PREFACE

Dental ceramics are the materials designed with the purpose of producing dental prostheses that in turn are used to replace missing or damaged dental structures. Dental ceramics mainly include porcelain, glasses, glass ceramics and highly crystalline structures and have good mechanical, physical, chemical and thermal properties. The present thesis has been divided into eight chapters.

Chapter 1: Introduction and literature review

This chapter focuses on the history of dental ceramics and their classifications and an overview of the literature on the synthesis and characterization of leucite and kalsilite and bioactive glass ceramic composites for restorative dentistry. Dental restoration has been divided in two categories; (i) Metal- ceramic restoration (MCR) and (ii) All ceramic restoration. MCR is a fixed restoration that employs a metal substructure on which a ceramic veneer is fused. A surface oxide layer lies between the metal substructure and veneer is considered as a separate component. Porcelain veneer has three layers, an opaque, dentin, enamel and a surface glaze. All ceramic restoration consists of composite of the glass and ceramic and they are processed into a complex shape using a glass shaping technology. The most outstanding advantages of metal-ceramic prostheses are their good aesthetic quality and high resistance to fracture. There is almost no wear of the porcelain occurs by abrasion and no staining along the interface between the metal and veneer.

The feldspathic porcelains are mostly preferred for metal-ceramic restoration. The compositions are based on the SiO_2-Al_2O_3-K_2O ternary system. Specifically, SiO_2 and potash feldspar ($K_2O{\bullet}Al_2O_3{\bullet}6SiO_2$) are the base for dental porcelains. Leucite ($KAlSi_2O_6$) is the most important

aspect for the development of feldspathic porcelain. The presence of leucite increases the thermal expansion coefficient of the porcelains to an extent that makes a good bonding between the porcelain and the metal substructure. Leucite content in commercial porcelain is from 6 vol% to 21 vol%. Leucite crystallizes by the heat treatment of a precursor glass containing K_2O, Al_2O_3 and SiO_2 together with other components like alkali fluxes, nucleating agents and grain growth inhibitors. A glass ceramic with high content of leucite crystals has also been prepared using solid state sintering, salt-bath, co-precipitation, sol–gel and hydrothermal synthesis processes. Though leucite glass-ceramic has been synthesized by several methods but, the synthesis of pure complete crystalline leucite powder below 900 °C has never been reported, as it is always accompanied by a large amount of glassy phase.

Kalsilite is a significant constituent in porcelain fused to metal (PFM) and ceramic restoration systems. It is used as the precursor of leucite. It has a framework of alumina silicates containing a network of tetrahedral Si and Al elements with charge balancing alkali metal ions. Kalsilite crystallizes as a meta-stable intermediate phase when synthesizing leucite. Becerroet et al. have been suggested a very simple and economical technique to synthesize the kalisilite from a precursor of kaolinite using hydrothermal synthesis route. Irma et al. has been synthesized kalsilite using sol-gel route at 750 ºC. However, there is a lack of research in the stabilization and implementation of kalsilite as PFM.

The dental porcelains are biocompatible but not bioactive and therefore incapable of interacting with the surrounding tissues. However, bioactive glasses are bioactive and interact with body fluid forms the calcium phosphate rich surfaces allows them to bond tightly to hard and soft tissues. Addition of these materials into the dental porcelains will improve their bioactivity behavior. For the last few years, research has been carried out for the development of bioactive

dental materials for a complete and effective attachment between the fixed prosthetic restorations and soft periodontal tissue. The feldspathic porcelains constituted by a glassy aluminosilicate and crystalline leucite is mostly used for MCR. Problems occur with the patient is the failure of fixed MCR due to secondary carries. This results in a plaque collection in the marginal area between the fixed tooth and restoration consequently encourages the bacterial attack, pulp irritation and the dissolution of the luting cement. A hypothetical tissue attachment on the margins of fixed tooth and restoration would eliminate the marginal gap and cement dissolution and subsequently secondary carries.

In the literature, many researcher have been reported the synthesis of bioactive glass ceramic composite material using sol-gel technique. However, there are limited literatures concerning the physicochemical properties of the wide range of dental ceramics used in the clinical practice. Microstructural analysis is also important because it provides an association among the composition, physical properties, and structural characteristics of the materials. Even less studies have focus on the biocompatibility or cytotoxicity of these prepared dental ceramics although they perform in direct contact with surrounding periodontal tissue. Furthermore no work has been reported on the synthesis of mechanochemically derived leucite and kalsilite based bioactive glass ceramic composites.

Chapter 2: Objective of the work

The present work aims to prepare new type of bioactive glass ceramic composites for veneering materials for PFM (Porcelain Fused on Metals) as these types of materials are not marketed up to now. Further, objective of research work will be to reduce the fabrication cost of dental implant by using inexpensive natural raw materials instead of organometallics types of materials. Low cost mechanochemical powder processing route will also be employed for the preparation

materials of high thermal expansion. A series of samples of the mixtures of mechanochemically derived leucite/kalsilite and LTF (low temperature frit) in different weight ratios will be prepared to optimize the thermal, mechanical and microstructural properties. To develop the bioactivity in leucite and kalsilite containing glass-ceramics, a bioactive glass will be prepared by melt and quenching method. This finely ground bioactive glass will be incorporated in the mechanochemically derived leucite and kalsilite glass-ceramics to make them bioactive veneering composites. The compositions which have optimum high thermal expansion phases and better thermal, mechanical and microstructural properties will be further investigated. Study of doping with materials having high mechanical properties such as Al_2O_3 will also be done in these bioactive glass-ceramic composites to enhance the mechanical properties without affecting the biological and thermal response. Batch compositions will be further modified to maintain the glossiness and bioactivity after addition of Al_2O_3.

The main objectives are as follows:

- To synthesize leucite/kalsilite containing glass-ceramics by mechanochemical synthesis route
- To prepare LTF (Low temperature frit) and bioactive glass by employing traditional melt and quenching method.
- To study the phase formation and crystal structure of the leucite/kalsilite containing glass-ceramics.
- To prepare the bioactive glass-ceramic composites by mixing leucite/kalsilite glass-ceramics with LTF and bioactive glass in different weight ratio. To study the mechanical and thermal expansion properties.

- To determine the concentration of ions (K^+, Na^+, Ca^{2+}) leaching of leucite and kalsilite glass-ceramic composites in different acidic agents using a flame photometer.
- To study the capability of the hydroxyapatite layer formation on bioactive glass ceramic composites and study the cytocompatibility of the composites employing cell viability, cell proliferation, and In-vitro cytotoxicity assay.
- To examine the cell morphology on the surface of the composites employing scanning electron microscope.

Chapter 3: Experimental work

This chapter deals with the experimental techniques which were used to synthesize and characterized the samples. All the leucite and kalsilite samples were synthesized using mechanochemical synthesis route. Bioactive glass and low temperature frit were prepared using traditional melt quenching methid. Bioactive glass-ceramic composites were prepared by mixing mechanochemically derived lecucite and kalsilite, bioactive glass and low temperature frit (LTF) in different weight ratios. Crystal structure and phase analysis of all the samples were studied using X-ray diffraction technique (XRD). Thermal expansion measurements were made employing a dilatometer. Flexural strength of all the samples was determined using universal testing machine. Ion leachebility from the surface of the leucite and kalsilite glass ceramics in different acidic agents has been studied using flame photometer. The capability of hydroxyapatite layer formation on the bioactive glass ceramic composites through immersion in SBF for several soaking periods was studied employing scanning electron microscope (SEM) and Fourier transform infrared spectroscopy. The cytocompatibility of the composite samples

was studied employing cell viability, cell proliferation and In-vitro cytotoxicity assay. The cell morphology on the surface of the composites was analyzed employing SEM.

Chapter 4: Results and Discussion

4.1 Mechanochemically Synthesized Leucite for Dental Veneering Glass Ceramics

The present chapter deals with the synthesis of nano crystalline leucite glass-ceramics at relatively low temperatures using mechanochemical synthesis route. Two blends in which, one containing Al_2O_3, SiO_2 and K_2CO_3 in the stoichiometric ratio of leucite and the other with same stoichiometric ratio with 2 wt% CaF_2 as an additive have been prepared. The starting mixes have been mechanochemically activated and heat treated at 900, 1000 and 1100 °C. The effects of mechanical activation and calcium fluoride addition on phase formation have been investigated using XRD. The compositions heat treated at 1000 and 1100 °C having high concentration of leucite than that of the sample heated at 900 °C. Therefore, these compositions were mixed with LTF in weight ratio of 25:75 for further characterizations. Further low temperature glass frits (LTF) based on alumino-alkalis-silica-boric oxide has been prepared using traditional melt quenching. The prepared leucite and LTF have been mixed in different proportions and characterized for their thermal expansion, flexural strength, surface morphology and flame photometer. Weibull statistical analysis has been done to interpret the flexural strength data of all the samples. Introduction of CaF_2 in leucite raw mixes suppressed the formation of kalsilite phase and promotes the crystallization of pure leucite. Coefficient of thermal expansion of the samples with the mixes of leucite nano crystalline powders and LTF nearly matched with the coping material (nickel-chrome alloy). The veneering dental glass–ceramics prepared by using

these materials may be used in various applications for making PFM crowns or bridges. Composition of these mixes can be adjusted to obtain different value of thermal expansion by varying prepared leucite content. Flexural strength of the CaF_2added leucite (MCL-C) sample is higher than that of the without CaF_2 (MCL). This is due to homogenous dispersion of leucite grains within the glassy matrix leads to its enhanced mechanical strength. Weibull modulus and nominal strength of the MCL-C samples are higher than that of the MCL samples. A high value of Weibull modulus confirms the reliability of these samples.

Weight loss of all the leucite samples is less in the acetic acid than that in the pine apple juice. Weight loss decreases with increasing the content of the nano crystalline leucite in the LTF matrix. This is due to homogeneous distribution of leucite throughout the matrix. MCL-C samples have less weight loss than that of the MCL samples. It is also in conformity with the results of flexural strength data that MCL-C samples have high flexural strength than the MCL samples.

4.2 Mechanochemical Synthesis of Kalsilite: Implementation as Dental Porcelain with Low Temperature Frit

This chapter describes the synthesis of nano crystalline kalsilite using mechanochemical synthesis route via high-energy ball milling of the mixture of Al_2O_3, SiO_2 and K_2CO_3 with stoichiometric ratio of (1:1:1). 2 wt% of MgF_2 has been added as an additive which incorporated into kalsilite precursors. This assessed the act of phase kinetics. The ground powders have been heat treated at different temperatures and characterized via powder X-ray diffraction technique (XRD). After heating at 1000 °C for 1 h, kalsilite sample [with (MKL-M) & without (MKL) MgF_2] has been mixed with different weight ratio of LTF (20:80, 25:75 and 30:70) and

characterized via CTE, flexural strength, apparent porosity (AP), bulk density (BD), scanning electron microscope and flame photometer.

All the MKL and MKL-M samples are suitable for PFM as its CTE value in the range 14.0 to 14.8 × 10^{-6} /°C is close to the standard CTE of nickel-chrome alloy (13.9 × 10^{-6} °C).Flexural strength increases with increasing the microfine kalsilite in the LTF matrix. Homogenous dispersion of microfine kalsilite grains within the glassy matrix leads to enhance the mechanical strength. MKL-M samples have higher flexural strength than that of the MKL samples.BD increases with increasing the content of kalsilite followed by a continuous decrease of AP. The micrographs show the homogenous distribution of hexagonal kalsilite throughout LTF matrix. There is no visible micro-crack appears due to the phase transformation. Therefore, this material may be a potential candidate for application in porcelain fused to metal.

Weight loss of all the samples is less in the acetic acid than that in the pine apple juice. Weight loss decreases with increasing the content of the fine kalsilite in the LTF matrix. This is due to homogeneous distribution of kalsilite throughout the matrix. MKL-M samples have less weight loss than that of the MKL samples.Therefore, it is concluded that the acidic environment had an effect on the surface and structural of the dental ceramic.

4.3 Mechanochemically synthesized leucite/kalsilite based bioactive glass ceramic composite for dental veneering

In this chapter, the work has been carried out to introduce a successful process for the synthesis of bioactive leucite and kalsilite based glass ceramic composite materials for dental applications, especially for PFM used for crown, bridges etc. Composites were prepared by mixing 40 wt% of mechanochemically derived leucite (heat treated at 1100 °C) and kalsilite (heat treated at 1000

°C), 45 wt% bioglass and 15 wt% LTF powder. Compositions were chosen on the basis of various optimizations such as; thermal expansion, glossiness of the surface and translucency.

The formation of calcium silicate ($2CaO.SiO_2$) and wollastonite ($CaO.SiO_2$) crystalline phases (after heat treatment) has been confirmed in the leucite based composites using XRD. These phases have high strength consequently improves the flexural strength of the leucite based composites.

In the kalsilite based composites, a sodium orthosilicate ($2Na_2O.SiO_2$) crystalline phase has been observed after heat treatment. This phase has less strength as compared to that of calcium silicate and wollastonite crystalline phases. This results in the lower flexural strength of the kalsilite based composites than that of the leucite based samples. Coefficient of thermal expansion (CTE) of all the samples is nearly same as the commercial dentine and nickel chrome alloy and the substrate made of VITA VMK95 opaque 1M2. Values of CTE for both the substrate and the composite are very close so that the applied heat treatment will not lead to peel off the coating.

The formation of hydroxyapatite layer on the whole surface of the composites has been confirmed using SEM and FTIR after immersion in SBF for 0, 7 and 14 days. Leucite and kalsiliteglass–ceramic composites are observed to be cyto-compatible and relatively nontoxic to buccal epithelial cells.

SCC-25 cells have been cultured on the leucite and kalsilite glass–ceramic composites compounds in order to demonstrate both the cyto-compatibility and biocompatibility of the compounds in the case of clinical application. We observed that leucite and kalsilite based glass–ceramic composites are tolerant to growth of the SCC-25 cells. The results suggest that the prepared composite materials perform better compared to the standard materials and allow growth of the cells efficiently over its surface.

4.4 Effect of Al_2O_3 on leucite based bioactive glass ceramic composite for dental veneering

This chapter describes the effect of addition of alumina to the leucite based bioactive glass ceramic composite. The results have also been compared with a commercial product (VITA VMK 95) to validate the feasibility of the prepared composite. The formation of a crystalline phase nepheline has been confirmed after firing (at 950 °C) along with some alumina crystalline phase subsequently decreasing the amorphous phase. Nepheline has the highest coefficient of thermal expansion and good mechanical strength which may further increase the mechanical properties of the prepared composites. Alumina added leucite glass ceramic composites show high flexural strength than that of the leucite based glass ceramic composite and commercial dentine. A uniform attachment of SSC-25 cells after 10 days of culture on the surface of the composites has been observed. It confirms that the addition of alumina to the leucite glass ceramic composite is a successful approach to improve its mechanical and biological properties.

Chapter 5: Conclusion and scope for the future work

- The present chapter describes the overall conclusion drawn from all the chapters. Scope of the future work is also proposed in this chapter.
- Nanocrystalline leucite and kalsilite has been successfully synthesized using mechanochemical route and characterized.
- All the MCL-C & MKL-M samples have better thermal and mechanical properties than that of the MCL and MKL samples.

- The bioactive leucite/kalsilite glass-ceramic composites have been successfully prepared by mixing mechanochemically derived leucite/kalsilite, LTF and bioactive glass in different weight ratios followed by heating at 960 ºC.
- The formation of calcium silicate (2CaO.SiO2) and wollastonite (CaO.SiO2) crystalline phases in the compositions, COMP-1 and COMP-2 improves their flexural strength.
- A sodium orthosilicate (2Na2O.SiO2) crystalline phase has been found in the kalsilite based composites. This phase has less strength as compared to wollastonate and calcium silicate. This results in the less flexural strength of the compositions COMP- 3 and COMP-4.
- CTE of all the composites have been found in the range 14.5 to 15.9×10 6 /°C. These values are very close to the nickel-chrome alloy and commercial dentine.
- Leucite and kalsilite glass–ceramic composites are observed to be cyto-compatible and relatively nontoxic to buccal epithelial cells.
- It has been observed that leucite and kalsilite based glass–ceramic composites are tolerant to growth of the SCC-25 cells.
- It is, therefore, concluded that the prepared bioactive leucite/kalsilite glass-ceramic composites may be used for PFM as well as for different purpose in implant custom ceramic abutments at collar or emerging profile region.
- The addition of alumina to the glass ceramic composites results in the formation of nepheline crystalline phase. This leads to enhance the CTE and flexural strength of the samples.
- A uniform attachment of SSC-25 cells after 10 days of culture on the surface of the composites has been observed. It confirms that the addition of alumina to the leucite glass

ceramic composite is a successful approach to improve its mechanical and biological properties.

Scope for the future work

- In-vivo testing of the prepared materials will be useful for their realistic application.
- Ion leachability test of the composite materials using AAS to confirm their chemical durability.
- Study of addition of fine Al_2O_3 toCOMP-2, COMP-3 and COMP-4 on the mechanical, thermal and biological properties.