

Phase evolution in polymer derived silicon carbonitride ceramic hybrids

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Abstract:

Polymer-derived ceramics (PDCs) like SiCN, SiBCN poses excellent creep and oxidation resistance. Their unique shaping advantage (due to liquid precursors) and nanostructure make them suitable for coating application, including TBCs and EBCs. SiC based coatings and composites, though perform well at high temperatures, usually disintegrate in atmosphere containing moisture. Polymer derived Si-ceramics are probable materials for applications as bond coats in such high temperature resistant coatings.

The purpose of the present work is to explore the evolution of nanostructure in PDC materials with the introduction of transition metal ions. Molecular sources of Zr and/or Hf can affect the nanostructure during the pyrolysis induced conversion of the polymeric phase to ceramic. In the current work, Zr was incorporated into a commercially available polyvinylsilazane and pyrolyzed in an inert atmosphere at different temperatures, ranging from 1000-1400 °C. The pyrolyzed SiZrCN ceramic hybrid appeared as a single phase amorphous ceramic at 1000 °C, and exhibited phase separation of Zr into nanocrystals of t-ZrO₂ with higher pyrolysis temperature. Interestingly the nanocrystals exhibited exceptional homogeneity in size (2-6 nm) and distribution in the amorphous SiCN matrix, as confirmed by HRTEM and XRD. The retention of tetragonal phase of ZrO₂ in the ceramic matrix, even after pyrolysis at 1400 °C, provides a significant advantage for achieving enhanced toughness of the bond coat. These findings will allow the fabrication of a bond coat material with better toughness, oxidation resistant, hot strength, and tailorable thermal expansion coefficient to match between SiC and other top-coat oxides.

(Keywords: *PDC; Silicon Carbonitride; ZrO₂; EBC; HRTEM*)



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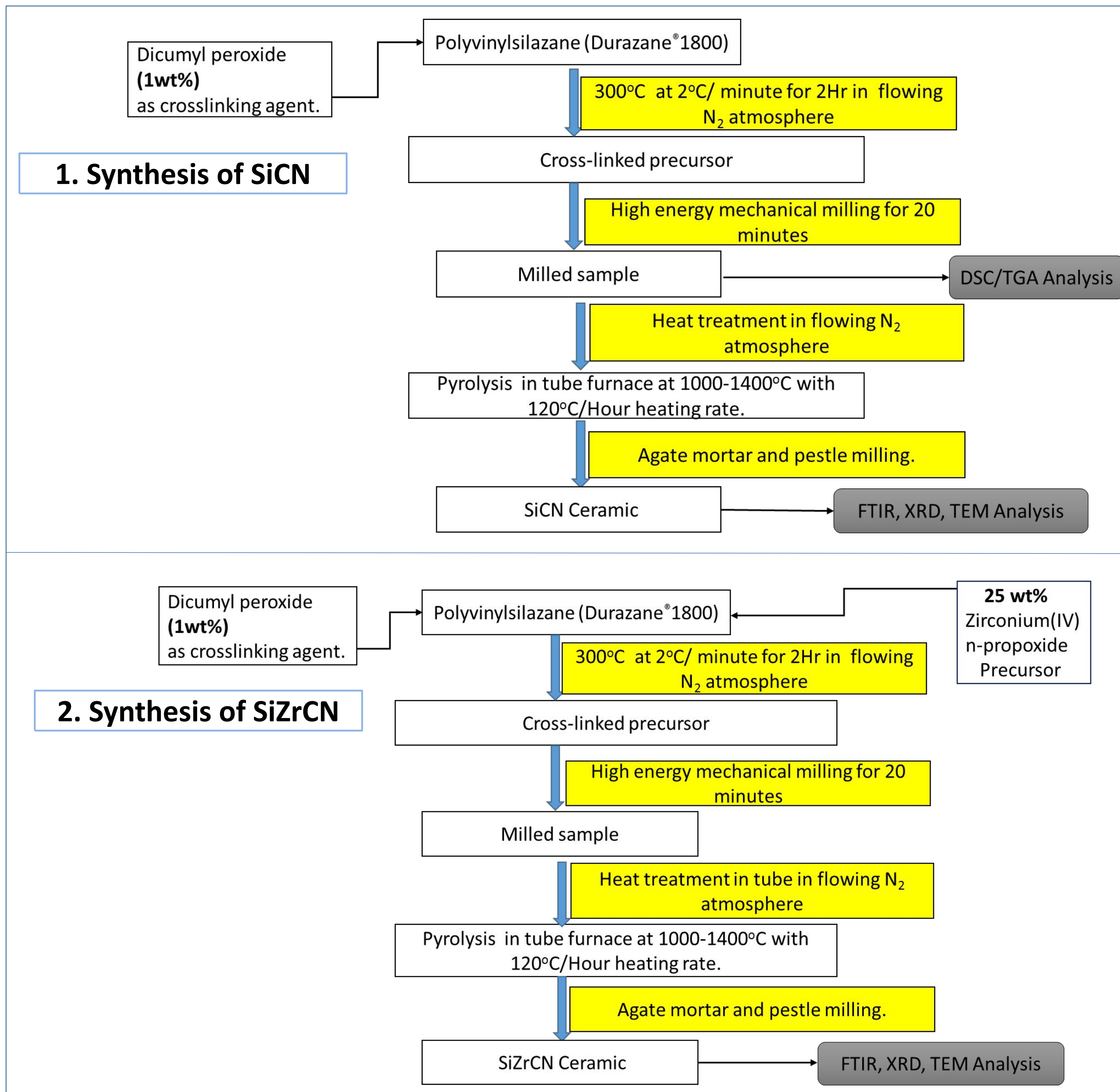
Abstract

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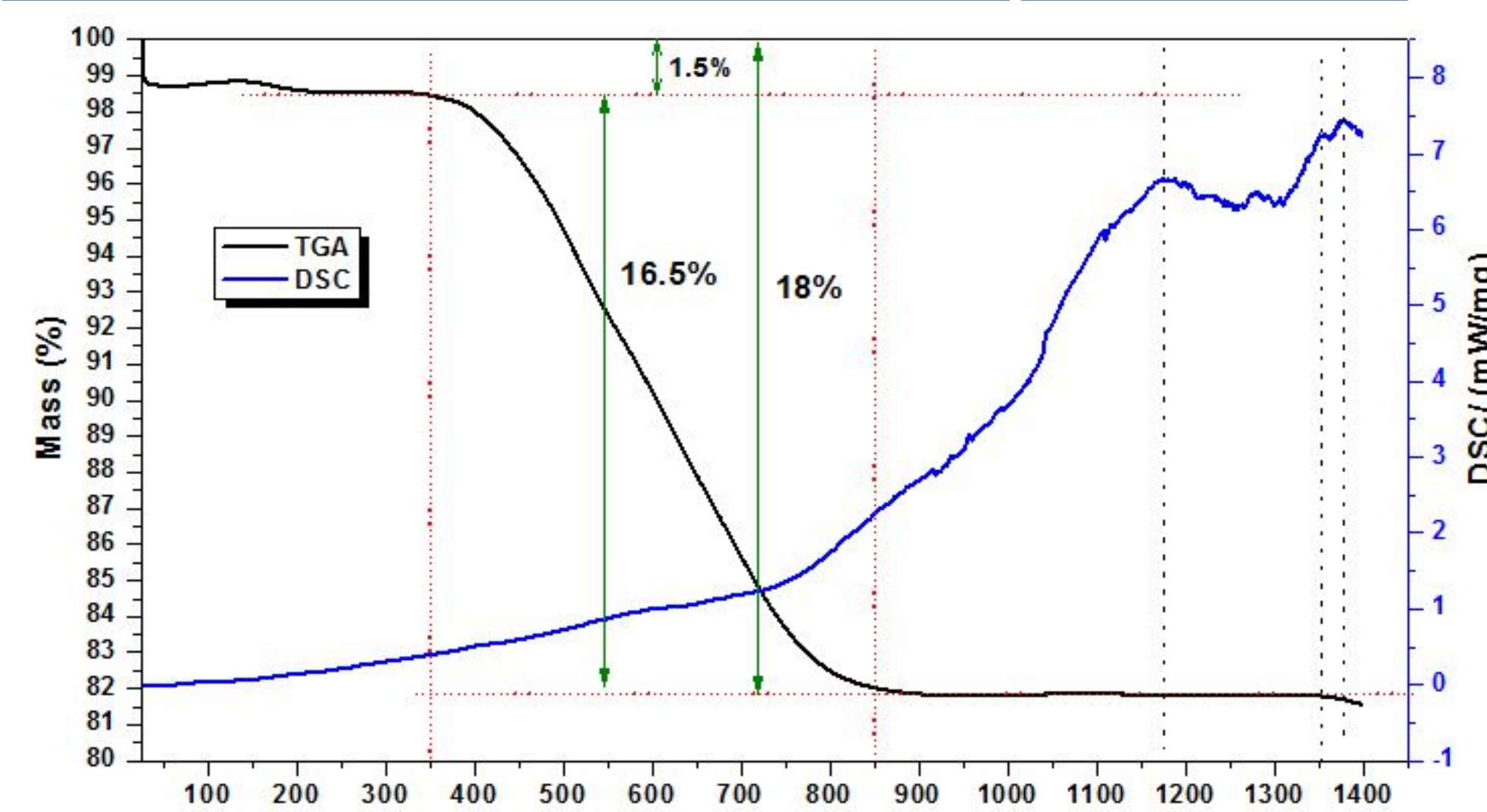
Introduction

Polymer derived ceramics (PDCs) are a novel class of complex nanostructured ceramics, which can be produced in an inert or reactive atmosphere upon cross-linking and controlled pyrolysis of suitable molecular precursors. Precursor-derived covalent ceramics have been gaining attention for their excellent thermo-mechanical properties, crystallization, or phase separation as well as resistance in oxidative and corrosive environments up to 1500°C and higher. Recent investigations have shown that in some special cases, namely in boron-containing SiCN ceramics, the high-temperature stability in terms of decomposition can reach 2200°C.

Methods and Materials

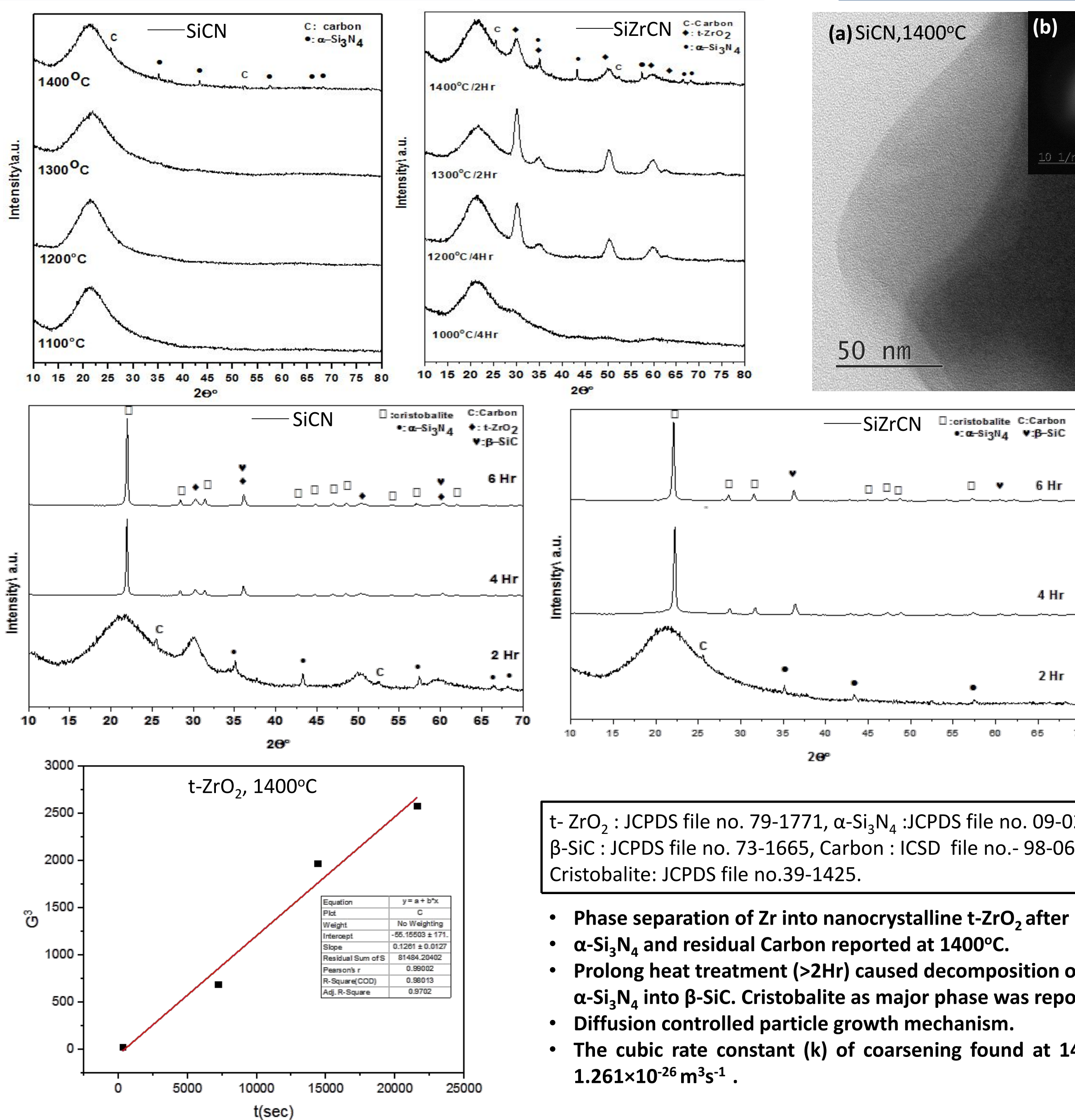


DSC-TGA Analysis



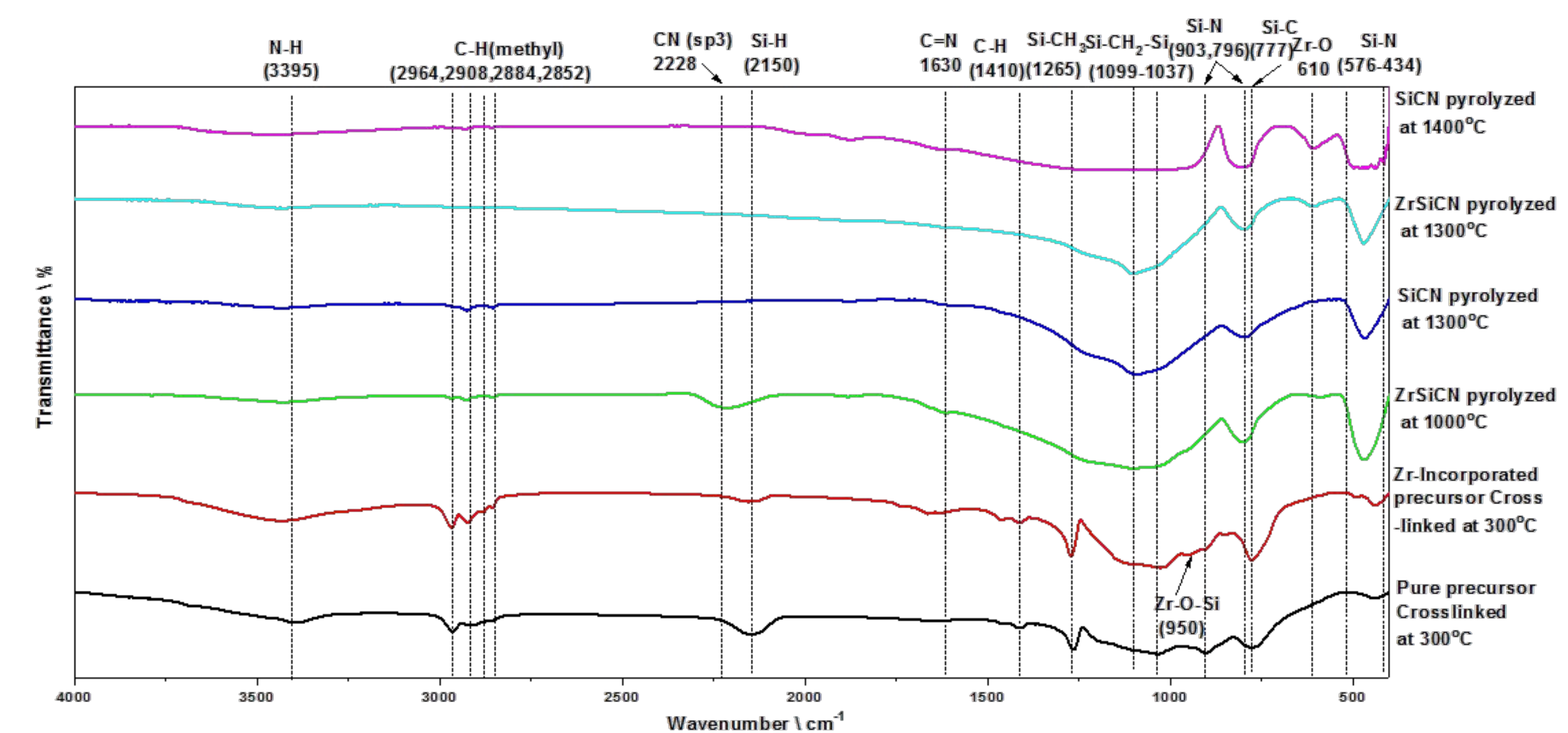
➤ Ceramic yield = 82%.

XRD Analysis

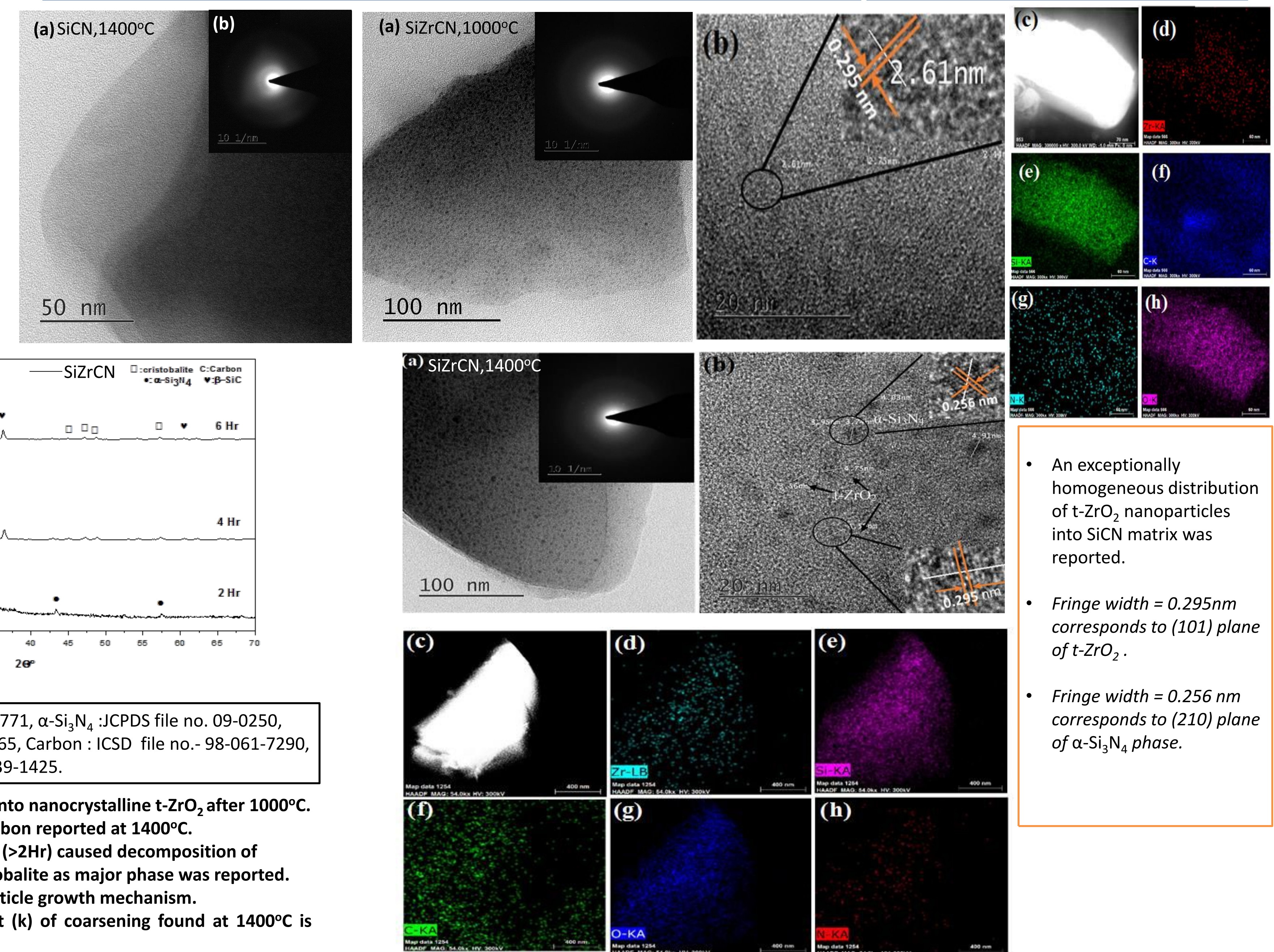


Results

FTIR Analysis



Microstructure Analysis



- An exceptionally homogeneous distribution of t-ZrO₂ nanoparticles into SiCN matrix was reported.
- Fringe width = 0.295nm corresponds to (101) plane of t-ZrO₂.
- Fringe width = 0.256 nm corresponds to (210) plane of α-Si₃N₄ phase.

Summary

In the current work, Zr was incorporated into Si-C-N(O) system successfully. The pyrolyzed SiZrCN ceramic hybrid appeared as a single phase amorphous ceramic at 1000°C, and exhibited phase separation of Zr into nanocrystals of t-ZrO₂ after 1000°C. Interestingly the nanocrystals exhibited exceptional homogeneity which is in size (2-9 nm) and distribution in the amorphous SiCN matrix, as confirmed by HRTEM and HAAD analysis. The SiCN and SiZrCN samples remain predominantly amorphous up to heat-treatment at 1400°C and therefore are stable against crystallization within this temperature range. Small amount of α-Si₃N₄ and residual carbon is detected locally. This indicated that the crystallization of SiCN and SiZrCN ceramics starts at around 1400°C. Prolonged heat treatment led to the cristobalite and β-SiC formation. The retention of tetragonal phase of ZrO₂ in the ceramic matrix, even at pyrolysis at 1400°C, provides a significant advantage for achieving coat application. The crystal size of t-ZrO₂ at 1400°C for various dwelling times was calculated and cubic grain growth rate constant (k) value for hybrid SiZrCN ceramic was found around 1.261×10⁻²⁶ m³s⁻¹.