SUMMARY AND CONCLUSION

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It has been mentioned in chapter 2 that macor and dicor glass-ceramics are the part of machinable glass-ceramics. Macor glass-ceramics is based on potassium fluorophlogopite mica (K\(\cdot\)Mg\(_3\)\cdot\)Al\(_3\)\cdot\)Si\(_3\)\cdot\)K\(_2\)O-F\(_2\)\(_2\)). Potassium fluorophlogopite mica forms a “house of cards” microstructure, when slowly crystallized from the parent glass in a controlled fashion. The most interesting aspect of macor glass-ceramics is that it can be machined with ordinary metal working tools to precise tolerances.

A review of existing literature relevant to the present work has been discussed in chapter 3. A critical survey of which shows that the various methods of formation of fluorophlogopite glass-ceramics, effect of various additives on the nucleation, crystal growth and ultimately the material properties.

Potassium fluorophlogopite presents an important problem - the mechanical strength is relatively poor. This has led to the development of compatible machinable glass-ceramics containing alkaline earth elements as the interlayer ions in place of potassium ions, which exhibit higher strength when compared with more conventional potassium fluorophlogopite glass-ceramics. Such materials reflect a compromise between the low strength/good machinability and high strength/moderate machinability.

In the present study, the effect of progressive substitution of potassium with barium in the potassium fluorophlogopite glass-ceramics has been investigated. For this purpose, a number of glass batches with variation in BaO content were prepared as per the procedure mentioned in Experimental (Sec. 5.1, page 53). Properly mixed batches were melted at about 1500°C to prepare a molten glass. With this molten glass rectangular slabs were fabricated in cast iron molds and subsequently annealed in an annealing furnace to remove the stresses of the glass slabs. The slabs were cut into small and thin pieces with the help of a precision cutting machine. Subsequently, the wafers like pieces were ceramised at different crystallization temperatures. Physical properties such as Density, Molar volume, Modulus of rupture, Fracture toughness,
Vicker’s hardness, Machinability etc. were examined and correlated with the respective microstructure, crystalline phase and also with the compositions.

The bulk densities of the glass-ceramics crystallized at different temperature are shown in Table 11. It can be seen from the above table that the densities increase with increasing heat treatment temperature in Ba05 and K10 samples. This increase in density may be attributed to the formation and growth of crystal phases viz. K-fluorophlogopite and Ba-fluorophlogopite in glass-ceramics systems, K10 and Ba05 respectively, whereas, in all the mixed system of glass-ceramics samples, except Ba04 containing both potassium and barium (viz. batches Ba01, Ba02 and Ba03) are somewhat different, density achieves the maximum value at 900°C, and beyond this, the density decreases with increasing heat treatment temperatures. In Ba04, the density of glass-ceramics samples, heat treated at 800-1150°C for five hours achieves the maximum value at 1100°C. Beyond this point, density decreases with increasing heat treatment temperatures. The change in density is rapid up to 900°C (Ba01, Ba02 and Ba03) and beyond this temperature density decreases drastically with increasing heat treatment temperature. The decrease in density may be associated with the partial decomposition of the initial mica phases. The other major reason for decrease in density may be due to the propagation of cracks into interlocking mica crystals accompanied by crystal growth.

The molar volumes of the samples containing different amounts of barium are shown in Table 13. With progressive addition of barium, molar volume decreases continuously and with a rapid rate. This may be due to the higher charge-density of barium ions and also due to the changes in the strength of modifier-glass structural unit interaction.

Substitution of potassium by barium results in increase hardness and glass transition temperature values. These effects are due to the replacement of \( O_{Nb} - K \) bridges by \( O_{NB} - Ba - O_{NB} \) terminations, with attendant increases in the level of association of the glass network and thus its rigidity.

From differential thermal analysis (DTA), it is observed that only one crystallization peak temperature appears in K10 and Ba05 samples, where the glass contains either potassium or barium respectively. The crystallization peaks are due to the formation of K-fluorophlogopite in K10 and Ba-fluorophlogopite in Ba05. But two crystallization peak temperatures appeared in Ba01, Ba02, Ba03, and Ba04 samples, where both potassium and barium are present in various amounts. Two crystallization peak temperatures correspond to K-fluorophlogopite and Ba-
fluorophlogopite. From calculation of Avrami exponent, first crystallization peak temperature (lower temperature) indicates that it is a case of bulk nucleation and two dimensional and second crystallization peak temperature (higher temperature) indicates that it is a case of bulk nucleation and three dimensional crystal growth for all batches of samples.

From X-ray diffraction (XRD), it is observed that K-fluorophlogopite and Ba-fluorophlogopite crystal phases grow as major phase in $K_{10}$ and $Ba_{10}$ samples respectively, whereas both the mica crystal phase appear simultaneously in $Ba_{101}$, $Ba_{102}$, $Ba_{103}$ and $Ba_{104}$ samples.

From scanning electron microscope (SEM) study, it is observed that the partial substitution of potassium by barium can lead to the formation of K-fluorophlogopite and Ba-fluorophlogopite crystal phases simultaneously, and forms interconnected “house of cards” microstructure.

In all the batches for different heat treatment temperature, the machinability parameter was calculated from Vicker’s hardness ($H_v$) values. It is clear from the results that the higher the hardness values, the lower the machinability parameter, whereas, at any particular temperature the machinability decreases with gradual increase in barium content. In all the batches for different heat treatment temperature, the fracture toughness was calculated from Vicker’s hardness ($H_v$) values. It is clear from the results that the higher the hardness values, the higher the fracture toughness. At any particular temperature the fracture toughness increases with gradual increase in barium content. Invariably in all the batches, crystallized at 1150°C, the sudden increase in hardness values may be due to the formation of other crystal phases like enstatite and barium aluminium silicate etc.

The modulus of rupture values of the samples containing different amounts of barium and ceramised at different temperatures are shown in the Table 22. It is clear from Fig.64 that the MOR values increase to a large extent on formation of the either potassium or barium, or both potassium fluorophlogopite and barium fluorophlogopite phases compared to that of original glasses. When the temperature is further increased, the modulus of rupture values gradually increase up to 1100°C. The modulus of rupture values decrease slightly beyond this temperature up to 1150°C, but the decrease is very low and sufficiently higher than those of the original glasses. The modulus of rupture of the glass-ceramics heated at 1150°C was not higher than that at 1100°C because the barium fluorophlogopite and potassium fluorophlogopite crystals grew large (~5μm), thereby probably introducing large sized critical flaws.

From the above findings it is observed that with progressive substitution of potassium by
barium, the machinability might have been reduced to some extent but the strength i.e. modulus of rupture has increased to a great extent. The MOR values ultimately got its maxima in the sample Ba_{0.5} i.e. the glass-ceramics sample containing only barium fluorophlogopite mica. Similarly, Vicker's hardness (H_v) and fracture toughness (K_{IC}) also increased progressively to their maximum values in the sample Ba_{0.5}. Moreover it can also be concluded that machinability and strength can be customized by judicious substitution of potassium by barium and also by the duration of crystallization.