

Introduction

Oxynitride glasses have attracted interest since the late 70's, when it was observed that an incorporation of nitrogen into silicate glasses causes profound alterations of mechanical properties, such as strength, toughness, elastic modulus, and hardness. It is furthermore found that upon introduction of nitrogen, the viscosity and tendency to devitrification decreases and that the thermal expansion coefficient decreases. The aim of the present work has been to develop synthesis techniques in order to increase the nitrogen content in Ca-Si oxynitride glasses. Obtained glasses in the Ca-Si-O-N system contain nitrogen contents up to 55 e/o.

Glass Formation:

The glass synthesis route involves reacting Ca metal with SiO₂ and Si₃N₄ in nitrogen atmosphere. As an example, a mixture of 0.40 g Ca metal, 0.30 g SiO₂, and 0.30 g Si₃N₄ was carefully ground inside an Ar-filled glove box. The mixture was pressed into a pellet and inserted into a Nb crucible which was sealed with Parafilm, in order to avoid oxidation of the Ca metal upon transfer to a graphite furnace, or alternatively a radio frequency furnace. The sample was heated to 1700°C in 2 hours, kept at this temperature for another two hours, and then cooled by lowering the sample to a cooler part of the furnace. Guinier-Hägg films were used to ascertain the presence or absence of any crystalline phases in the glass matrix. The cation compositions of the glasses were determined by energy dispersive X-ray (EDX) micro-analysis in a scanning electron microscope and the oxygen and nitrogen contents by combustion analysis.

A new crystalline phase was also obtained by crystallization of a glass phase with the nominal composition of Ca₉Si_{10.5}O₉N₁₄. The same crystalline phase could later be grown as larger single crystals by slow cooling of the melt. The crystal structure of this phase was determined and refined using single crystal XRD.

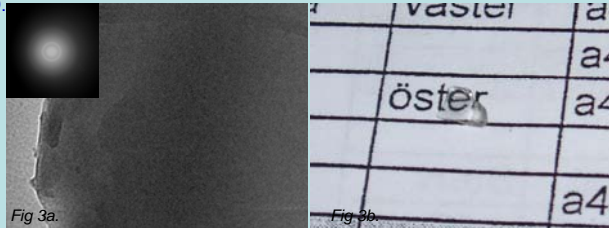


Fig 3a. A high-resolution electron microscopy image with the corresponding electron diffraction pattern (inset) of the nominal composition Ca₉Si_{10.5}O₉N₁₄. Fig 3b. shows the appearance of the glass.

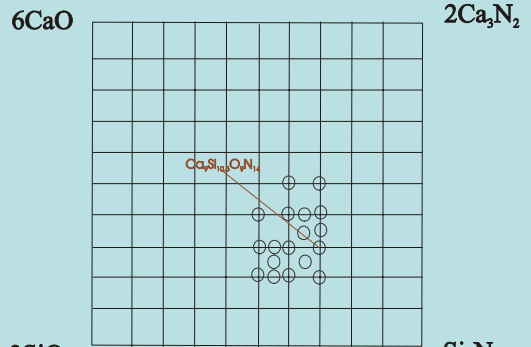


Fig 1. Nominal composition of nitrogen rich glasses achieved in the Ca-Si-O-N system, illustrated by circles.



Fig 2. Radio frequency furnace used for the synthesis .

A new crystalline phase

Single crystals of an oxynitrido-silicate phase with ideal composition Ca₃Si₂O₄N₂ were obtained by crystallizing a glass with nominal composition Ca₉Si_{10.5}O₉N₁₄. The crystal structure was determined using single crystal diffraction data, recorded using MoK α radiation and a CCD camera detector. The phase crystallizes in space group Pa3 and has an unit cell parameter of a = 15.11 Å. The structure contains Si₁₂O₂₄N₁₂ rings of 12 Si(O/N)₄ tetrahedra. There are 4 such rings in the unit cell, centred at (1/2,0,0), (0,1/2,0), (0,0,1/2) and (1/2,1/2,1/2), which are held together by Ca²⁺ ions. A preliminary structural model, yielding RF = 4.1% for all 1986 unique reflections, includes disorder and vacancies at several Ca atom sites and accords with a real composition of Ca_{2.89}Si₂O_{4.22}N_{1.78}. The structure is similar to those of Ca₂Al₂O₆ and (Na_{8/3}Ca_{2/3})Si₂O₆, which can both be described as intricate superstructures of ABO₃ perovskite. However, whereas the latter structures contain rings of 6 tetrahedra, the structure of Ca₃Si₂O₄N₂ contains rings of 12 tetrahedra.

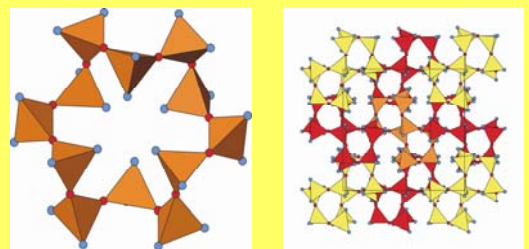


Fig 4. The oxynitrido-silicates network is built up by 12 ring units.

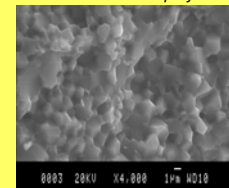


Fig 5. SEM micrograph of an oxynitrido-silicate phase with the composition of Ca₃Si₂O₄N₂.

Concluding remarks

Glass forming region in Ca-Si-O-N system is much larger than usually obtained in the oxynitride glass systems. Either by crystallization of the glass in the Ca-Si-O-N system or by slow cooling of the melt, a new crystalline phase was obtained.

References

- [1] Abbas S.Hakeem, Rachel Dauce, Ekaterina Leonova, Matthias Eden, Zhijian Shen, Jekabs Grins and Saeid Esmailzadeh. Adv.Mater.2005, 17, 2214-2216.
- [2] Mondal.P, Jeffery.J.W. Acta Crystallogr.,Sect B 1975, B31, 689.
- [3]Stuart Hampshire. Journal of Non-Crystalline Solids 316 (2003) 64-73.