

CHAPTER 8

SUMMARY AND FUTURE SCOPE OF WORK

In this chapter the salient features of the present investigations are summarized. The structural aspects of melt-derived bioactive glass and their correlation with ion transport properties are discussed. The structural, textural and morphological aspects and their correlation with in-vitro bioactivity for sol-gel prepared mesoporous bioactive glasses in the light of current experimental results are discussed. The scope of future work in this area is discussed.

8.1 SUMMARY

The thesis work is focused on two aspects of bioactive glasses

First, to provide new insights onto the ion transport properties in bioactive glasses, i.e. the effect of local atomic structure on the ion transport mechanism.

Secondly, we have investigated the effect of composition and texture on the in-vitro bioactivity of sol-gel derived mesoporous bioactive glasses.

8.1.1 Melt-derived Bioactive Glasses

Temperature-dependent dc conductivity of alkali ion conducting bioactive and bioinert silicate glasses shows non-Arrhenius behavior below their glass transition temperature. The observed non-Arrhenius behavior is completely reproducible in nature even after prolonged annealing close to the glass transition temperature of the respective glass sample. These results are manifestations of local structural changes of the network formers with temperature and give rise to different local environments into which the alkali ion hop, revealed by in situ high-temperature Raman spectroscopy.

In order to remove the observed non-Arrhenius behavior, an effort has been made by tuning the chemical composition, i.e. with constant alkali and by changing the alkaline-earth content by silica. The present study clearly demonstrates that the prevalence of fewer Na-Na and Na-Ca pairs and provide the strong evidence of

interaction among the network-modifying cations. The preference for dissimilar pair plays an important role in the strong compositional dependence of the transport properties of these glasses, including Na^+ diffusivity with CaO content. We find that the measured dc conductivity of alkali-alkaline-earth ion conducting silicate glasses increase with decreasing alkaline-earth oxide content and the observed behavior is aided by the anionic units in these glasses. On the basis of available structural data, we could able to explain the composition dependence dc ionic conductivity in these glasses. The present results directly supports the impeding effect on alkaline-earth oxide ion the diffusion mechanism of alkali ion as reported in theoretical simulation studies. Furthermore, it is observed that presence heavier and much less mobile Ca^{2+} ions expected to occupy the favorable sites for Na migration and hence partially blocking alkali migration pathway.

8.1.2 Sol-gel derived Mesoporous Bioactive Glasses

A novel method to prepare mesoporous alkali-oxide containing bioactive silicate glasses has been reported. Wormhole-like bioactive mesostructured glasses with different compositions have been synthesized by acid assisted sol-gel method followed by evaporation induced self-assembly process using non-ionic block copolymer as structure directing agent.

- i. For first time, we reported, the mesostructured sodium silicate glasses with alkali oxide content and a systematic trend between textural and structural parameters has been observed. The observed composition dependent textural properties are explained on the basis of local atomic structure. The glass with less alkali oxide content shows the high surface area and smaller pore size and vice versa. The effect of textural parameters on the rate of apatite formation has been observed. The glasses with superior textural parameters i.e. high surface area showing faster formation kinetics of apatite phase.
- ii. Furthermore, we have extended the binary glass synthesis procedure to ternary and quaternary phosphorous- bearing (P-bearing) and phosphorus- free (P-free) silicate glasses and the role of phosphorus/calcium has been investigated on *in-vitro* bioactivity of these glasses. It has been observed that the P-bearing

mesoporous glasses show the rapid hydroxycarbonate apatite (HCA) crystallization than P-free mesoporous glasses independent of calcium content. The present study reveals that the presence of phosphorous jointly with calcium in the bioactive glass system significantly enhances the rate of apatite formation as well as crystallization. Additionally, presence of the sodium orthophosphate rich phase enhances the solubility when exposed to body fluid and further accelerate the kinetics of apatite formation. The influences of the chemical composition and their superior textural properties upon bioactivity are explained in terms of the unique structure of mesoporous bioactive glasses.

- iii. In mesostructured quaternary bioactive glass and glass ceramics, the influence of alkaline-earth oxide content on the glass structure followed by textural property has become more evident. The pristine glass samples exhibit a wormhole-like mesoporous structure, whereas the glass-ceramic found to be in two different crystalline phases: hydroxyapatite and wollastonite and a residual glassy phase as observed in Cerabone® A/W. It is interesting to note that this new quaternary glass compositions with minimal alkali oxide content show superior textural properties than the earlier reports on mesoporous bioactive glasses. The *in vitro* studies on these glasses reveal the role of mesostructure and local atomic structure on the hydroxycarbonate apatite (HCA) formation. On the other hand, different phases present in glass-ceramic sample inhibits or delays the kinetics of apatite formation.

8.2 SCOPE OF FUTURE WORK

- Further experimental investigations are necessary to fully understand the effect of structural peculiarities on the ion transport mechanism. For example, for drawing more quantitative comparison between exchange of various structural species and ion transport, local probes such as in situ high temperature NMR studies would be highly desirable.
- It would be great challenge to probe the different stages of hydroxycarbonate apatite (HCA) i.e. the formation of amorphous calcium phosphate on the

surface and its subsequent crystallization into HCA by conducting in-situ NMR experiments on the samples after soaking in SBF.

- It is equally important to understand the as synthesized glass structure and to correlate with the HCA formation by using the various techniques. Thus, within this proposed topic the research work, it would be emphasized towards exploring the structural roles of different nuclei by MAS and double quantum NMR techniques; the proximities of Si and P to protons will be studied through the cross-polarization based experiments, including ^1H - ^{29}Si and ^1H - ^{31}P hetero-nuclear 2D correlation spectroscopy.
- Again, it would be a great challenge in the present scenario to synthesis mesoporous multicomponent glass system with high alkali-alkaline-earth oxide content close to 45S5 glass.