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Ferroelectric Glass-Ceramic Systems for Energy Storage Applications

Abdulkarim Ziedan Khalf

Abstract

An overview of ferroelectric glass ceramics, some literature review and some of the important previous studies were focused in this chapter. Nanocrystalline glass–ceramics containing ferroelectric perovskite-structured phases have been included. All modified glasses having ferroelectric ceramics which prepared by different methods are discussed, that producing nanocrystalline glass–ceramics. Then particular tested to their use as dielectric energy storage materials. These materials exhibit promising dielectric properties, indicating good potential for high energy density capacitors as a result of their nanocrystalline microstructures. The results of the analysis are summarised in this chapter to provide an overview of the energy storage characteristics of the different materials produced during the study.

Keywords: ferroelectric, glass-ceramics, BaTiO₃, KNN, energy storage, crystallisation

1. Introduction

Nanocomposite materials can be obtained through the crystallisation of the grain-boundary glass phase in a ceramic matrix; the electrical and structural properties are improved with glass additives [1]. Over the last few decades, the field of electronic ceramics applications has been progressing. Some newer applications, such as in low temperature co-fired ceramics (LTCCs) and dynamic random access memories (DRAMs), utilise the material's dielectric properties. LTCC applications require the sintering temperature to be below the melting point of the electrode materials [2]. The chemical processes of adding glass and using starting materials with ultra-fine particle sizes improve the characteristics of ceramics at low sintering temperatures [3]. Glass additives can have useful effects on the dielectric constant due to their effect in broadening the diffusive phase transition at the Curie temperature, something that is desirable in the application of multilayer ceramic capacitors [4].

Glass–ceramics are ceramic materials that are produced through the controlled nucleation and crystallisation of glass through thermal treatment. Depending upon the chemical composition and microstructure of glass–ceramics, they can exhibit useful thermal, optical, chemical, mechanical, electrical, and magnetic properties. Useful composite materials can be produced by combining glass–ceramics and other materials, such as metals [5]. Low sintering temperatures and high relative permittivity are of primary importance in the manufacture of ferroelectric ceramics. Typical

dielectric ceramic materials, such as barium titanate (BaTiO_3) and lead titanate zirconate (PZT), have found many applications in the electronics industry. Certain additives for BaTiO_3 and PZT, such as LiF and $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$, can reduce their sintering temperatures to around 900°C and improve their ferroelectric properties, making them suitable for a range of different electronic applications [6, 7].

It is known that the functional properties of ceramic materials are strongly dependent on microstructure, which provides opportunities to develop new or improved ceramic materials through microstructural engineering. One of these approaches involves combining ferroelectric perovskite with glass-forming oxides in order to form ferroelectric glass-ceramics [5, 8]. The microstructure of such materials comprises ferroelectric nanocrystals dispersed within a glass matrix [9], giving rise to novel materials having pore-free, fine-grained microstructures, low thermal expansion coefficients, high mechanical strength, high chemical stability and good dielectric properties [10]. Such materials have potential applications in high energy density capacitors [11], as well as piezoelectric [12] and electro-optic devices [10, 13]. The glass-ceramic processing route can provide well-controlled microstructure, formed by the crystallisation of chemically and microstructurally homogeneous glasses, at relatively low cost [5, 8].

2. Fundamentals of Ferroelectrics

Ferroelectrics are insulating solids that have spontaneous polarisation. This means that they contain a permanent polarisation at the unit cell level, even in the absence of external electric fields. Additionally, ferroelectric materials exhibit the ability to alter the orientation of their polarisation between two or more directions when under the influence of external electric fields. In order to exhibit spontaneous electric polarisation, there must be a noncentrosymmetric arrangement of the ions and their electrons in these materials. Many ferroelectric materials have perovskite structures with a general chemical formula of ABO_3 . ABO_3 -type oxides are known to stabilise with a wide range of A (Pb, Ba, Ca, Sr) and B (Ti, Zr, Sn) ions, with A ions having larger ionic radii than B ions.

Ferroelectrics have typical properties which are essential for their use in electronic devices. High relative permittivity and low-loss dielectric characteristics are most important in multilayer ceramic capacitors (MLCC), which are widely used in electronic devices. There have been progressive developments in the manufacture of MLCCs to increase both the relative permittivity and the number of layers, as well as decreasing the layer thickness, t , according to the equation below [14, 15].

$$C = \frac{\epsilon_0 \epsilon_r A}{t} \quad (1)$$

where ϵ_r is the relative permittivity or relative dielectric constant. The capacitance itself is dependent upon ϵ_r , the area of the parallel plates, A , and the thickness of the dielectric material, t .

Ferroelectrics are polar crystals with the ability to alter their polarisation direction upon the application of an external electric field. They exhibit spontaneous polarisation, even in the absence of external electric fields. In the unit cell, net permanent dipole moments are present in ferroelectric materials. In polycrystalline ceramics, the orientation of the dipole moments are random and therefore a net polarisation is not normally present after cooling through TC in the absence of an external electric field. The overall orientation of the dipole moments in

polycrystalline and single crystal ferroelectrics are not completely random at the scale of the unit cell, since they form ordered groups, referred to as domains. Within the domains, there is a uniform alignment of dipoles, with neighboring domains being separated by boundaries known as domain walls.

The direction of spontaneous polarisation in ferroelectrics can be altered through an applied electric field, as shown in **Figure 1**. With the increase of the electric field, the domains begin to align, giving rise to an increase and saturation in the polarisation at high field. In the absence of an external electric field, some of the domains remain aligned. Thus, the crystal displays remnant polarisation. If the field is reversed, the domains change direction. The direction of polarisation flips and produces a hysteresis loop when the external electric field alternates between negative and positive [16, 17].

2.1 Energy storage in capacitors

Significant improvements over the last couple of decades in both the energy storage density and reliability of capacitors have been achieved through a combination of novel materials, diagnostic methods, and manufacturing techniques. Capacitors, inductors, and batteries are means through which electrical energy is stored. **Figure 2** depicts a graph of the specific energy for different energy conversion and storage devices plotted against their specific powers [18].

The characteristics of energy-storage in four types of the most highly studied dielectric materials, namely, relaxor ferroelectrics, polymer-based ferroelectrics, antiferroelectric, and dielectric glass–ceramics were reviewed by Hao [19].

The changes in polarisation upon the application of an electric field are a critical aspect of energy storage dielectrics. This response can be used to estimate the stored energy, which should exclude hysteresis losses. Dielectrics may be grouped into being either linear or non-linear, according to the relationship between the applied electric field and the polarisation. A simple equation (below) may be used to describe their behavior [20].

$$D = \epsilon_0 E + P = \epsilon E \tag{2}$$

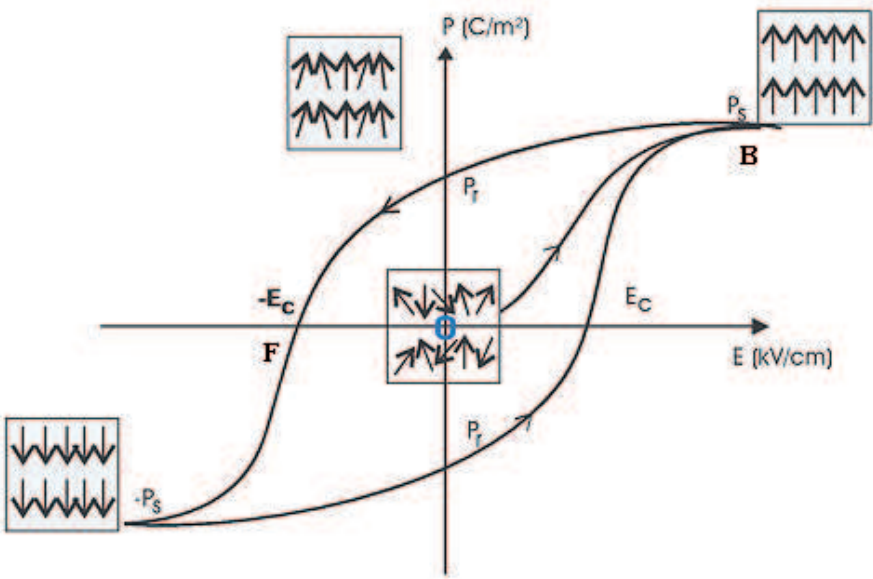


Figure 1.
Illustration of the polarisation-electric field relation, P-E hysteresis loop, for a typical ferroelectric crystal [16].

Therefore:

$$P = \epsilon_0 (\epsilon_r - 1)E = \chi_e \epsilon_0 E \tag{3}$$

where χ is dielectric susceptibility and D is the dielectric displacement.

Energy density, U , is a measure of the energy stored per unit volume. For dielectrics, this can be obtained by the following relationship:

$$U = \int_0^{E_{\max}} P dE \tag{4}$$

Using formula above (Eq. (4)), the U values of the dielectrics can be obtained through the numerical integration of the area between the polarisation and curves for the electric-field polarisation (P - E) loops. **Figure 3**, shows that upon reaching the maximum electric field strength (E_{\max}), the polarisation approaches its

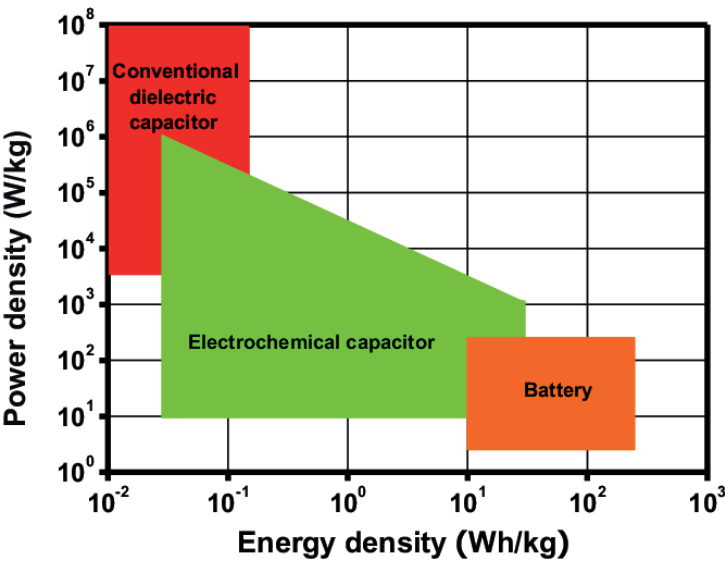


Figure 2. Diagram of power density as a function of energy density in different energy-storage devices [19].

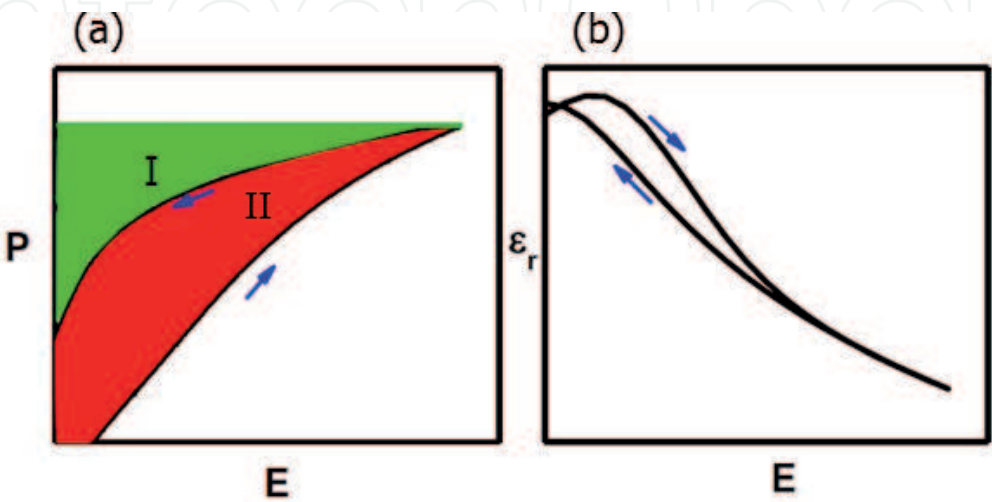


Figure 3. The typical dependence of (a) polarisation and (b) relative permittivity on the electric field of ferroelectrics in the first quarter shows the charge–discharge cycle. The area I (green shaded area) corresponds to the discharged or recoverable, energy density and area II (red shaded area) correspond to the energy density loss [19].

maximum (P_{\max}) and the capacitor holds the electrical energy (U_{store}), as illustrated by the red and green areas.

The recoverable electrical energy density (U_{rec}) is released during the discharge process when the electrical field reduces from E_{\max} to zero. This is represented by the green area in **Figure 3**. Therefore, an amount of the stored energy (the red segment surrounded by the loops) is dissipated during the process of depolarisation, denoted the hysteresis loss, U_{loss} [19, 21].

The above analysis indicates that there are three prerequisites to designing an effective dielectric material for practical use with high efficiency and high recoverable energy-storage density. These three requirements need to be satisfied simultaneously and are small remnant polarisation, large saturation polarisation, and a high electric breakdown field [22].

Figure 4(a)-(d) depicts typical P-E loops and an illustration of the energy-storage of four types of dielectrics: (a) linear dielectric with constant permittivity (e.g. Al_2O_3 , glass), (b) antiferroelectric with zero net remnant polarisation (e.g. PbZrO_3), (c) ferroelectric with spontaneous polarisation (e.g. PbTiO_3 , BaTiO_3), and (d) relaxor ferroelectrics with nanosized domains, e.g. $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$.

Even though linear dielectrics often have lower energy losses and higher breakdown fields, small polarisation values resulting from the use of low-permittivity dielectrics can reduce their effectiveness for high-energy storage purposes, unless very high breakdown fields can be achieved. Ferroelectrics generally have moderate electric field endurences and larger saturated polarisations, however, due to their larger remnant polarisations, they are often less efficient and have smaller energy-storage densities. **Figure 4** demonstrates that antiferroelectrics and relaxor ferroelectrics are more attractive for high energy storage due to their relatively moderate breakdown fields, smaller remnant polarisations, and larger saturated polarisations.

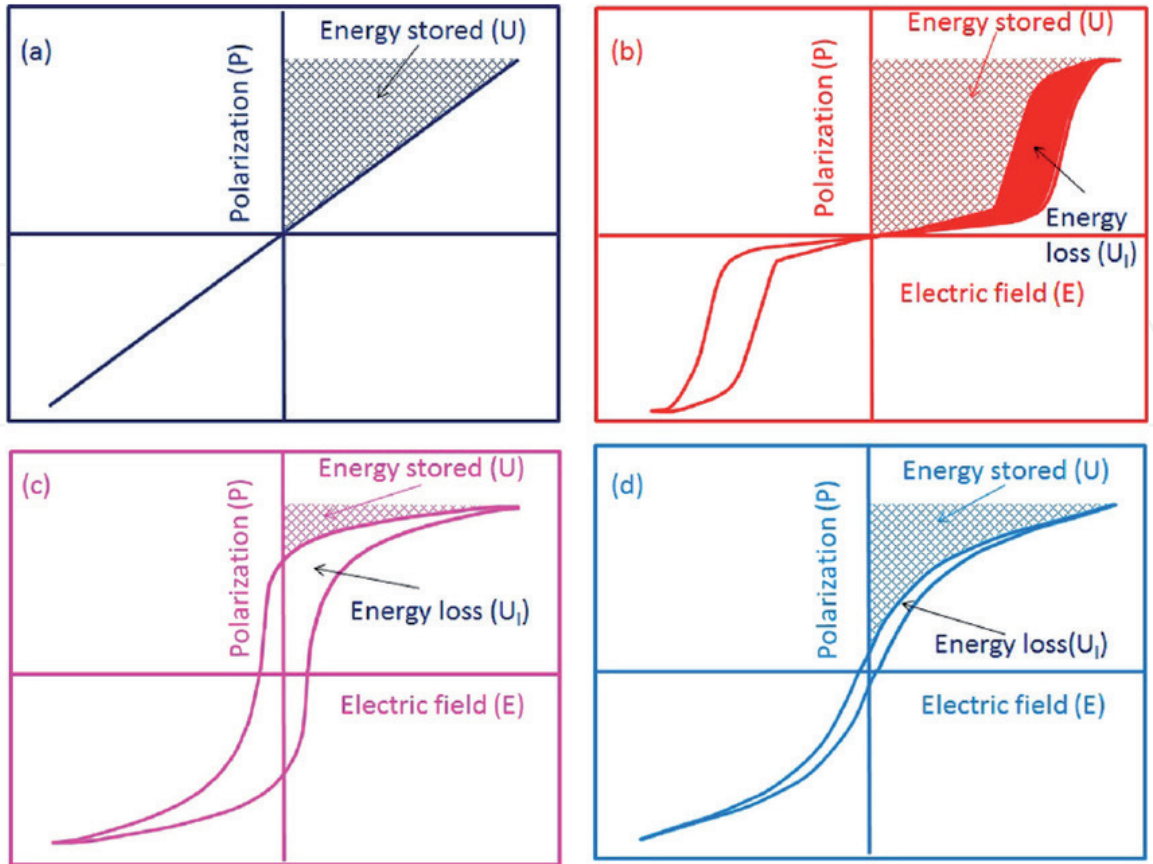


Figure 4. Schematic description of the energy storage characteristics of (a) linear dielectrics, (b) antiferroelectrics, (c) ferroelectrics, and (d) relaxor ferroelectric ceramics [23].

Novel manufacturing processes, such as the use of composite technology and glass-crystallisation techniques, have allowed for the production of ceramic-polymer composites and glass-ceramics. These materials could potentially combine the larger polarisations of ferroelectrics and the higher breakdown fields of linear dielectrics. Therefore, amongst the aforementioned four groups of dielectrics, namely, relaxor ferroelectrics, ceramic-polymer composites, glass-ceramics, and antiferroelectrics, the former two are generally thought to be the most useful for high energy storage purposes and therefore much research has been conducted on these two types of material [19, 23].

Pb(Zr,Ti)O₃ (PZT) based materials have been widely used in energy storage applications because of their high dielectric constant. However, the environmental issues derived from the use of lead have encouraged many searches for more environmentally friendly materials.

The perovskite structure of BaTiO₃, capable of high dielectric constant values, spontaneous polarization, low dielectric loss and ferroelectricity offers an alternative for lead-based capacitors. As mentioned earlier on, for energy storage applications a high dielectric breakdown strength is required to allow device miniaturization. It is well known that the energy storage properties of BaTiO₃ based ceramics can be improved by reducing the porosity [24], tuning the grain size [25], the addition of glass additives [26], presence of secondary phases, etc. For example, the relative permittivity of BaTiO₃ increases as the grain size decreases [27], reaching a maximum of 5000 at grain sizes of about 0.8 to 1.1 μm [28]. This was attributed to domain size and stress effects. Further reductions in the grain size resulted in a rapidly decreased permittivity. Furthermore, the dielectric breakdown strength increases with decreasing grain size [29], being about 8.5 kV mm⁻¹ when the grain size is 3.5 μm [30].

The addition of glass additives to induce liquid phase sintering is a widely used technique to improve the energy storage capabilities of BaTiO₃ based ceramics. During the liquid phase sintering, a thin layer of the fluxing agent coats the BaTiO₃ grains leading to improved relative densities and reduced sintering temperatures. Until now, the use of several glass additives in BaTiO₃ ceramics has been proved to show promising results for energy storage applications. For example, Sarkar and Sharma [31] demonstrated that the addition of B₂O₃ and PbB₂O₄ to BaTiO₃ significantly reduced the sintering temperature to about 800°C, which is suitable for commercial applications as multilayer capacitors. Moreover, they doubled the dielectric breakdown strength of BaTiO₃ by the addition of 10 mol% of PbB₂O₄ [31]. However, this improvement in the dielectric breakdown strength was accompanied by a small decrease in the dielectric constant.

The aliovalent substitution at the Ba²⁺ and/or Ti⁴⁺ sites in the perovskite structure of BaTiO₃ has been demonstrated [32] to be an effective approach to tailor the energy storage properties of BaTiO₃ to meet industrial application requirements. Recently, Puli et al. [33] investigated the dielectric, ferroelectric and energy density properties of (1-x){BaZr_{0.2}Ti_{0.8}O₃}-(x){Ba_{0.7}Zr_{0.3}TiO₃} where x = 0.1, 0.15 and 0.20, hereinafter denoted BCZT. They reported a dielectric of the permittivity of 8400 when x = 0.15 and a low loss (tan δ) of 0.014 in samples sintered at 1600°C. **Figure 5** shows the discharge energy density, charge energy density, and energy storage efficiency reported by Puli and co-workers, measured at a maximum electric field of 80 kV cm⁻¹ [33]. They achieved an energy storage efficiency of about 70% when x = 0.15.

Wang et al. [34] achieved an energy density of 0.52 J cm⁻³ in a (Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O₃ ceramic prepared by the sol-gel method. They attributed it to the improved microstructure compared to that obtained by the conventional solid-state reaction method. In order to simultaneously attain high dielectric breakdown

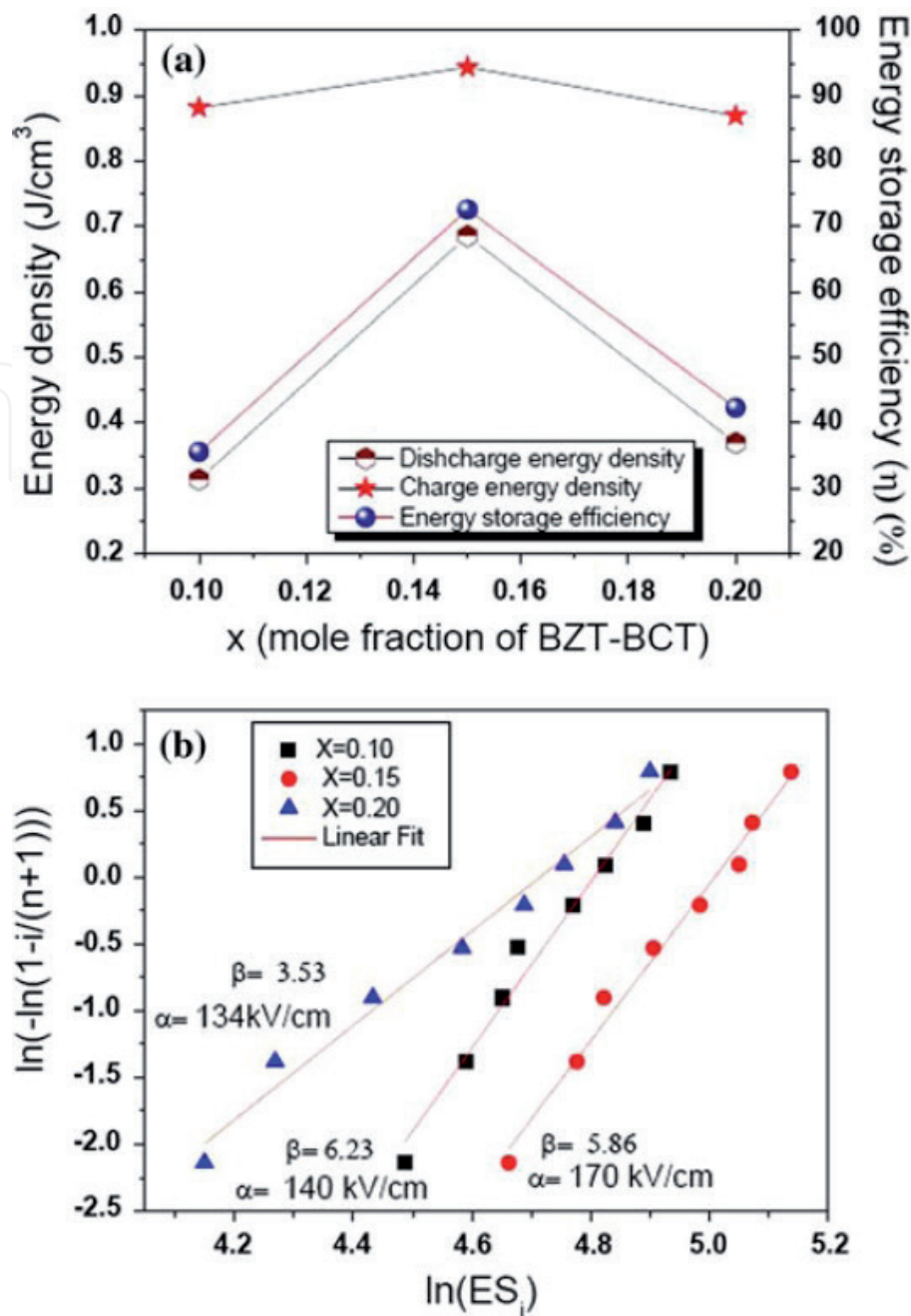


Figure 5.
(a) Composition dependence of recoverable energy density (U_{rec}), stored energy density (U_{stor}), and energy storage efficiency (η %) of $(1-x)\{\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\}-(x)\{\text{Ba}_{0.7}\text{ZCa}_{0.3}\text{TiO}_3\}$ where $x = 0.1, 0.15$ and 0.20
(b) Weibull plots of the breakdown strength of BCZT ceramics sintered at 1600°C [33].

strength, high energy density and a high dielectric constant in a material, the glass–ceramic concept has been devised. Here, the high dielectric breakdown of the linear dielectric (glass) and the high dielectric constant/large polarization typical of ferroelectric ceramics are combined in a nanostructured composite-type material. Puli et al. [35] followed the glass–ceramic approach to improve the energy storage properties of BCZT ceramics. They added 15 wt% of two different alkali-free glass compositions, namely $0.1\text{BaO} + 0.4\text{B}_2\text{O}_3 + 0.5\text{ZnO}$ and $0.3\text{BaO} + 0.6\text{B}_2\text{O}_3 + 0.1\text{ZnO}$, to BCZT, they reported a slight improvement in the dielectric breakdown field to about 28 kV mm^{-1} but a lower energy density compared to glass-free BCZT. The low energy density values reported were attributed to the low relative permittivity values (≈ 270) for glass–ceramic composition.

Another lead-free perovskite material that exhibits useful ferroelectric properties is the solid solution system potassium-sodium niobate (KNN). The solid

solution in the binary system $\text{KNbO}_3\text{-NaNbO}_3$ crystallises as an orthorhombic perovskite, [36], with the composition around $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ being the most popular due to its closeness to the morphotropic phase boundary (MPB) which occurs at about 52.5% Na [37]. The solid solution $(\text{K},\text{Na})\text{NbO}_3$ exhibits ferroelectric behaviour which diminishes at high sodium additions until it completely disappears due to the nonpolar, antiferroelectric end-member NaNbO_3 [38, 39]. The dielectric constant of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ at room temperature is about 290 [38] and reaches 990 at 473 K. The use of additives to reduce the grain size and to improve the energy storage abilities of KNN ceramics has shown promising results. Qu et al. [40] achieved an energy storage density of 2.48 J cm^{-3} and a breakdown strength of 29.5 kV mm^{-1} by reducing the grain size of KNN to $0.5 \mu\text{m}$ through the addition of $\text{Sr}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (SSN), although they reported the presence of porosity at the grain boundaries. Highly dense KNN-SNN samples were achieved through the addition of 0.5 mol% ZnO , leading to a breakdown strength of 40 kV mm^{-1} and an energy storage density of 2.6 J cm^{-3} [41].

3. History and definition of glass-ceramics

Glass-ceramics are classified as ceramic materials. They are polycrystalline materials that are formed by controlling the crystallisation of an amorphous glass. These materials are an important type of electroceramic and were successfully developed during the 1940 and 1950s. During this period, S. D. Stookey (Corning, USA) successfully used glass-ceramics as electrical insulators in electronics technology [5, 20]. The fundamental patent of Stookey was based on the concept that the TiO_2 works as a nucleating agent in a glass system. Additionally, ZrO_2 was used by Tasiro and Wada [5], in 1963 as a nucleating agent. Another discovery was made in the 1950s by Hummel, who discovered the crystal arrangement of the $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-2SiO}_2$ system [42].

Figure 6 shows three types of an atomic structure with different atomic arrangements. A crystalline solid is one which has a long-range order in its atomic structure; an amorphous solid is one in which there is no long-range order in its atomic structure. Crystalline solids have two subdivisions, single crystal and polycrystalline. A single crystal has a periodic atomic arrangement. In this case, there are no grain boundaries. A polycrystalline solid contains many grain boundaries in the structure due to the differences in the orientations of the grains (that have a short-range order) [43].

It is difficult to specifically define a glass since the behaviour of a glass alters with changes in temperature. There are two points at which a glass can be defined; the

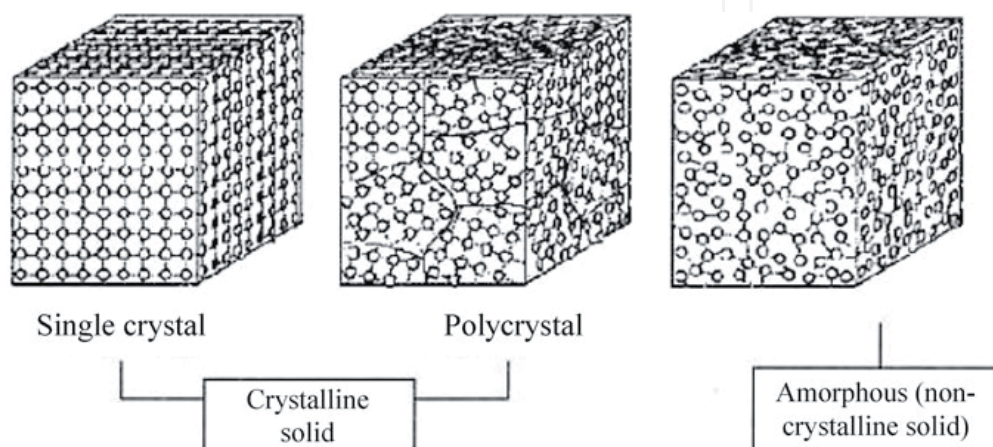


Figure 6.
The structure of ceramics [43].

first is at high temperature, when the glass is a liquid, while the second is at a lower temperature when the glass is considered as a supercooled liquid. Although there are important structural differences between glasses and polycrystalline ceramics, their mechanical and functional properties at room temperature can be similar.

The traditional definition of glass is that it is a supercooled liquid. According to the American Society for Testing and Materials (ASTM), the definition of glass is that it is an inorganic product of fusion which has cooled to a solid state without being crystallized. However, there are alternate definitions for glass, one being that glass is a type of amorphous solid material that lacks long-range order (not a random arrangement) in its atomic structure. Another definition, also put forward by ASTM, is that a glass is a liquid that has lost its ability to flow [5, 16].

3.1 Heat treatment of glass-ceramics

The heat treatment of glass leads to the occurrence of many transitions. Differential scanning calorimetry (DSC) is a form of thermal analysis that depends upon the change in a material's physical properties [42]. In DSC, there is a difference in temperature (ΔT) that is seen between the sample and the reference. Here ΔT represents differences in heat flow as ΔQ . The two quantities, ΔT and ΔQ , are functions of thermal resistance (R), as shown in equation below.

$$\Delta Q = \frac{\Delta T}{R} \quad (5)$$

In the first step of the glass transition, some of the physical properties change for amorphous materials. This change occurs in the heat capacity, which can be measured by DSC as an endothermic change in the sample. The transitions in glass due to the effects of temperature occur in the range of temperature which is known as the glass transition temperature (T_g). Therefore, below T_g , materials display a rigid glassy structure. When the temperature is increased above T_g , these materials display a flexible structure.

Another transition which occurs due to changing temperature is crystallisation. In this case, the amorphous materials are transformed into a crystalline structure. With an increase in temperature, the next conversion is melting. At this point, the crystalline structure converts to a viscous amorphous structure. The melting point is dependent upon the chemical impurity of the materials. After the melting stage, a reaction inside the material causes an increase in the density of the material [5, 42].

3.2 Crystallisation of glass-ceramics

Generally, since 1960, there has been much research undertaken regarding glass systems in the field of glass-ceramics. Glass-ceramics are very important in many fields of application. They have demonstrated many desirable thermal, optical, biological, chemical, and electrical properties. Some of these properties provide advantages to glass-ceramics over more traditional materials. A glass-ceramic is a polycrystalline material formed by controlling the crystallization of glass. Therefore, in order to make glass-ceramics from glass, the main manufacturing process needs to be a thermal one. **Figure 7** shows the steps of glass transforming into glass-ceramic. These steps begin at a low temperature with the formation of nuclei, then at higher temperatures crystallisation occurs by growth of the nuclei; this continues to produce the polycrystalline a glass-ceramic microstructure [5, 43].

Microstructural control is said to be easier when the temperature required for crystallisation lies between but is significantly different from both the glass transition temperature and that of matrix devitrification. In such a case, the desired crystalline phase can be induced to form without devitrification of the glass matrix. The crystallite size generally increases with increasing temperature, as shown by the micrographs in **Figure 8** [44].

In **Figure 9**, the typical thermal preparation of glass–ceramic can be seen. In this case, the raw materials, Li_2CO_3 and SiO_2 , are used to create lithium disilicate. There are two main stages in obtaining glass–ceramics: glass formation and glass crystallisation. In each stage, there are many steps which depend upon both temperature and time. The first stage begins by melting the components and then quickly cooling them. The nucleation and crystal growth occurs in the second stage. During this stage, controlled crystallisation of the glass produces nanoscale crystals [5].

3.3 Glass-ceramic properties and applications

Glass-ceramics can be containing a substantial glassy phase if the range is highly crystalline. As a result of that, glass–ceramics can contain grain boundaries as well as it can range from transparent to opaque. Therefore, the properties of glass–ceramics depending on the microstructure and the chemical composition, which can be tuned to meet demanding requirements. In general, the most important of glass–ceramics properties that can be exhibited is about zero thermal expansion with high toughness. as well as, have a high impact resistance with resistant to thermal shock [5, 8].

The potential applications of glass–ceramics in energy storage capacitors was investigated by Du et al. [11]. Here, the $\text{Na}_2\text{O-PbO-Nb}_2\text{O}_5\text{-SiO}_2$ glass–ceramics system achieved a highest relative permittivity of >600 after heated the sample at 850°C . The results given by Gorzkowski et al. [46] shown that the interfacial

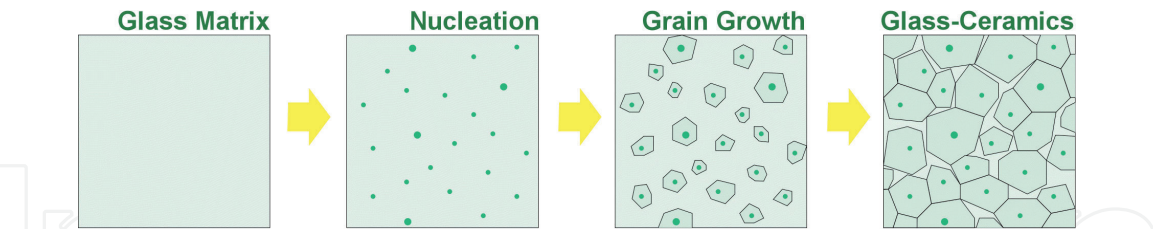


Figure 7. Schematic representation of glass–ceramic processing [5].

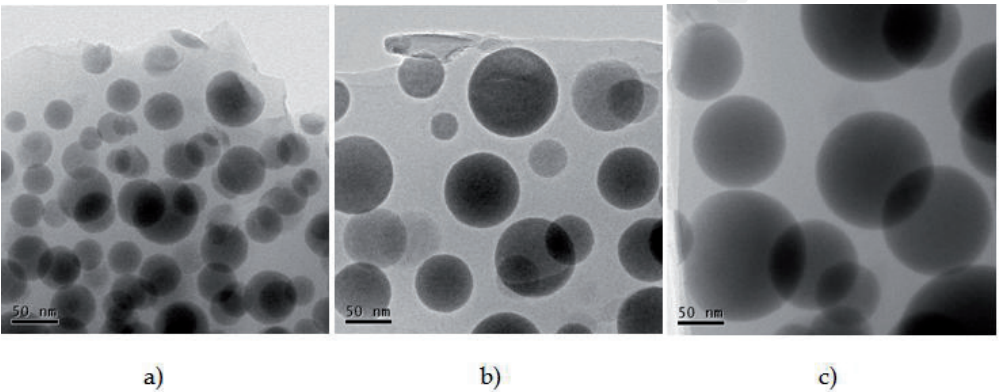


Figure 8. TEM micrographs showing Nanoscale crystallites precipitated from a glass matrix of $\text{SiO}_2/\text{Lu}_2\text{Si}_2\text{O}_7$ heat-treated at 1100°C (a), 1200°C (b) and 1300°C (c) [44].

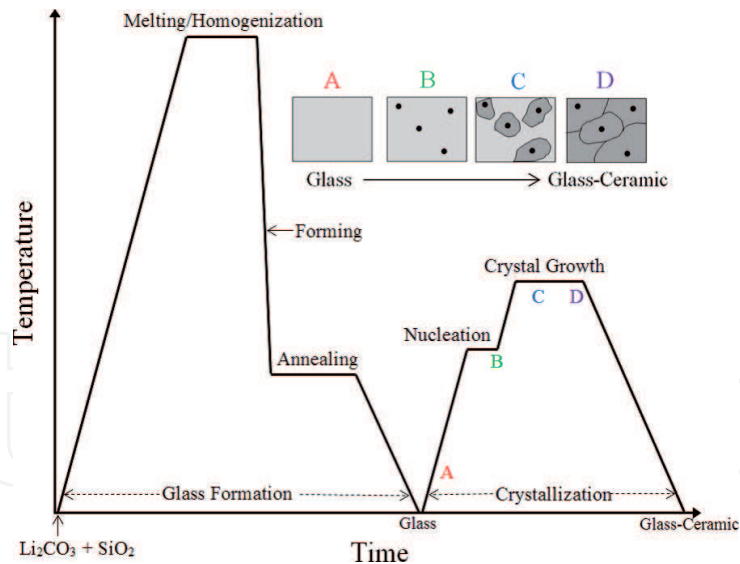


Figure 9.
 Schematic of glass processing in the formation of a glass ceramic [45].

polarization due to the difference in the dielectric and conductivity of glass phase and ceramic phase large hysteresis loss, led to low energy density (Max. 0.9 J cm^{-3}) and breakdown strength (Max. 800 kV cm^{-1}) of the BST glass–ceramics that expected much higher energy density ($\approx 3.5 \text{ J cm}^{-3}$ in case assuming is it ideal linear dielectric behavior) [46].

As the energy crisis intensifies, the search for novel, high performance and environmentally friendly energy storage devices have attracted wide attention. For a material to possess high energy density capabilities, a high relative permittivity and dielectric breakdown strength are needed; this is a challenging task since theoretical and experimental studies on crystalline materials usually show a contrary relationship between these properties [47]. Compromises between relative permittivity and dielectric breakdown strength have encouraged the search for more efficient materials such as polymers and glasses. Recently, a high relative permittivity and a high dielectric breakdown strength were found in fluoropolymers, with energy density values up 25 J cm^{-3} being reported [48]. A high dielectric breakdown of $\approx 12 \text{ MV cm}^{-1}$ (1.2 MV mm^{-1}) was also reported [49] in a low relative permittivity ($\epsilon_r \approx 6$) alkali-free glass, showing the possibility to reach an energy density of 35 J cm^{-3} . These results are very promising since the relationships between relative permittivity and dielectric breakdown strength in inorganic glasses are not well established.

Xue et al. [38] studied the effect of glass concentrations on the energy storage capabilities of niobate glass ceramics $(100-x)(40\text{BaO}-10\text{Na}_2\text{O}-50\text{Nb}_2\text{O}_5)-x(63\text{SiO}_2-12\text{BaO}-16\text{B}_2\text{O}_3-9\text{Al}_2\text{O}_3)$ prepared via controlled-crystallization. They achieved dielectric breakdown strength of about 130 kV mm^{-1} and a charge–discharge efficiency of 92.5%, with a relative permittivity of about 50, see **Figure 10** below.

Glass-ceramics are amongst the most important hosts for transition metal ions [51]. There are several benefits of adding glass to ceramics, such as improving their dielectric properties and reducing both the sintering temperature and the porosity [6]. In glass–ceramics, the ferroelectric and dielectric properties are highly dependent on the characteristics of the glass matrix as well as the crystal volume fraction and crystal size [52]. Glass-ceramics are crucial in the development of more efficiently produced and controlled energy. They are thought to be efficient cathodes or solid electrolyte materials when used in lithium batteries. Dielectric glass ceramics are also of interest due to their uses in high-power microwave systems, distributed power systems, power electronics, and pulsed power.

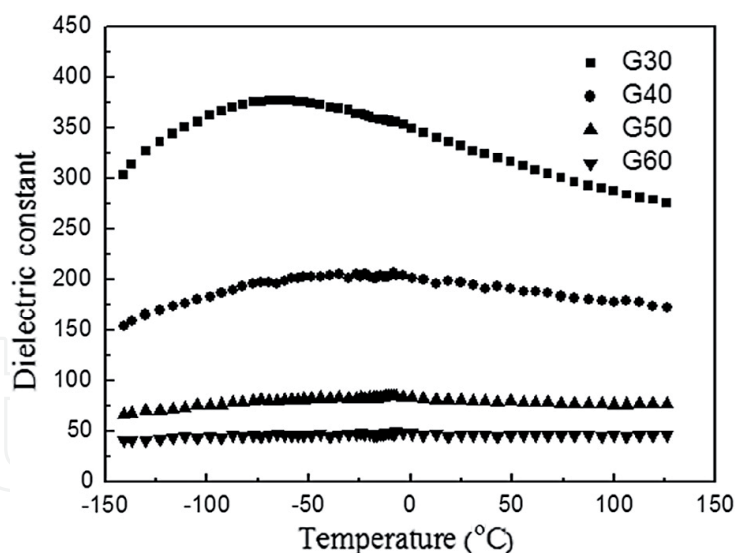


Figure 10.

Relative permittivity versus temperature curves of niobate glass–ceramics prepared via the controlled-crystallisation route, samples were annealed at 1100°C. When the glass content was 30–60%, the samples were labelled G30 to G60, respectively [50].

To decrease the thickness of the dielectric layers in a capacitor and reduce the weight of portable pulsed power systems, it may be necessary to have high dielectric breakdown strength in the materials. In any case, improved control of the porosity, along with enhanced energy storage capabilities, are important aspects of improving the performance of glass–ceramics [53]. The significance of glass–ceramics in many applications lies in the possibility of utilizing key properties such as transparency, strength, resistance to abrasion, and the controlled coefficient of thermal expansion. All these properties can be manipulated by the controlling the composition, extent of crystallisation, crystal morphology, crystal size, and aspect ratio of the materials [54]. Glass-ceramics are used in a range of applications across different fields such as telecommunication, radar, and navigation. With respect to the use of high-density electron device packages, the materials which are used in LTCC applications need to have good dielectric properties and a large coefficient of thermal expansion (CTE). These characteristics are important in order to achieve thermal matching between the components of the package [55, 56].

3.4 Chemical compositions of glass-ceramic systems

3.4.1 Alumina-silica systems

Silicates are salts of silicic acid, H_4SiO_4 . Most of the silicates contain SiO_2 , while in the case of SiO_2 or quartz glass, only SiO_2 is present. For all other types of glass, additional oxides, such as: Li_2O , BaO , B_2O_3 , Na_2O , K_2O , MgO , CaO , or Al_2O_3 are employed as network formers or modifiers. Alkaline and alkaline earth oxides are important in glass due to their effects on the network. Therefore these additives work as effective network modifiers [57]. The alumina-silica system, Al_2O_3 - SiO_2 , is amongst the most important binary oxides and ceramic systems. **Figure 11** shows the phase diagram of the binary Al_2O_3 - SiO_2 system. The low solid solubility for SiO_2 in Al_2O_3 , and vice versa, can be seen in this diagram. At a high temperature below 1890°C, part of the Al_2O_3 component is transformed to a molten state, while the other part remains solid. This also occurs with SiO_2 at a temperature below 1600°C. The effect of the SiO_2 ratio in reducing the melting point of Al_2O_3 - SiO_2 , can be seen [58].

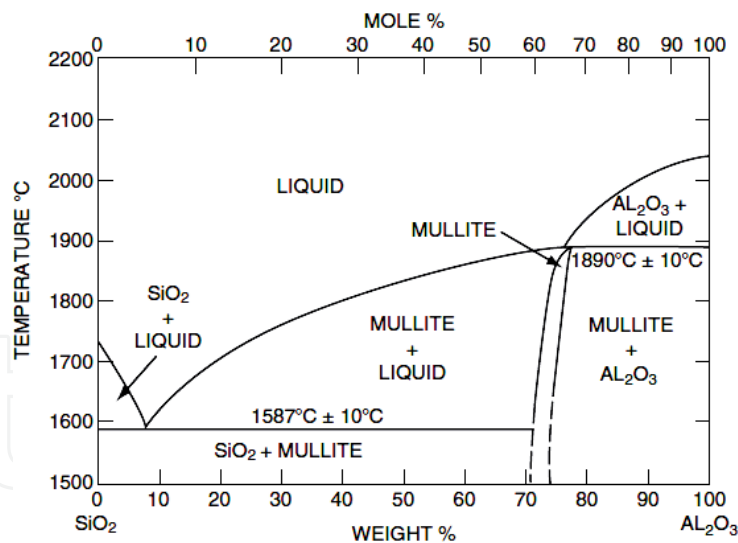


Figure 11.
Phase diagram of the binary alumina-silica system [58].

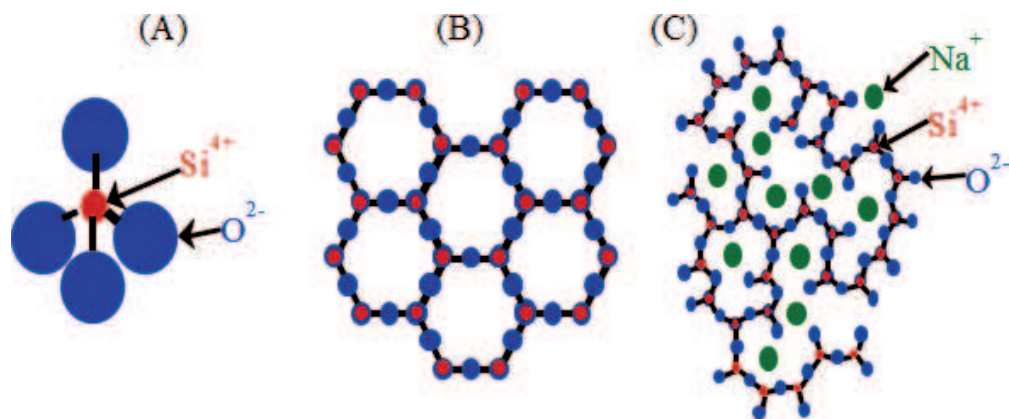


Figure 12.
Silica network structure: (A) silica tetrahedron, (B) pure silica quartz, (C) and a soda lime silicate [57].

Figure 12 shows the silica structure as a network. In **Figure 12-A** the basic units for silica are represented; these are Si⁴⁺ with O²⁻. The network of pure silica, also known as quartz, is presented in **Figure 12-B**, while **Figure 12-C** shows the structure of this 2D network with the addition of some alkaline additives as modifiers [57].

3.4.2 Alkaline and alkaline earth silicates

Glass-ceramics can be modified by a formulation process. Alkaline and alkaline earth oxides are modifiers of glass networks and act to decrease the connectivity of the glass network, effecting changes in the properties of the glass. There are many oxides that are used to modify glass-ceramics, such as: Ba, Li, B, Ca, Na, etc. [57]. These glass-ceramic systems contain binary and ternary systems. Both types of systems contain oxides, such as: BaO, B₂O₃, MgO, CaO, PbO, ZnO, Al₂O₃, SiO₂, and SrO [5]. Some of the oxides contained within the glass are popular as sintering aids for ceramics. This is because of the high stability of their structures and the low glass transition temperatures, in addition to their thermal and electrical properties. The systems of PbO-containing glasses (e.g. PbO-B₂O₃-SiO₂ and PbO-B₂O₃-ZnO) are important due to the aforementioned reason [59, 60].

Other glass systems include Bi₂O₃-B₂O₃, BaO-CaO-Al₂O₃-B₂O₃-SiO₂, CdO-Bi₂O-PbO-B₂O₃, and BaO-B₂O₃-SiO₂ which have all been used to reduce the sintering temperature [3, 61]. The structure of PbO is not easy to crystallise, even with a high percentage of it within the glass, because PbO₄ is formed within the glass system. Recently, many glass systems have been developed as alternative lead-free materials. In this research, BaO, ZnO, and Bi₂O₃ are used instead of PbO [61]. Most glasses containing a high proportion of PbO are undesirable due to the toxicity of lead oxide causing environmental problems during or after production. Therefore, most researchers focus on decreasing the PbO content or replacing it with other oxides. This issue was addressed by Bobkova and Khot'ko [62], who were studied the ZnO-SrO-B₂O₃ system. They found that the optimum glass was produced when it contained a high ZnO and low B₂O₃ content. In addition, two ternary systems, B₂O₃-CaO-SiO₂ and B₂O₃-CaO-Al₂O₃, have been studied by Vartanyan et al. [63]. They found that these two systems successfully produced lead-free materials for low-temperature simultaneously fired ceramics (LSCs).

Glass manufacturing processes can be generally complex due to the materials which undergo different changes during the melting and cooling. The ternary systems of B₂O₃-CaO-Al₂O₃, B₂O₃-CaO-SiO₂, and B₂O₃-ZnO-SiO₂-BaO were developed at low melting points below 1000°C then used as sintering aids with ceramics at low sintering temperatures [62, 63]. Consequently, these systems (BaO-B₂O₃-SiO₂) and (BaO-B₂O₃-SiO₂-Al₂O₃) possess their own particular thermal physical properties, where achieved a coefficient of thermal expansion (11–17 ppm °C⁻¹) and low permittivity (≈7) [64]. B₂O₃-Bi₂O₃-SiO₂-ZnO (BBSZ) is commonly used as an appropriate additive to reduce the sintering temperature of many dielectric materials and make them suitable for LTCC applications [65, 66]. Therefore in order to improve the electromagnetic properties of Ni-Cu-Zn ferrite (NCZF) and BaTiO₃, the BBSZ glass was chosen as a melting agent [67]. Glass-ceramics based on the CaO-MgO-SiO₂ system has been studied with the additives B₂O₃, P₂O₅, Na₂O, and CaF₂. The results showed that these systems required high melting points and the final crystallisation of the glass-ceramic occurred with temperatures of 900°C, producing high levels of density [68].

3.4.3 Barium borate system

The binary system of BaO-B₂O₃ is used in a wide range of glass ceramic production, oxide cathodes and the coloured materials in paints. In addition, these systems are used as sintering aids for low temperature co-fired ceramic applications due to the low softening temperature of the B₂O₃ [69]. **Figure 13** shows the phase diagram for the binary system of BaO-B₂O₃ [70]. The procedures of melting and cooling the BaO-B₂O₃ systems lead to glass formation. In the phase diagram, it can be seen that the lowest melting point with high stability for these systems occurs with approximately 60 to 80% B₂O₃. In practise, the optimum ratio also depends upon the rate of cooling of the glass [70].

The binary system of BaO-B₂O₃ was modified by SiO₂ or Al₂O₃ as a network modifier. Therefore, it was expected that the mineral phase with odd physical characteristic would be obtained. Therefore, glass ceramics are prepared with low sintering temperatures [64]. It should be noted that the melting point of B₂O₃ is around 450°C, which is much lower than SiO₂, which has a melting point of around 1710°C. However, the crystalline glass of B₂O₃ is much more difficult to produce than that of SiO₂ [70].

SiO₂ added to borate glasses generally leads to an improvement in the density of the glass and an increase in its T_g and chemical durability [71]. The effect of the Al₂O₃ on the characteristics of BaO-B₂O₃-SiO₂ was reported by Lim et al. [72].

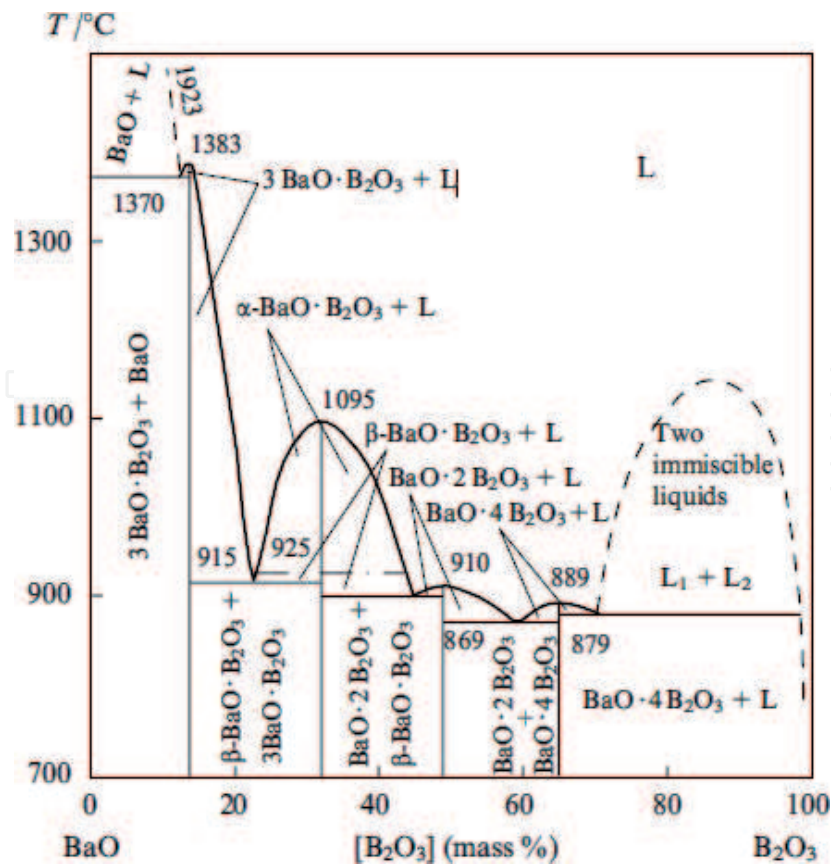


Figure 13.
Phase diagram of the BaO-B₂O₃ system [59].

It was found that the crystallisation temperature, sintering temperature, and glass transition temperature increased with increased amounts of Al₂O₃ in the glass systems. The ternary glass system BaO-B₂O₃-SiO₂ was studied by Lim et al. [61, 69]. The SiO₂ ratio was fixed at 10% and the effects of the amount of BaO/B₂O₃ on the thermal and physical properties of the glass system were studied. Increasing B₂O₃ content gave rise to a clear increase in the dielectric properties. The electrical conductivity of solid silicates shows a complex dependence on glass formation processes, devitrification, and temperature. Here, a slight change in the composition of the glass can lead to marked differences in the electrical conductivity values. In spite of the fact that most studies are about the binary systems, however, there is a scarcity of experimental data on the electrical conductivity of the glasses. Accordingly, the study of the influence of the metal oxide on the electrical conductivity is important for the multicomponent silicate glasses for electrical purposes [73, 74].

It was reported that the electrical conductivity is decreased by the presence of the K⁺ ions in the alumina-silica glasses while the glass transition temperature increased [73]. Wang et al. noted that the addition of Na₂CO₃ into Ba_{0.4}Sr_{0.6}TiO₃ (BST) ceramics caused a decrease in the room temperature dielectric constant of BST, while the highest Na⁺ and K⁺ content produced an increase in the energy storage density [75].

4. Ferroelectric glass-ceramic systems

The following sections summarise the results of previous research on the use of glass additives into ferroelectric ceramics, producing ferroelectric glass-ceramic and composites, and on the heat treatment of amorphous glasses to produce glass-ceramics containing nanocrystalline ferroelectric phases. The emphasis of the

present research is on lead-free ferroelectric materials and therefore previous work on lead titanate and PZT-based glass-ceramics is not included here.

4.1 Barium titanate systems

BaTiO₃-based ceramics have been widely used in a number of electronics and electrical industries, due to their excellent dielectric properties [76]. Glass additives have been used during the sintering process of ceramic materials to form a liquid phase to improve the sintering behaviour of well-known ferroelectric ceramics such as BaTiO₃, PZT and KNN. During this process, the reactive liquid formed by the glass additives wets the solid particles and facilitates their rearrangement. This rearrangement of particles gives more effective packing and higher densities, desirable for ferroelectric applications. Furthermore, the capillary pressure developed at each inter-particle space provides an additional driving force for particle rearrangement and re-shaping during sintering, inducing densification.

The pioneering work of Stookey in 1949 [77] on photosensitive glasses led to the discovery of methods for heterogeneous nucleation, where crystal growth takes place from many nuclei dispersed in the glass matrix after the glass has been formed [78]. Later on, Herczog [79] studied the properties and composition of glasses suitable for crystallization of BaTiO₃ from glasses. Perovskite BaTiO₃ with a minor amount of BaAl₂Si₂O₈ was obtained by heat treating glasses of compositions corresponding to $(x)(\text{BaTiO}_3) + (100-x)(\text{BaAl}_2\text{Si}_2\text{O}_8)$. The grain size was controlled in the range 0.01 to 1 μm by varying the heating rate and the final heat treatment temperature. When the volume content of BaTiO₃ in the glass-ceramic increased from 30 to 60% and the grain size was about 1 μm , the dielectric constant increased from 100 to 1200. For grain sizes less than or equal to 0.2 μm , the relative permittivity was further decreased and found to be independent of temperature; this was attributed to the presence of surface defects in the fine grains. The highest relative permittivity of 1300 at room temperature was achieved at average grain sizes of about 1 μm , as can be observed in **Figure 14**; the breakdown strength and electrical resistivity of this ceramic were also reported to be high.

Nano-sized BaTiO₃ (20–80 nm) was produced by McCauley et al. [80] following the same approach as Herczog [79] and using different heat treatments and compositions. They observed intrinsic size effects at crystal sizes lower than 80 nm and predicted a critical size of 17 nm, at which BaTiO₃ cannot support a ferroelectric transition. Takahashi et al. [81] reported the glass-ceramic of 0.65(Ba_{1-x}Sr_x)TiO₃–0.27SiO₂–0.08Al₂O₃ (BSTS). The heating temperature of glass-ceramics was 1000°C with a small amount of Sn or Zr; also the relative permittivity also decreased with the addition of both of the Sn and Zr. The ϵ_r -T relationship showed a broadening and shift of the Curie point towards room temperature, as shown in **Figure 15**.

The use of solid state reaction for the preparation of BaTiO₃ ceramics has advantages where the products have good crystallinity and low cost, as well as a high level of accuracy of stoichiometric control [82]. However, many ferroelectric materials have high sintering temperatures (>1200°C), making them unsuitable for certain applications, such as LTCC. In this case, it is necessary to include some additives to reduce the sintering temperature. There have been many studies aimed at lowering the sintering temperature of BaTiO₃. The typical additives used include ZnO, CuO, LiF, and CdO. Amongst these additives, LiF proved to be a very effective sintering aid. The effect of LiF in BaTiO₃ was investigated and the results indicate that the sintering point is reduced to approximately 900°C [83, 84].

The use of glass additives in BaTiO₃ was also shown to improve densification behaviour and reduce the required sintering temperature. Jeon et al. [85] studied the effects of BaO-B₂O₃-SiO₂ (BBS) glass in BaTiO₃ ceramics. It was found that the

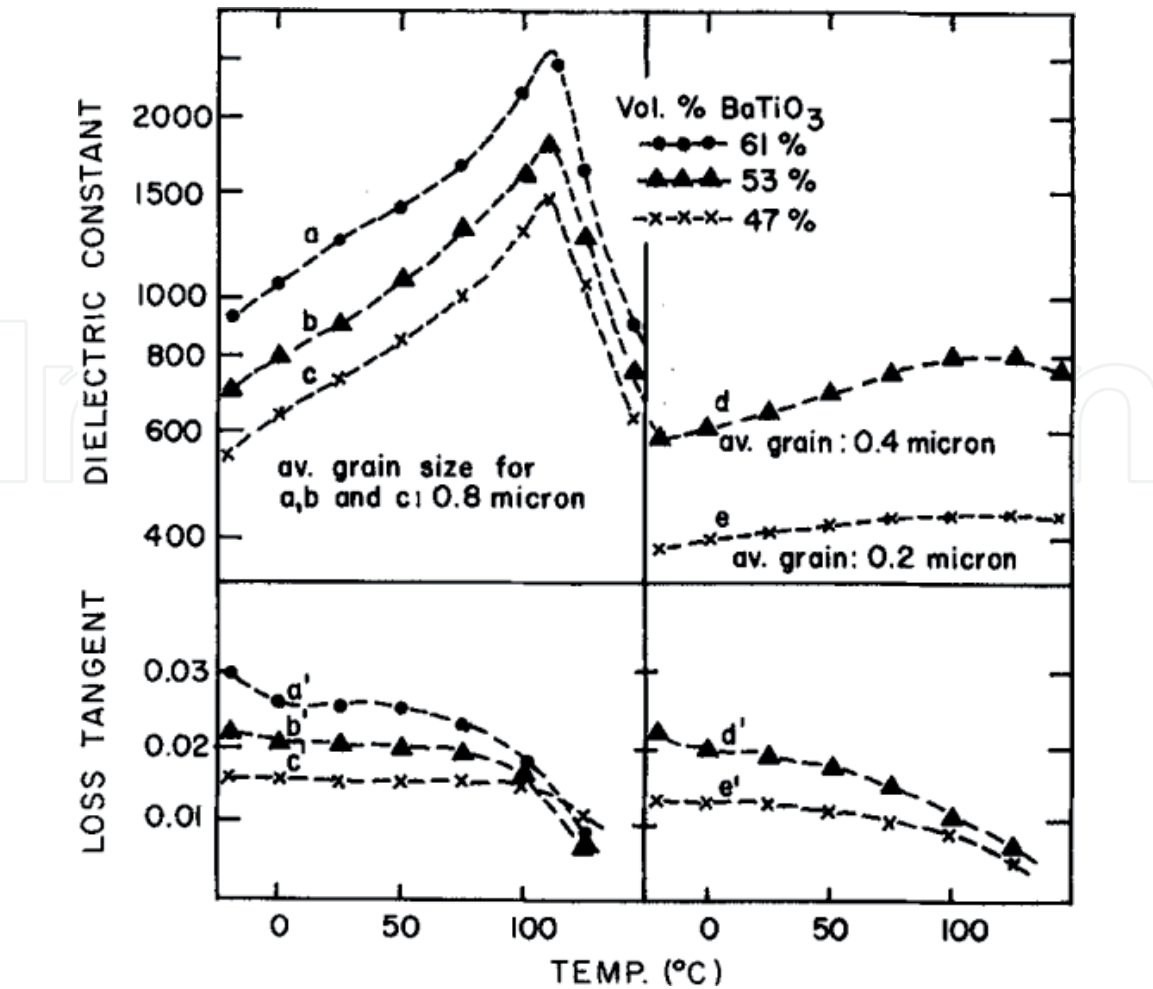


Figure 14.
Variation of dielectric constant and loss tangent with the temperature at 1 kHz [79].

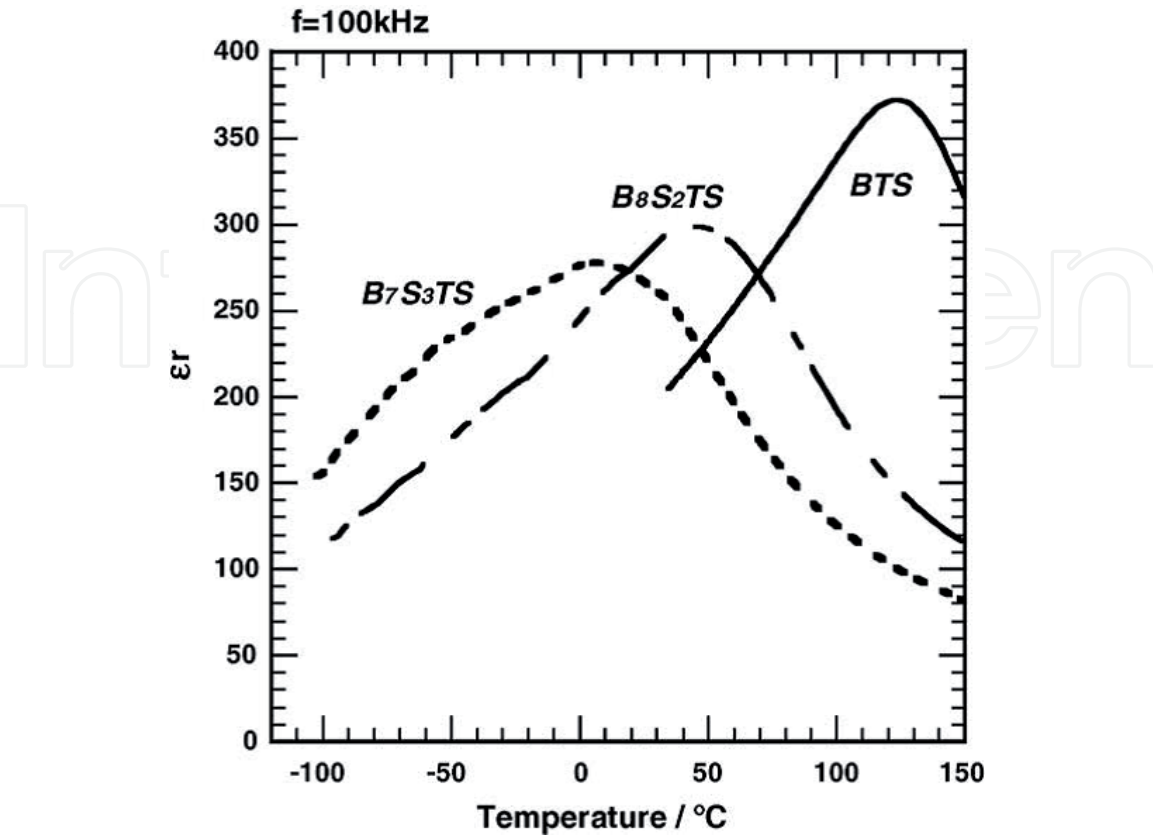


Figure 15.
The ϵ_r -T relationship for BSTS bulk glass-ceramic derived from SnO₂-containing glasses [81].

sintering temperature required to reach a high density ($\approx 93\%$) could be reduced to $\approx 1000^\circ\text{C}$. The influence of glasses on the sintering behavior and properties of ceramics is dependent upon the glass additive content as well as the chemical reaction between the glass and ceramic phases. Three different glass additives for BaTiO_3 were studied by Hsianga; these were $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ (BBS), $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ (PBS), and $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ (ZBS). It was reported that the glasses containing PbO and BaO led to degradation of the dielectric properties and densification of the ceramic. In addition, adding both BBS and PBS caused the formation of a large number of secondary phases [3].

Lin et al. [86] added a manganese oxide-silica glass to pure BaTiO_3 and reported the effect of the liquid phase on the dielectric and ferroelectric properties of the material. The addition of the Mn-Si-O glass enabled densification of the nanocrystalline powder at temperatures in the range $1175\text{--}1300^\circ\text{C}$. At high glass concentrations, they observed the formation of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and a Mn solid solution in BaTiO_3 grains growing at the grain boundaries and inhibiting grain growth. **Figure 16** shows the influence of glass content on the structural and dielectric parameters [86]. It can be observed, that the ceramics with grain sizes in the range of $0.7\text{--}1\text{ }\mu\text{m}$ have the higher relative permittivity. Meanwhile, for the glass doped samples, the higher tetragonality of BaTiO_3 induced through the liquid phase sintering led to larger dielectric permittivity. However, the dielectric loss was also affected by the Mn solid solution in BaTiO_3 and the $\text{Ba}_2\text{TiSi}_2\text{O}_8$ phases.

More recently, Chen et al. [87] studied the addition of $50\text{--}90\%$ of $\text{B}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-SiO}_2\text{-ZnO}$ (BBSZ) glass on the dielectric and ferroelectric properties of BaTiO_3 . By this means, the sintering temperature was reduced to $400\text{--}450^\circ\text{C}$. The second phase of $\text{Bi}_4\text{Si}_2\text{O}_{10}$ was observed when samples were sintered at 450°C and the BBSZ concentration was higher than $60\text{ wt}\%$. Once the solubility limit of BBSZ on BaTiO_3 was exceeded ($\text{BBSZ} > 60\text{ wt}\%$) and the formation of the $\text{Bi}_4\text{Si}_2\text{O}_{10}$ and glass phases took place, some pores of about $1\text{--}2\text{ }\mu\text{m}$ appeared due to the capillary pressure, rearranging the particles and affecting the packing; this reduction in density led to a lower relative permittivity for the $60\text{ wt}\%$ modified samples. When the amount of liquid increased (up to $70\text{ wt}\%$), the porosity decreased and relative permittivity values of 132 and 207 were achieved at 100 kHz and 100 MHz , respectively. The dielectric loss remained at the same level as that of the pure glass at 100 kHz (0.006). At higher BBSZ concentration (80 and $90\text{ wt}\%$), the overall dielectric properties of the samples decreased due to the lower relative permittivity of the glass phase.

Choi et al. [88] reported that the addition of 1 to $7\text{ wt}\%$ of BBS into BaTiO_3 (prepared using flame spray pyrolysis) reduced the sintering temperature at 1000°C , yielding an improvement in relative permittivity in comparison with pure BaTiO_3 sintered at 1300°C . It was also found that the glass additives improved the density

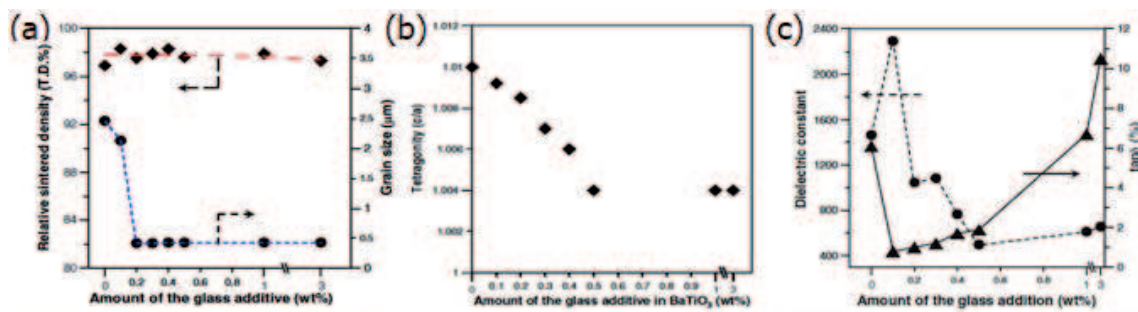


Figure 16.

Effect of glass addition on the (a) grain size (b) tetragonality and (c) dielectric constant and loss of die-pressed BaTiO_3 [86].

of the material with an increase in the grain size by several microns. Wang et al. [26] found that the sintering temperature of BaTiO₃ ceramics could be reduced to about 1100°C using a glass with the composition 27.68BaCO₃–6.92SrCO₃–29TiO₂–22SiO₂–12Al₂O₃–2.4BaF₂ (mol %). The effect of this additive was a reduction in the average grain size. It was also found that the energy storage density of the ceramics increased gradually with increasing glass concentration; the highest energy density value of 0.32 J cm⁻³ was obtained for the sample with 7 mol% of the glass. The influence of glass additives on modified barium titanate ceramics was reported by Puli et al. [35], who studied the dielectric and ferroelectric properties of glass-modified BCZT, specifically the composition 0.85(BaZr_{0.2}Ti_{0.8}O₃)–0.15(Ba_{0.7}ZCa_{0.3}TiO₃). The addition of 15 wt% (0.1BaO + 0.4B₂O₃ + 0.5ZnO) and (0.3BaO + 0.6B₂O₃ + 0.1ZnO) glass powders yielded dielectric breakdown field strengths of 260 and 280 kV cm⁻¹, with recoverable energy density values of about 1.12 and 0.50 J cm⁻³, respectively. The resulting samples were composites comprising a mixture of two phases, BCZT and the glass phase. They attributed the high breakdown strength to the presence of alkali free glass composition, and the low loss dielectric to the low dielectric loss of BZT–BCT ceramic composition.

The effect of up to 9 wt% of CaO–B₂O₃–SiO₂ (CBS) glass additions on the microstructure and electrical properties of Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O₃ (BCZT) was studied by Lai et al. [89]. Samples were sintered at 1300°C for 4 hours in air; in the CBS-free sample, they observed the coexistence of orthorhombic and tetragonal BCZT phases with a small amount of CaTiO₃ secondary phase by means of XRD. The addition of the CBS glass induced a phase transformation to pseudocubic, a shift of the reflections towards lower 2θ values and the coexistence of the orthorhombic and tetragonal phases disappeared. These phase transformations were accompanied by the appearance of another secondary phase, reported to be Ba₂TiSi₂O₈. The density of the BCZT samples increased with CBS content, reaching a maximum when the addition of CBS was 2 wt%, and then slowly decreasing at higher CBS concentrations. Regarding the electrical properties, the sample with 2 wt% CBS exhibited the best ferroelectric properties, a dielectric constant of 8874 (at 106 Hz), a Curie temperature of 116°C, Pr of about 3.18 μC cm⁻², and d₃₃ of 159 pC N⁻¹ due to the improved density achieved by the addition of CBS.

4.2 Potassium sodium niobate systems

KNN is one of the most promising candidates for energy storage properties, yet at present much research has focused on the development of, for example, (BaO,SrO)-TiO₂ [90, 91], (BaO,SrO)-Nb₂O₅ [50] and (BaO,Na₂O)-Nb₂O₅ [92] glass-ceramics. Therefore, the study of KNN glass-ceramics still needs more exploration and in-depth research [93]. Many studies have been conducted on sintering of KNN, but there are currently few reports of true glass-ceramics.

Some previous studies have reported the formation of KNN in a glass-ceramic form [56]. Vernacolota et al. [94] reported that glass-ceramics containing KN and KNN phases can be obtained using silicate glasses prepared with alkali metal and niobium additions. The effects of substituting K by Na on thermal and crystallisation behaviour of KNN-SiO₂ glass-ceramics were reported by Aronne et al. [95]. Kioka et al. [96] and Kongputhon et al. [97] studied the control of the crystallisation behaviour in KNN-SiO₂, by varying the K:Na ratio, as a means of modifying the dielectric properties. Alumina-silicate glasses have also been used to fabricate glass-ceramics containing ferroelectric KNN and their dielectric properties reported by Yongsiri et al. [54]. The influence of CeO₂ as a nucleation agent in borosilicate glasses containing KNN have been reported for energy storage capacitor application by Hanyu et al. [93]. On the basis of their results, Yongsiri et al. [54] suggested that

KNN glass-ceramics could be favourable for use in electro-optical applications. The microstructure, crystallite sizes, and crystal quantity of the KNN glass-ceramics were studied as a function of the heat treatment conditions. The heat treated glass-ceramics were found to contain a KAlSiO_2 phase at heat treatment temperatures between 600 and 675°C, while the perovskite KNN phase was observed at a higher temperature of 700°C, **Figure 17**. The glass-ceramic containing 23.75 mol% of SiO_2 exhibited a relative permittivity value of ≈ 260 and loss tangent ≈ 0.02 at 10 kHz.

The use of a two-stage incorporation method, which involved the separate preparation of KNN and glass powders prior to melting, was also studied by Yongsiri et al. [98]. The calcined KNN powder was mixed with 25 mol% of SiO_2 then melted at 1300°C using the conventional melt-quenching technique. The glass was heat treated at temperatures from 525 to 575°C for crystallisation. Increasing heat treatment temperatures were found to improve the crystal size and crystallinity, which in turn plays an important role in controlling the properties of the glass ceramics, including physical, optical, and dielectric properties. It is clear from the SEM results, **Figure 18** that the crystallisation of the KNN phase occurred at temperatures lower than the observed crystallisation temperature of 648°C from the DTA results. Furthermore, the amorphous XRD patterns were observed in the glass-ceramic samples heat treated at temperatures lower than 550°C. The highest relative permittivity value was 474 at a heat treatment temperature of 550°C, while the transparency decreased with increased temperatures.

KNN ceramics prepared by solid state reaction usually require reaction temperatures around 800°C or, sometimes, the double calculation in order to obtain a homogenous powder; sintering temperatures are usually in the range 1100–1200°C [99]. The three starting materials used in KNN are Nb_2O_5 , with a high melting point of 1520°C, and two alkali metal carbonates, K_2CO_3 and Na_2CO_3 , with melting points of 891°C and 851°C, respectively. Therefore, the alkali metal carbonates/oxides become volatile during the calcination, making it difficult to achieve a chemically homogeneous material. Excess alkali carbonate is used in order to compensate the losses during calcination and to obtain a single phase perovskite product [100]. The studies reported in [96, 100] indicated that a 5 mol% excess of K_2CO_3 and Na_2CO_3 in the raw materials leads to increased stability during calcination at 800°C. The other effect of this excess is an increase in particle size, which is probably due to the liquid phase which forms during the calcination [100]. By adding 3% and 1% excess alkali carbonate the density of KNN has improved and, at the same time, this excess leads to reduce the sintering temperature to 1000°C [101, 102].

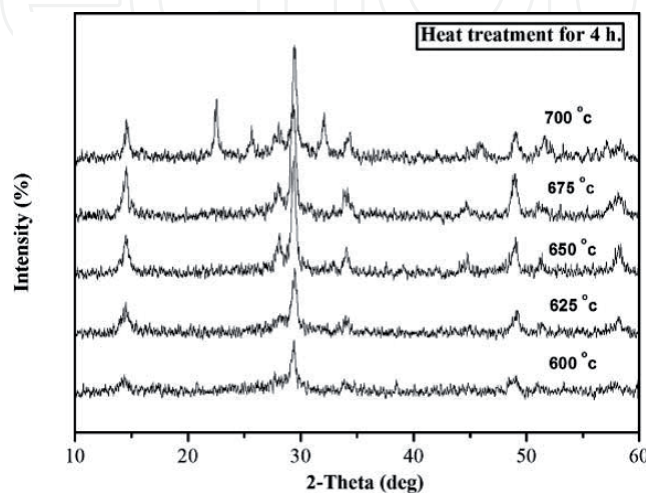


Figure 17.

XRD patterns of the glass-ceramic sample with 5 mol% alumina and 23.75 mol% SiO_2 subjected to different heat treatment temperatures [54].

Sintering temperatures for KNN ceramics are usually $>1000^{\circ}\text{C}$. This needs to be lowered in order to decrease the alkali evaporation during the periods of high temperature, as well as to make it suitable for many desired applications [103]. If lithium additives are added to KNN, the sintering temperature reduces to lower than 1000°C , there is a shift in TC to a higher temperature, and there is an increase in the dielectric constant [104]. Barium borosilicate-based frit (BaO-B₂O₃-SiO₂-Na₂O-K₂O-CuO-CaO) (abbreviated as BBS) was one glassy additive used previously as a sintering aid to KNN. It has been shown to reduce the sintering temperature to 1000°C . In addition, the additive led to an increase in the mechanical properties and a decrease in the dielectric loss, whilst the TC remained high at 400°C ; samples with 1.5 wt% glass frit showed optimal properties as follows: $\epsilon_r = 410$, $\tan\delta = 0.57$ and $d_{33} = 108 \text{ pC N}^{-1}$, **Figure 19** [105].

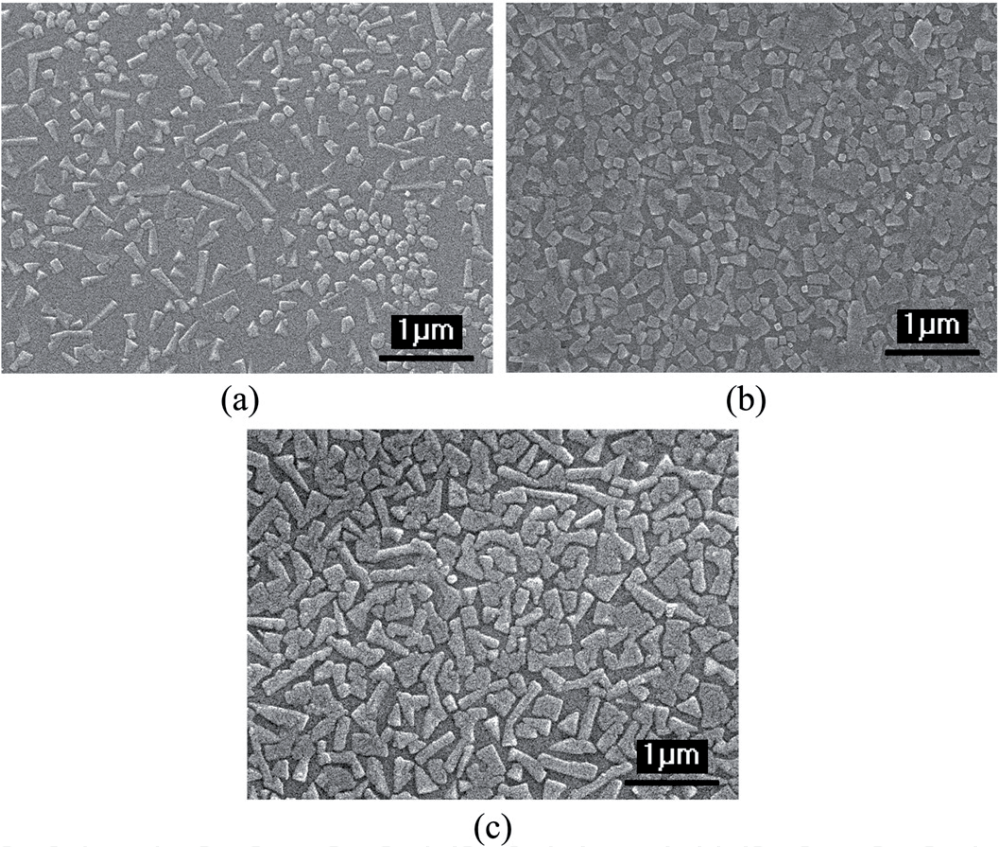


Figure 18. SEM micrographs for glass-ceramic samples heated at different temperatures. (a) 525°C , (b) at 550°C , (c) 575°C [98].

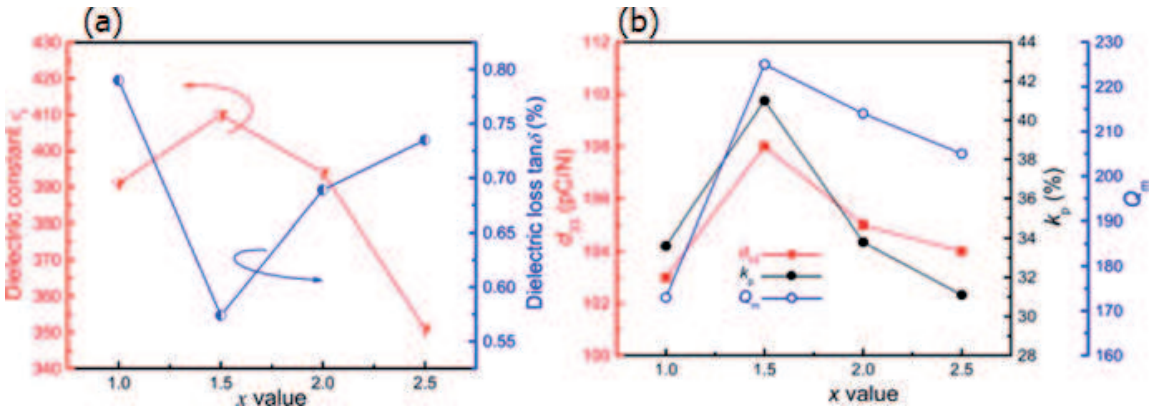


Figure 19. (a) ϵ_r and $\tan\delta$ (b) d_{33} , k_p and Q_m of KNN + x wt% BBS ceramics as a function of the x value [105].

5. Conclusion

Several different ferroelectric glass-ceramics systems were discussed in this chapter. All glasses types were mixed with ceramics, resulting in much improved densification behaviour at reduced sintering temperatures. In addition, nanocrystalline glass-ceramics containing perovskite-structured ferroelectric phases have been researched. These studies indicate that the materials exhibit promising dielectric properties and good stability of relative permittivity values at low heat treatment temperatures comparison with conventional preparation methods, although relatively high dielectric losses were evident. This review suggests that ferroelectric glass-ceramics exhibit promising dielectric properties with good potential for use as energy storage dielectrics at high electric field levels as a result of their nanocrystalline microstructures.

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