



# **PHYSICAL CHEMISTRY 2006**

## *Proceedings*

*of the 8<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry*

September 26-29,  
Belgrade, Serbia

ISBN 86-82139-26-X  
Title: Physical Chemistry 2006. (Proceedings)  
Editors Prof. dr A. Antić-Jovanović  
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia  
Publisher: Society of Physical Chemists of Serbia  
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia  
Printed by: "Jovan" Printing and Published Comp;  
250 Copies; Number of Pages: x + 442; Format B5;  
Printing finished in September 2006.  
Text and Layout: Aleksandar Nikolić  
*250 – copy printing*

## PHASE EVOLUTION OF $\text{Si}_3\text{N}_4$ WITH Mg-EXCHANGED ZEOLITE ADDITIVE

M. Pošarac<sup>1</sup>, S. Bošković<sup>1</sup>, A. Devečerski<sup>1</sup>, T. Husović<sup>2</sup> and B. Matović<sup>1</sup>

<sup>1</sup>INN Vinča, Material Science Lab. 11001 Belgrade

<sup>2</sup>TMF, Belgrade

### Abstract

This paper deals with the chemical reactions and phase evolution during pressureless sintering of  $\text{Si}_3\text{N}_4$  with Mg-exchanged zeolite as sintering additive. The XRD data show that the first MgO-rich liquid forms at as low as 1250 °C, which as a consequence results in a significant reduction of sintering temperature. At 1300 °C the  $\beta$ - $\text{Si}_3\text{N}_4$  phase had disappeared indicating its dissolution into the liquid phase. At 1500 °C the secondary phase had been completely converted into a glassy phase, however, no phase transformation from  $\alpha$ - $\text{Si}_3\text{N}_4$  to  $\beta$ - $\text{Si}_3\text{N}_4$  had taken place. Thus the composition of this material consists of  $\alpha$ - $\text{Si}_3\text{N}_4$  embedded in magnesium silicon oxynitride glassy phase.

### Introduction

Since silicon nitride is a covalently bonded solid compound. The self-diffusivities of Si and N in pure  $\text{Si}_3\text{N}_4$  are very low [1]. Therefore it cannot be sintered to full density without additives that form liquid phase upon firing [2]. Various types of sintering additives have been used which react with the adherent silica on the powder surface of  $\text{Si}_3\text{N}_4$  and form a melt and thus promote liquid phase sintering [3]. The liquid acts as a medium for mass transport during densification. Thus, liquid-phase sintering is the only method applied for densification of  $\text{Si}_3\text{N}_4$  ceramics. Magnesium aluminosilicate is known to melt at relatively low temperatures and is, in addition a low cost material. Moreover,  $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$  (Mg-Z) glasses can be crystallized easily [4] being a base for the development of good mechanical properties.

Mg-Z can be prepared from different sources, but the synthesis route starting from ion-exchanged zeolites offers several advantages [5]. This route represents a low-cost method that leads to formation of an amorphous phase with high chemical reactivity compared to crystalline phases. Ion-exchanged zeolites (Ba- and Li-zeolite) have been the only used additives for  $\text{Si}_3\text{N}_4$  composite materials [6, 7], so far. No study has yet been performed by using Mg-exchanged zeolite as sintering additive for pressureless sintering of  $\text{Si}_3\text{N}_4$ , although some good mechanical properties may be expected in the compositions containing Mg ions.

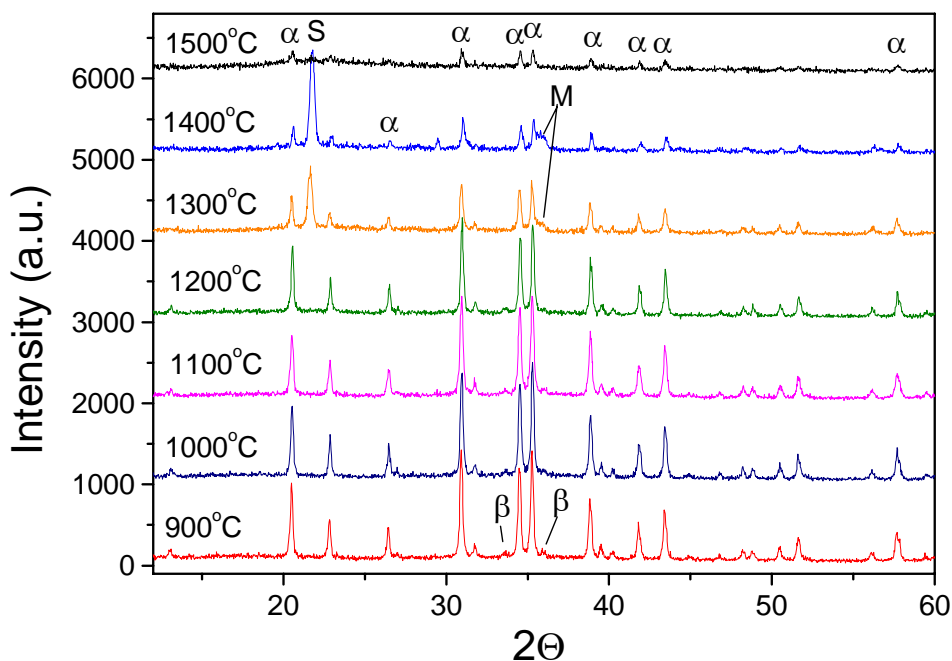
### Experimental

The starting powders were commercial  $\text{Si}_3\text{N}_4$  (UBE) and homemade Mg-exchanged zeolite (Mg-Z) powder. The Mg-exchanged zeolite was produced by ion exchange using water solution of  $\text{MgCl}_2$ . The procedure was repeated several times to ensure

complete substitution of Mg for Na in synthetic LTA-zeolite. It was found that Mg-Z powder become XRD amorphous after heat treatment at 850 °C.  $\text{Si}_3\text{N}_4$  powder with 10 wt% of amorphous Mg-Z powder was prepared by vibro milling in the presence of alcohol. Green pellets were obtained by applying cold uniaxial pressing under 100 MPa. Sintering was accomplished in a graphite-heated furnace under 0.1 MPa nitrogen atmospheres, in the temperature range from 900° to 1500 °C, with a heating rate of 100°C/min. The phase analysis of the quenched samples was performed by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation.

## Results and Discussion

The phase evolution of samples with 10 wt% of Mg-Z additive after heat treatments at temperatures between 900° and 1500 °C for 5 min is shown in Fig. 1. The main crystalline phase is  $\alpha\text{-Si}_3\text{N}_4$  for all stages of annealing. At 900 °C the initial Mg-Z sintering additive is present in an amorphous state due to collapse of Mg-zeolite structure at about 850 °C. At 1300 °C the  $\beta\text{-Si}_3\text{N}_4$  has completely disappeared indicating its dissolution into the liquid phase. Also, the presence of a new phase ( $\text{SiO}_2$ ) is associated with excess silica, which had crystallized from the liquid during cooling.



**Fig. 1.** Phase evolution during heating of mixture ( $\text{Si}_3\text{N}_4/\text{Mg-Z}$ ) at different temperature for 5 min of soaking time.  
( $\alpha\text{-Si}_3\text{N}_3$ ,  $\beta\text{-Si}_3\text{N}_3$ , S- $\text{SiO}_2$ , M-Mg-Al-Si-N-O).

Thus, the appearance of the liquid in the sample starts between 1200° and 1300 °C. According to the phase diagram the lowest eutectic temperature in the system MgO-

$\text{Al}_2\text{O}_3\text{-SiO}_2$  is 1345 °C [8], however, the overall liquid forming temperature is lower than the nominal eutectic temperature because of the present nitrogen in the liquid phase. This confirms that Mg-Z acts as a very good flux and a solvent for  $\text{Si}_3\text{N}_4$  which is also a prerequisite for a good sintering additive.

At 1300 °C, XRD pattern shows remarkable broadening and decrease of intensity of the diffraction lines especially in the region around 35–36° 2 $\theta$  which can be explained by the dissolution of  $\alpha\text{-Si}_3\text{N}_3$  in the liquid phase based on Mg-Z composition. Thus, resulting liquid belongs to Mg-Al-Si-N-O system. The result also indicates that nucleation and crystallization of this liquid takes place in the temperature region at the onset of liquid formation. However, the secondary phase starts to re dissolve into the liquid as the temperature exceeds 1400 °C. Therefore, the total liquid content increases substantially and at 1500 °C, which upon cooling formed amorphous glassy phase. At this temperature the crystalline  $\alpha\text{-Si}_3\text{N}_4$  phase, traces of silica as well as, oxynitride glassy phase are the only present phases.

Having in mind that  $\alpha\text{-Si}_3\text{N}_4$  has a very high hardness as does magnesium silicon oxynitride glassy phase [2], the final ceramics might have promising mechanical properties. in spite of the low sintering temperature.

## Conclusion

On the basis of the experimental results, it can be concluded that that Mg-exchanged zeolite acts as a very good solvent for  $\text{Si}_3\text{N}_4$  resulting in silicon oxynitride glassy phase. Composition of material sintered at 1500 °C has potential for enhanced hardness.

## Acknowledgement

We acknowledge the support of the project No. 142016 by the MSEP of Serbia.

## Reference

- [1] F. Riley, *J. Am. Ceram. Soc.*, 2000, **83**, 245.
- [2] G. Petzow and M. Herrmann, in *Structure and Bonding*, Springer-Verlag, Berlin, 2002, **102**, 51.
- [3] G. Ziegler, J. Heinrich, G. Wötting, *J. Mater. Sci.*, 1987, **22**, 3041.
- [4] Z. Panek, *J. Mater. Sci.*, 1994, **29**, 5383.
- [5] V. Dondur, R. Dimitrijevic, *J. Solid State Chem.*, 1986, **63**, 46.
- [6] S. Boskovic, D. Kosanovic, V. Dondur, R. Dimitrijevic, *Ceram. Int.*, 2000, **26**, 33.
- [7] B. Matovic, G. Rixecker, F. Aldinger, *Proceedings 10th International Ceramics Congress, Firenca (2002)* 183.
- [8] M. Keith, J. Schairer, *J. Geol.*, 1952, **60**, 182.