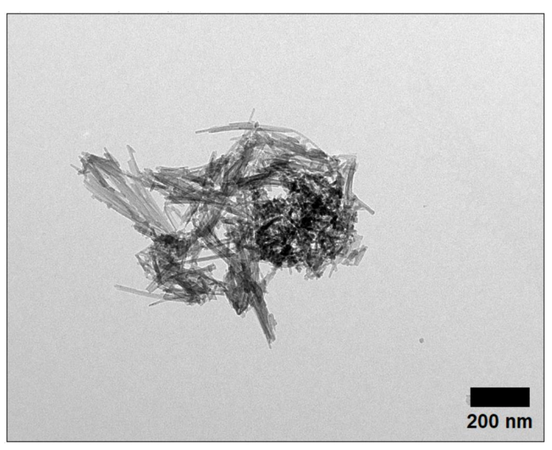


RESULTS & DISCUSSION

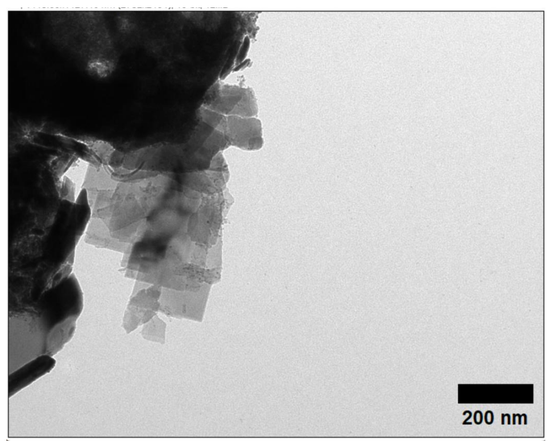
X-ray Diffraction (XRD) analyses demonstrate the effectiveness of the syntheses performed, with only a few cases showing impurities in the diffractogram.



Transmission Electron Microscopy (TEM) confirms that the morphology variation in the samples is directly correlated to the matrix effect of the reactants.

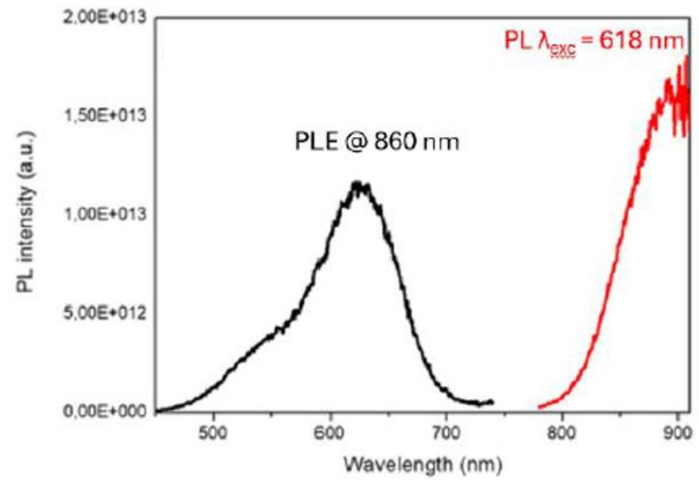


$CaCuSi_4O_{10}$_NaRUB18



$BaCuSi_4O_{10}$_Cu/SiO_2

The pure Egyptian Blue compound emits in the near-infrared (NIR) region between 910 and 930 nm, with a broad excitation spectrum in the green-red wavelengths. Its fluorescence quantum yield is very high (11%) compared to typical NIR fluorescent dyes, such as indocyanine green (ICG), and it exhibits a long emission lifetime (100-150 µs)[4].



$CaCuSi_4O_{10}$_Cu/SiO_2

CONCLUSION

The different syntheses yielded products which, after the exfoliation process, exhibited distinct morphological characteristics, as evidenced by XRD and TEM analyses. This initial step is crucial for verifying whether these differences will translate into useful properties for applications in optoelectronic devices.

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