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Investigation of lithium, magnesium-aluminosilicate solid solutions crystallized in some cordierite–zircon ceramics containing lithium

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The crystallization of Li,Mg-aluminosilicate solid solutions in lithium-bearing zircon and/or cordierite-based ceramics is studied as a function of firing temperature up to 1500° C. X-ray diffraction, electron microprobe analysis and microscopic techniques were used for the identification of the studied phases. Keatite solid solution (ss) coexists with zircon and/or cordierite at temperatures up to 1300° C. On raising the temperature to 1400–1500° C, β-quartz ss is crystallized at the expense of both keatite and cordierite with the precipitation of spinel on cooling from such high temperatures. In bodies containing zircon, the dissociation of zircon at 1400–1500° C into its constituents epitaxially enhances the nucleation of β-quartz ss crystallization.

1. Introduction

During the crystallization of lithium-bearing aluminosilicate melts, varieties of phases could be precipitated depending on the chemical as well as the crystallization parameters of the system. A series of aluminosilicate structures can be derived from SiO_2 structures, where aluminium atoms replace a portion of the silicon atoms in the framework. The lower valency of Al^{3+} relative to Si^{4+} is compensated by incorporating other positive ions in the structural vacancies. If the small Li^+ ions are the main stuffing ions, β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) and/or β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) phases are resulted. When other cations of similar sizes, e.g. Mg^{2+}, Be^{2+}, Zn^{2+} and Fe^{2+} are also incorporated, β-eucryptite-like and β-spodumene-like phases can be obtained. These solid solutions are recently referred to as β-quartz and keatite solid solutions (ss) since they are structurally analogous to the SiO_2 polymorphs β-quartz and keatite, respectively [1–5].

In a previous work on low thermal expansion electrical insulators [6], vitrified cordierite–zircon bodies were prepared by firing some kaolin–talc–zircon mixtures up to 1400° C. When small amounts of Li_2O (1–2%) were added a considerable amount of liquid phase was developed at temperature as low as 1275° C, which was enough to vitrify the bodies fired at this temperature. Also, a Li,Mg-aluminosilicate solid solution phase identified to be analogous to a Be-bearing β-spodumene phase [5], was crystallized on cooling from the formed liquid phase beside the main phases cordierite and zircon.

The aim of the present work is to study the effect of composition and temperature on the formation and stability of such Li,Mg-aluminosilicate solid solution phase(s) in some zircon and/or cordierite-based ceramics.

2. Experimental details

2.1. Raw materials

Egyptian kaolin, talc and zircon as well as a reagent grade lithium carbonate were used for batch preparation. The chemical analyses of the raw materials are given in Table I.

2.2. Processing and investigation

Table II shows the details of the studied mixtures. The original base mixture (Mix-O) was designed [6] to give vitrified ceramic body composed mainly of cordierite and zircon in addition to smaller amounts of mullite and crystobalite. Mix-1 is the same but contains 2% Li_2O in excess. The batch composition of Mix-1 is prepared under the same processing conditions as that in which the aforenamed β-spodumene-like phase was previously developed. In Mix-2, zircon is omitted and the ratio of kaolin–talc–lithium carbonate is the same as in Mix-1.

The two mixtures were prepared from the powdered raw materials ($-76\,\mu m$) by adopting Leopoldo's method [7]. The prepared mixtures were intimately wet-mixed in a porcelain ball mill and then dried overnight at 110° C. Cylinders of 1 cm diameter and 1 cm height were semi-dry pressed under $100\,kg\,cm^{-2}$. The pressed samples of Mix-1 were dried overnight at 110° C, loaded on a platinum foil and subsequently fired in a Globar furnace for 6 h at 1275, 1300, 1400 and 1500° C. On the other hand, samples of Mix-2 were fired directly at 1500° C for 6 h and the obtained samples were reprocessed and heat-treated for 6 h at 1000, 1200 and 1400° C.

TABLE I Chemical analysis of raw materials used

Oxides	Kaolin (wt %)	Talc (wt %)	Zircon (wt %)
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	Nil	Nil	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

The crystalline phases developed in the fired samples were determined by XRD technique using a Phillips type PW 1050 diffractometer with Ni filtered Cu*K* radiation. All the instrument settings were maintained for all the analyses and a silicon disc was always used as an external standard to test this maintenance. This was necessary to make the comparative phase frequency, based on the peak height more accurate.

The electron microprobe analysis (EMPA) technique was also adopted to determine the chemical composition of the crystalline and the amorphous phases, which were formed on firing samples of Mix-2 at 1500° C. By using a computerized microprobe analyser type JXA-50A JEOL, the mean values of 12-point analysis were done to determine the oxide composition as well as the chemical formula of the investigated phases [8]. Li_2O could not be detected by EMPA and therefore its content was determined by difference.

Some thin sections were made and investigated under the polarizing Carl Zeiss research microscope.

3. Results and discussion

Table III gives the crystalline phases encountered during ceramming Mixes 1 and 2.

The samples of Mix-1, which were fired at 1275 and 1300° C are almost fully vitrified, i.e. the densification process took place through the formation of a Li-bearing liquid phase as enough as to fill almost all their open-pore structure. On the other side, the samples fired at 1400 and 1500° C are partially fused. This is due to the excessive development of the liquid phase as a result of the powerful fluxing agent of lithium and other impurities, brought into by raw materials such as Fe_2O_3, CaO, K_2O and Na_2O at such high firing temperatures.

The XRD patterns of the firing products of Mix-1 cured for 6 h at 1275 and 1300° C (Figs 1a and b) are almost similar revealing zircon ($ZrSiO_4$), cordierite ($Mg_2Al_4Si_5O_{18}$) and keatite ss. This indicates that the as-added raw zircon was consistently fired to 1300° C without any significant change and cordierite was formed as a result of the reactions occurring between the calcination products of talc and kaolin. Keatite ss was mainly crystallized from the Li,Mg-aluminosilicate-liquid phase which was formed during the fluxing action of Li_2O and other impurity oxides on cordierite constituents. Keatite ss is verified by the characteristic *d*-spacings 0.458, 0.390, 0.346, 0.313 and 0.187 nm (Fig. 1).

The ease of crystallization of keatite ss could be

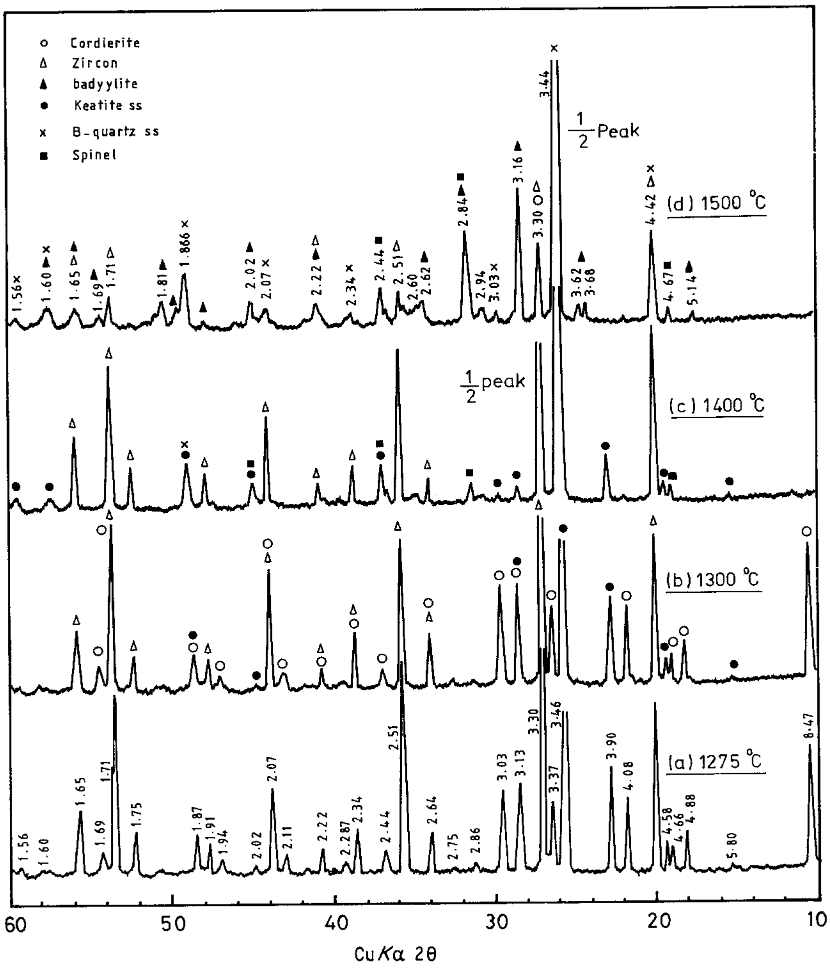

Figure 1 XRD patterns of Mix-1 heat-treated up to 1500° C.

TABLE II Composition of mixes investigated

Mix number	Batch composition (wt %)				Oxide composition on calcined basis (wt %)										Calculated phase composition in the solid state (wt %)			
	Kaolin	Talc	Zircon	Li_2CO_3	SiO_2	ZrO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Li_2O	Na_2O	K_2O	Cordierite	Zircon	Mullite	Crystobalite
0	55.0	20.0	25.0	–	49.29	17.63	22.98	1.30	0.65	6.90	0.67	–	0.28	0.28	50.1	27.5	13.7	8.7
1	52.3	19.1	23.8	4.8	48.22	17.25	22.48	1.28	0.64	6.75	0.66	2.18	0.27	0.27				
2	68.7	25.0	–	6.2	58.27	–	27.16	1.55	0.77	8.16	0.80	2.63	0.33	0.33				

TABLE III Phases resulting from various heat treatments

Compound number	Heat treatment	Crystalline phases
Mix-1	1275° C, 6 h	Cordierite + zircon + keatite ss
Mix-1	1300° C, 6 h	Cordierite + zircon + keatite ss
Mix-1	1400° C, 6 h	Zircon + β-quartz ss + keatite ss + spinel
Mix-1	1500° C, 6 h	β-quartz ss + badydlite + zircon + spinel
Mix-2	1500° C, 6 h (1st-step)	β-quartz ss + keatite + spinel
Mix-2	1st-step + 1000° C, 6 h	Keatite ss + cordierite (m)
Mix-2	1st-step + 1200° C, 6 h	Keatite ss + cordierite
Mix-2	1st-step + 1400° C, 6 h	β-quartz ss + spinel(m) + α-quartz (m)

m = minor.

ascribed to the well known effect of Li^+ in reducing the viscosity of the melts, which consequently facilitates the mobility of ions during the ceramming process.

On raising the firing temperature to 1400° C (Fig. 1c), the diffraction lines of cordierite are almost completely disappeared and the crystalline phases detected in this sample are zircon, keatite ss in addition to minor β-quartz ss and spinel ($MgO \cdot Al_2O_3$). The existence of β-quartz ss was verified by the increase of the intensity of the diffraction lines 0.442, 0.346 and 0.187 nm and by the decrease of the lines 0.390 and 0.313 nm. The latter lines are characteristic to keatite ss phase. The disappearance of cordierite indicates its complete dissolution into the liquid phase at 1400° C. Also, some of the zircon phase begins to break down as indicated by the slight reduction of its diffraction lines. The enrichment of the lithium-bearing liquid phase by Si^{4+}, Al^{3+}, Mg^{2+} and some Zr^{4+} ions as a result of the dissolution of cordierite and some of the zircon phase led to the crystallization of minor β-quartz ss phase beside the keatite ss.

The crystallization of some β-quartz ss from the liquid phase is mainly due to the effect of zirconia which epitaxially favours its nucleation [9–11]. The formation of β-quartz ss is accompanied by the crystallization of minor spinel phase ($MgO \cdot Al_2O_3$). The latter phase may be precipitated on cooling from the keatite ss phase or directly crystallized from the liquid phase, which became rich in MgO and Al_2O_3 after the dissolution of cordierite. The precipitation of spinel from keatite ss phase is in agreement with the results of Ray [12] who found that the crystallization stability of keatite ss was decreased with increasing MgO and/or SiO_2 content. The replacement of Li^+ by Mg^{2+} in keatite lattice increases the degree of charge imbalance. This was considered more important than the availability of favourable sites (for the interstitial cations) in limiting the extent of such replacement and in governing the formation of keatite ss and its stability range.

Figure 1d shows that zircon is dissociated at 1500° C into ZrO_2 (baddylite) and SiO_2. No keatite ss is detected and the Li,Mg-aluminosilicate ss phase seems to be crystallized almost entirely as β-quartz ss

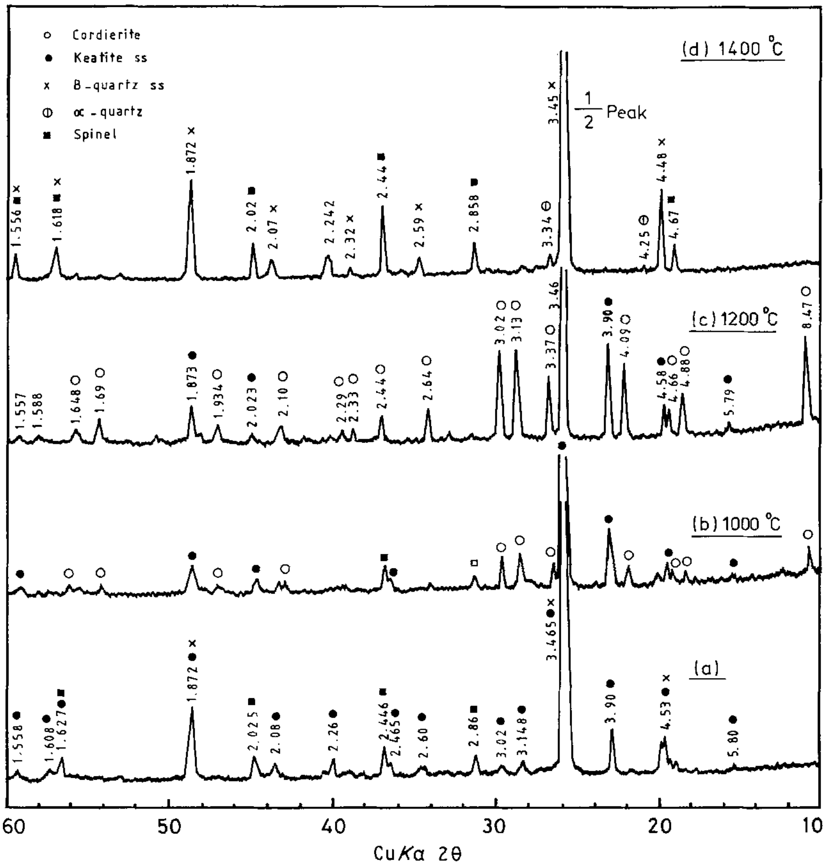

Figure 2 XRD patterns of Mix-2 fired at 1500° C (a) and reheated at 1000, 1200 and 1400° C.

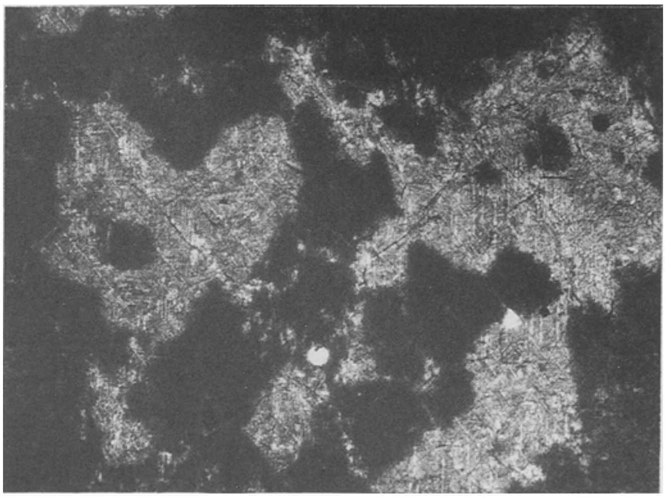

Figure 3 Photomicrograph of Mix-2 fired at 1500° C showing keatite and β-quartz ss crystallites in a glassy groundmass (crossed polars; ×70).

which associated also with minor spinel phase. This is mainly attributed to the dissociation of zircon. The liberated ZrO_2 epitaxially nucleates and favours the crystallization of high quartz ss and hinders, meanwhile, the formation of keatite structure [10, 11]. Also, the enrichment of the developed liquid phase by SiO_2 released from zircon may be an additive factor. The structure of β-quartz has a higher ability to incorporate ions, especially SiO_2 as solid solution than that of the keatite structure at their stability fields of crystallization [10, 13].

In order to eliminate the effect of zircon or its ingredients on the crystallization of the Li,Mg-aluminosilicate ss, Mix-2 devoided of zircon was made and fired directly at 1500° C for 6 h. The details of composition and the developed crystalline phases are given in Tables II and III.

Figure 2a exhibits the XRD pattern of Mix-2 fired at 1500° C. The phases identified in this sample are mainly β-quartz ss and keatite ss with minor spinel. The crystallization of keatite ss beside β-quartz ss in Mix-2 is mainly attributed to the elimination of zircon (ZrO_2, SiO_2), which has a significant effect in stabilizing the high-quartz ss structure, as indicated in case of Mix-1 under the same firing conditions.

Under the polarizing microscope, the thin sections of the fired sample of Mix-2 are seen to be an inhomogeneous glass containing in some parts abundant interlocked dendrites of tiny keatite ss crystallites having a net-like structure together with some optically negative β-quartz ss patches (Fig. 3).

TABLE IV Mean values of EMPA of amorphous and crystalline phases

Oxide	Crystalline solid solution		Amorphous phase	
	% Oxide	Formula	% Oxide	Formula
SiO_2	55.85	3.14	55.36	3.08
Al_2O_3	29.11	1.93	28.70	1.88
TiO_2	1.68	0.10	2.50	0.11
FeO	0.78	0.04	0.93	0.04
MgO	7.49	0.63	9.07	0.75
CaO	0.31	0.02	0.37	0.03
Na_2O	0.32		0.26	0.03
K_2O			0.08	0.01
Li_2O	4.46	0.38	2.73	0.10

The mean values of the chemical composition as well as the chemical formula of the crystalline and amorphous phases present in Mix-2 as determined by EMPA are summarized in Table IV.

These results indicate that the crystallized solid solution phase is composed mainly of Li_2O, MgO, Al_2O_3 and SiO_2 and contains higher lithia and lower magnesia than those in the glassy phase. The chemical formula obtained for this solid solution phase is $Li_{0.20}Mg_{0.39}Al_{1.16}Si_{1.88}O_6$ which defines a β-quartz–keatite solid solution. In such silica derivatives Al^{3+} readily replace Si^{4+} in tetrahedral coordination with the charge balanced by both the modifying ions Li^+ and Mg^{2+}. The enrichment of the crystalline phase with lithia rather than the glassy phase (Table IV) may be interpreted by its higher mobility at such elevated temperatures. Evidently lithium ions are very mobile at such temperatures and could accompany more readily the replacement to maintain the charge balance than Mg^{2+}.

To define the thermal stability fields of the lithium-bearing ss phases, reprocessed samples of the 1500° C ceramic body of Mix-2 (devoided of zircon) were thermally cured for 6 h at 1000, 1200 and 1400° C. Figures 2b–d shows the X-ray diffraction patterns of these samples. At 1000° C, keatite ss with minor cordierite are developed. The amount of cordierite is considerably increased on firing at 1200° C as shown in Fig. 2c.

The crystallization of keatite ss at these temperatures is mainly attributed to the formation of cordierite, which includes much Mg^{2+}, Al^{3+} and Si^{4+} in its structure. This led to increase the stability of keatite ss, which can coexist with cordierite at 1000–1200° C. On reheating at 1400° C (Fig. 2d), β-quartz ss as well as minor spinel and α-quartz phases are detected. Also, the lines of β-quartz ss show a noticeable shift to lower 2θ angles revealing a more solid solution process.

The predominance of β-quartz ss at such high firing temperature (1400° C) is most probably due to that the composition of the resultant β-quartz ss is close to eucrypitite ($Li_2O : Al_2O_3 : 2\ SiO_2$) stoichiometry as the result of the dissolution of cordierite ($MgO : Al_2O_3 : 2.5\ SiO_2$). The stability of β-quartz ss to such high temperature is conformable with the findings of Ray and Muchow [14] who showed that high-quartz ss are stable to melting when n in $Li_2O:MgO \cdot Al_2O_3:nSiO_2$ is less than 3.5. Also, the appearance of some lines relevant to α-quartz is mainly attributed to the crystallization of some of the excess SiO_2, which could be available in such system at 1400° C.

4. Conclusions

In conclusion, the crystallization of Li,Mg-aluminosilicate solid solution in lithium-bearing zircon and/or cordierite-based ceramics is mainly sensitive to heat-treatment process. Keatite ss is stable and can coexist with cordierite at temperatures up to 1300° C. On raising temperature to 1400–1500° C, β-quartz ss is crystallized on cooling from such high temperatures at the expense of keatite ss and cordierite with the precipitation of spinel and α-quartz. Also, the disassociation of zircon in such system into its ingredients favours the crystallization of β-quartz ss.

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