

Low thermal expansion electrical insulators

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Vitrification, thermal expansion and electrical resistivity of some mixtures within the system: $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$ were studied in the light of their phase composition. The effect of adding 1 to 2% Li_2O on the phase composition and properties of these mixtures was also investigated. All of the investigated mixtures vitrify between 1200 and 1400°C. The vitrified bodies show low thermal expansion and reasonable electrical resistivity. The increase of cordierite, at the expense of cristobalite and mullite phases, decreases the thermal expansion and increases the electrical resistivity. In mixtures containing Li_2O , an LiMg -aluminosilicate phase crystallizes leading to a further decrease in thermal expansion and to a slight deterioration of electrical resistivity.

1. Introduction

Cordierite bodies are characterized by their low thermal expansion as well as their high thermal shock resistance. They are usually produced from kaolin, talc and alumina raw materials [1, 2]. Densification of the great majority of silicate systems on firing takes place in the presence of a viscous liquid phase, a process known as vitrification. For a satisfactory firing, the amount and viscosity of the liquid phase must be such that the densification occurs in a reasonable time without deformation. The degree of vitrification is followed by the determination of bulk density and linear change. Due to the short vitrification range of cordierite bodies, some refractory materials having low thermal expansion, e.g., zircon and/or alumina are added to cordierite in producing vitreous bodies [3, 4].

The present work aims to study the possibility of preparing vitrified cordierite-zircon bodies as low thermal expansion electrical insulators using Egyptian kaolin, talc and zircon raw materials. Three mixtures were made from the latter raw materials according to the available phase relationships of the system ($\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$) [5-7]. These mixtures were designed to compose mainly, after firing, of cordierite ($2\text{MgO-2Al}_2\text{O}_3\text{-5SiO}_2$) and zircon ($\text{ZrO}_2\text{-SiO}_2$), in addition to lesser amounts of mullite ($3\text{Al}_2\text{O}_3\text{-2SiO}_2$) and cristobalite (SiO_2). Li_2O is added with amounts of 1 to 2% to the mixture containing the highest amount of cordierite in order to lower its vitrification temperature. The relationship between the phase composition and the vitrification as well as the thermal expansion and electrical resistivity of the fired mixtures were also studied.

2. Experimental procedure

2.1. Raw materials

Local Sinai kaolin, talc from Eastern Desert and zircon from the Egyptian Black Sand Company, Alexandria were the raw materials used in the present investigation. Chemically pure lithium carbonate (Riedel-de Haenag) is also used. The chemical analysis

of kaolin, talc and zircon raw materials were carried out using the appropriate schemes of silicate analysis (Table I).

2.2. Processing and testing

The raw materials were separately ground to pass through a 76 μm sieve. Five cordierite-zircon mixtures were made from the powders of the raw materials on the basis of the available phase equilibrium data. Mixes containing Li_2O were prepared according to the method described by Leopold [8]. The prepared mixtures were intimately wet-mixed for 1 h in a porcelain ball mill and then dried overnight at 110°C. Discs of 3 cm diameter and 3 mm thickness were semi-dry pressed under 300 kg cm^{-2} . The formed samples were dried overnight at 110°C and subsequently fired up to vitrification at temperatures between 1200 and 1400°C, with intervals of 50°C, in an electric furnace. The vitrification of the fired samples was indicated by determining their total linear shrinkage, bulk density and water absorption according to the ASTM C₂₀₋₇₄. The effect of soaking time for 1, 3 and 6 h on the vitrification was also studied at the final temperature of vitrification of each body.

Samples in the form of bars (7 cm \times 0.5 cm \times 1 cm) were processed under the same conditions and fired up to vitrification at the selected maturing

TABLE I Chemical constitution of the raw materials

Oxides (wt %)	Raw material		
	Kaolin	Talc	Zircon
SiO_2	43.23	62.00	32.50
Al_2O_3	36.55	1.60	0.92
TiO_2	1.94	traces	0.42
Fe_2O_3	0.85	0.40	0.17
ZrO_2	—	—	63.40
CaO	0.63	0.49	0.62
MgO	0.25	30.30	traces
Na_2O	0.34	0.32	traces
K_2O	0.42	0.11	traces
Ignition loss	14.80	4.70	0.39

temperatures to measure the reversible thermal expansion of the studied mixtures. A horizontal dilatometer was used and a heating rate of $5^{\circ}\text{C min}^{-1}$ up to 1000°C was adopted.

In order to determine the electrical resistivity of the fired samples, the vitrified 1 inch discs were covered on both sides by a filled circle of 2 cm diameter of silver paint. These discs were dried for 2 h at 110°C and then fired for 0.5 h in a muffle furnace at 700°C . The silver cover works as two electrodes on both sides of the test discs in measuring their electrical resistivity.

The phase composition of the vitrified cordierite–zircon mixtures was calculated from the available phase equilibrium data. It was also qualitatively determined by X-ray diffraction (XRD) technique using $\text{CuK}\alpha$ radiation and CaF_2 as an internal standard. A favourable line for each crystalline phase was selected and the relative intensities of these lines against the 4.711 nm line of CaF_2 were calculated. The used lines of XRD analysis were: cordierite, 0.855 nm; zircon, 0.443 nm; mullite, 0.536 nm; cristobalite, 0.405 nm and LiMg –aluminosilicate phase, 0.348 nm.

3. Results and discussion

Fig. 1 shows the vitrification curves of the fired mixtures in terms of their total linear shrinkage, bulk density and water absorption as a function of firing temperature. These curves indicate that the rate of vitrification of mixes I to III is clearly increased on firing for 1 h from 1350 to 1400°C . This can be seen from the higher bulk density and linear shrinkage as well as the lower water absorption of samples fired at 1400°C in comparison with the corresponding values of samples fired at $\leq 1350^{\circ}\text{C}$. From Fig. 1 it is also evident that, at 1400°C the vitrification decreases from mix I to III.

The presence of limited amounts ($< 2\%$) of the fluxing oxides Fe_2O_3 , CaO , Na_2O and K_2O in mixes I to III has allowed the formation of considerable amounts of liquid phase on firing these mixes between 1350 and 1400°C . This led to the vitrification of the later mixes at temperatures as low as 1400°C . On the other hand, the decrease of kaolin/talc ratio from mix I to III has decreased the amount of liquid phase formed in these mixes at the same sequence, on firing up to 1400°C . This effect can be seen when the composition of mixes I to III are plotted on the phase diagram of the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [9]. Therefore, mix I is fully vitrified at 1400°C , showing only 0.5% water absorption, and the degree of vitrification is decreased down to mix III as shown in Fig. 1.

The vitrification temperatures of mixes IV and V, which contain, in addition to the above mentioned fluxing oxides, 1 and 2% Li_2O , respectively, are appreciably lower than those of mixes I to III. Mix IV is vitrified between 1300 and 1350°C , whereas the vitrification of mix V occurs between 1250 and 1275°C . This was expected due to the severe fluxing effect of Li_2O in such a system.

The influence of soaking time on the vitrification parameters of the investigated mixes (I to V) at the respective firing temperatures is illustrated in Table II. These results reveal that as the duration of firing

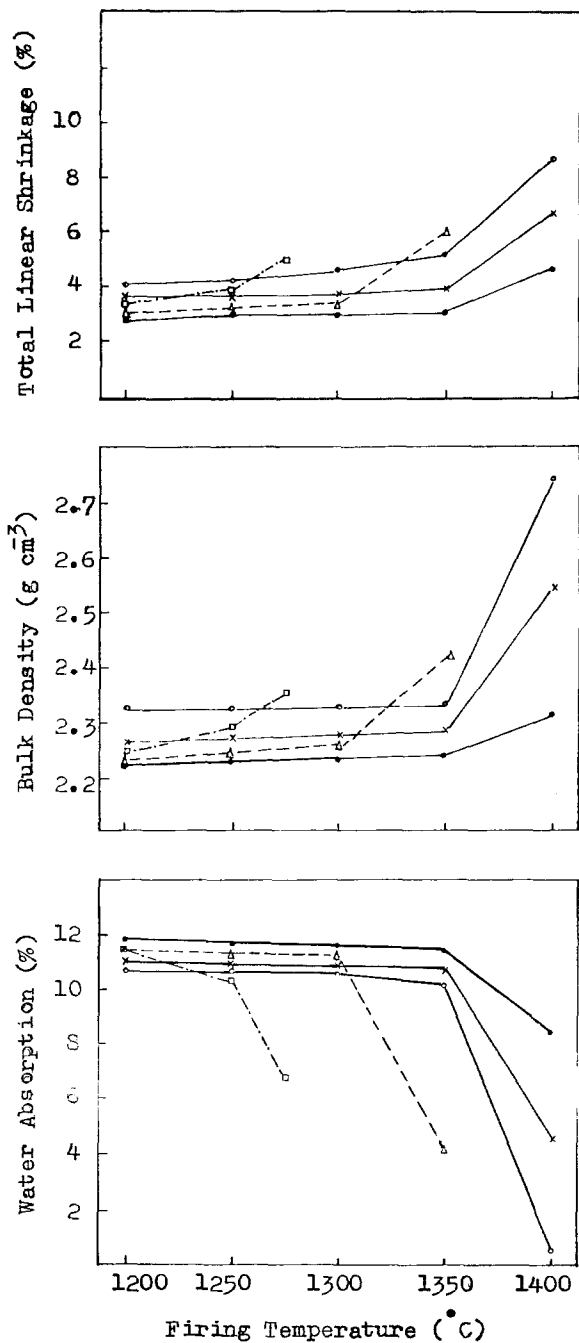


Figure 1 Vitrification parameters of the fired mixes against firing temperature. (O) Mix I; (x) mix II; (●) mix III; (Δ) mix IV; (-□-) mix V.

increases from 1 to 6 h the vitrification of all the fired mixtures is consequently improved. Therefore, mixes I to III, IV and V were fired for 6 h at 1400, 1350 and 1275°C , respectively, in order to obtain mature samples for the study of their phase composition and physical properties.

Table III summarizes the mix composition as well as the calculated phase composition of the investigated mixtures. The phase equilibrium data of the system: cordierite–mullite–cristobalite–zircon, within which mixes I to III exist, indicates that zircon coexists with the other phases in the solid state up to 1400°C [5–7]. Therefore, the weight percentages of cordierite, mullite and cristobalite of mixes I to III were calculated from their kaolin and talc contents using the ternary system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [9]. Zircon content was recalculated on a calcined basis from the original

TABLE II Effect of soaking time on the vitrification parameters of the fired mixtures

Mix No.	Vitrification temperature (°C)	Soaking time (h)								
		1			3			6		
		L Shr	BD	WA	L Shr	BD	WA	L Shr	BD	WA
I	1400	8.70	2.74	0.46	9.67	2.77	0.36	10.67	2.91	0.10
II	1400	6.70	2.54	4.52	8.00	2.67	1.51	9.33	2.73	0.21
III	1400	4.70	2.31	8.54	5.00	2.43	4.96	5.70	2.61	1.57
IV	1350	4.70	2.41	4.08	5.33	2.43	2.59	5.60	2.47	1.48
V	1275	4.00	2.34	6.88	4.33	2.35	4.59	5.00	2.42	2.59

L Shr = linear shrinkage (%).

BD = bulk density g cm^{-3} .

WA = water absorption (%).

mix composition. These calculations were done assuming that the phases are formed in the solid state, neglecting the formation of the liquid phase due to the presence of some of the impurity oxides in the raw materials. For mixes IV and V, which contain 1 and 2% Li_2O , respectively, the above calculations could not be applied. This is due to the unavailable data relevant to the five component system $\text{Li}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{ZrO}_2$. The calculated phase composition of mixes I to III indicates that as the kaolin/talc ratio decreases from mix I to III, the content of cordierite increases at the expense of mullite and cristobalite contents. The level of zircon content is more or less constant.

Fig. 2 exhibits the variation of the relative amounts of the crystalline phases in the fired mixes I to V, as detected qualitatively by XRD. These results confirm the calculated phase composition of mixes I to III. Thus, the cordierite content increases from mix I to III, whereas that of mullite and cristobalite decreases. Zircon content seems to be more or less constant. The presence of 1 and 2% of Li_2O in mixes IV and V, respectively, results in decreasing amounts of the crystalline phases: cordierite, mullite, cristobalite and zircon. Meanwhile, a new crystalline LiMg-aluminosilicate phase appears in these mixes and its amount increases with the increase of Li_2O from mix IV to V. Due to the unavailable XRD data for the later phase, it is identified according to the ASTM card of the $\text{Li}_{0.34}\text{Be}_{0.88}\text{Al}_{0.66}\text{Si}_{0.98}\text{O}_6$ phase (card No. 27-1219), which agrees well with this phase. Be^{2+} can be substituted by Mg^{2+} giving the LiMg-aluminosilicate phase. The crystallization of the LiMg-aluminosilicate phase is attributed to the dissolution of cordierite, cristobalite and mullite phases in the lithium-bearing liquid phase. Hence, in addition to Li^+ the liquid phase becomes rich in Mg^{2+} , Al^{3+} and $(\text{SiO}_4)^{4-}$ ions. Therefore, LiMg-aluminosilicate phase is crystallized on cooling in such mixes. As the

Li_2O content increases from mix IV to V the amount of the crystallized LiMg-aluminosilicate is consequently increased. Zircon shows on the other hand higher resistance to dissolution in the lithium-bearing liquid phase as revealed from its relative intensity, which decreases slightly in mixes IV and V in relation to mixes I to III.

Fig. 3 shows the thermal expansion curves of the vitrified mixtures I to V on firing between 20 and 1000°C . The values of thermal expansion coefficients at 1000°C were calculated and illustrated in Table IV. It is evident that the percentage of thermal expansion decreases gradually from mix I to V during firing up to 1000°C . The thermal expansion coefficient at 1000°C ranges between 4.03×10^{-6} for mix I to 1.58×10^{-6} for mix V. This range of thermal expansion is rather low, when compared with that of the conventional porcelain electrical insulators, which usually have thermal expansion coefficients $\geq 6.0 \times 10^{-6}$. These results can be attributed to the phase composition of the prepared mixes, which consist mainly of the low thermal expansion phases cordierite, zircon and glassy phase. The increase of cordierite content with simultaneous decrease of cristobalite and mullite phases from mix I to III are responsible for the decrease in thermal expansion of these mixes in the same order. The continuous decrease of thermal expansion from mix III to V is due to the crystallization of the LiMg-aluminosilicate phase in mixes IV and V. The latter phase would have, as the other Li-aluminosilicate phases, very low thermal expansion coefficient up to 1000°C . As the amount of this phase increases from mix IV to V, the thermal expansion coefficient in consequently decreased down to 1.58×10^{-6} . The presence of appreciable amounts of cristobalite in mixes I to III leads to the appearance of its characteristic expansion step on their thermal expansion curves between 100 and 250°C , due to the conversion of low-high form of

TABLE III Mix composition and calculated phase composition of the fired mixtures

Mix No.	Mix composition (wt %)				Calculated phase composition in the solid state (wt %)			
	Kaolin	Talc	Zircon	Li_2O	Cordierite	Mullite	Cristobalite	Zircon
I	65	10	25	—	28.0	25.5	18.8	27.7
II	60	15	25	—	39.0	19.7	13.7	27.6
III	55	20	25	—	50.1	13.7	8.7	27.5
IV	55	20	25	1.00	—	—	—	—
V	55	20	25	2.00	—	—	—	—

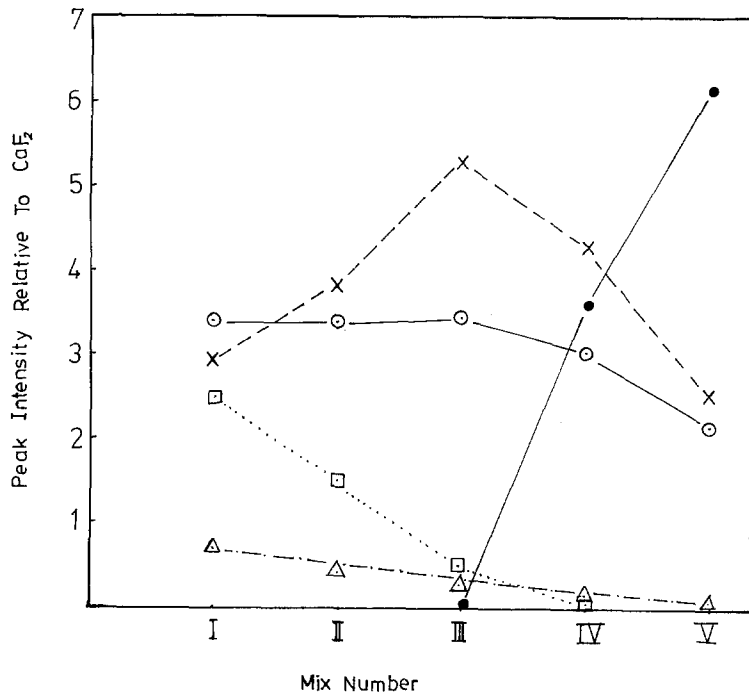


Figure 2 Variation of the relative intensity of the crystalline phases as detected in the vitrified mixes by XRD. (○) Zircon, 0.443 nm; (x) cordierite, 0.855 nm; (△) mullite, 0.536 nm; (□) cristobalite, 0.405 nm; (●) LiMg-aluminosilicate, 0.348 nm.

cristobalite (see Fig. 2). The intensity of this expansion step is clearly decreased with the decrease of cristobalite content from mix I to III. The thermal expansion curve of mix III shows, as those of mixes IV and V, no evidence of the presence of cristobalite. The low cristobalite content of these mixes is dissolved almost entirely in the liquid phase during vitrification.

Table IV illustrates the volume resistivity of the vitrified mixes I to V as a function of firing tem-

perature (20 to 500°C). The prepared bodies give reasonable electrical resistivity between room temperature and 400 to 500°C. These values decrease generally with increases of temperature. The increase of cordierite content from mix I to III leads to the increase of their electrical resistivity in this direction. Also, the electrical resistivity decreases in mix IV and V, due to the presence of Li₂O [10]. The electrical resistivity of the prepared bodies are not affected

TABLE IV Properties of the vitrified cordierite-zircon mixes

Mix No.	Vitrification 6 h at temperature (°C)	Thermal expansion coefficient at 1000°C (× 10 ⁻⁶)	Volume resistivity (Ω)ohm cm ⁻¹ at temperature (°C)						
			20	100	200	300	400	450	500
I	1400	4.03	3.0 × 10 ¹¹	1.0 × 10 ¹¹	1.0 × 10 ⁹	2.0 × 10 ⁸	1.8 × 10 ⁷	7.0 × 10 ⁶	
II	1400	3.20	2.0 × 10 ¹²	1.1 × 10 ¹²	3.0 × 10 ¹⁰	3.0 × 10 ⁸	1.4 × 10 ⁷	3.8 × 10 ⁶	
III	1400	2.68	7.0 × 10 ¹²	6.0 × 10 ¹²	6.5 × 10 ¹⁰	3.5 × 10 ⁹	1.8 × 10 ⁸	7.0 × 10 ⁷	2.0 × 10 ⁷
IV	1350	1.86	3.0 × 10 ¹¹	2.1 × 10 ¹¹	5.0 × 10 ⁹	2.2 × 10 ⁷	7.0 × 10 ⁶		
V	1275	1.58	2.5 × 10 ¹¹	1.0 × 10 ¹¹	4.0 × 10 ⁹	1.0 × 10 ⁷	4.0 × 10 ⁶		

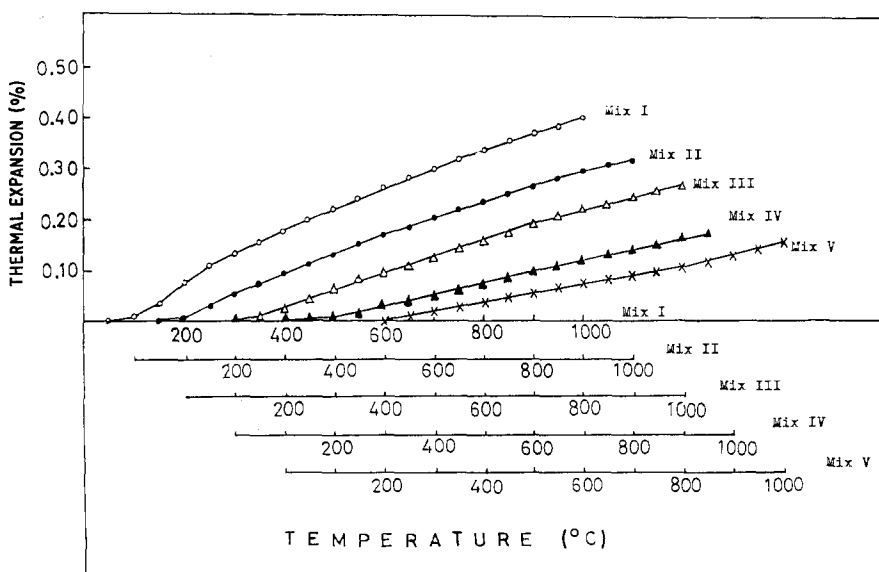


Figure 3 Thermal expansion curves of the vitrified mixes.

appreciably by the slight difference in their apparent porosity values.

4. Conclusions

According to the above discussion the following conclusion can be drawn:

1. It is possible to prepare vitrified low thermal expansion electrical insulators composed mainly of cordierite, zircon and liquid phase from Egyptian kaolin, talc and zircon raw materials. These materials are mixed by weight ratios as in mix III, semi-dry pressed and fired up to 1400°C for 6 h.

2. The addition of 1% Li₂O to mix III (mix IV) is enough to decrease the vitrification temperature of the fired body down to 1350°C without shortening its vitrification range. The crystallization of the LiMg–aluminosilicate phase in mix IV decreases its thermal expansion, where its electrical resistivity up to 500°C slightly deteriorates.

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