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Control of properties of PZT ceramics during liquid-phase sintering

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A PZT ceramic modified by 0.4Pb–(1 − x)(B_2O_3)–x(GeO_2) glass, and glass–ceramics modified by V_2O_5, have been obtained. The influence of the chemical composition of the glasses on the mechanical strength and dielectric parameters of these ceramics is investigated. The mechanical and electrical parameters of PZT ceramics are considerably improved by small additions of glass ($\leqslant$ 1 mass %) of suitable composition. During heat treatment, the mobility of the domain walls may be changed as a result of the interaction of smelt glass with the surface layer of the crystallites (resulting from a change of V''_{Pb} vacancy concentration in grains and decreased mechanical tension on the grain boundaries). By introducing the glass, we can decrease the porosity of the ceramics and thus decrease the attenuation of surface acoustic waves in piezoelectric filters. The origin of the liquid phase during sintering of the PZT glass–ceramics prevents PbO evaporation. This determines the preservation of the solution's stoichiometry. The glass addition leads to a decrease in the sintering temperature of PZT, which simplifies the technological process. The glass ceramics are obtained by common ceramic technology which is used for commercial piezoceramic production. The main technological problem is choosing the chemical composition and concentration of the glass and thermal process parameters.

1. Introduction

Small additives of glass-forming oxides and glasses of special composition are able simultaneously to reduce the ferro- and piezoelectrical ceramic sintering temperature (T_s) and to increase its mechanical and electrical properties. This is of great importance in piezomaterial technology based on $PbTiO_3$ (PT) and the solid solution of Pb (Zr, Ti)O_3 (PZT). The T_s reduction leads to decreased PbO losses during piezoelement calcining, and a rise in mechanical strength causes a safety increase in their functioning in the conditions of the cycle symbol variable assignments [1]. Since there is little information on the theoretical choice of glass modificator composition for piezoelectrical materials, research on the glass components' influence on the mechanical and electrical properties of piezoceramics is of great importance. Glasses of the PbO–B_2O_3–GeO_2 type have been used to modify piezoceramics. They possess high discrystallization stability and have no cations, which could enter the solid solution crystal lattice, changing the ferroelectric phase transition or (at the heterovalent replacements) increasing its electroconductivity, the latter being undesirable. The optimal amount of PbO in the glass (40 mol %) has previously been published [2]. It is a compromise between the tendency to reducing glass smelt viscosity by T_s, and the undesirable poly lead-glass electroconductivity rise, leading as a rule to a reduction of electrical strength and to changes in the characteristics of piezoelectrical ceramics.

2. Results and discussion

The V_2O_5 oxide was introduced into a glass with equal B_2O_3 and GeO_2 content (1–6 mol %) to regulate both the high-temperature viscosity and smelt-wetting capacity. The PZT solid solution (5–15 mol %) was also introduced in order to discover the significance of the solubility and precipitation processes of the crystal phase substance by studying the influence of sintering and intercrystal layer composition on the piezoceramics characteristics.

The ceramics samples with glass additives were made by means of traditional ceramics technology. The glass was smelted in PbO, B_2O_3 and GeO_2 oxides (the PZT solid solution and V_2O_5 were also used) in the platinum crucible at 1573 K, then pounded to particles of $\bar{r} \leqslant 50$ μm, and finally introduced into the ceramics at the grinding stage of the material after synthesis. Due to the higher sensitivity of piezoceramics to modification, the amount of glass introduced was chosen as 1 mol %. The model (diameter 12 mm, height 2 mm) was pressed at a pressure of 98.10^6 Pa. The T_s value of 1533 K was optimal for the given structure. The final size of samples after sintering and mechanical treatment was 10 mm in diameter and 1 mm in height. The mechanical strength of the

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piezomaterial during the tension σ_t was determined, using the disc-crushing method [3], and the electrical properties were determined by means of existing standards.

Not less than ten samples of the same substance and sintering regime were examined. In the course of statistical analysis, the average $\langle a \rangle$ value, average quadratic deviation, $S_{\langle a \rangle}$, from the average, and medium width of the suggestive interval $\pm S_{\langle a \rangle} \cdot t(p, n)$ for suggestive probability $p = 0.95$ were calculated.

As shown in Fig. 1, the $\langle \sigma_t \rangle$ value of piezoceramics is maximal with $x = 0.2$–0.3 in the composition of the glass modifier $0.4\text{PbO} + (0.6\text{–}x)\text{B}_2\text{O}_3 + \text{GeO}_2$, and sharply decreases with $x = 0.4$–0.5. The observed changes $\langle \sigma_t \rangle$ considerably surpass the mistakes, and although the amount of additives (1 mol %) is small, this proves to be due to its composition modification. On the other hand, as our own and other investigators' data show, the glass phase does not change the PZT solid solution composition, and does not form a new crystal substance in ceramics (which is deduced, for example, from analysing the pseudo-binary state diagrams of the initial composition glass–PZT solid solution state). Thus, in accordance with the existing heterophasal ceramic materials strength theory [4], the modifications obtained are connected primarily with changes in σ_g (the glass-like layer strength). Employing IR sectroscopy, we find that the $0.4\text{PbO} + (1\text{–}x)\text{B}_2\text{O}_3 + \text{GeO}_2$-glass composition structure is most homogeneous and organized, with x being 0.2–0.3, but in other cases it represents the combination of local structural groupings of various chemical compositions, where glass forming atoms are in various coordination states.

These types of glass are characterized by light and consequently by decreased structural strength. Data defining the dependence of glass molar volume V_m from the content GeO_2 (Fig. 2) in their composition serve as evidence for this conclusion. The V_m value, x being zero, coincides with the calculated one, provided ~ 40% of boron atoms in the glass composition are in the 4-coordinated state, which coincides with the existing investigators' data. The type of dependence $V_m = f(x)$ differs greatly from the linear one, especially with x being 0.2–0.3, this being evidence of general glass-structure compaction at the expense of the supplementary transition $[\text{BO}_3] \rightarrow [\text{BO}_4]$; thus the increase in strength of the glass-like layer is the original cause of piezoceramic growth $\langle \sigma_t \rangle$.

The introduction of V_2O_5 (up to 3 mol %) and PZT solid solution (up to 10 mol %) into the glass composition leads to a further increase in $\langle \sigma_t \rangle$. V_2O_5 oxide is, firstly, a glass structure depolymerizer, causing a decrease in smelt viscosity leading at ceramic sintering to denser packing of grains. Secondly, it possesses surfacial active properties, and consequently increases the

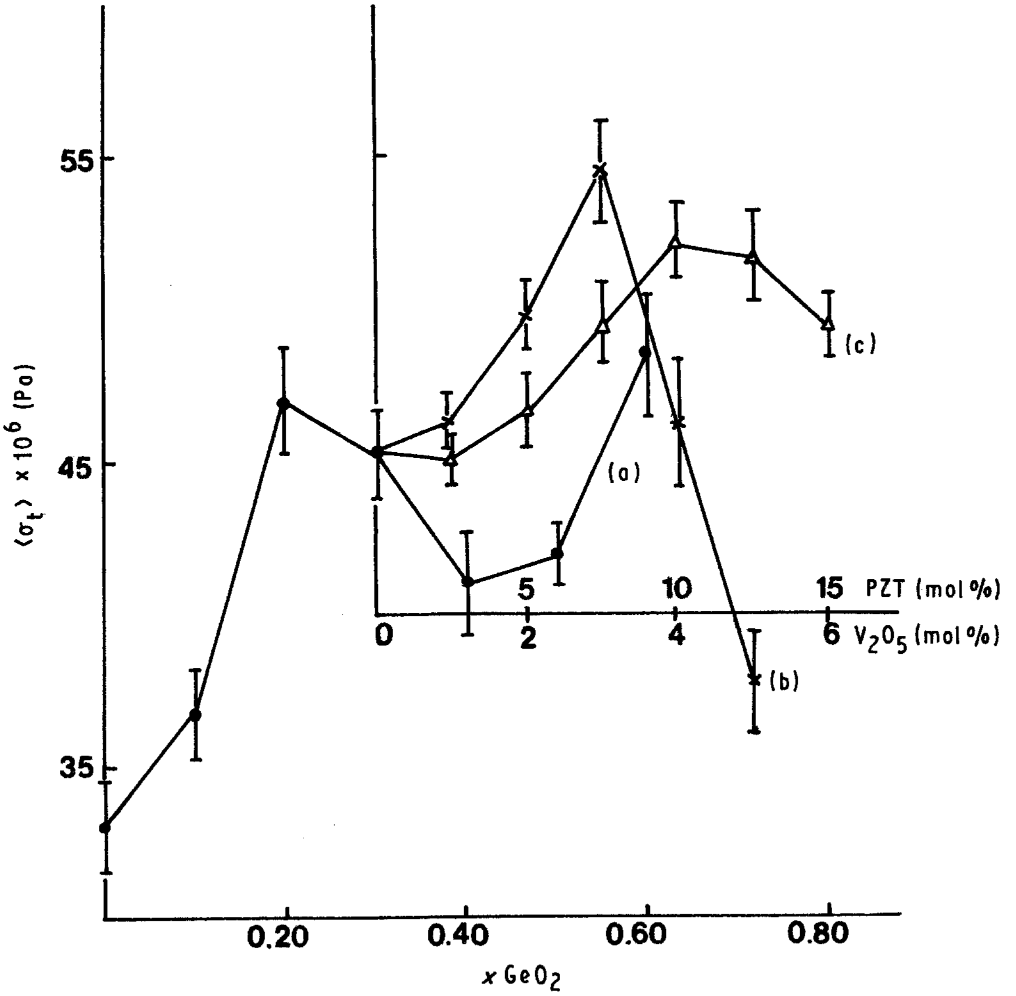

Figure 1 The influence of cation composition in (a) the 0.4PbO–$(1 - x)\text{B}_2\text{O}_3$–$x\text{GeO}_2$ glass system, (b) V_2O_5 oxide additive, and (c) PZT solid solution on the mechanical strength of piezoceramics. Glass content = 1 mass %, calcining temperature = 1533 K.

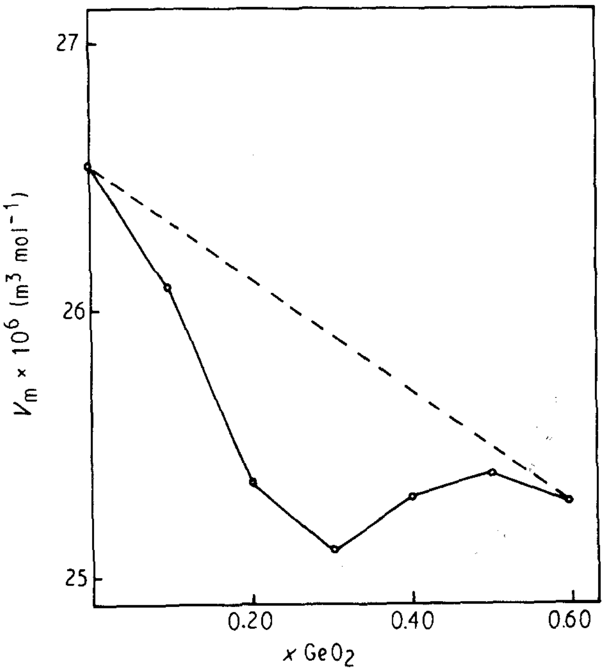

Figure 2 V_m, molar volume change of the $0.4PbO-(1-x)B_2O_3-xGeO_2$ glass system, dependent on GeO_2 content.

wetting capacity of the lead–boron–germanium smelt, and leads to interphase strength growth at the expense of chemisorptional strengthening during the growth of the crystal grain surface with such reactions as

$$PbTiO_3 + V_2O_5 \rightarrow PbO \cdot V_2O_5 + TiO_2 \quad (\Delta G_T^\circ = -1.15 \cdot 10^5\ J\,mol^{-1})$$

$$PbZrO_3 + V_2O_5 \rightarrow PbO \cdot V_2O_5 + ZrO_2 \quad (\Delta G_T^\circ = -1.04 \cdot 10^5\ J\,mol^{-1})$$

However, at a V_2O_5 content higher than 3 mol %, new phase isolation of the $PbO \cdot V_2O_5$ composition must take place, and $\langle \sigma_t \rangle$ decreases again. According to our results, the introduction of a $Pb(TiO_{0.47}Zr_{0.53})O_3$ solid solution into the composition during the glass smelting (this being the main piezomaterial component) approaches the thermal expansion coefficient of the material grains and layer. This introduction reduces strains in the glass ceramics and thus leads to $\langle \sigma_t \rangle$ growth.

Analysing the influence of various cation compositions of glass wall additives on piezoceramics, one must keep in mind that piezoceramic glass modification differs greatly from oxide or crystal composite modification. Glass-forming atoms (B, Si, Ge) do not form a solid solution with PZT material and can react with the crystalline phase, although the layer of surface grains change their point or linear defect concentrations and also change their mechanical tension value, influencing the grain in the polycrystal (for example at the expense of the difference of grain and layer in the thermal expansion coefficient).

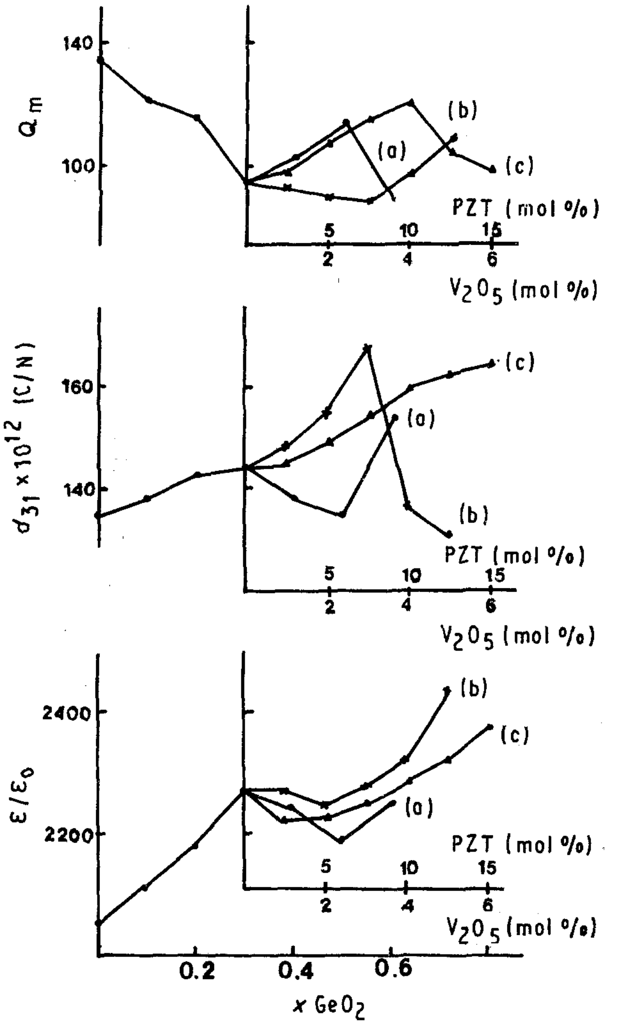

Figure 3 The influence of cation composition in (a) the $0.4PbO-(1-x)B_2O_3-xGeO_2$ glass system, (b) V_2O_5 oxide additive, and (c) PZT solid solution on the electrical properties of piezoceramics. Glass content = 1 mass % calcining temperature = 1533 K.

Fig. 3 shows the dependence of single electrical properties such as dielectric constant $\varepsilon/\varepsilon_0$, piezomodule d_{31} and mechanical durability Q_M of PZT piezoceramics, containing 1 mol % glass with different B_2O_3 and GeO_2 oxide correlations, amounts of V_2O_5 oxide, and PZT solid-solution components. All the above-mentioned factors regularize and in a complex manner influence the properties of piezoceramics. But the observed changes cannot be explained as simply due to the influence of glass composition. In our opinion, such changes indicate the leading role of the electrical condition of the crystal grain surfacial layers.

Thus the $\varepsilon/\varepsilon_0$ of glass is comparatively low (10–20) and depends weakly on its composition. At the same time, $\varepsilon/\varepsilon_0$ of piezoceramics reaches 2000–3000 (at 293 K). We introduced 1% glass, having the $(1-y)0.4PbO + (0.6-x)B_2O_3 + xGeO_2 + yV_2O_5$ composition, which allows $\varepsilon/\varepsilon_0$ to change by 10–20%, depending on the value of x and y (Fig. 3). The same active role of glass is seen in its influence on the d_{31} and Q_M values. The glass smelt–PZT solid solution interaction takes place on the crystal grain surface. Thus the observed influence of cation glass composition on the ε, d_{31}, Q_M values of piezoceramics will take place, whilst having a simple domain structure. In our opinion, the influence of the glass phase is connected with V''_{Pb} vacancy concentration changing (as at heterovalent replacements in the solid solution lattice). The conclusion drawn is connected both to the experimental data, devoted to $Pb(Ti, Zr)O_3$ solid-solution solubility research on glass smelts of different compositions, and to the results of thermodynamic estimations of the reactions, passing at the smelt interaction with ceramics crystal phase.

It is known [5] that the extent of selective solubility of PbO from the crystal phase composition (i.e. V''_{Pb} concentration in the surfacial grains layers) will depend on the isobar–isothermal potential value during the reaction between PbO and local structural grouping compositions, available in the initial glass. The chemical composition of local structural groupings is different in glasses of several different types. The relative content of the structure $[B_mO_n]$ complexes is the dominant factor here. The extent of PbO solubility (from the PZT composition) is proportional to the non-combined amount of B_2O_3 (the composition $5PbO \cdot 4B_2O_3$ with ΔG°_T being $-4.9795 \cdot 10^6$ J mol^{-1} is formed at the reaction). This extent will be maximum for x at 0.3 in the $0.4PbO + (0.6 - x)B_2O_3 + GeO_2$-glass composition, and minimum for x at 0.5.

The PbO solubility in the glass of $0.4PbO + 0.6GeO_2$ composition is also considerable in the reaction $2(PbO \cdot GeO_2) + PbO \rightarrow 3PbO \cdot 2GeO_2$ with $\Delta G^\circ_T = -3.50 \cdot 10^5$ J mol^{-1}. Thus it is possible that the maximum amount of vacancy formation in the surfacial layer of the ceramic crystal grains takes place at $x = 0.2$–0.3 and 0.6, and consequently that the expansion of the domain-wall mobility, which leads at the mentioned level to ε and d_{31} growth and Q_M increase, also takes place at this value. Using the same results it is possible to explain the observed piezoceramics electrical property dependences from the V_2O_5 content of the glass and the PZT solid solution. At first (up to 3 mol% V_2O_5), ε and d_{31} are growing with the increase in V''_{Pb} content (as an interaction result of PbO and V_2O_5) and then they reduce, due to the non-ferroelectrical $PbO \cdot V_2O_5$ phase formation. The introduction of PZT increases the PbO content in the glass under discussion, and therefore acts in another way. With a high PZT content, the solid solution may crystallize out of fusion (during ceramic sintering) and as a result we have a decrease in the amount of glass phase, and an increase in ε and d_{31}.

3. Conclusions

The mechanical and electrical characteristics of piezoceramics are considerably changed by means of cation glass content (even at a low content of ~ 1 mass %). The main condition for the production of maximum-strength piezoceramics is that the glass should have a homogeneous and compact structure. The local structural grouping of the chemical composition exchange of the glass exerts an influence on the amount of V''_{Pb} in the crystal-grain layers, and in this way influences the domain structure lability, and thus its dielectrical and piezoelectrical properties.

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