PZT – BASED GLASS - CERAMICS

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Some of the contents presented in this chapter have appeared in the following research publication

6.1 Introduction

Ferroelectric glass ceramics are composites in which ferroelectric crystallites are dispersed in a continuous glass matrix. Glass-ceramics comprising micro-crystallites that are capable of exhibiting piezo-, pyro- and ferroelectric properties have been in increasing demand and recognized to be potential multifunctional materials. Glass ceramics based on PZT are increasingly being used in the formulation of thick film inks for devices such as thick film actuators etc. PZT-based thick film actuators are gaining attention due to the simultaneous requirements of device miniaturization, lower operating voltages and device integration [1-5]. These device requirements have necessitated the use of thick and thin films based structures. In the case of thin films, the thermal stresses influence their performance and limit their crack free area. These effects could be minimized in the case of thick films. Therefore thick film devices assume significance. Thick films having a thickness in the range 10-100µm, will fill an important technological gap between thin film and bulk materials. The thick film technique is a very flexible and cost-effective technology for producing functional layers on green or fired ceramics. Usually, thick-film pastes are formulated from fine powders of the functional constituent and glass phase. In this glass + ceramic approach, homogeneity of the mixture of the functional ceramic with the glass constituent is limited. This can be circumvented through the use of glass-ceramic method. The glass-ceramic technique results in finer crystallites and a more homogeneous mixture of the PZT and glass phases. In addition to this glass-ceramics have low sintering temperature. The low sintering temperature of the materials makes it better compatible with cheaper metal electrodes. Another advantage of using glass-ceramics for thick film technology is that it can form vitreous bonds with the substrate and thereby improves the adhesion between
ferroelectric layer and substrate. Glass forming oxides form covalently bonded network. This covalent network is modified to form glass. The glass formers include silicates, phosphates, sulfates etc. and to a lesser extent fluorides and sulfides. The glass network modifier include alkali metal cation, alkaline earth metal and many of the transition metal ions and lanthanides. Only those anionic structural units having a co-ordination number 4 can form a three dimensional network as shown in the two dimensional representation (figure 6.1) for silicate glass. $\text{SiO}_4^{4-}$ forms a tetrahedral unit in which each Si$^{4+}$ ion is surrounded by four oxygen ions.

![Fig. 6.1](image)

**Fig. 6.1 (a)** Silica: crystalline state **(b)** Silica: amorphous state

It is clear from the figure that considerable difference in structure exists between crystalline and amorphous phases, even though they may have identical chemical composition. Also the volume occupied by the same number of tetrahedron is greater for the amorphous state as compared to the crystalline phase.

A multicomponent glassy structure in which the silica network is modified by several cations, each having its own degree of coordination is shown in figure 6.2. In silica, each silicon forms four covalent bonds and thus
forms a three dimensional network. When network modifiers such as Al₂O₃ or B₂O₃ is added to this network, Al³⁺ replaces Si⁴⁺ forming only three covalent bonds with its neighbouring atoms. Therefore addition of these network modifiers breaks the 3D network structure as shown in figure 6.2.

The glass containing network formers yield two or more phases during crystallization. The minor phase significantly controls the grain growth of major phase. This is advantageous in ferroelectric glass ceramics where the temperature dependence of dielectric permittivity is reduced due to the controlled growth of the ferroelectric crystallites. Crystallisation of a continuous glass should result in pore – free material. Therefore network forming oxides ensure structural continuity and also particle size control during crystallization. The amount of network forming additions must be sufficient to ensure workability of the glass. i.e, the glass should be stable enough to be heated to a temperature range where it softens without crystallization.

Fig.6.2 A schematic representation of a multicomponent glass
For the glass–ceramics, net-work forming oxides must be chosen properly to minimize interactions between the constituents of the glass and the desired crystalline phase. In glass –ceramics, choice of the glass constituents depends on the following factors [6];

1) Glass composition should have high mechanical strength.

2) The glass composition should be chemically compatible with the ceramics.

3) Glass forming elements should not affect the physical and chemical property of crystalline phase.

4) The softening temperature of glass component should be higher than the precipitation temperature of crystalline phase.

5) Glass constituents should not act as substituents in the ceramic phase

6) The host glass matrix should facilitate crystallization of ceramic phase

There are several methods for preparing ferroelectric glass ceramics. The various methods reported are;

1. Mixing of glass and ceramic powders.

   In this method chemical composition of glass and ceramic are adjusted independently. This method often leads to inhomogeneity.

2. Coating of ceramic powders with glass forming sol.

   Glass forming sol is synthesized first by wet chemistry route. Then ceramic powders are mixed and dispersed in sol. After gelation ceramic particles are coated with glass forming component.

In this all glass and ceramic components are melted together and cooled down rapidly to form metastable glass. The glass is then annealed at high temperature to induce crystallization.

The different steps used in processing a glass – ceramic by the conventional melt-quenching technique are illustrated schematically by the temperature – time cycle shown in figure 6.3. Glasses containing a major portion of ferroelectric phase produce crystallites of ferroelectric phase in glass through a suitable heat treatment. The material is melted and formed at elevated temperatures and then rapidly cooled to ambient, at which additional processing steps may be carried out.

![Fig.6.3 Schematic temperature–time cycle for the controlled crystallization of glass–ceramic body.](image)

[Source: Introduction to Ceramics by W.D. Kingery, H.K. Bowen, D.R. Uhlmann, p.369]
The material at this stage is homogeneous, or it may contain some crystals of the nucleant phase. After nucleation is completed, the material is heated further to effect the growth of the major crystalline phase. The maximum temperature for growth is generally chosen to maximize the kinetics of crystal growth. Conventional methods suffer several disadvantages.

1. Homogeneity is less.
2. Volatilization of low melting components.
3. Powder size is coarse.
4. Lack of chemical purity.

These limitations are overcome to a large extent by sol-gel processing. Sol-gel processing offers significant advantages such as high purity, chemical homogeneity and controlled particle size of materials. Besides lowering the processing temperature, the main advantage of this process is in achieving chemical homogeneity of the desired product due to mixing of constituents at molecular levels [7]. Glass – ceramics processing can be used to form solids with zero porosity and fine crystallite size. Properties of glass-ceramics are determined mainly by the intrinsic properties of the major crystalline phase. Some of the important factors that influence the properties of the major crystalline phase in a glass-ceramic are the surrounding glass matrix, their crystallization kinetics and nucleation mechanism, particle size and presence of other crystalline phases.

Thick-film actuator applications require materials with large values of electromechanical coupling factor, $k_p$, and piezoelectric constant, $d_{33}$ and should also possess lower sintering temperatures. Previously we have reported...
[8] that the composition, \((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.997}\text{Mn}_{0.004}\text{O}_3\) (PSZTM) exhibited good piezoelectric characteristics with values of \(k_p = 0.55\) and \(d_{33} = 451\) pC/N indicating its suitability for actuator applications. Ferroelectric glass–ceramics, with a high fraction of the crystalline phase, \((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.997}\text{Mn}_{0.004}\text{O}_3\) (PSZTM) are therefore of interest for the fabrication of thick film actuators. For the glass–ceramics, net-work forming oxides must be chosen properly to minimize interactions between the constituents of the glass and the desired crystalline phase [9–13]. In the PbO-TiO\(_2\)-B\(_2\)O\(_3\) ternary phase diagram, the glass compositions PbO.B\(_2\)O\(_3\) and 2PbO. B\(_2\)O\(_3\) have been reported [9] to be suitable for crystallization of PbTiO\(_3\). We have reported [14] the glass system, 5PbO. B\(_2\)O\(_3\). SiO\(_2\) for the crystallization of PZT. The advantage of selecting these glass systems is that due to the small ionic radii and coordination number of the glass forming constituent cations, such as B\(^{3+}\) and Si\(^{4+}\), they do not substitute the elements in the PZT lattice and also facilitate the crystallization of PZT-phase.

The objective of the present study, therefore, is to identify the optimum glass matrix from the three systems, PbO. B\(_2\)O\(_3\) (PB), 2PbO. B\(_2\)O\(_3\) (2PB) and 5PbO. B\(_2\)O\(_3\). SiO\(_2\) (PBS) by studying the influence of their composition on the crystallization of the major perovskite phase and the piezoelectric characteristics.

### 6.2 Experimental procedure

Three different glass–ceramic systems, as given below, each with glass content of 2, 5, 10 and 20 mol% were prepared by sol–gel method.

(i) \((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.997}\text{Mn}_{0.004}\text{O}_3.5\text{PbO. B}_2\text{O}_3. \text{SiO}_2)(\text{PSZTM–PBS})\)
(ii) \((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.997}\text{Mn}_{0.004}\text{O}_3 \cdot 2\text{PbO} \cdot \text{B}_2\text{O}_3\) (PSZTM–2PB)

(iii) \((\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.997}\text{Mn}_{0.004}\text{O}_3 \cdot \text{PbO} \cdot \text{B}_2\text{O}_3\) (PSZTM–PB).

Fine PZT glass-ceramics with a high fraction of the crystalline PZT phase are difficult to fabricate by conventional melting method because of the high volatility of \(\text{B}_2\text{O}_3\). Solid state method is the easiest way to prepare ferroelectric glass–ceramics. But the solid state method would result in coarse grained powder and also the homogeneity of the resulting glass–ceramic system is rather poor. Therefore, in this work, solution-sol-gel method has been used for the synthesis of BST-based glass ceramics because of its advantages such as high chemical homogeneity, molecular level mixing, low temperature processing, nanosized crystallites and ability to form high fraction of ceramic constituent. For the preparation of the precursor solution, stoichiometric amounts of basic lead acetate, \((\text{CH}_3\text{COO})_2\text{Pb}\cdot\text{Pb(OH)}_2\) (ACS reagent-grade, Merck, Mumbai, India), Strontium acetate, \(\text{Sr(CH}_3\text{COO)}_2\) (99.9% purity, Aldrich, Steinheim, Germany), Zirconium acetyl acetonate, \(\text{Zr(CH}_3\text{COCH=CH}_2\text{CH}_3)}_4\), (>98% purity, Merck, Hohenbrunn, Germany), Manganese(III) acetylacetonate, \(\text{Mn(CH}_3\text{COCH=CH}_2\text{CH}_3})_3\), (tech.-grade, Aldrich Steinheim, Germany) were dissolved in acetic acid, \([\text{CH}_3\text{COOH}]/[\text{Zr+Ti+Mn}]=25\), and was mixed with Titanium tetraisopropoxide, \(\text{Ti(OCH}_3\text{H}_2)}_4\) (97% purity, Aldrich, Steinheim, Germany) in iso-propyl alcohol under constant stirring condition. To the above metal salt solution, the clear solution obtained by refluxing stoichiometric amounts of boric acid, \(\text{H}_3\text{BO}_3\) (Merck, India) and tetraethyl orthosilicate, \(\text{Si(OCH}_2\text{CH}_3)}_4\) (Merck, Germany) in ethyl alcohol was added under stirring condition.
Fig. 6.4 Process flow chart for sol-gel processing of PSZTM-glass
Water was added ([H₂O/Ti]=2) to induce hydrolysis and the solution was kept for gelation at room temperature. A sample of the dried gel was used for differential thermal analysis (DTA) under flowing dry air on a thermal analyzer (Model-SDT Q 600, TA Instruments, USA). The dried gel was powdered and calcined at 600 °C. The calcined powder was isostatically pressed at 200 MPa into pellets of diameter 10 mm and thickness 1 mm. The specimens were sintered, over a temperature range of 900–1200 °C for 3 h in an oxygen atmosphere under constant PbO atmosphere maintained using a mixture of PbZrO₃ + ZrO₂ as reported [15, 16]. All XRD measurements were done on sintered and powdered samples on a X-ray diffractometer (Model- D5005, Bruker, Karlsruhe, Germany). The sintered specimens were polished and electroded with silver paste and subsequently cured at 700 °C for 30 min and poled by applying a DC electric field of 2.5 kV/mm at temperatures around 90 °C for 60 min in a silicone oil bath. The piezoelectric characteristics were measured 24 h after poling. Electromechanical characteristics were calculated from the resonance measurements[17]. The d₃₃ constant was measured using a d₃₃ meter (Model Pennebaker 8000, APC Inc., PA, USA). The dielectric properties of the sintered compacts were determined at 1 kHz using an impedance analyzer (Model 4294A, Agilent Technologies, Palo Alto, CA, USA). The microstructures of sintered pellets were recorded using scanning electron microscope (SEM; Model JSM-840A, JEOL, Tokyo, Japan).
Fig. 6.5(A) XRD patterns of PSZTM-PBS system glass-ceramics sintered at 1200°C / 3hr; ★ = PbO; ○ = TiO$_2$
Fig. 6.5(B) XRD patterns of PSZT-2Pb system glass-ceramics sintered at 1200°C/3hr; ★ = PbO; ⚫ = TiO₂; □ = t-ZrO₂.
Fig. 6.5(C) XRD patterns of PSZTM-PB system glass-ceramics sintered at 1200°C / 3hr
Fig. 6.6 TGA-DSC curves of the xerogels (a) PSZTM.xPBS (b) PSZTM.x2PB and (c) PSZTM.xPB; x=10 mol%, $\phi = 10^\circ$C/min. Inset shows the crystallization exotherms.
6.3 Results and discussion

X-ray diffraction patterns, shown in Figure 6.5, indicate that PbO, TiO₂ and t-ZrO₂ are present in small amounts in the glass–ceramic systems containing higher fractions of PbO (Figure 6.5(A) and(B)) whereas in the system, PSZTM-PB(Figure. 6.5C) no secondary crystalline phases are formed.

Fig. 6.7 Evolution of crystalline PSZTM as a function of temperature (a) 400, (b) 500, (c) 560 and (d) 600°C

The DTA patterns of the three different glass–ceramics recorded at a heating rate of 10 °C/min are shown in Figure 6.6. The exotherms around 275 and 500 °C correspond to the decomposition of organic moieties. The exotherm
around 550 °C correspond to the crystallization of the perovskite phase, while that around 575 °C (Figure 6.6 (c)) correspond to the transformation from the rhombohedral to the tetragonal phase (Figure 6.7). In the case of the PBS-based system, the crystallization of the PSZTM phase is not facile as evidenced by the very weak exotherm (Figure 6.6(a)-inset).

In the glass-ceramic, an understanding of the crystallization behaviour is necessary to optimize the thermal annealing conditions. Therefore study of the kinetics of crystallization is very important in this system. The various methods used to study the kinetics of crystallization are Johnson – Mehl – Avarami (JMA) method, Ogawa method, Kissinger method etc. JMA equation is [21].

\[ x = 1 - e^{-(kt)^n} \] ................................. (6.1)

where \( x \) is the amount of material crystallized at time ‘t’. \( n \) is Avrami exponent describing the nature of nucleation and growth of a crystal and \( k \) is the kinetic factor which depends on temperature according to Arrhenius equation,

\[ k = A e^{-\frac{E_a}{RT}} \]

Equation 6.1 takes the form,

\[ \ln(1-x) = -(kt)^n \] ....................................................... (6.2)

If \( n = 1 \), the JMA equation reduces to first order rate equation as shown below

\[ \ln(1-x) = -kt \] .......................................................(6.3)

This equation forms the basis of Kissinger equation. For this glass – ceramic system, Kissinger method, which is applicable only if the reaction
follows first order kinetics, is adopted to evaluate the kinetic parameters associated with the crystallisation. Therefore in order to find out, whether the crystallization of PSZTM from glass phase follows first order kinetics, the volume fraction of the PSZTM phase crystallized, $f_c$ was determined from the densities of the amorphous gel compacts isothermally annealed at 800 °C, for different time durations, $t$, using the method of mixtures $\rho = \sum_{i=1}^{n} \rho_i f_i$, where $\rho$ and $\rho_i$ are the densities of the glass–ceramic and the ith phase, respectively and $f_i$ the volume fraction of the ith phase. The densities of the components are 8.003 for PSZTM, 5.5, 6.5 and 5.46 g/cm³ for PB, 2 PB and PBS glass respectively [18].

Fig. 6.8 Plots of $\ln f_c$ versus time for (a) PSZTM.2PB and (b) PSZTM.PB glass-ceramic systems.
The linear relationship of ln $f_c$ with $t$ (Figure 6.8) indicates that the crystallization of PSZTM phase in the two glass-ceramic systems follows first order kinetics.

The kinetic parameters associated with the crystallization of the perovskite phase in the two glass–ceramic systems were determined by the method reported by Kissinger [19, 20]. The Kissinger equation is,

$$\ln \frac{\phi}{T_m^2} = -\frac{E_a}{R} \frac{1}{T_m} + \ln \frac{A}{E_a/R}$$

(6.4)

where $\phi$, $E_a$, $R$, $A$ and $T_m$ represent heating rate, activation energy of crystallization, universal gas constant, pre-exponential frequency factor and crystallization temperature respectively.

The crystallization temperature ($T_m$) of PSZTM in the two different glass matrices at different heating rates ($\phi$) was studied through DTA. Figures 6.9(B) & 6.9(B) shows the evolution of crystallization exotherms upon increasing the heating rate ($\phi$) for the amorphous gel powder. It is clear that the crystallization temperature ($T_m$) increases with $\phi$ along with an increase in intensity, which is characteristic of an activation controlled process. The activation energy of crystallization, $E_a$ determined from the slope of the plot of $\ln [\phi/T_m^2]$ vs. $1/T_m$ (Figure 6.10), the pre-exponential frequency factor, $A$, determined from the $y$-intercept and the reaction rate constant $k$ determined from the Arrhenius equation at a temperature of 500 °C are shown in Table 6.1.
Fig. 6.9 (A) Crystallization exotherm of PSZTM in PSZTM.2PB at $\phi (^\circ C/min.)=(a)10; (b)12.5; (c)15$

Fig. 6.9 (B) Crystallization exotherm of PSZTM in PSZTM.PB at $\phi (^\circ C/min.)=(a)10; (b)15; (c)20$
Fig. 6.10 Plots of $\ln[\phi/T_m^2]$ versus $1/T_m$ for (a) PSZT.2PB and (b) PSZT.4PB glass-ceramic systems

The crystal growth dimension, $n$, was estimated, as reported [21] earlier from the relation,

$$n = 2.5 \left( \frac{R}{E_a} \right) \frac{T_m^2}{\Delta T_{FWHM}}$$ ........................................................ (6.5)

where $\Delta T$ is full-width at half-maximum (FWHM) of the crystallization peak, $R$, universal gas constant and $E_a$, the activation energy of crystallization. From the kinetic parameters (Table 6.1) it is seen that, though the activation energy of crystallization of PSZTM in the PB glassmatrix is higher than that in the 2PB system, the pre-exponential frequency factor $A$, is extremely high indicating a rapid transition from the activated state to the crystalline state. Hence the rate constant, $k$ is also higher in the PB system. The value of $n = 3.7$ for PSZT–PB
system indicates that in this glass–ceramic system bulk nucleation of the perovskite crystallites is predominant. From these results it can be inferred that the crystallization of the ceramic phase is rapid and homogeneous in the PB glass.

**Table 6.1** Kinetic parameters obtained for the crystallization of PSZTM from the two glass systems

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>PSZTM.2PB</th>
<th>PSZTM.PB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy (E_a)</td>
<td>220.5 kJ/mol</td>
<td>395.7 kJ/mol</td>
</tr>
<tr>
<td>Frequency factor (A)</td>
<td>3.5 x 10^{13} s^{-1}</td>
<td>5.9 x 10^{24} s^{-1}</td>
</tr>
<tr>
<td>Reaction rate constant (k)</td>
<td>0.4677 s^{-1}</td>
<td>0.9695 s^{-1}</td>
</tr>
<tr>
<td>Crystal growth dimension (n)</td>
<td>5.4</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Figure 6.11 shows the effect of glass content on the microstructure in the PSZTM–xPB system. In glass–ceramics, the grain size depends on the number of nuclei in the glass matrix and their growth rate. Further grain growth due to liquid phase assisted process results in a maximum grain size of ~9 µm in the 5 mol% glass containing composition (Figure 6.11B). Increase in glass content beyond this resulted in grain size reduction. This is due to the presence of excess glass at grain boundaries restraining grain growth of the PSZTM phase (Figure 6.11C and D). The dielectric and piezoelectric properties of the three glass–ceramic systems are shown in Figure 6.12 and Figure 6.13. In the PSZTM–xPB system, the piezoelectric constant, d_{33}, the electromechanical coupling coefficient, kp and the relative permittivity, ε_r decrease with increasing glass content. Optimum dielectric and piezoelectric properties are obtained for the composition containing 5 mol% glass which is in agreement with the microstructure (Figure 6.11b) and the MPB composition (Figure 6.5C).
Fig. 6.11 SEM images of PSZTM$_x$ PB glass-ceramic system with $x$(mol%) = (A) 2; (B) 5; (C) 10; (D) 20
A similar trend is observed in the variation of the dielectric and piezoelectric characteristics of the 2PB-based glass–ceramic system. Higher values of $d_{33}$, $k_p$ and $\varepsilon_r$ obtained in the PB-based system is attributed to the better crystallization behaviour of the piezoelectric phase in this glass matrix (Table 6.1) and also due to the absence of secondary crystalline phases.

**Fig. 6.12** Dielectric characteristics of the three glass-ceramic systems

- $\blacklozenge$ - PSZM-PBS
- $\bullet$ - PSZM-2PB
- $\Delta$ - PSZM-PB
Fig. 6.13 Piezoelectric characteristics of the three glass-ceramic systems

-PSZTM-PBS, -PSZTM-2PB, -PSZTM-PB
6.4 Conclusion

Glass–ceramics based on PSZTM have been synthesized from three different glass systems. The effects of the different glass systems on the crystallization of the perovskite phase and the piezoelectric characteristics have been investigated. The glass system, PbO . B₂O₃ has been found to be suitable for the crystallization of phase-pure PSZTM ceramic, thereby enabling to achieve properties close to that of PSZTM ceramic. Optimum dielectric and piezoelectric properties are obtained in this glass–ceramic system containing 5 mol% glass. Bulk nucleation of the perovskite phase in this glass–ceramic system also offers promise for its application in fabricating thick films for actuator applications.

References