

## CRYSTALLIZATION STUDY OF A BIOGLASS™ BY TEM

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In the early '70s, L. L. Hench et al. discovered a Bioglass™ from an  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5$  glass system that underwent chemical bonding to bone [1]. However, its poor mechanical properties inhibit its use in load bearing applications. On the other hand, if this glass is subjected to a controlled heat treatment, fine crystals will precipitate from the glass matrix, enhancing its mechanical properties. Most glasses contain small quantities of dissolved water and this water has long been known to affect the kinetics of phase transformations in glass-forming systems, increasing the nucleation and growth rates of crystals [2].

At first, we were concerned with the effect of  $\text{OH}^-$  as a potential nucleating agent of a Bioglass™. Batches containing  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5$  were melted under normal, wet air and vacuum atmospheres in order to obtain glasses with different contents of residual hydroxyl. The different contents of water were confirmed by IR spectra. The glass melted under vacuum (47.5  $\text{SiO}_2$  - 23.3  $\text{Na}_2\text{O}$  - 23.3  $\text{CaO}$  - 6  $\text{P}_2\text{O}_5$  wt %, in a Pt crucible at  $1300^\circ$  for 1h), showed the smallest amount of  $\text{OH}^-$  as predicted. However, contrary to our expectation, after heat treatment it showed the largest density of crystals, suggesting that nuclei were formed on the cooling path from melting to glass transition. Being so, the aim of the present study was to determine the presence of nuclei in the glass melted under vacuum and to identify them.

Transmission electron microscopy (TEM) associated with selected area electron diffraction (SAD) was used to identify those nuclei. To prepare microscopy specimens, a small piece of glass was crushed into a powder, which was then ultrasonically dispersed in pure ethyl alcohol. Few drops from the top portion of the liquid were placed on a carbon-coated 200 mesh copper grid. Finally, ethyl alcohol evaporated, leaving behind the fines particles of glass powder on the grid surface. TEM analyses were carried out at 120 kV using a Philips EM-420T microscope at the Materials Research Center at Lehigh University – USA. The electron diffraction patterns were indexed according to the method described by P. Goodhew [3], using the software CaRIne v3.0 [4].

Figures 1 and 2 show TEM micrographs and the related electron diffraction patterns of crystals observed in the glass melted under vacuum without heat treatment, confirming that the nuclei were formed during cooling. The crystals were indexed as Combeite:  $\text{Na}_4\text{Ca}_4\text{Si}_8\text{O}_{18}$  (R-3m - trigonal).

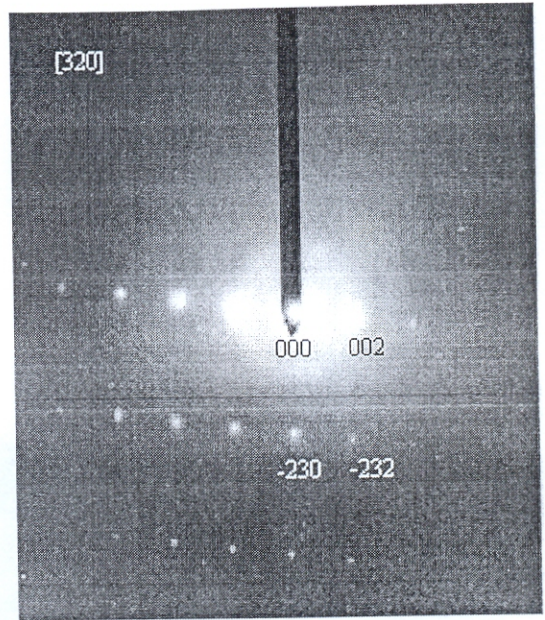
### REFERENCES

1. L. L. Hench, T. K. Greelee, R.J. Slinger and W.C. Allen, J. Biomed. Mater. Res. Symp. 2 (1971) 117.
2. C.J.R. Gonzalez-Oliver, P.S. Johnson and P.F. James, J. Mat. Science 14 (1979) 1159-69.
3. P. Goodhew – “*Electron Diffraction*”, [www.matter.org.uk/diffraction/electron/](http://www.matter.org.uk/diffraction/electron/)
4. CaRIne Crystallography Software version 3.0 (1996) France.





(a)

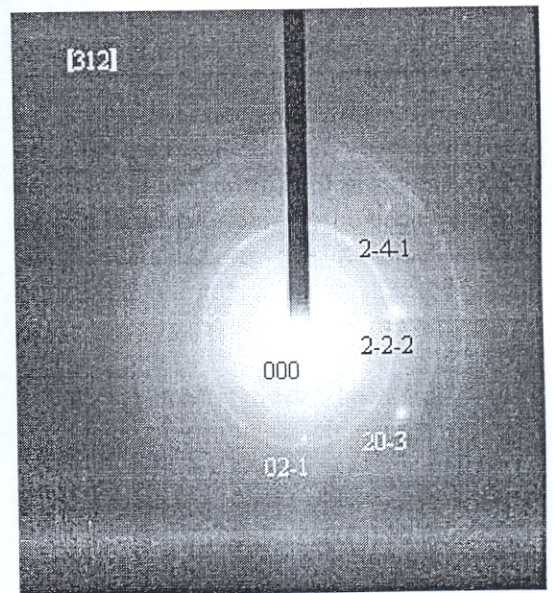


(b)

**Figure 1.** Electron micrograph showing a combeite crystal (a) and the corresponding electron diffraction pattern (b). Indexed as Combeite trigonal [320].



(a)



(b)

**Figure 2.** Electron micrograph showing a combeite crystal (a) and the corresponding electron diffraction pattern (b). Indexed as Combeite trigonal [312].