CHAPTER 3

THE EFFECT OF Li₂CO₃ ADDITION ON THE STRUCTURAL, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF PZT CERAMICS

3.1 Introduction

Lead based perovskites have been widely exploited for their technological properties like high dielectric constant and piezoelectric coefficient which makes them excellent candidates for device applications such as multilayer capacitors, transducers and actuators. The Pb(ZrₓTi₁₋ₓ)O₃ system and its modified solid solutions are known to exhibit excellent dielectric, elastic and piezoelectric properties at the ‘Morphotropic Phase Boundary (MPB)’[18]. As previously stated this MPB was earlier believed to be a coexistence region of two phases namely, tetragonal and rhombohedral phases [120,132-139].

The processing of these perovskites requires sintering at high temperatures above 1280°C (as already discussed in Chapter1) which limits their use in device applications, where the high firing temperature results in the compositional fluctuation due to the evaporation of PbO which not only deteriorates the electromechanical, piezoelectric, dielectric properties but also causes the environmental pollution. Further, the application of these materials in multilayer piezoelectric devices requires the sintering temperatures below 1000°C in order to reduce the cost of expensive electrodes like platinum and palladium [110,111]. The high firing temperature is undesirable for Ag/Pd electrodes as the diffusion of Ag leads to the deterioration in the performance of the device due to the formation of interfacial microdefects. Thus, it is desired to lower the sintering temperature for the improved, reliable and reproducible material properties of these ceramics. Some of the methods employed for achieving low sintering temperature without forfeiting the properties of materials include the use of ultra-fine powder [140], liquid phase sintering [141], use of additives [142], hot pressing [143] which enhance the solid state sintering.

Liquid phase sintering is the process of incorporating specific weight percent of low melting point additives known as sintering aids into the unsintered ceramics. Generally, the metal
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oxides considered as sintering aids have eutectic below the sintering temperature of the sample. Hence, the formation of liquid phase at temperature lower than the firing temperature assists in the densification process by the transportation of mass and reprecipitation [112]. The “wetting” action of the particles due to the formation of liquid phase results in the promotion of densification. The capillary forces which result due to the creation of curved surfaces of the liquid meniscus are responsible for bringing the particles together [144]. Further, the reorientation of the powder particles results into the compact and dense structure of the sample. Therefore, proper choice of the liquid phase additive is required for accelerating the densification process as well as for reducing the sintering temperature.

The lowering of sintering temperature in these lead based ceramics could be achieved by the addition of various metal oxides such as CuO, ZnO, Bi$_2$O$_3$, LiBiO$_2$(LBO), Fe$_2$O$_3$, Li$_2$CO$_3$ and has been reported earlier [112, 145-153]. Generally, the addition of these oxides led to the deterioration of piezoelectric properties or the sintering temperature could not be reduced much. Hence, efforts have been made in the direction to reduce the sintering temperature of these ceramics without degrading the material properties.

Fan et al. recently investigated the influence of Li$_2$CO$_3$ and Sm$_2$O$_3$ additives on PZT-PZN ceramics. The sintering temperature was found to reduce to 950°C without much degradation in the piezoelectric properties of the ceramics [146]. Liang et al. studied the effect of LBO addition on Pb$_{0.87}$La$_{0.03}$(Zr$_{0.53}$Ti$_{0.43}$)$_{0.9925}$O$_3$ and found that by controlling the soaking time and concentration of LBO, these ceramics could be sintered at 950°C and yielded high $S_{11}$ of 0.22% under 3kV/mm [148]. Sen et al. also tried LBO as a sintering aid and could sinter PZT ceramics at ‘ultra’ low temperature 750°C though the synthesis method adopted was intricate and sensitive [150]. Hayashi et al. had also explored LBO as a sintering aid for various lead based PZT system [152, 153]. Wang et al. synthesized PZT–Pb(Zn,Sb)–Pb(Ni,Te)O$_3$ ceramics at 980°C using Li$_2$CO$_3$–Bi$_2$O–CdCO$_3$ as sintering aid and found that $k_p$ of the sintered ceramics to be as high as 0.71 [112].

It has been seen from the literature that Li$_2$CO$_3$ is one of the most commonly used sintering aids for the synthesis of PZT based solid solutions. However, the effect of Li addition on the structural and material properties of PZT system has not been explored in detail. In this chapter, we have adopted low temperature calcination route to synthesize PZT ceramics which results in fine particles thereby making the sintering mechanism easier [42, 154]. Further, a detailed and systematic investigation is carried out to study the effect of Li$_2$CO$_3$
addition on the sinterability, structural, dielectric and piezoelectric properties of the PZT system. Since, Zr/Ti ratio plays a crucial role in deciding the phases and hence, the material properties of the PZT based system, therefore, Zr/Ti ratio is chosen to be 50/50 and later tailored to regain the MPB in the Li added PZT system with an objective to obtain superior dielectric and piezoelectric properties.

### 3.2 Materials and Methods

The nominal composition of PbZr\(_{0.5}\)Ti\(_{0.5}\)O\(_3\) was synthesized by two-step solid-state reaction via low temperature calcination method [42]. The analytical grade of raw materials such as PbO, ZrO\(_2\) and TiO\(_2\) were taken in stoichiometric ratio, mixed in ethanol medium and were kept for calcination at 700°C for an hour. 0.1, 0.2 and 0.3 wt% of Li\(_2\)CO\(_3\) was added in the solution form to the nominal composition after the calcination stage and was preheated at 500°C to remove all the volatile components. These powders were pelleted and kept at different sintering temperatures from 900°C to 1280°C in a lead controlled atmosphere. X-ray diffraction data were collected on the ceramic samples at normal scanning rate of 1°/minute with a step size of 0.02° using Philips diffractometer. The sintered pellets were polished and were gold coated. The electrical properties such as dielectric constant, dielectric loss of the sintered pellets were measured using HP – 4194 impedance/ gain-phase analyzer. The gold coated sintered ceramics were poled in silicone oil bath close to 300°C by applying a dc electric field of 2KV/cm and cooling down to room temperature for the characterization of piezoelectric coupling coefficient \(d_{33}\). The ceramics were aged for 24 hours prior to their measurements. The values of \(d_{33}\) were obtained using a Berlincourt piezo \(d_{33}\) meter.

### 3.3 Results and Discussion

#### 3.3.1 Density measurements

The density of the sintered ceramic samples was evaluated using modified Archimedes three-weight method as discussed in Chapter 2. Figure 3.1 shows the variation of relative density of PZT ceramics with the sintering temperature and with the amount of Li\(_2\)CO\(_3\) added to the system.
It can be seen from the figure that the densification of pure PZT ceramics could only be achieved at 1280°C with the maximum density of 85% of the theoretical density. However, the densification and sinterability was found to improve with the incorporation of Li⁺ ions in the system. This increase in the density is attributed to the addition of Li₂CO₃ as sintering aid, which promoted liquid phase sintering. This liquid phase sintering not only resulted in the improved sinterability and densification of PZT powders but also helped in lowering the sintering temperature. Further, the local charge imbalance due to addition of Li⁺ ions may also have facilitated the diffusion and densification rates.

![Figure 3.1: The variation of relative density (%) with the sintering temperature for various wt% of Li₂CO₃ added PZT ceramics.](image)

The maximum density of 92% of the theoretical density was obtained for 0.2 wt% Li₂CO₃ added PZT samples and the sintering temperature could be lowered to 1000°C as compared to the maximum relative density of 88% for 0.1 wt% Li₂CO₃ added systems at 1100°C. It is seen that the addition of 0.3 wt% Li₂CO₃ in the system resulted in the relative density of 90% of the theoretical density of PZT ceramics and the sintering temperature could not be lowered.
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further. Hence, it could be stated that the high amount of sintering aid beyond 0.2 wt% of Li$_2$CO$_3$ in the system did not further improve the density or lower the sintering temperature.

3.3.2 Structural analysis

XRD

The formation of the perovskite phase of the PZT based systems has been studied and analyzed using XRD patterns of the sintered ceramics. The characteristic peaks of the perovskite phase of the PZT samples were confirmed using the JCPDS data against the observed experimental peaks. The diffraction patterns of all the sintered ceramics with or without Li added PZT systems showed the formation of a pure perovskite phase with no impurity peaks observed within the limit of X-ray detection.

It is known that the (200) pseudocubic reflection is splitted into two peaks for tetragonal phase while the triplet splitting of this reflection is an indication of the presence of both

![X-ray diffraction pattern of sintered PZT ceramic](image)

**Figure 3.2:** X-ray diffraction pattern of sintered PZT ceramic (Zr/Ti =50/50)
monoclinic and tetragonal phases in the system. Figure 3.2 shows the diffraction profile of sintered PZT ceramic with Zr/Ti = 50/50. The inset of the figure shows the zoomed plot of the diffraction pattern in the range 20 between 40° and 60°. The peaks corresponding to (200), (210) and (211) pseudocubic reflections lie within this range of 20. It is clearly evident from the triplet splitting of (200) reflection that the PZT system synthesized with Zr/Ti = 50/50 lies in a coexistence region (MPB) comprising of two phases viz. monoclinic phase and tetragonal phase [43].

![Figure 3.2: The X-ray diffraction profile patterns in the range 35-50° for various wt% of Li$_2$CO$_3$ addition in the PZT ceramics.](image)

The effect of Li$_2$CO$_3$ addition on the structural evolution of PZT ceramics has been investigated. Figure 3.3 shows the x-ray diffraction profiles of PZT and Li added PZT systems in the range 35°-50° to examine the (200) reflection for MPB. It can be seen from the

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figure that with the addition of Li$_2$CO$_3$ in the PZT system (b-d), there is gradual transformation of the triplet splitting of the peaks into two peaks. This observation indicates that the Li$^+$ addition favors tetragonal phase in the system. It is well known that PZT based systems exhibit excellent dielectric and piezoelectric properties, for compositions around MPB, which is desired for device applications such as sensors and actuators. Since, the sinterability and densification was found to be optimum for 0.2 wt% Li$_2$CO$_3$ added PZT system, hence, an effort was made to regain the MPB in 0.2 wt% Li$_2$CO$_3$ added PZT system with an intention to obtain better dielectric and piezoelectric properties.

It was observed from the earlier results that the desired phases (viz. monoclinic and tetragonal phases) can be controlled and hence, the material properties of PZT based system can be tailored by varying Zr/Ti ratio [43, 154]. Since, the addition of Li$^+$ content is found to shift the MPB towards tetragonal phase, the Zr/Ti content in the 0.2 wt% Li$_2$CO$_3$ added PZT system.

**Figure 3.4:** The X-ray diffraction profile patterns in the range 35-50° for various Zr/Ti ratio of 0.2 wt% Li$_2$CO$_3$ added PZT system.
system was varied to restore the MPB. Thus, Zr/Ti ratio was varied from 52/48 to 56/44 to regain MPB in 0.2 wt% Li$_2$CO$_3$ added PZT system.

Figure 3.4 shows the diffraction patterns for 0.2 wt% Li$_2$CO$_3$ added PZT compositions with varying Zr/Ti content in the range 35°-50°. It can be seen that the increasing Zr/Ti ratio resulted in the increase in the content of monoclinic phase in the samples which is evident by the prominent singlet peak of monoclinic (200) phase. It can also be clearly seen from the figure that the system completely transformed to a monoclinic phase for Zr/Ti = 56/44. It can further be seen that the system regains its MPB for Zr/Ti = 52/48 as the triplet splitting of (200) pseudocubic reflection is observed from the figure.

3.3.3 Functional analysis

Dielectric properties

![Graph showing dielectric constant vs. temperature for various wt% of Li$_2$CO$_3$ addition in PZT system at 1kHz.]

Figure 3.5: The variation of dielectric constant with temperature for various wt% of Li$_2$CO$_3$ addition in the PZT system at 1kHz.
Figure 3.5 shows the variation of dielectric constant (1 kHz) with temperature for the studied PZT systems. It can be seen from the figure that the addition of Li in the PZT system led to the shift in the transition temperature as expected. The transition temperature $T_c$ was found to reduce to 370°C for 0.3 wt% Li$_2$CO$_3$ added PZT system as compared to 409°C for the parent system. It can also be seen that the dielectric properties are maximum for 0.2 wt% Li$_2$CO$_3$ added PZT system. The dielectric loss could also be controlled by the addition of Li$^+$ in the system up to 0.2 wt% addition of Li$_2$CO$_3$ in the PZT system. The addition of further Li$^+$ in the PZT system was not seen to improve the density or reduce the sintering temperature, however, it deteriorated the dielectric and piezoelectric properties. Hence, the optimized amount of Li$_2$CO$_3$ to be added to the PZT system was found to be 0.2 wt% for the improved performance.

The dielectric properties at 1 kHz for the various studied systems have been summarized in Table 3.1.

Table 3.1: Summarized dielectric properties of various Li$_2$CO$_3$ added PZT (Zr/Ti = 50/50) compositions

<table>
<thead>
<tr>
<th>System</th>
<th>$\varepsilon_{RT}$</th>
<th>$\delta_{RT}$</th>
<th>$T_c$(°C)</th>
<th>$\varepsilon_{max}(T_c)$</th>
<th>$\delta_{Tc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT</td>
<td>827</td>
<td>0.06</td>
<td>409</td>
<td>8801</td>
<td>0.1</td>
</tr>
<tr>
<td>PZT - 0.1 wt% Li$_2$CO$_3$</td>
<td>987</td>
<td>0.04</td>
<td>402</td>
<td>11346</td>
<td>0.09</td>
</tr>
<tr>
<td>PZT - 0.2 wt% Li$_2$CO$_3$</td>
<td>1023</td>
<td>0.02</td>
<td>388</td>
<td>13808</td>
<td>0.07</td>
</tr>
<tr>
<td>PZT - 0.3 wt% Li$_2$CO$_3$</td>
<td>797</td>
<td>0.1</td>
<td>370</td>
<td>12484</td>
<td>0.2</td>
</tr>
</tbody>
</table>

It has been stated that the MPB is regained in PZT ceramics by varying the Zr/Ti ratio, hence, a systematic dielectric study was carried out for PZT ceramics with different Zr/Ti ratio to establish the superior dielectric properties in the MPB region.

Figure 3.6 shows the variation of dielectric constant with temperature for different Zr/Ti content of the said system. It is seen that the transition temperature decreases as the content of Zr increases in the PZT system. The transition temperature is found to reduce from 388°C to 312°C with the variation in the Zr/Ti ratio from 50/50 to 56/44. It is seen that for 0.2 wt%
Li$_2$CO$_3$ added PZT ceramics with Zr/Ti ratio as 52/48 exhibited the most promising dielectric properties. This may be accounted due to the coexistence region in the system as stated earlier. The dielectric loss remained invariant with the variation of Zr/Ti ratio.

![Image of dielectric constant vs temperature graph]

**Figure 3.6**: The variation of dielectric constant with temperature for various Zr/Ti ratio of 0.2 wt% Li$_2$CO$_3$ added PZT system.

Table 3.2 summarizes the dielectric properties of various Zr/Ti ratios for 0.2 wt% Li$_2$CO$_3$ added PZT compositions.

**Table 3.2**: Summarized dielectric properties of various Zr/Ti ratios for 0.2 wt% Li$_2$CO$_3$ added PZT compositions

<table>
<thead>
<tr>
<th>Zr/Ti</th>
<th>$\varepsilon_{RT}$</th>
<th>$\delta_{RT}$</th>
<th>T$_C$(°C)</th>
<th>$\varepsilon_{max}(T_C)$</th>
<th>$\delta_{Tc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>1023</td>
<td>0.02</td>
<td>388</td>
<td>13808</td>
<td>0.07</td>
</tr>
<tr>
<td>52/48</td>
<td>1456</td>
<td>0.02</td>
<td>378</td>
<td>16158</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Piezoelectric properties

The high dielectric constant and piezoelectric coefficients are required for the materials to be used as sensor and actuator applications. Hence, piezoelectric coupling coefficient $d_{33}$ was measured to evaluate the performance of the synthesized PZT ceramics.

Figure 3.7 shows the variation of piezoelectric coupling coefficient $d_{33}$ with different compositions of PZT. It can be seen from the figure that $d_{33}$ increased with the addition of Li$_2$CO$_3$ up to 0.2 wt% in the PZT system. It was found to be 207 pC/N and maximum for 0.2 wt% Li added PZT (Zr/Ti = 50/50) compared to 155 pC/N for the parent system.

![Figure 3.7: The variation in the piezoelectric coupling $d_{33}$ for various compositions of PZT ceramics.](image-url)
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This improvement in $d_{33}$ values was attributed to the better sinterability and densification for Li added PZT system. However, it deteriorated with the further addition of Li content in the system which may be explained on the basis of solid solubility limit of Li in the system. The addition of Li content beyond the solid solubility may lead to its segregation in the grain boundary and hence, is detrimental to the dielectric and piezoelectric properties.

It is reported in the literature that the Zr/Ti ratio can be tuned to tailor the crystal structure and hence the material properties of PZT based system. Hence, the Zr/Ti ratio was varied to restore the MPB region in the PZT system as it was seen that the Li addition shifts the MPB region towards the tetragonal phase. 0.2 wt% Li added PZT (Zr/Ti =52/48) showed the maximum $d_{33}$ of 220 pC/N compared to 207 pC/N for Zr/Ti=50/50 which is attributed to the restoration of MPB region in the system.

3.4 Conclusions

The sinterability, structural, dielectric and piezoelectric properties of Li added PZT system have been studied. It is found that by controlling the concentration of Li in the system, PZT ceramics could be densified and sintered at 950$^\circ$C without forfeiting the material properties. The Li addition in PZT system is found to improve the sinterability remarkably and resulted in the reduction of the sintering temperature which in turn, led to the enhancement in the dielectric and piezoelectric properties of the ceramics. It is seen that an optimized amount of Li content in the PZT system is responsible for better sinterability and improved dielectric behavior and further addition of Li is found not to influence the sinterability but deteriorated the dielectric properties. 0.2 wt% of Li$_2$CO$_3$ in the PZT system was found to be an optimum concentration for exhibiting superior dielectric properties. The Li addition is found to favor the tetragonal phase and hence, Zr/Ti ratio was varied to regain the MPB in the system. It is found that the Li added PZT in the morphotropic region exhibited better dielectric and piezoelectric properties.