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Thermal and dielectric properties of zirconyl phosphate compact

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Experimental results are presented on the measurements of thermal expansion (up to 1500 °C), thermal conductivity (up to 1000 °C), dielectric constant (up to 450 °C) and tan δ (up to 800 °C) of zirconyl phosphate compacts obtained by sintering at 1600 °C. The thermal expansion coefficient of the samples at the temperature below 1100 °C was less than $1.7 \times 10^{-6}\,°\mathrm{C}^{-1}$. The samples showed a definite shrinkage at temperatures of 1110 and 1470 °C due to the phase transformations. The expansion at 1500 °C was less than that at 1100 °C probably because of the phase transformation. The thermal conductivity at room temperature was a very small value (0.0046 to 0.0065 $\mathrm{cal\,s^{-1}\,cm\,°C^{-1}\,cm^{-2}}$). The dielectric constant was close to 9. The value of tan δ ($\simeq 0.0001$) measured is one of the lowest values for ceramic materials.

1. Introduction

Zirconyl phosphate [$(ZrO)_2P_2O_7$] is a low thermal expansion compound known to be stable up to 1600 °C [1]. Usually it is not possible to sinter this compound without any additives. The single oxides, ZnO, MgO, CoO, Fe_2O_3, MnO_2, Nb_2O_5 and Ta_2O_5, are added to obtain a dense compact at temperatures ranging from 1300 to 1550 °C [2, 3]. The mixed oxide of Nb_2O_5–La_2O_3 is effective in raising the sintering temperature to 1600 °C [4]. The addition of SiO_2–Ta_2O_5 improves the strength [3].

The crystal of zirconyl phosphate expands anisotropically. For example, its expansion coefficient is positive in the direction of the a axis and the c axis while it has a negative coefficient in the b axis direction at temperatures up to 1000 °C [2]. This anisotropic expansion tends to cause microcracking which reduces the strength [2–4]. In order to improve the strength, several approaches have been attempted to remove the microcracks, lowering the grain size [2, 3] and aligning the crystal axis [4].

The highest heat-resisting temperature for the low expansion ceramics is about 1400 °C which is the decomposition temperature of cordierite [5]. Zirconyl phosphate, however, can withstand a temperature 200 °C higher than the decomposition temperature of cordierite. Zirconyl phosphate can, thus, be useful in applications of heat-resistant materials. However, because of its relatively low strength it is not suitable as a structural material. Both zirconyl phosphate and cordierite are good insulating materials due to their poor electrical conductivity. A good insulator is required to have a low dielectric constant and low tan δ, so that it reduces dielectric losses. Dense cordierite has relatively poor dielectric properties and is not considered to be an excellent insulator at high temperatures [6]. The dielectric and thermal properties of zirconyl phosphate have not been previously reported except for the report on the thermal expansion in the temperature range up to 1000 °C.

The present study was undertaken to characterize the thermal and dielectric properties of zirconyl phosphate. The results of the measurements of thermal expansion (up to 1500 °C), thermal conductivity (up to 1000 °C), dielectric constant (up to 450 °C) and tan δ (up to 800 °C) are presented.

2. Experimental procedure

Zirconyl phosphate was sintered at 1600 °C using amorphous zirconyl phosphate as a raw material with Nb_2O_5 (99.9%) and La_2O_3 (99.9%) as additives [4], that is, amorphous zirconyl phosphate powder was mixed with Nb_2O_3 and La_2O_3 additives with ratio Nb:La = 1:1. Three different amounts of the additive were used: 1.43, 1.6 and 1.8 wt %. The resulting powder mixture was fired at 1100 °C for 1 h in air. The fired powder was then mixed with the water solution of 2 wt % polyethylene glycol. After drying and grinding, the powder sample was moulded in a plate ($7.5 \times 5 \times 36\ \mathrm{mm}^3$ or $8 \times 13 \times 35\ \mathrm{mm}^3$) using a steel die. First, the sample was pressed with 70 MPa by a uniaxial press and then with 140 MPa by a hydrostatic press. The amorphous zirconyl phosphate contains some evaporative materials, and when this is heated to 1600 °C, a weight loss of about 3.9 wt % is observed. In order to prevent the cracking of compacts with these gases, the following processing scheme was used: 20 to 400 °C at 3 °C min^{-1}, at 400 °C for 1 h, 400 to 950 °C at 15 °C min^{-1}, at 950 °C for 1 h, 950 to 1300 °C at 15 °C min^{-1}, at 1300 °C for 1 h, 1300 to 1600 °C at 5 °C min^{-1}, and at 1600 °C for 1 h in air.

The thermal expansion was taken on a Rigaku 1700TMA dilatometer. The measurements were first

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conducted using alumina as standard, and the measurement errors were determined. A 20 mm long sample was then used to measure the thermal expansion from room temperature to 1500 °C raising the temperature at the rate of 10 °C min^{-1}. The thermal expansion of the sample was determined at each temperature by subtracting the expansion of alumina from the measured values. Among the samples used for measurements that obtained by use of 1.43 and 1.8 wt % of additive showed orientation in the *a* and *c* axis direction, and those samples were cut along that axis. The sample obtained by use of 1.6 wt % additive showed no orientation.

The thermal conductivity was found by the laser flash method using ULVAC TC-3000. The sample used was a 10 mm diameter disc with a thickness of 1 mm [7].

For the dielectric measurements, plate-like samples with dimensions 11 × 7 mm^2 and thickness up to 1 mm were used. The sample surface was coated by 200 nm thick gold film by sputtering and a platinum wire was pasted on top of the gold layer with gold paste. The dielectric constant and loss factor were measured in the 3×10^4 to 10^6 Hz range with a wide band capacitance bridge of AS-4079K TR-1C (Ando Electric Co.).

3. Results and discussion

Zirconyl phosphate is sintered by use of the additives obtained by combining Nb_2O_5 and La_2O_3 at a ratio of Nb:La = 1:1. The bulk densities of the resulting compacts were 3.64, 3.25 and 3.62 g cm^{-3}, respectively, for Compact-1 with 1.43 wt % additives, Compact-2 with 1.6 wt % additives and Compact-3 with 1.8 wt % additives [4]. The porosity calculated from the difference between the theoretical density of 3.80 g cm^{-3} [8] and measured density was 4.5% for Compact-1 and 14.5% for Compact-2. Compact-2, having a higher porosity, was found to be composed of non-oriented particles less than 10 μm and there was no crystalline orientation in the structure. On the other hand, the particle in Compact-1 and -3 were slightly oriented in the direction perpendicular to the pressure direction of a uniaxial press. They were thus aligned in the *a* plane and *c* plane [4]. These orientations are the result of the crystal growth in the process of sintering needle-like crystals that are formed in the powders calcined at 1100 °C. These needle-like crystals are aligned in a certain direction by the uniaxial press [9].

The thermal expansions of Compact-2 and -3 are shown in Figs 1 and 2. The expansion characteristics of Compact-1 and Compact-3 were very similar. The expansion up to 1100 °C is larger for Compact-3 than Compact-2. This difference was probably due to the difference in the direction of measurements. The expansion of Compact-3 was measured along the direction oriented *a* and *c* axis directions. Usually the expansion in these directions is greater than that in the *b* axis. The thermal expansion coefficient for Compact-3 was, however, less than 1.7×10^{-6} °C^{-1}. Compact-3 was thus classified as a low thermal expansion ceramic.

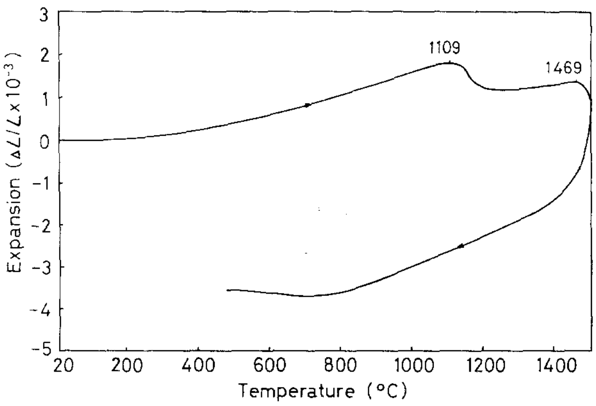

Figure 1 Plots of thermal expansion against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.6 wt %.

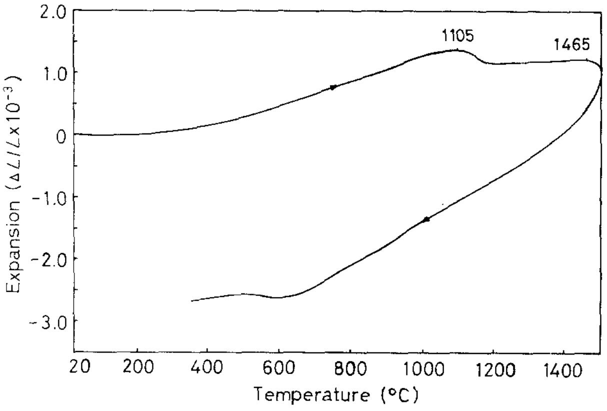

Figure 2 Plots of thermal expansion against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.8 wt %.

As is clearly shown in the figure the compacts changed from expansion to shrinkage at temperatures between 1100 and 1470 °C. This shrinkage is probably due to a phase transformation. The elongation at 1500 °C was less than that at 1100 °C.

The expansion coefficient of zirconyl phosphate in the *b* axis direction is known to be negative up to 1000 °C. One example of a compound that shows negative expansion coefficient is cordierite. Cordierite is an anisotropic crystal, and the negative expansion is explained by a counter-clockwise rotation of the six-membered ring formed in alternate layers. This rotation takes place following the elongation of the coordination octahedron [10, 11]. The structural characteristics of zirconyl phosphate suggest the occurrence of the rotation just as that which occurs in cordierite. These rotations will result in negative expansion in the *b*-axis direction. The phase transformation found in the temperature at 1110 and 1470 °C by the measurement of thermal expansion can also be thought of as the result of these elongations and rotation. The phase transformation of phosphate compounds at high temperature has been studied by use of the following compounds. Calcium phosphate is transformed from trigonal to monoclinic crystals at 1120 °C [12, 13]. The phase transformation of aluminium orthophosphate parallels that of silica in the temperature range 700–1100 °C [14, 15]. In this way, the phase transformation of phosphate compounds takes place rather easily.

Fig. 3 shows the temperature dependence of the thermal conductivity of samples up to a temperature of 1000 °C. The thermal conductivities for Compact-1, -2 and -3 at room temperature, were 0.0046, 0.0054 and 0.0065 $\mathrm{cal\,s^{-1}\,cm\,{}^\circ C^{-1}\,cm^{-2}}$, respectively. The difference between these thermal conductivities corresponds to the difference in the amount of additives used in each of the sample compacts. The value of thermal conductivity is quite small and these values are similar to that of a silica glass and PSZ. The behaviour of the conductivity curve is also close to that of PSZ [16].

Since the pores reduce the phonon mean free path [16, 17], the thermal conductivity is expected to decrease more for highly porous Compact-2 than for Compact-1. More than 10% higher porosity of Compact-2 did not, however, decrease the conductivity. This result suggests that for zirconyl phosphate the effect of the porosity on the thermal conductivity is rather insignificant but the amount of additives is a more significant influence. Among the additives used, niobium oxide tends to solidify on the zirconyl phosphate, while lanthanum oxide tends to stay at the grain boundary [4]. Usually any impurities within the crystal or in a grain boundary should lower the conductivity because of their promotion of the phonon scattering [16]. The results of this present study, however, show a contrary trend (i.e. higher thermal conductivity for compounds with higher amount of additives). This result indicates that a solid solution of zirconyl phosphate and niobium oxide actually does not promote any phonon scattering, and the thermal conductivity of the solid solution is indeed higher than that of zirconyl phosphate. The grain boundary impurity of lanthanum oxide may be too small to affect the conductivity.

The dependence of a dielectric constant on temperature and on frequency is illustrated in Figs 4, 5 and 6. The frequency range used in the measurements is considered to be an important range in practical applications. The increase of 10% porosity from Compact-1 to Compact-2 reduced the dielectric constant at room temperature by about 4%. The curves in Figs 4, 5 and 6 are analogous to that of steatite. The

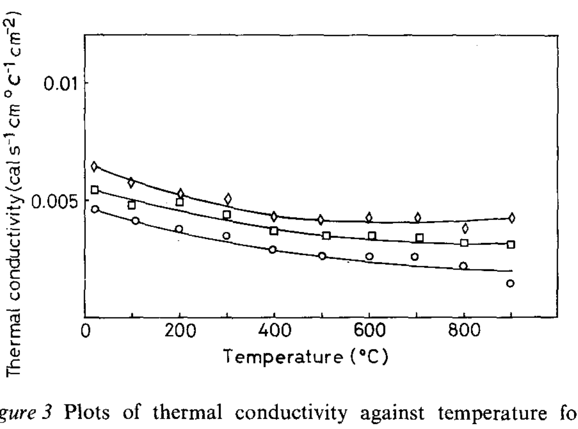

Figure 3 Plots of thermal conductivity against temperature for $Zr_2P_2O_9$ compact (○ 1.43 wt %, □ 1.6 wt %, ◇ 1.8 wt %).

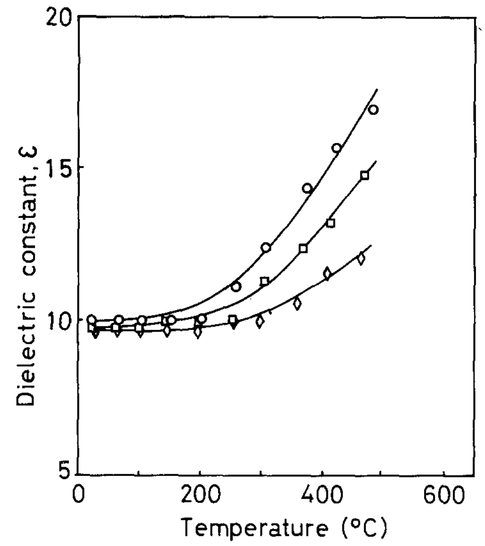

Figure 4 Plots of dielectric constant against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.43 wt % (○ 3×10^4 Hz, □ 1×10^5 Hz, ◇ 1×10^6 Hz).

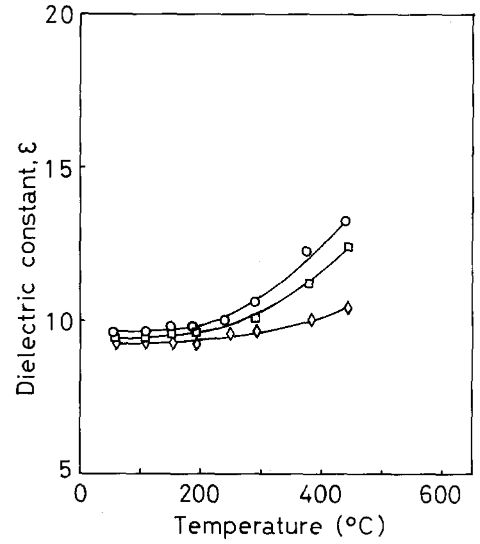

Figure 5 Plots of dielectric constant against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.6 wt % (○ 3×10^4 Hz, □ 1×10^5 Hz, ◇ 1×10^6 Hz).

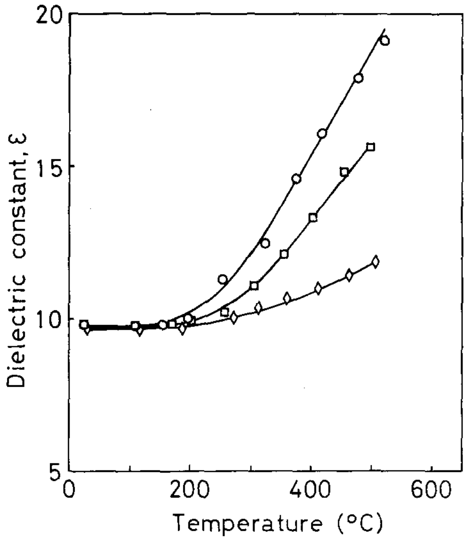

Figure 6 Plots of dielectric constant against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.8 wt % (○ 3×10^4 Hz, □ 1×10^5 Hz, ◇ 1×10^6 Hz).

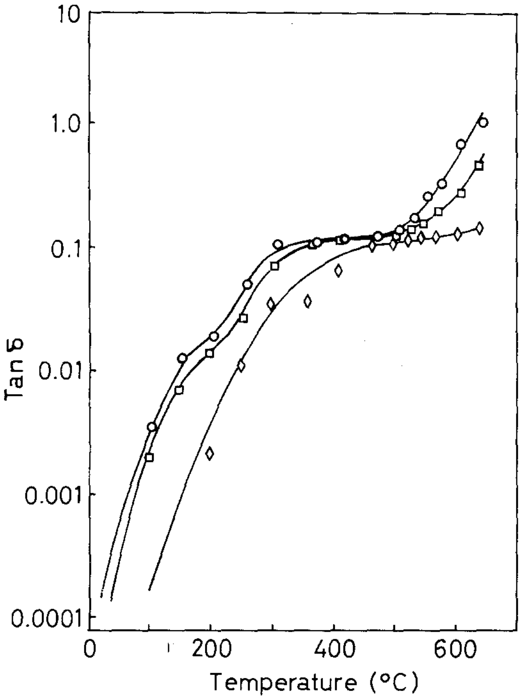

Figure 7 Plots of tan δ against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.43 wt % (○ 3×10^4 Hz, □ 1×10^5 Hz, ◇ 1×10^6 Hz).

dielectric constant of 9 at room temperature is close to that of Al_2O_3, LiF, $ZrSiO_4$ and MgO [18].

Figs 7, 8 and 9 show the dependence of tan δ on temperature and on frequency. The value at room temperature is so small that it falls below the accuracy of the instrument. The extrapolation of this curve to room temperature yields a value of $\simeq 0.0001$. This value is close to the value given for diamond, silica glass and forstelite, and is among the lowest for ceramics [18].

The curves in Figs 7 and 9 for Compact-1 and Compact-3 show the variation in temperature range of 200 to 300 °C. In the frequency range of this measurement and at a temperature below 500 °C, the ion jump and dipole losses based on a Nb^{5+} and ionic polarization become important in determining the value of tan δ [18]. The effect of these losses differs depending on the axes of anisotropic crystals. The tan δ of the oriented Compact-1 and Compact-3 was thus influenced in the temperature range of 200 and 300 °C. When the temperature exceeds several hundred degrees centigrade, the effect of the conductivity on tan δ becomes more important to make all the curves same [18].

4. Summary

1. The zirconyl phosphate compact expands with temperatures up to 1100 °C. It then shrinks near 1100 and 1470 °C because of the phase transformation. The thermal expansion coefficient was less than 1.7 $\times 10^{-6}$ °C^{-1} between room temperature and 1100 °C.

2. The thermal conductivity increased from 0.0046 to 0.0065 cal s^{-1} cm °C^{-1} cm^{-2} proportionally with the amount of additive and not influenced by the porosity.

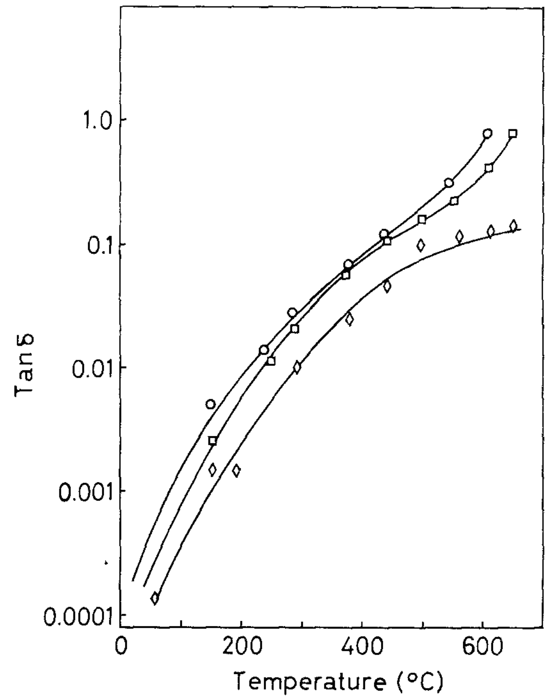

Figure 8 Plots of tan δ against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.6 wt % (○ 3×10^4 Hz, □ 1×10^5 Hz, ◇ 1×10^6 Hz).

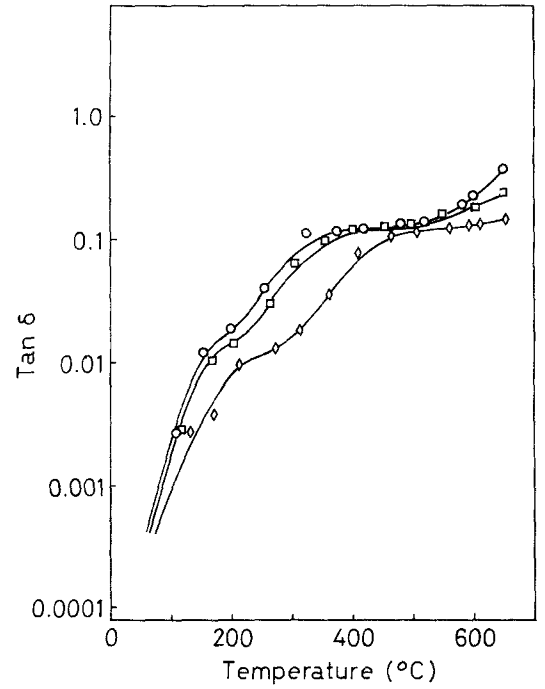

Figure 9 Plots of tan δ against temperature for $Zr_2P_2O_9$ compact with $LaNbO_4$ of 1.8 wt % (○ 3×10^4 Hz, □ 1×10^5 Hz, ◇ 1×10^6 Hz).

3. The measured dielectric constant of 9 is close to that of Al_2O_3. The value of tan δ was very small and is one of the lowest of the ceramics.

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