

in the molar volume. These increases are explained by a greater cross-linking of the vitreous network since the trivalent nitrogen substitutes the divalent oxygen. Indeed, when a nitrogen atom, bonded to three silicon atoms, replaces the oxygen atom, bonded to two silicon atoms, the structure of the glasses is then reinforced. The density measurements were carried out using the helium pycnometry method on these glasses. The results show that the density increases strongly with the nitrogen ratio. Indeed, when a nitrogen atom, bonded to three silicon atoms, replaces the oxygen atom, bonded to two silicon atoms, the structure of the glasses is then reinforced. Thus, the molar volume decreases due to the increase in the cross-link density of the network.

### 3.4.6 Mechanical properties Si-Ca-Na-O-N and Si-Ca-Na-O-F-N (Bachar et al., 2013b)

According to the analysis of Fig. 3.16, the addition of nitrogen involves an increase of the hardness, of the Young modulus, and of fracture resistance for all the glasses due to the formation of the Si-N bonds in the form of  $[\text{SiO}_3\text{N}]$  and  $[\text{SiO}_2\text{N}_2]$  species confirmed by  $^{29}\text{Si}$  NMR spectroscopy.

Indeed, Young's modulus evolves from  $E=64$  GPa for GN0 to  $E=85.2$  GPa for GN4, and from  $E=64$  GPa for GFN0 to  $E=92.5$  GPa for GFN4.

Concerning the hardness, the value of Hv also increases with the nitrogen rate since it evolves from 5.3 GPa for the GN0 glass to 6.2 GPa for GN4 and from 5.3 GPa for GFN0 to 6.7 GPa for GFN4. Hv increases more rapidly as nitrogen content increases, because a power law can model the curve.

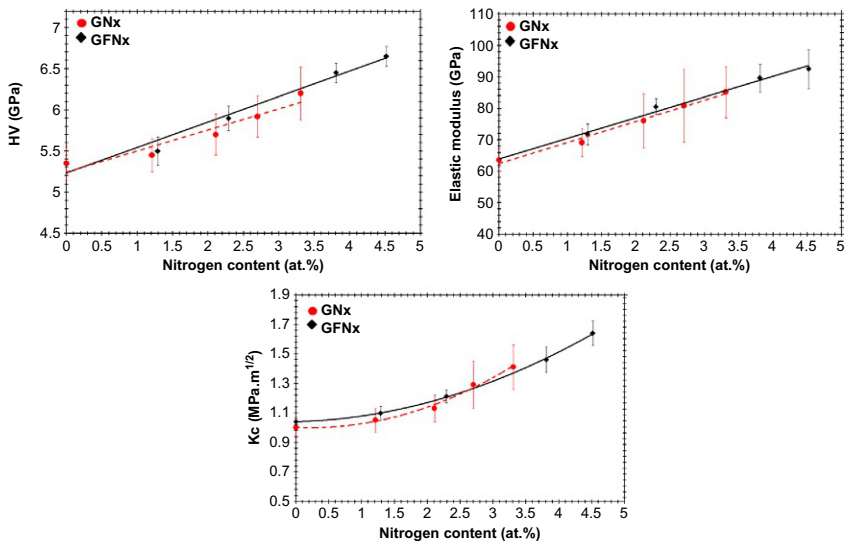


FIG. 3.16 Effect of nitrogen doping on (A) Vicker's hardness (HV), (B) elastic modulus (measured by Knoop indentation), and (C) Vicker's Indentation Fracture (VIF) resistance (Kc) for GNx and GFNx glasses.