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# Effect of silica precursor on the synthesis of Zn<sub>2</sub>SiO<sub>4</sub>-based material

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#### ABSTRACT

The synthesis of zinc silicate  $(Zn_2SiO_4)$  powders via the solid-state method was studied using amorphous and crystalline silica precursors. This work explores the impact of reaction temperature (700–1300 °C) on phase evolution and microstructural changes. A comprehensive characterization was carried out using X-ray diffraction, Raman spectroscopy, and scanning electron microscopy. X-ray diffraction analysis revealed a progression from unreacted precursors at lower temperatures to a mixed-phase composition ( $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> and  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub>) at intermediate temperatures, ultimately resulting in a single-phase  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> at 1300 °C. Notably, Raman spectroscopy detected the presence of the metastable  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> phase. Morphological analysis using scanning electron microscopy demonstrated the important role of precursor type and reaction conditions on particle characteristics: crystalline silica yielded larger, more uniform particles, while amorphous silica promoted the formation of spherical Zn<sub>2</sub>SiO<sub>4</sub> particles with an average diameter of approximately 1 µm. These findings are of significant interest for tailoring the properties of Zn<sub>2</sub>SiO<sub>4</sub> ceramics to be used for advanced applications in optoelectronics and luminescence technologies.

## 1. Introduction

Zinc silicate  $(Zn_2SiO_4)$  has gained significant attention owing to its outstanding luminescence properties, which make it an indispensable material for diverse applications such as phototherapy, dosimetry, and optoelectronic devices [1,2]. The material exists in five polymorphic forms: I ( $\alpha$ ), II ( $\beta$ ), III, IV, and V, with the  $\beta$ -phase being metastable and transforming into the thermodynamically stable  $\alpha$ -phase at elevated temperatures. The functional properties of  $Zn_2SiO_4$  are highly dependent on its crystalline structure and morphology, which are significantly influenced by the synthesis method and processing conditions [3]. Notably,  $Mn^{2+}$ -doped  $\alpha$ - $Zn_2SiO_4$ exhibits green emission, whereas  $Mn^{2+}$ -doped  $\beta$ - $Zn_2SiO_4$  produces yellow emission [2]. This tunable emission behavior between the  $\alpha$  and  $\beta$  phases highlights the potential for tailoring luminescent properties through crystal structure control.

Solid-state synthesis is widely employed for the production of  $Zn_2SiO_4$  due to its simplicity, cost-effectiveness, and scalability [4]. This method involves high-temperature reactions between precursor oxides such as zinc oxide (ZnO) and silica (SiO<sub>2</sub>). However, achieving high phase purity, controlled morphology, and optimal particle size necessitates careful consideration of precursor characteristics and reaction parameters. SiO<sub>2</sub>, a critical reactant in  $Zn_2SiO_4$  synthesis, exists in various forms, including amorphous and crystalline phases. These forms exhibit distinct reactivity and thermal behavior, which can profoundly influence phase formation, particle morphology, and ultimate functional properties.

This study systematically investigates the influence of silica precursor type (amorphous and crystalline) on the synthesis of  $Zn_2SiO_4$  powders via the solid-state method. The work focuses on understanding the effects of reaction temperature (700–1300 °C) on phase evolution, as well as the morphology and particle size distribution. The complementary analysis of X-ray diffraction (XRD) and Raman spectra, particularly in identifying metastable phases, offers valuable insights into the mechanisms of reactions. The main objectives of this work were to elucidate the role of precursor type in the formation of  $Zn_2SiO_4$  phases, including the metastable  $\beta$ -phase, and to provide recommendations for optimizing synthesis conditions to adapt the properties of  $Zn_2SiO_4$  to specific technological applications.

#### 2. Experimental section

#### 2.1. Materials and synthesis

ZnO (Symrise GmbH, 99.5%), amorphous silica (Thermo Fisher Scientific, 99.9%), and crystalline silica with quartz polymorph (Alfa Aesar, 99.5%) were used to synthesize  $Zn_2SiO_4$  powders via the solid-state method. The average particle sizes of the precursors were as follows: ZnO ~400 nm, amorphous SiO<sub>2</sub> ~500 nm, and crystalline SiO<sub>2</sub> ~1.21 µm. Stoichiometric amounts of ZnO and SiO<sub>2</sub> powders were initially mixed using an agate mortar and pestle to ensure initial homogeneity. Subsequently, the mixture was further homogenized by planetary ball milling (Model YKM-1) at 250 rpm for 8 hours using yttria-stabilized zirconia (YSZ) balls and zirconia jars under dry conditions. After ball milling, the homogenized powder mixtures were heat-treated in air at temperatures ranging from 700 to 1300 °C for 2 hours.

#### 2.2. Characterization

Phase identification was performed using XRD on a Rigaku SmartLab SE system with Cu K $\alpha$  radiation in Bragg-Brentano geometry (2 $\theta$  range: 10–80°). Raman spectroscopy employed a Horiba LabRAM HR800 with a 532 nm Nd:YAG laser for excitation. Morphological and microstructural analyses were conducted using a Zeiss ULTRA-55 field-emission scanning electron microscope (SEM).

# 3. Results and discussion

### 3.1. Phase evolution

Figure 1a,b shows the X-ray diffraction patterns of the samples synthesized at 700, 900, 1100, and 1300 °C using crystalline and amorphous silica precursors, respectively.

At 700 °C, both samples exhibit ZnO characteristic peaks observed at  $2\theta = 31.77^{\circ}$ ,  $34.43^{\circ}$ ,  $36.24^{\circ}$ ,  $47.52^{\circ}$ ,  $56.60^{\circ}$ ,  $62.85^{\circ}$ , 67.96°, and 69.07°, corresponding to the reflection planes (100), (002), (101), (102), (110), (103), (112), and (201), respectively, and correlated with the standard JCPDS card No. 36-1451. The material synthesized using crystalline silica, hereinafter referred to as the crystalline-based sample, also shows SiO<sub>2</sub> XRD peaks (JCPDS No. 33-1161) due to the crystalline nature of this precursor. In both materials no Zn<sub>2</sub>SiO<sub>4</sub> formation was detected at this temperature. At 900 °C, the material synthesized using amorphous silica, designated as the amorphous silica-derived sample, displayed  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> (JCPDS No. 37-1485) and  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> (JCPDS No. 14-0653) phases, alongside residual ZnO and silica polymorphs (quartz, cristobalite, and tridymite). In contrast, the crystalline silica-based sample exhibited only low-intensity  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> peaks, with residual ZnO and quartz. The enhanced formation of  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> in the amorphous silica-based sample can be attributed to the higher reactivity of amorphous silica, which facilitates the formation of metastable phases.



Fig. 1. XRD patterns of Zn<sub>2</sub>SiO<sub>4</sub> powders synthesized at 700, 900, 1100, and 1300 °C using (a) crystalline silica and (b) amorphous silica as precursors.



Fig. 2. Raman spectra of Zn<sub>2</sub>SiO<sub>4</sub> powders synthesized at 700, 900, 1100, and 1300 °C using (a) crystalline silica and (b) amorphous silica as precursors.

The transformation of amorphous silica to tridymite and cristobalite at 900 °C may further promote the formation of metastable  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub>, as this phase is derived from a distorted tridymite- or cristobalite-like framework, where zinc atoms partially replace silicon in the lattice, while additional zinc ions occupy interstitial positions [5]. This observation suggests that utilizing amorphous silica as the silica source for solid-state synthesis with ZnO may enhance the formation of  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> compared with the direct use of quartz. Stabilizing the metastable  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> phase could further enhance the functional versatility of the synthesized materials, enabling applications that leverage its unique properties.

At 1100 °C,  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> became the dominant phase in both samples. However, residual ZnO and quartz persisted in the crystalline silica-based sample, while the amorphous silica-based sample showed ZnO as a minor phase. Upon elevating the crystallization temperature to 1300 °C, a singlephase rhombohedral  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> structure developed in the samples from both precursor types, indicating the completion of the phase transformation. Raman spectroscopy corroborated the phase evolution observed during the XRD analysis and provided additional structural insights (Fig. 2a,b).

For the crystalline silica-based sample, the Raman spectrum at 700 °C revealed prominent peaks at 333, 381, 438, and 586 cm<sup>-1</sup>, corresponding to the  $E_1^{high} - E_2^{low}$ ,  $A_1(TO)$ ,  $E_2^{high}$ , and  $E_1(LO)$  vibrational modes of ZnO, respectively [6]. Six Raman modes associated with quartz were also observed at 131, 206, 268, 361, 464, and 803 cm<sup>-1</sup>, assigned to the E(TO + LO),  $A_1$ , E(TO + LO),  $A_1$ ,  $A_1$ , and E(LO) modes, respectively [7]. In contrast, only ZnO Raman modes were detected in the sample prepared with amorphous silica at this temperature.

At 900 °C, Raman analysis of the crystalline silica-based sample revealed the presence of both  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> peaks and a low-intensity peak at 173 cm<sup>-1</sup>, associated with  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> [8]. This observation, not detectable by XRD, demonstrates the higher sensitivity of Raman spectroscopy in detecting even small amounts of the metastable  $\beta$ -phase, highlighting its complementarity to XRD in phase analysis.



**Fig. 3.** SEM micrographs of  $Zn_2SiO_4$  powders synthesized at 700, 900, 1100, and 1300 °C using (a–d) crystalline silica and (e–h) amorphous silica as precursors.

For the amorphous silica-based sample, additional peaks appeared at 900 °C, including a weak peak at 464 cm<sup>-1</sup> attributed to residual quartz. Raman bands at 121, 170, 204, 218, 242, 311, 866, 922, and 968 cm<sup>-1</sup> were assigned to  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> [8], while a low-intensity peak at 284 cm<sup>-1</sup> was attributed to  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub>.

At 1100 °C, Raman peaks associated with ZnO diminished significantly for both samples using the two precursor types, reflecting the progression of the reaction between ZnO and silica to form Zn<sub>2</sub>SiO<sub>4</sub>. Above 1100 °C, the spectra were dominated by prominent peaks at 116, 145, 162, 175, 193, 217, 236, 284, 298, 384, 400, 552, 595, 627, 871, 908, and 947 cm<sup>-1</sup>, attributed to  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> [8]. These modes correspond to vibrations of the [SiO<sub>4</sub>]<sup>4-</sup> and [ZnO<sub>4</sub>]<sup>6-</sup> tetrahedra in the  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> structure. Notably, the intense band at 872 cm<sup>-1</sup> is associated with symmetric Si–O stretching (v<sub>1</sub>(A)) vibrations, while the peaks at 908 and 947 cm<sup>-1</sup> are attributed to asymmetric stretching vibrations (v<sub>3</sub>(F<sub>2</sub>)) [9]. At 1300 °C, only  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> peaks were observed in both precursor types, confirming the complete transformation.

The XRD and Raman analyses indicate the presence of multiple polymorphs of zinc silicate that coexist in the material synthesized at 900 and 1100 °C, underscoring the com-

plex composition and structural variation obtained by this route. The stabilization of the metastable  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> phase sheds light on its potential applications in various fields.

#### 3.2. Morphological analysis

The SEM analysis (Fig. 3) elucidates the influence of precursor selection and synthesis temperature on the morphology of  $Zn_2SiO_4$  powders.

For crystalline silica-based samples (Fig. 3a–d), notable morphological evolution was observed with increasing synthesis temperature. At 700 °C, distinct particle types were evident: smaller, whiter ZnO particles and larger, irregularly shaped SiO<sub>2</sub> particles, which were attributed to the quartz present in the precursor mixture. As the temperature increased to 900 °C and 1100 °C, the emergence of smaller, spherical Zn<sub>2</sub>SiO<sub>4</sub> particles alongside the larger irregular particles was observed. At 1300 °C, particle growth and coalescence resulted in a more uniform particle size distribution.

In contrast, amorphous silica-based samples (Fig. 3e–h) exhibited a different morphological evolution. At 700 °C, smaller ZnO particles were observed alongside spherical SiO<sub>2</sub> particles. At 900 °C, the ZnO particles were more uniformly distributed around the SiO<sub>2</sub> particles, facilitating surface reactions and the formation of small zinc silicate particles [10]. These particles subsequently grew and coalesced to form spherical  $Zn_2SiO_4$  structures. At 1100 °C, the particles exhibited increased size and uniformity, with an average diameter of approximately 1 µm, which is relatively small for particles synthesized via the solid-state method. At 1300 °C, significant sintering occurred, leading to the formation of interconnected particles with evident necking between them.

The findings highlight the importance of the nature, initial reactivity, and particle size of the silica precursor in tailoring the morphology and structural properties of the zinc silicate material. These findings contribute to our understanding of the underlying mechanisms governing  $Zn_2SiO_4$  synthesis.

#### 4. Conclusions

This work studied the influence of silica precursor type and synthesis temperature on the phase evolution and morphological characteristics of Zn<sub>2</sub>SiO<sub>4</sub> powders produced via the solid-state method. A combined approach employing XRD, Raman spectroscopy, and SEM analyses was utilized to comprehensively characterize the synthesized powders. XRD analysis revealed a temperature-dependent phase evolution. At the lower temperature of 700 °C, unreacted precursors were observed. With an increase in temperature to 900 °C, a mixedphase composition comprising  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> and  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> emerged. Raman spectroscopy detected the presence of the metastable β-Zn<sub>2</sub>SiO<sub>4</sub> phase, complementing the XRD analysis. At 1300 °C, the single-phase  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> was developed for both precursor types. Morphological SEM analysis revealed distinct particle characteristics influenced by the type of silica precursor. Crystalline silica yielded larger particles, while amorphous silica facilitated the synthesis of smaller, spherical Zn<sub>2</sub>SiO<sub>4</sub> particles with an average diameter of approximately 1 µm at 1100 °C.

These findings underscore the critical role of precursor selection and reaction conditions in tailoring the phase composition, particle size, and morphology of  $Zn_2SiO_4$  powders, which are crucial parameters for their performance in various applications, such as luminescent materials and advanced technologies.

#### Data availability statement

All research data are contained within the article and can be shared upon request from the authors.

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# Ränidioksiidi eelkäija mõju Zn<sub>2</sub>SiO<sub>4</sub>-põhise materjali sünteesile

#### Jallouli Necib, Irina Hussainova ja Rocío E. Rojas-Hernandez

Tahkefaasilise meetodi abil uuriti tsinksilikaadi (Zn<sub>2</sub>SiO<sub>4</sub>) pulbrite sünteesi, kasutades amorfseid ja kristalseid ränidioksiidi eelkäijaid. Töö keskendus reaktsioonitemperatuuri (700–1300 °C) mõjule faasimuutustele ja mikrostruktuurilistele muutustele. Läbiviidud põhjalik analüüs hõlmas röntgendifraktsiooni, Ramani spektroskoopiat ja skaneerivat elektronmikroskoopiat. Röntgendifraktsioonanalüüs näitas, et madalamatel temperatuuridel esinesid reageerimata eelkäijad, keskmistel temperatuuridel tekkis segafaasiline koostis ( $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub> ja  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub>) ning 1300 °C juures moodustus ühefaasiline  $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub>. Ramani spektroskoopia tuvastas metastabiilse  $\beta$ -Zn<sub>2</sub>SiO<sub>4</sub> faasi olemasolu. Skaneeriva elektronmikroskoopia abil tehtud morfoloogiline analüüs näitas, et eelkäijate tüüp ja reaktsioonitingimused mängivad olulist rolli osakeste omaduste kujunemisel: kristalne ränidioksiid andis suuremad ja ühtlasemad osakesed, samas kui amorfne ränidioksiid soodustas ligikaudu 1 µm läbimõõduga sfääriliste Zn<sub>2</sub>SiO<sub>4</sub> osakeste moodustumist. Tulemused on olulised Zn<sub>2</sub>SiO<sub>4</sub>-põhise keraamika omaduste kohandamiseks, et seda saaks kasutada kõrgtehnoloogilistes rakendustes optoelektroonikas ja luminestsentstehnoloogiates.