Subsolidus phase equilibria in the PbO-poor part of the TiO_2–PbO–SiO_2 system and its application in low-temperature thick-film dielectrics

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Subsolidus equilibria in the PbO-poor part of the TiO_2–PbO–SiO_2 diagram were studied with the aim of investigating possible applications for low-temperature thick-film dielectrics. The tie lines are between $PbTiO_2$ and $PbSiO_3$, and between $PbTiO_3$ and SiO_2. The results show that the TiO_2, when added to low-temperature softening point glasses, reacts with the PbO from the glass, so forming $PbTiO_3$. These results were applied to a low-temperature firing dielectric, consisting of a lead-rich PbO–SiO_2–B_2O_3 glass filled with a TiO_2 powder. The conversion of TiO_2 to the $PbTiO_3$ crystalline phase was observed above firing temperatures of approximately 600 °C. The kinetics of the reaction depend on the particle size of the TiO_2.

I. INTRODUCTION

The standard thick-film technology for applications in electronics and sensors normally makes use of ceramic alumina substrates, which have a good thermal and chemical stability. In this case, conductors, multilayer dielectrics, and resistors are screen printed and fired at a standard temperature of 850 °C. However, this processing temperature is not compatible with many potentially useful substrates. For instance, high-strength steel,[1] Ti,[2] and Al alloys have much better elastic properties than Al_2O_3, and hence are better suited to piezoresistive sensors. Al, Al-Si, and Al-SiC composites are promising materials for power electronics because of their good thermal conductivity. Finally, thick films on glass have promising applications in display technology, chemical microreactors, and biotechnology. These substrates all require processing temperatures limited roughly to the range 500 °C–600 °C because of melting (Al, Al-Si, and Al-SiC), excessive oxidation (Ti alloys), degradation of mechanical properties (steels), and softening (glass).

Suitable thick-film dielectrics are needed as insulating layers on metallic substrates as well as for multilayer or overglaze compositions. However, the dielectric layer ought to be densely sintered after first firing, but upon later firings of conductors and resistors at the same temperature on its surface, it ought not to melt or soften again. These desirable characteristics can be obtained with crystallizable glass, a mixture of glass and ceramics (e.g., Al_2O_3), or a combination of both. In this work, we endeavor to investigate the combination of a low-melting, lead-rich glass with a reactive TiO_2 filler. The glass is based on the lead borosilicate system, similar to the glass phase used in thick-film resistors[3] and overglazes. Resistors, which are usually fired around 850 °C, have a PbO/SiO_2 molar ratio of about 1/2. The overglaze compositions, which have lower firing temperatures in line with our requirements (500 °C–600 °C), are richer in PbO: the PbO/SiO_2, analyzed with an energy-dispersive x-ray analyzer (EDS), is roughly 45 mol% PbO/55 mol% SiO_2. The addition of a reactive TiO_2 filler in these glasses would presumably result in the following reaction during firing

PbO (from glass) + TiO_2 ⋙ $PbTiO_3$ (+ glass depleted in PbO)

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The above-mentioned reaction will stabilize the dielectric by increasing the softening point of the glass (by depleting it in PbO) and increasing the crystalline volume fraction by a factor of around 2, as the reduced cell volumes for TiO_2 and $PbTiO_3$ are 33.9 A^3 (JCPDS 86-4921) and 63.3 A^3 (JCPDS 72-1135), respectively, assuming that the solubility of the TiO_2 in the glass is small.

In this work, we first investigated the subsolidus phase equilibria (in air) in the PbO-poor part of the TiO_2–PbO–SiO_2 system. The results would indicate possible interactions between the PbO-SiO_2 glass and the TiO_2. Subsequently, we extend these results to the fabrication and study of a thick-film dielectric comprised of a low-melting PbO–B_2O_3–SiO_2 glass and crystalline TiO_2 powder with two grain sizes.

The binary compound $PbTiO_3$ in the PbO–TiO_2 system melts congruently at 1285 °C. The melting temperatures of the eutectics are 838 °C on the PbO side and 1240 °C on the TiO_2 side.[4] Four binary compounds, $PbSiO_3$, Pb_2SiO_4, Pb_3SiO_5, and Pb_4SiO_6, exist in the PbO–SiO_2 system.[5] The eutectic composition on the SiO_2-rich side of the system is at 62% PbO and the eutectic temperature is 739 °C. Two more eutectics are formed between $PbSiO_3$ and Pb_2SiO_4, and between Pb_2SiO_4 and Pb_3SiO_5, with melting temperatures of 714 °C and 711 °C, respectively. The Pb_4SiO_6 compound melts incongruently at 725 °C. No binary compound exists in the SiO_2–TiO_2 system. The eutectic composition on the SiO_2-rich side of the system is at 90% SiO_2 and the eutectic temperature is 1550 °C.[6]

II. EXPERIMENTAL

A. TiO_2–PbO–SiO_2 phase equilibria

The starting powders were TiO_2 (99%; Fluka, Buchs, Switzerland), PbO (99.99%; Johnson Matthey, London, UK), and SiO_2 (99.9%; Riedel de Haen, Lisbon, Portugal). The oxides were mixed in isopropyl alcohol, pressed into pellets, and fired up to five times in air at 700 °C with intermediate grinding. During firing, the pellets were placed on platinum foils. Heating rate was 10 K/min and the time at the temperature 18 h. X-ray analysis of reacted samples indicated completed reactions even (in some cases) after only two firing cycles. However, five "firings" were used to be reasonably sure that the equilibria were obtained. The compositions of the relevant samples in the PbO-poor part of the TiO_2–PbO–SiO_2 system are shown in Fig. 3. The SiO_2/PbO molar ratio in the glass phases is marked near the $PbSiO_3$ compound in the PbO–SiO_2 system.

The fired materials were characterized by x-ray powder diffraction (XRD) analysis using an x-ray diffractometer (PW 1710; Philips, Eindhoven, The Netherlands) with CuKα radiation. XRD spectra were measured from $2\Theta = 20°$ to $2\Theta = 70°$ in steps of 0.02°. A scanning electron microscope (SEM; 5800; JEOL, Tokyo, Japan) equipped with a link ISIS 300 EDS was used for the overall microstructural and compositional analysis. Samples prepared for the SEM were mounted in epoxy in a cross-sectional orientation and were then polished using standard metallographic techniques. Before analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and to avoid charging effects. The microstructures of the polished samples were studied by back-scattered electron imaging using compositional contrast to distinguish between the phases that differ in density (average atomic number = Z).

B. Glass–TiO_2 dielectric

The preparation conditions for the PbO–SiO_2–B_2O_3 glass frit are identical to previous work on dielectrics and resistors with low firing temperature.[7] The glass had a nominal starting molar composition of 44.9 PbO + 33.3 SiO_2 + 19.2 B_2O_3 + 2.6 Al_2O_3, with B_2O_3 further depressing the firing temperature,[8] and Al_2O_3 inhibiting crystallization.[9] After the fabrication of the frit, the glass was mixed with two different TiO_2 powders (99.9%, 5000 nm; Aldrich, Milwaukee, WI, and 99.5%, 21 nm; Degussa Aeroxide, Dusseldorf, Germany) and a suitable printing vehicle[7] to form thick-film pastes. These pastes were then printed on 96% Al_2O_3 substrates (Kyocera A–476) and fired in a Sierratherm belt furnace. The chosen firing schedules subjected the films to a dwell time of 15 min at the indicated firing temperature, with temperature rise and fall rates of approximately 50 K/min.

The degree of conversion of TiO_2 to $PbTiO_3$ was assessed by XRD (D500; Siemens, New York, NY) and measurements of the areas of the TiO_2 and $PbTiO_3$ peaks.

III. RESULTS AND DISCUSSION

A. TiO_2–PbO–SiO_2 phase equilibria

The results of the XRD analysis of the relevant samples, fired in air at 700 °C, are summarized in Table I. The nominal compositions of the samples and the phases identified after firing are given there.

TABLE I. Results of the XRD analysis of some compositions in the TiO_2-PbO-SiO_2 system, fired in air at 700 °C.

Nominal composition	Phases identified
$TiO_2 + SiO_2$	$TiO_2 + SiO_2$
$TiO_2 + PbO + SiO_2$	$PbTiO_3 + SiO_2$
$TiO_2 + PbO + 2\ SiO_2$	$PbTiO_3 + SiO_2$
$TiO_2 + 2\ PbO + SiO_2$	$PbTiO_3 + PbSiO_3$
$TiO_2 + 3\ PbO + SiO_2$	$PbTiO_3 + PbSiO_3$
$TiO_2 + 2\ PbO + 2\ SiO_2$	$SiO_2 + PbTiO_3 + PbSiO_3$
$2\ TiO_3 + PbO + SiO_2$	$PbTiO_3 + TiO_2 + SiO_2$

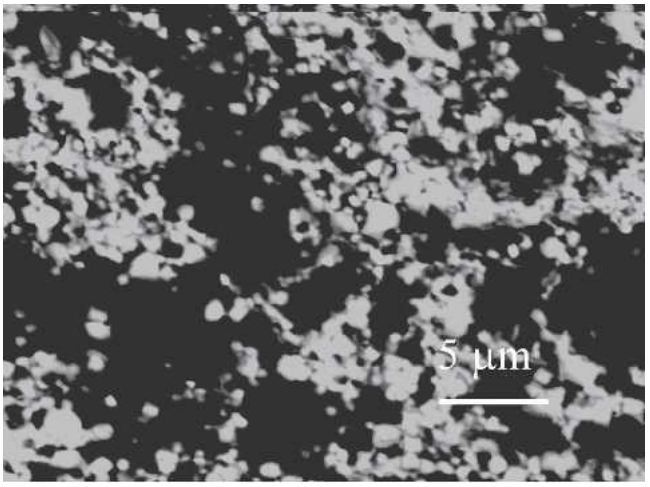

FIG. 1. Microstructure (backscattered electrons) of the sample with the nominal composition TiO_2 + PbO + SiO_2 fired at 750 °C. The material is a two-phase mixture of SiO_2 (dark phase) and $PbSiO_3$ (light phase).

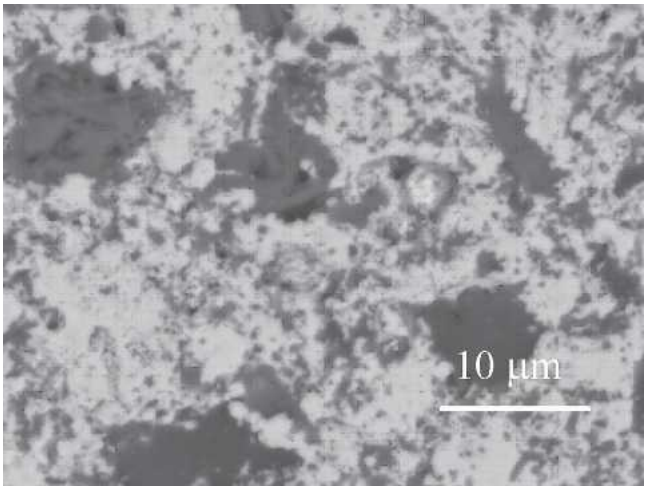

FIG. 2. Microstructure (backscattered electrons) of the sample with the nominal composition 2 TiO_2 + PbO + SiO_2 fired at 750 °C. The material is a three-phase mixture of TiO_2 (light gray phase), SiO_2 (dark phase), and $PbTiO_3$ (light phase).

The microstructures of the materials with the nominal compositions TiO_2 + PbO + SiO_2 and 2 TiO_2 + PbO + SiO_2 are shown in Figs. 1 and 2, respectively. The TiO_2 + PbO + SiO_2 sample is a two-phase mixture of SiO_2 (dark phase) and $PbSiO_3$ (light phase), whereas the 2 TiO_2 + PbO + SiO_2 sample is a three-phase mixture of TiO_2 (light gray phase), SiO_2 (dark phase), and $PbTiO_3$ (light phase).

Based on the results obtained by XRD and EDS, a subsolidus PbO-poor part of the TiO_2–PbO–SiO_2 diagram, shown in Fig. 3, was constructed. No ternary compound was found. The tie lines are between $PbTiO_3$ and $PbSiO_3$, and between $PbTiO_3$ and SiO_2. The upper, PbO-rich part of the phase diagram, which was not

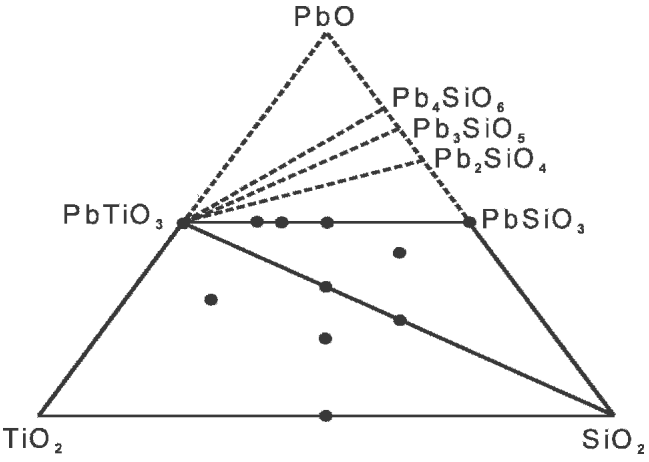

FIG. 3. The proposed subsolidus ternary phase diagram of the PbO-poor part of the TiO_2–PbO–SiO_2 system. The PbO-rich part of the phase diagram, which was not investigated, is shown with dotted lines.

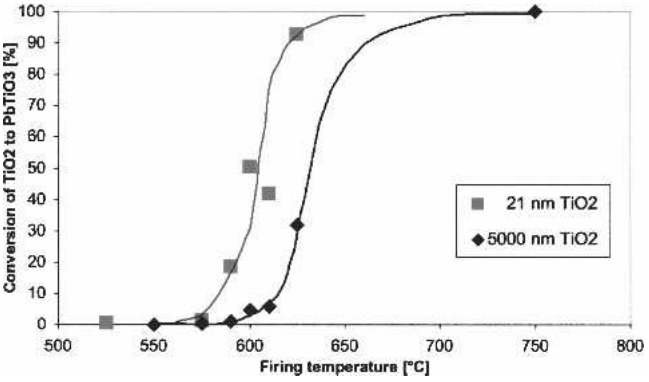

FIG. 4. Degree of conversion of TiO_2 to $PbTiO_3$, estimated from the XRD measurements.

investigated, is shown with dotted lines. Based on the phase equilibria and the compounds in the PbO-SiO_2 system,[5] the tie lines between $PbTiO_3$ and Pb_2SiO_4, $PbTiO_3$ and Pb_3SiO_5, and $PbTiO_3$ and Pb_4SiO_5 were envisaged.

Therefore, the results indicate that the TiO_2, if added, reacts with the PbO in the low-temperature-melting glass, forming $PbTiO_3$ and thus decreasing the PbO concentration of the glass phase and increasing its melting temperature.

B. Glass–TiO_2 dielectrics

The XRD results for dielectrics consisting of 86% V6 glass + 14% TiO_2 by mass are shown, in Fig. 4, as a function of firing temperature and for both TiO_2 sizes. The composition has a Ti/Pb molar ratio of approximately 0.63 and, as expected from the above results, complete conversion of TiO_2 to $PbTiO_3$ takes place, with the (kinetically limited) transition occurring between 580 °C and 630 °C for the nanoscale TiO_2 powder. This

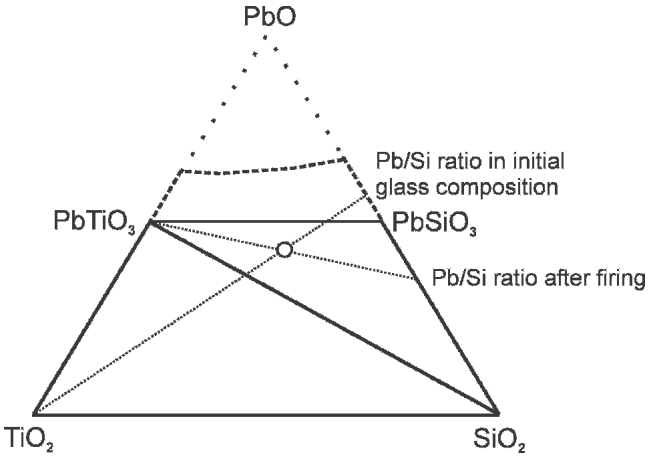

FIG. 5. The composition of 86 wt% glass and 14 wt% TiO_2 projected onto the TiO_2–PbO–SiO_2 phase diagram. The PbO/SiO_2 molar ratio before and after the formation of $PbTiO_3$ is indicated by dotted lines.

temperature range is shifted by approximately 25 °C to higher temperatures for the larger powder. The conversion is accompanied by a change of color, from almost white to yellowish, which is characteristic for $PbTiO_3$.[10] The PbO/SiO_2 molar ratio in the initial glass composition is 1.35. After firing and the formation of the $PbTiO_3$, the PbO/SiO_2 ratio in the glass phase is changed to 0.49. This is schematically depicted in Fig. 5. The composition of 86 wt% glass and 14 wt% TiO_2 is shown projected onto the TiO_2–PbO–SiO_2 phase diagram. The composition is denoted as an open circle. Dotted lines through this composition show the initial PbO/SiO_2 ratio and the ratio after the formation of the $PbTiO_3$.

These promising results indicate that we can obtain

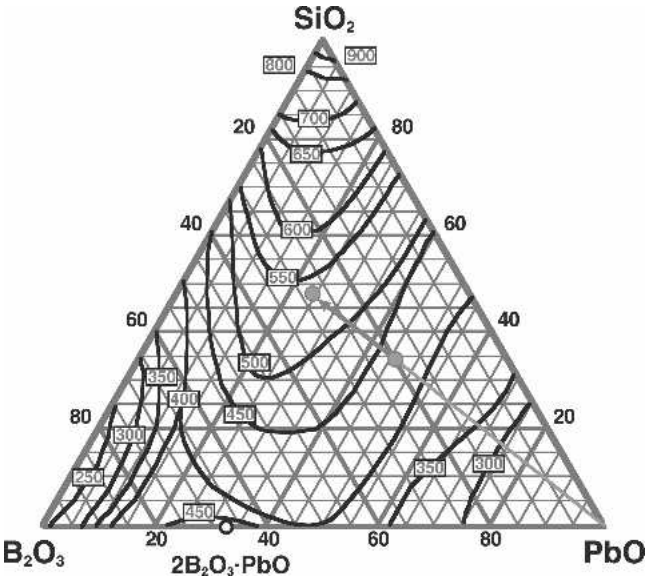

FIG. 6. Glass transition temperatures[11] in lead borosilicate glasses as a function of molar composition, with the starting and ending compositions of the glass in our dielectric.

stabilized low-firing dielectrics: the estimated shift in the glass composition, depicted in Fig. 6,[11] entails an increase of approximately 100 °C in the glass-transition temperature, and the filler volume fraction is estimated to increase from about 17%–35%.

However, the first tests to apply this dielectric onto aluminum substrates were not successful because it tended to spall off from excessive compressive stresses. This is because of the low thermal coefficient of expansion (TCE) of both phases (the glass and the $PbTiO_3$) of the resulting dielectric: PbO depletion results in a strong decrease in the TCE of the glass,[11] and $PbTiO_3$ actually has a negative TCE up to its Curie point at 490 °C.[10] This makes the dielectric useful for applications involving low-expansion substrates such as float glass or probably even 3.3 borosilicate glass. However, the application on most metallic substrates would need a higher thermal expansion and a slightly lower reaction temperature (550 °C would be ideal). This could probably be accomplished by starting with a glass that has a higher lead content, and by limiting the amount of reactive TiO_2 filler or the degree of reaction.

IV. CONCLUSIONS

An extensive study of the lead-poor region of the TiO_2–PbO–SiO_2 system was carried out. The important result is that TiO_2 has a strong affinity for PbO, so forming $PbTiO_3$. This feature was used in the formulation of a stabilized low-firing thick-film dielectric comprised of PbO–B_2O_3–SiO_2 (–Al_2O_3) glass frit and a dispersed TiO_2 powder. The latter should be nanoscale to improve the reaction kinetics. In such a case, the TiO_2 also reacted with the PbO in the glass at around 600 °C, forming $PbTiO_3$ and thus stabilizing the dielectric by increasing the filler volume fraction and through depletion in PbO, by increasing the softening point of the glass. Such dielectrics have a low thermal expansion coefficient and are thus very useful on certain substrates such as glasses.

Although lead-bearing glasses for electronics are still allowed as an exception to the European Union Restriction of Hazardous Substrates (RoHS) directive,[12] there is a strong trend toward making thick-film materials fully lead-free if possible. Therefore, further work will be focused on studying and developing similar low-temperature, lead-free materials systems and dielectrics.

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