Synthesis and characterization of Co_2SiO_4 from rice husk ash

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ABSTRACT

Silicate pigments with the general formula $MSiO_4$ are widely used in the paint, ceramic, and protective coating industries due to their high thermal and chemical stability. In this study, nano-silica was synthesized from rice husk ash (RHA) as a bio-based raw material via the sol–gel method and employed as the silica source for pigment preparation. Subsequently, cobalt silicate (Co_2SiO_4) pigment was successfully synthesized through the sol–gel process, resulting in a desirable blue coloration.

*The structural and phase composition of the synthesized pigment was characterized by X-ray-diffraction (XRD), confirming the formation of the cobalt silicate crystalline phase. The morphology and particle size distribution were investigated using scanning electron microscopy (SEM). In addition, the optical properties of the pigment were evaluated by UV–Vis diffuse reflectance spectroscopy (DRS), which revealed strong absorption in the visible region responsible for the blue color of the cobalt silicate pigment. The colorimetric properties were further quantified using the CIE L*a*b* color space, demonstrating high color intensity.*

The results indicate that RHA-derived nano-silica is a suitable and sustainable precursor for the synthesis of cobalt silicate pigments, offering an eco-friendly approach for the development of thermally and chemically stable inorganic pigments with promising optical and colorimetric performance.

Keywords: **Silicate pigments - Cobalt silicate- Rice husk ash - Nano-silica - Sol-gel method**

1. *INTRODUCTION*

Inorganic silicate pigments have long been recognized as essential materials in ceramic glazes, coatings, and protective applications owing to their outstanding thermal stability, chemical resistance, and color durability. Pigments with the general formula $MSiO_4$ are particularly attractive because their crystal structures can effectively accommodate chromophore ions, leading to stable and intense coloration. Among them, cobalt silicate (Co_2SiO_4), which crystallizes in an olivine-type structure, is well known for its vivid blue color and excellent stability at elevated temperatures. However, the industrial production of cobalt silicate pigments is still largely based on conventional solid-state reactions that require high calcination temperatures, extended processing times, and significant energy consumption, while offering limited control over particle morphology and homogeneity [1].

To address these limitations, wet-chemical synthesis techniques, particularly sol–gel methods, have gained increasing attention for the preparation of cobalt-containing silicate materials [2,3]. The sol–gel approach enables molecular-level mixing of precursors, leading to improved compositional homogeneity, reduced crystallization temperatures, and finer particle sizes compared to traditional ceramic routes. Previous studies have demonstrated the successful incorporation of cobalt species into silica networks and the formation of cobalt–silica or cobalt silicate phases with controlled microstructures using sol–gel-derived precursors [2,3]. Nevertheless, most of these studies predominantly rely on commercial silica sources such as tetraethyl orthosilicate (TEOS), which increases synthesis costs and diminishes the environmental sustainability of the process.

In parallel with advances in synthesis methods, increasing attention has been directed toward the utilization of renewable and low-cost raw materials in ceramic and pigment production. RHA, an abundant agricultural byproduct generated in large quantities worldwide, contains a high proportion of amorphous silica (approximately 85–95%) and represents a promising alternative silica source [4]. Extensive research has demonstrated the feasibility of extracting high-purity nano-silica from RHA through chemical and precipitation-based methods, yielding highly reactive silica suitable for advanced material synthesis [5]. The use of RHA-derived silica not only reduces material costs but also contributes to waste valorization and environmental protection.

RHA-derived silica has been successfully employed in the synthesis of various silicate-based ceramic materials and pigments, particularly zinc silicate (willemite) systems, confirming its suitability as a functional silica precursor [6–8]. However, despite the well-established role of cobalt ions as chromophores in ceramic pigments, the direct synthesis of cobalt silicate (Co_2SiO_4) pigments using nano-silica extracted from RHA has received comparatively little attention. In particular, there is a lack of systematic studies focusing on the phase formation behavior, structural characteristics, and morphological features of Co_2SiO_4 pigments synthesized via sol–gel routes employing bio-based silica sources.

In this context, the present work aims to develop a sustainable and efficient sol–gel synthesis route for cobalt silicate (Co_2SiO_4) pigment using nano-silica derived from RHA as the sole silica source. By combining a bio-based precursor with the sol–gel method, this study seems to achieve improved homogeneity and controlled microstructure while reducing environmental impact and reliance on commercial silica reagents. The synthesized pigment exhibits a desirable blue coloration and was systematically characterized by XRD to investigate its phase composition and crystallinity, as well as by SEM to analyze its morphology. The findings of this study highlight the potential of agricultural waste–derived nano-silica for the sustainable production of thermally and chemically stable cobalt silicate pigments suitable for ceramic and coating applications.

2. EXPERIMENTAL PROCEDURE

The materials used in this study include RHA as the silica source, hydrochloric acid (HCl) and sodium hydroxide (NaOH) for silica extraction, and cobalt acetate as the cobalt precursor. Distilled water was used throughout the experiments to prepare solutions and gels. All chemicals were of analytical grade and used without further purification.

Initially, the rice husk was calcined in a muffle furnace at 1000 °C with a heating rate of 5 °C/min and maintained at this temperature for 2 hours to obtain RHA. 2.0 g of the resulting ash were treated with HCl (2 M, ۱۹،۲mL) and refluxed at 90 °C for 3 h. The mixture was then repeatedly washed with hot water (90 °C) until the pH reached 7, followed by drying at100°C.

The dried ash was subsequently mixed with NaOH (3M, 34 mL) and the mixture was left to reflux overnight. The gel was obtained after evaporation of the solvent and then neutralized using 6 M HCl to induce the initial precipitation. Subsequently, cobalt acetate solution (0.6 M, 10 mL) was added, resulting in the appearance of a blue coloration.

The precipitate was separated by centrifugation and washed three times with distilled water. Finally, the washed precipitate was heated at 90 °C for 24 hours to the formation of Co_2SiO_4 pigment.

The phase composition and crystalline structure of the synthesized cobalt silicate pigment were analyzed using a Bruker axs Company, D8 ADVANCE diffractometer (Germany). The XRD patterns were recorded using Cu Kα radiation (λ = 1.5406 Å) over an appropriate 2θ range at room temperature.

The surface morphology and microstructural features of the synthesized pigment were examined by a (SEM, MIRA III, TESCAN Company).

DRS was employed to evaluate the optical properties of the synthesized cobalt silicate pigment. The UV–Vis diffuse reflectance spectra were recorded using a UV–Vis spectrophotometer equipped with an integrating sphere, in the wavelength range of 200–800 nm at room temperature. $BaSO_4$ was used as a reference material.

*Colorimetric analysis of the synthesized cobalt silicate pigment was carried out using a color measurement system based on the CIE L*a*b* color space. The color parameters, including lightness (L*), red–green coordinate (a*), and yellow–blue coordinate (b*), were determined under standard illumination conditions at room temperature. The measurements were performed to quantitatively evaluate the color characteristics and chromatic performance of the pigment.*

3.RESULTS AND DISCUSSION

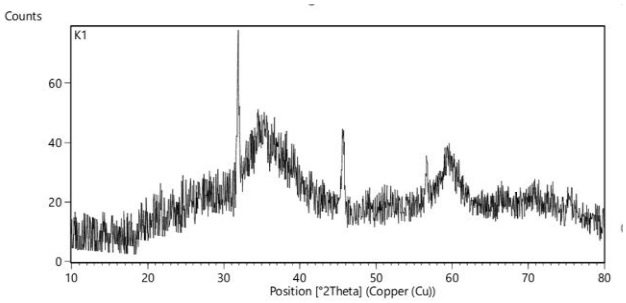


***Fig. 1**. XRD pattern of the Co_2SiO_4 pigment.*

3.1. XRD Analysis

Fig. 1 presents the XRD pattern of the synthesized cobalt silicate pigment, recorded in the 2θ range of 10–80° using Cu Kα radiation. The diffractogram reveals a dominant sharp reflection at 2θ = 32.0°, which matches the (131)/(220) planes of orthorhombic Co_2SiO_4 (JCPDS card No. 15-0865) [۹]. This prominent peak provides evidence for the presence of crystalline cobalt silicate as a significant phase in the pigment.

A characteristic reflection at 2θ ≈ 45° corresponds to the (220) plane of cubic NaCl (JCPDS card No.05-0628)[10], consistent with residual sodium chloride from the RHA silica extraction process.

Additionally, a weaker peak at 2θ ≈ 57.2° aligns with the (332) reflection of Co_2SiO_4 or possibly minor Co_3O_4 (JCPDS No.42-1467)[11].

Several lower-intensity reflections are also attributable to cubic Co_3O_4. The pronounced amorphous background indicates that Co_2SiO_4 crystallites are embedded within an amorphous silicate matrix derived from RHA silica. This partially crystalline nanostructure is typical of sol-gel synthesized cobalt silicate pigments and favorable for pigment applications.

The XRD results demonstrate the successful formation of a multiphase system containing crystalline Co_2SiO_4, Co_3O_4, and residual NaCl within an amorphous silicate network, which accounts for the observed intense blue coloration.

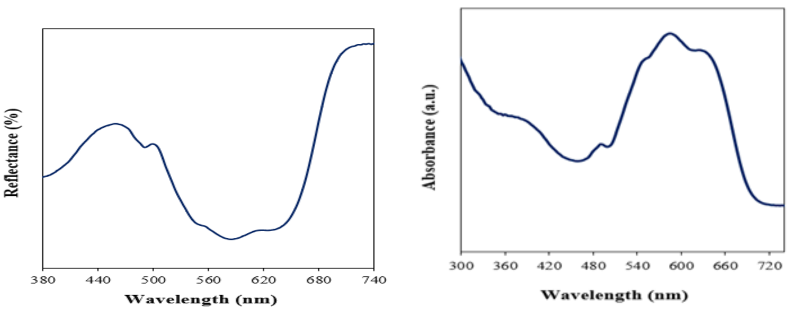


***Fig. 2**. DRS spectra of the Co_2SiO_4 pigment in the UV–Vis range*

3.2. DRS

DRS was employed to investigate the optical properties of the synthesized cobalt silicate pigment.

The reflectance spectrum, recorded in the wavelength range of 380–740 nm, exhibits a pronounced decrease in reflectance across the visible region, indicating strong visible light absorption characteristic of blue pigments.

A broad absorption band spanning 500–650 nm, with a minimum reflectance centered at 560–620 nm, is observed. This absorption profile is attributed to d–d electronic transitions of Co^{2+} ions in Co–O coordination environments within the silicate structure.

The $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transition around 580–600 nm is responsible for the intense blue coloration. Above 680 nm, a sharp reflectance increase occurs, corresponding to reduced absorption in the red to near-infrared region. This selective absorption in the yellow-orange-red spectrum (500–650 nm) and high reflectance in the blue region (<450 nm) produces the characteristic blue hue through complementary color mechanisms.

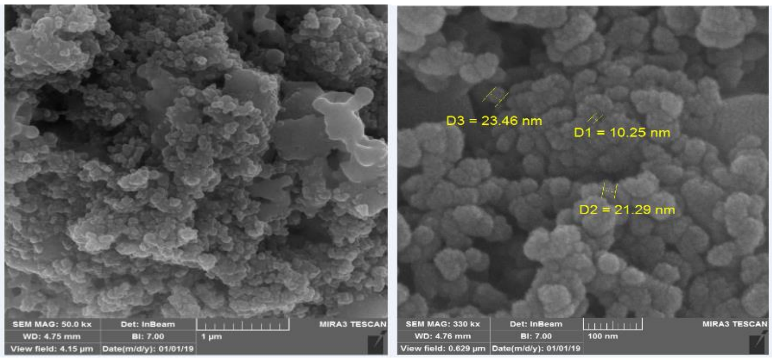


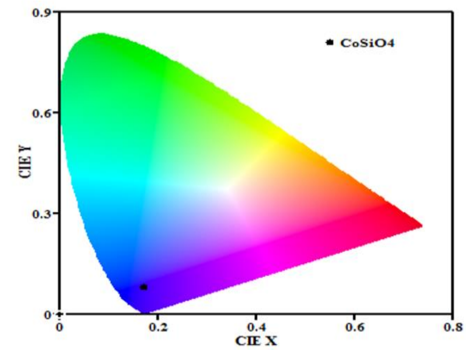
Fig. 3. *SEM images of the Co_2SiO_4 pigment*

3.3. SEM Analysis

Fig. 3 presents SEM micrographs of the synthesized cobalt silicate pigment, obtained to investigate surface morphology and microstructure. Low-magnification images reveal agglomerated clusters with irregular shapes, forming secondary particles in the micron range .

This agglomeration behavior is typical of silicate-based nanomaterials synthesized via sol-gel routes, driven by high surface energy of the primary nanoparticles. High-magnification images show that these agglomerates comprise nanosized primary particles exhibiting quasi-spherical morphology with rough surfaces, confirming the nanocrystalline character of the material.

The SEM observations demonstrate successful formation of nanostructured cobalt silicate with granular morphology, optimal for pigment applications requiring high surface area and dispersibility.



Entry	*L**	*a**	*b**	*X*	*Y*	*Z*
1	*35.1*	*67.9*	-۹٤,٥	*0.181*	*0.085*	*0.816*

Table ۱. *CIE L*a*b* and CIE XYZ color coordinates of the synthesized Co* ۲ *SiO_4 pigment.*

Fig. 4. *CIE L*a*b* color coordinates of the Co_2SiO_4 pigment*

*3.4. Colorimetric Analysis (CIE L*a*b*)*

*The colorimetric properties of the synthesized cobalt silicate pigment were quantitatively evaluated using the CIE L*a*b* color space. The measured color parameters are: L* = 35.1, a* = 67.9, b* = −94.5, with tristimulus values X = 0.181, Y = 0.085, Z = 0.816. The low L* value (35.1) indicates dark and intense coloration, desirable for inorganic pigment applications requiring high color strength [12].*

The strongly negative b value (−94.5) confirms dominant blue component, characteristic of cobalt silicate pigments [13].*

The positive a value (67.9) indicates magenta/reddish contribution, originating from the Co^{2+} coordination environment within the silicate matrix [14]. These parameters yield chroma (C*) = 104.8 and hue angle (h°) ≈ 305.8°, positioning the pigment in the blue-violet quadrant of the CIE L*a*b* space, optimal for ceramic and coating applications.*

4.CONCLUSIONS

In this study, cobalt silicate (Co_2SiO_4) blue pigment was successfully synthesized using silica extracted from RHA as a sustainable and bio-based precursor. The sol–gel route enabled effective incorporation of Co^{2+} ions into the silicate network, leading to the formation of a cobalt silicate pigment with a distinct blue coloration. The deliberate elimination of the gel-aging step proved beneficial for preserving color quality and avoiding excessive network condensation.

XRD analysis confirmed the formation of the cobalt silicate phase with a low to moderate degree of crystallinity, which can be attributed to the nanoscale nature of the synthesized material and the presence of amorphous bio-derived silica. SEM observations revealed a relatively uniform microstructure.

*DRS showed strong absorption in the visible region, particularly in the orange–red wavelengths, which accounts for the observed blue coloration of the pigment. In addition, colorimetric measurements in the CIE L*a*b* color space confirmed the high chromatic intensity of the synthesized cobalt silicate pigment.*

Overall, the DRS results indicate that the synthesized cobalt silicate pigment exhibits significant visible-light absorption and favorable optical characteristics, highlighting its potential applicability in pigment, coating, and ceramic formulations. The relatively low crystallinity observed in the XRD patterns should not be considered a limitation but rather a controlled structural feature that contributes to enhanced color performance and improved color uniformity in this system.

Finally, the results demonstrate that RHA can be effectively utilized as a renewable and low-cost silica source for the synthesis of cobalt silicate pigments. This approach not only offers an environmentally friendly route for producing inorganic pigments but also adds value to agricultural waste materials, underlining the potential application of the synthesized pigment in sustainable coating and ceramic industries.

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