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Sol–gel synthesis of zircon–effect of addition of lithium ions

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The sol–gel method was applied to the preparation of zircon, $ZrSiO_4$ powders. The addition of lithium ions to the $ZrO_2{\cdot}SiO_2$ gels was found to be very effective to produce zircon at temperatures as low as 800–900 °C. The zircon formation process in the gels was followed by using X-ray diffraction and i.r. analysis methods. A possible mineralizing mechanism of lithium ions, which is essentially different from the previous ones for the solid-state reaction, was proposed. Namely, the formation of orthosilicate such as Li_4SiO_4 as an intermediate compound was considered to trigger the zircon formation at low heat-treatment temperatures. © *1998 Kluwer Academic Publishers*

1. Introduction

Zircon, $ZrSiO_4$, is one of the technologically important oxide ceramic materials known for its high refractoriness, low thermal expansion and low thermal conductivity [1]. However, it is well known that the production of zircon powders is not so easy and usually requires the heat-treatment temperature to be as high as 1500 °C. Then, so far, much effort has been paid to lower the heat-treatment temperature for zircon processing, and many kinds of mineralizers have been found to be effective for that purpose.

Among mineralizers, fluorides easily react with SiO_2 to form SiF_4 which is readily vaporized during heat treatment, enhancing the diffusion of Si to the surface of ZrO_2 particles via vapour phase and lowering the formation temperature of zircon [2–4]. Several alkali and/or alkaline earth halides and carbonates have been found also to work successfully to lower the zircon formation temperature. Above all, lithium compounds allowed the solid-state reaction between SiO_2 and ZrO_2 to start around 750 °C [5]. Several plausible mechanisms have been proposed for the mineralizing effect of lithium compounds: the low temperature melting of lithium compounds to form liquid phase in the raw powder mixture, through which counterdiffusion of Si^{4+} and Zr^{4+} ions may be accelerated [6, 7], and the formation of $Li_2Si_2O_5$ crystalline species which reacts with ZrO_2 to form zircon [5].

The sol–gel method, which is known as a low temperature processing of ceramics and glasses, has been also applied to the fabrication of zircon ceramics, where any mineralizer was not utilized to obtain high purity products. However, unfortunately, required processing temperature was still much higher than 1000 °C [8–10], unless the precursor gel was seeded with zircon particles [11, 12].

Owing to its high chemical durability as well as thermal resistivity, zircon is also an interesting material in the glaze industry [13]. Conventionally, zircon-based pigments have been produced above $\sim$ 1200 °C through the solid-state reaction using NaF as a mineralizer, followed by vigorous mechanical crushing and grinding. The sol–gel method have been employed to produce V-zircon [14] and Ni-zircon [15] pigments around 1000 °C or lower. The chromophore elements act as mineralizers by themselves.

In the previous paper, the present authors also have applied the sol–gel method to the preparation of zircon-based pigments containing rare earth elements such as Pr, Nd, Sm, Eu and Er as chromophores [16], and the zircon-based pigments which were only weakly sintered and easily pulverized to fine powders have been successfully obtained at the heat-treatment temperature as low as 900–1000 °C. It has been also found that the addition of LiCl as a mineralizer was very effective in producing those pigments as in the case of the solid-state reaction method.

In the present work, the authors examined the formation process of zircon in the sol–gel derived $SiO_2 \cdot ZrO_2$ gels added with different kinds of lithium compounds, in connection with the previously reported sol–gel fabrication of the zircon-based pigments. The role of the lithium compounds in the zircon formation was discussed, comparing it with the solid-state reaction.

2. Experimental procedure

2.1. Preparation of samples

In the present work, the sol–gel method and conventional solid-state reaction method were employed to prepare zircon samples.

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2.1.1. Sol–gel method

Zirconium oxychloride hydrate, $ZrOCl_2 \cdot 8H_2O$ (Wako Pure Chemical Industries, Ltd., hereafter abbreviated as ZOC) or zirconium tetra-iso-propoxide, $Zr(OC_3H_7)_4$ (ZIP) (Aldrich Chemical Company) was used as a source of ZrO_2, and tetraethyl-orthosilicate, $Si(OC_2H_5)_4$ (TEOS) (Wako Pure Chemical Industries, Ltd.) as a source of SiO_2. Lithium compounds used as additives or mineralizers were LiCl, $CH_3COOLi \cdot H_2O$ (LiOAc) and $Li(OCH_3)$ (LiOMe). As a reference, sodium acetate hydrate, $CH_3COONa \cdot H_2O$ was also used as an additive. All the commercially available chemicals were used without any further purification. The amount of Li or Na additives was 0.3 in the molar ratio to the $ZrO_2 \cdot SiO_2$, because this amount was revealed to be most effective in the production of rare earth-containing zircon-based pigments. Two different procedures, Process I and II, were adopted to prepare the Li-containing $ZrO_2 \cdot SiO_2$ gels (equimolar composition) as shown in Fig. 1a and b. Only the order of addition of the chemicals was different from Process I to Process II.

In Process I, TEOS was pre-hydrolysed with water (of which amount was 1.0 in molar ratio to TEOS, or $r = 1$) in ethanol using HCl as a hydrolysis catalyst. The solution consisting of ZOC or ZIP (equimolar to TEOS), dissolved with ethanol, water and a lithium compound was mixed well at 50 °C for 1 h and added to the pre-hydrolysed TEOS solution. The gelation was achieved by heating the mixed solution at 80 °C, the result being a transparent to translucent gel.

In Process II, ethanolic solution of ZIP was added to and mixed with TEOS solution pre-hydrolysed with water of $r = 1$ in ethanol at 0 °C under stirring. Lithium compound was then added to the mixed solution, followed by the addition of water of $r = 9$ to complete the hydrolysis reaction. The solution set to gel just after adding excess amount of water. The resultant gels were dried at 60 °C in the ambient atmosphere.

The dried gels prepared by Process I and Process II were calcined at 600 °C for 5 h in the air, and then heated to various temperatures from 700 to 1000 °C with a heating rate of 3 °C min^{-1} and held there for 3 h.

2.1.2. Solid-state reaction method

The equimolar amounts of commercially available monoclinic zirconia powders and high-purity quartz (SiO_2) sand were well mixed together with LiCl or Li_2CO_3 (the molar ratio of Li to ZrO_2 and/or SiO_2 was 0.3) using a pestle and mortar, and pressed into pellets. The pellets were heated to various temperatures up to 1000 °C in the air and held there for 1 h.

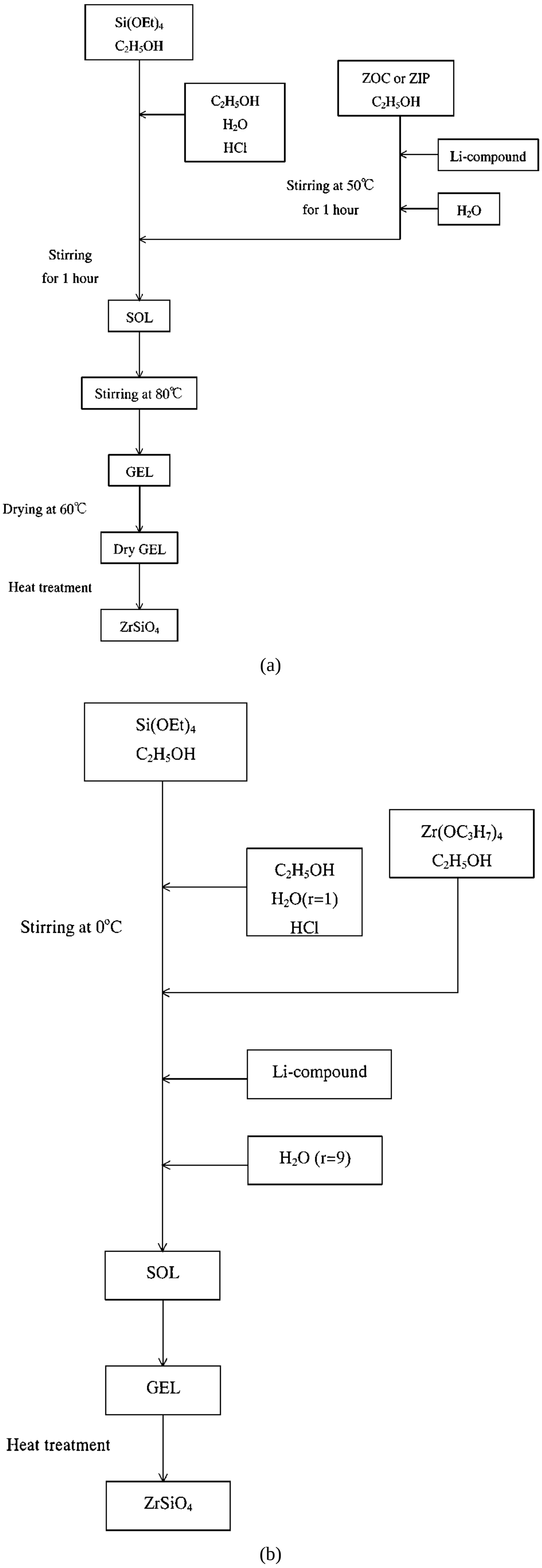


Figure 1 Flow chart of the preparation of $ZrO_2 \cdot SiO_2$ gels containing different additives: (a) Process I; (b) Process II.

2.2. Characterization of the samples

The formation process of zircon was followed by using X-ray diffraction (XRD; Shimadzu XD-610) and infrared (i.r.) spectroscopy. Ni-filtered CuK_α radiation was used as an X-ray source. The diffraction profile covering the diffraction angle 2θ from 10 to 60° was measured to identify the precipitated crystalline species. The fraction of zircon, $\alpha(ZR)$ in all the crystalline species was estimated on the basis of the intensity of diffraction peaks appearing in 2θ range from 20 to 30°, i.e. (2 0 0) line of zircon, (1 1 1) and $(1\ 1\ \bar{1})$ lines of monoclinic ZrO_2 and (1 0 1) line of tetragonal ZrO_2 following Equation 1 [9]

$$\alpha(\mathrm{ZR}) = I_{\mathrm{ZR}}(2\ 0\ 0)/(I_{\mathrm{ZR}}(2\ 0\ 0) + I_{\mathrm{M}}(1\ 1\ 1) + I_{\mathrm{M}}(1\ 1\ \bar{1}) + I_{\mathrm{T}}(1\ 0\ 1)) \qquad (1)$$

where subscripts ZR, M and T stand for zircon, monoclinic ZrO_2 and tetragonal ZrO_2, respectively, and the numbers in the parentheses indicate respective diffraction lines. The weight fraction of zircon in the whole sample (including not only crystalline compounds but also the amorphous material) was estimated from the diffraction intensity of (2 0 0) line of zircon by using a calibration curve made beforehand for the mixtures consisting of known amounts of pure zircon and SiO_2 glass powders.

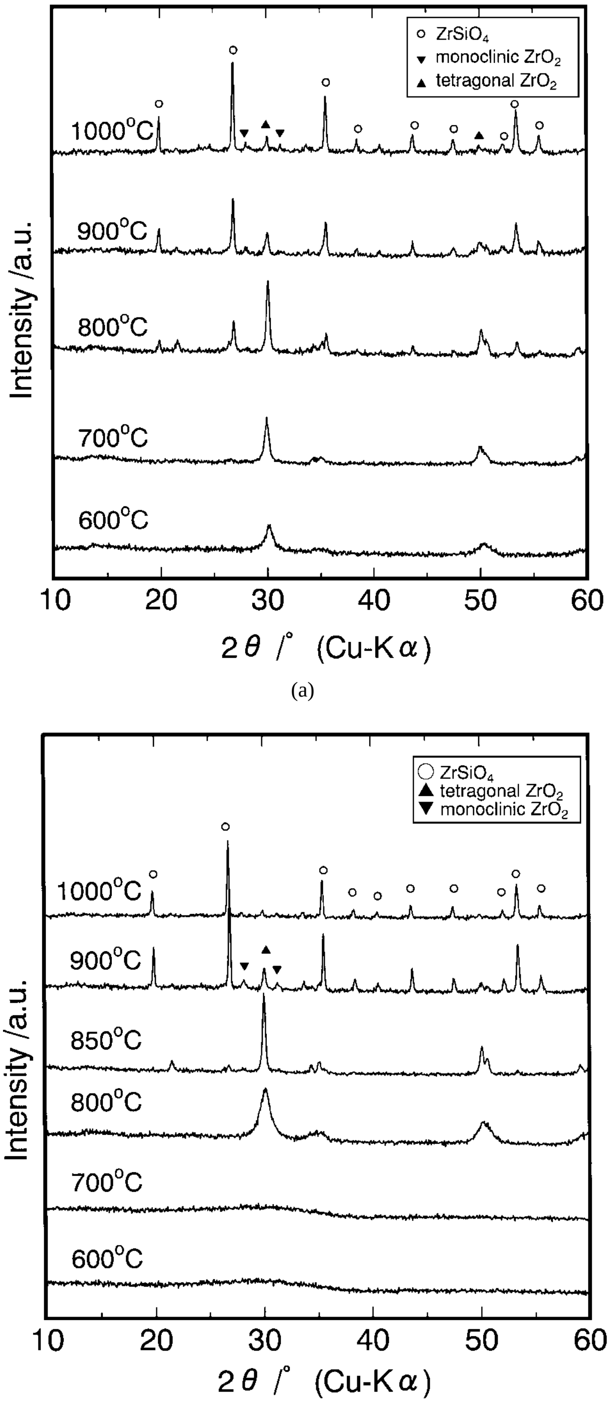
The i.r. spectra were measured in the wavenumber range from 300 to 2000 cm^{-1} with an Fourier transform infrared (FTIR) spectrometer FT/IR-550 (Nihon Bunko Kogyo, Co. Ltd). The KBr pellet method was employed. The assignment of i.r. absorption peaks was referred to Pecharroman *et al.* [17].

3. Results

Fig. 2a and b show the heat-treatment temperature dependence of XRD pattern for the representative gels made by Process I and Process II. For the Process I gel, tetragonal ZrO_2 was precipitated already at the calcination temperature of 600 °C. No other diffraction peaks than those of tetragonal ZrO_2 were detected in the 700 °C-treated gel. Zircon starts to be formed at 800 °C and is increased in diffraction intensity at the expense of zirconia at higher temperature. At 1000 °C, a part of the remaining tetragonal ZrO_2 is transformed to monoclinic ZrO_2. In the Process II gel, tetragonal ZrO_2 is crystallized at 800 °C, a relatively higher heat-treatment temperature than in the Process I gel; then zircon is formed at the expense of zirconia at higher temperature. The other Process II gels from those shown in Fig. 2b, i.e. gels made from ZIP/TEOS/LiOAc and ZIP/TEOS/LiOMe combinations showed a similar tendency of crystallization behaviour.

It is noted in Fig. 2a and b, that a small diffraction peak is detected at $2\theta = \sim 21.5°$, which may not be attributed to either zircon or zirconia. This diffraction peak appears in XRD patterns of all other gels during zircon formation. Because this peak is decreased with increasing the heat-treatment temperature, the corresponding crystalline species is considered to be metastable or some intermediate compound, which will be discussed in the next section.

In Fig. 3, the fraction of zircon, α(ZR) is plotted against heat-treatment temperature for all the gels. The change of α(ZR) in the gel made from the ZIP/TEOS/LiOAc/HCl combination by Process I with the heat-treatment temperature is almost same as in the gel made from the ZOC/TEOS/LiCl combination by Process I, although the data points are not given in Fig. 3 for the simplicity of the figure. It is seen that in the gels made by Process II, zircon starts to be formed at a slightly higher temperature than in the gels made by Process I. The α(ZR) is as high as 90–95% at 900–1000 °C, depending on the combination of chemicals and the process for making gels. However, the weight fraction of zircon itself was still 40 to 50 wt %, indicating that an important part of the heated product remains as an amorphous phase even at such a high temperature.



(a)

(b)

Figure 2 Change of XRD pattern of the $ZrO_2 \cdot SiO_2$ gels with heat-treatment temperature. (a) Gel made from ZOC/TEOS/LiCl combination by Process I. (b) Gel made from ZIP/TEOS/LiCl combination by Process II.

For a first reference, XRD patterns of the gel made from the chemicals combination of ZIP/TEOS/NaOAc by Process II and heat-treated at different temperatures

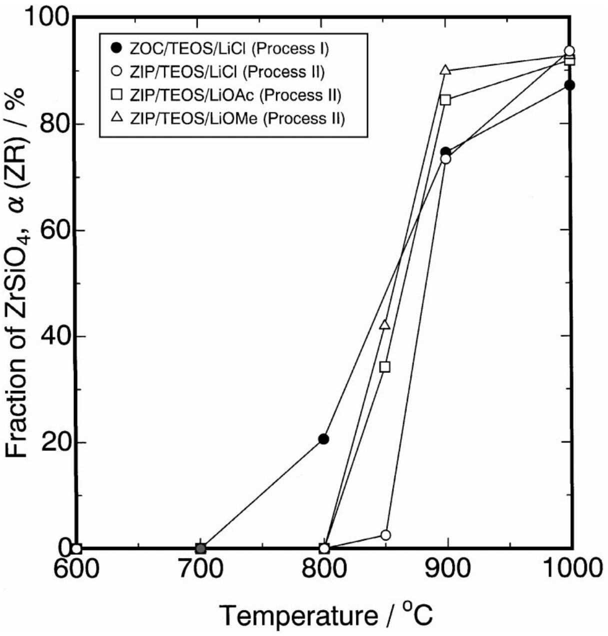


Figure 3 Plots of the fraction of zircon, α(ZR), as a function of heat-treatment temperature for $ZrO_2 \cdot SiO_2$ gels made from different chemical combinations.

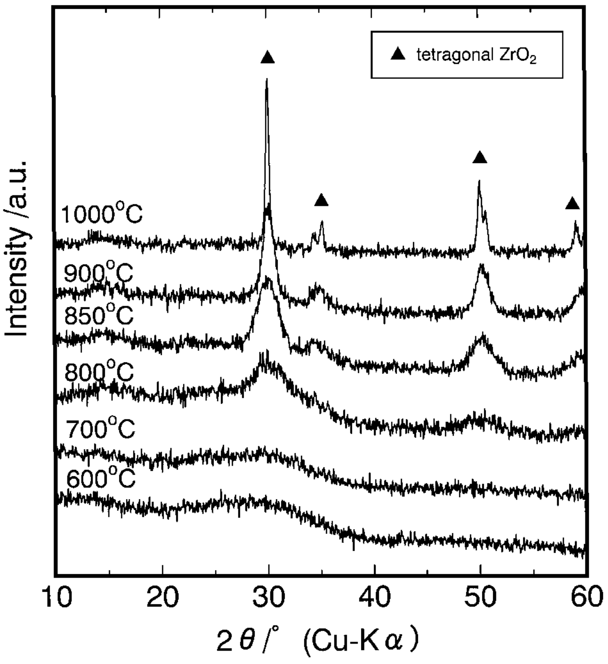


Figure 4 Heat-treatment temperature dependence of XRD pattern of the $ZrO_2 \cdot SiO_2$ gel made from ZIP/TEOS/NaOAc combination by Process II.

up to 1000 °C are shown in Fig. 4. In the gel, only the tetragonal ZrO_2 is detected up to 1000 °C, and no zircon formation occurs.

The change of crystalline phase caused by heat-treatment in the solid-state reaction in the $ZrO_2/SiO_2/LiCl$ powder pellets is shown in Fig. 5, as a second reference. It is seen that the zircon starts to be formed at 1000 °C. The α(ZR) is shown in Fig. 6 as a function of heat-treatment temperature, together with the result for the $ZrO_2/SiO_2/Li_2CO_3$ powder mixtures. The results are consistent with those reported previously by Nurishi *et al.* [5] (although they did not provide quantitative data).

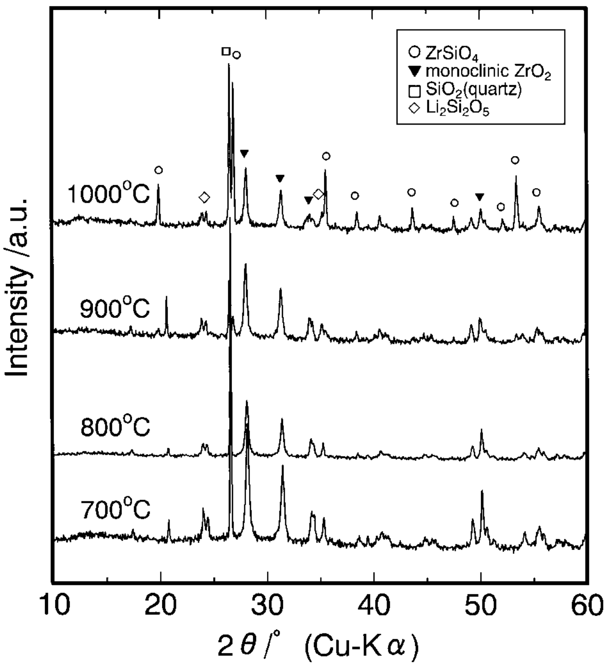


Figure 5 XRD patterns of the powder mixture of SiO_2, ZrO_2 and LiCl heat-treated at indicated temperature.

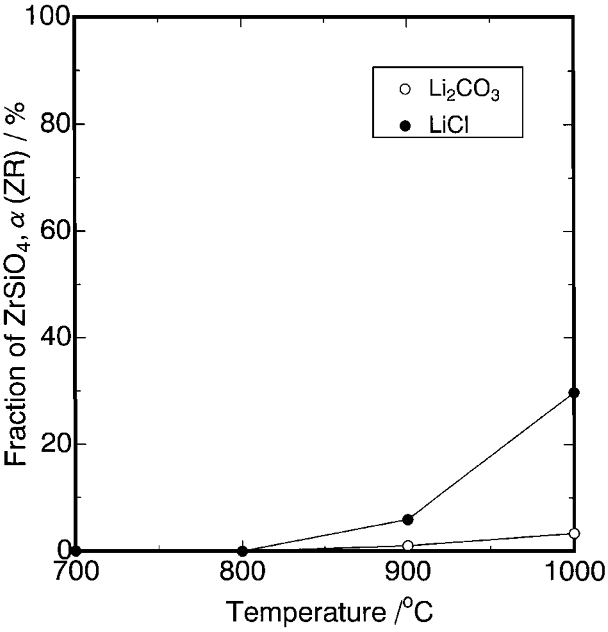
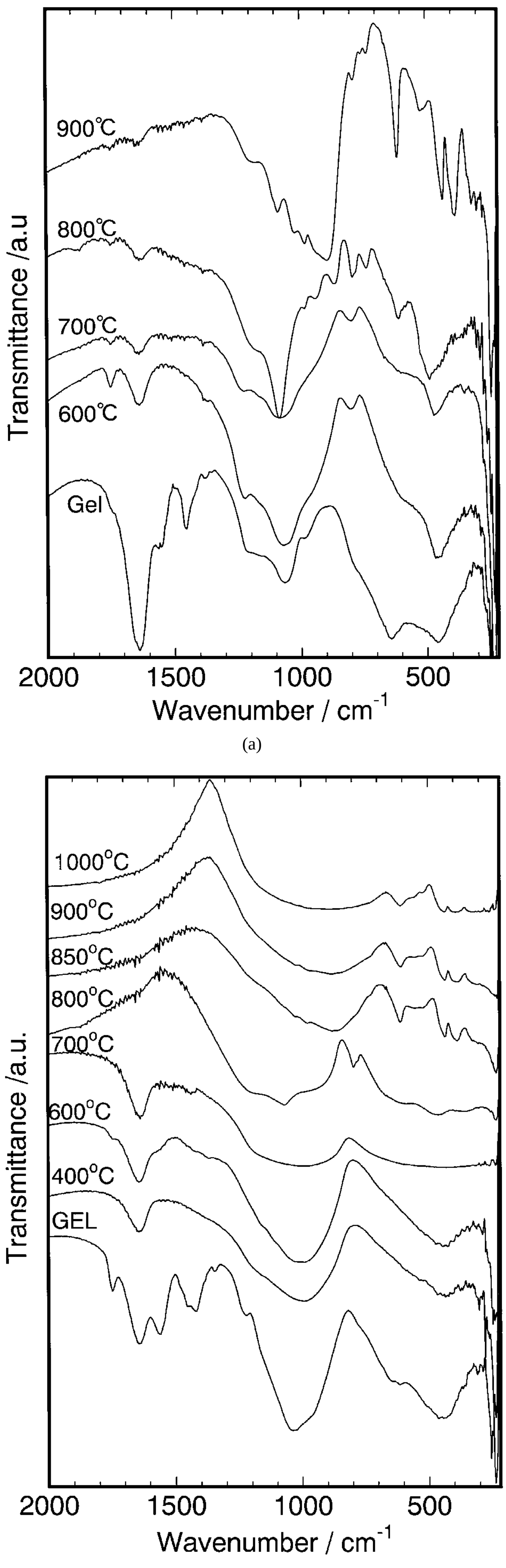


Figure 6 Change of α(ZR) with heat-treatment temperature for the $SiO_2/ZrO_2/LiCl$ powder mixture (●) and the $SiO_2/ZrO_2/Li_2CO_3$ powder mixture (○).

Infrared spectra of the Process I gel made from the ZIP/TEOS/LiOAc/HCl combination and heat-treated at various temperatures are shown in Fig. 7a, and those of the Process II gel made from ZIP/TEOS/LiOAc in Fig. 7b. Fig. 8 shows the heat-treatment temperature dependence of i.r. spectrum for a reference gel sample made from the ZIP/TEOS/NaOAc combination by Process II. The wave number of the main i.r. absorption peak around 1000 cm^{-1} of Si–O–Si stretching vibration is plotted against the heat-treatment temperature in Fig. 9, for all the gels prepared in the present study. It is seen from these figures that the i.r. peak is sited around



(a)

(b)

Figure 7 Change of i.r. spectrum with heat-treatment temperature for (a) the gel made from ZIP/TEOS/LiOAc/HCl combination by Process I and (b) the gel from ZIP/TEOS/LiOAc combination by Process II.

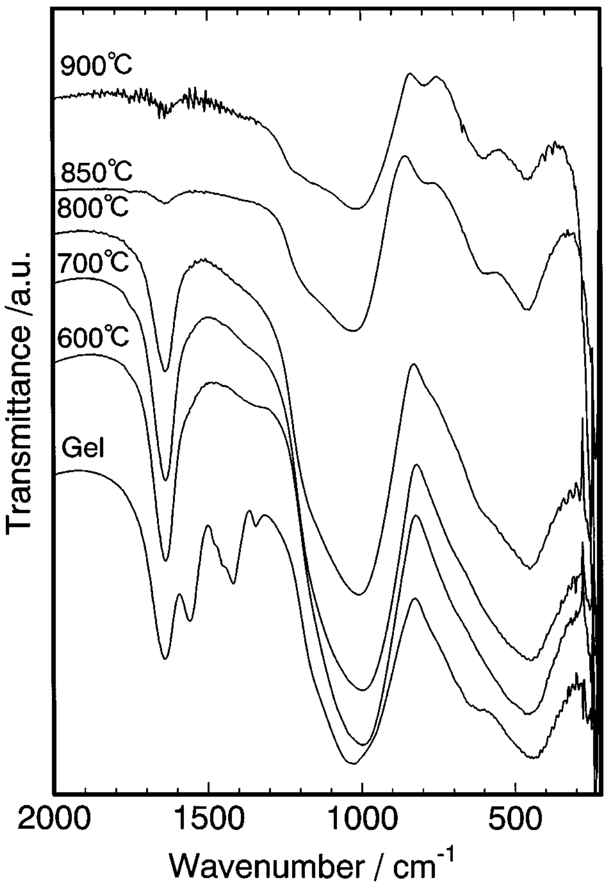


Figure 8 Infrared spectra of a reference gel made from ZIP/TEOS/NaOAc by Process II and heat-treated at indicated temperatures.

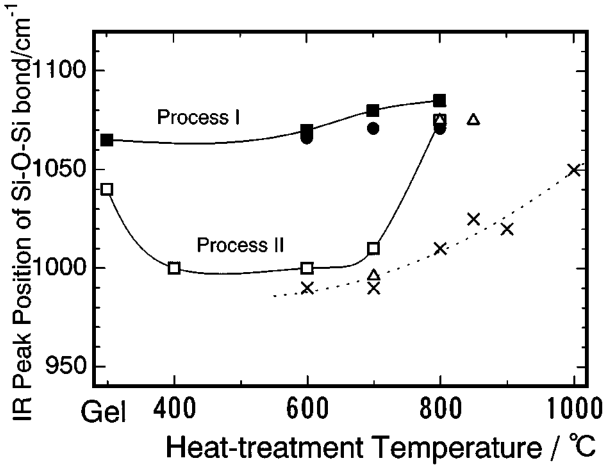


Figure 9 The change of wavenumber of i.r. absorption peak due to Si–O–Si vibration with heat-treatment temperature for all the gel samples prepared in the present work. ●:ZOC/TEOS/LiCl (Process I); ■:ZIP/TEOS/LiOAc/HCl (Process I); □:ZIP/TEOS/LiOAc (Process II); △:ZIP/TEOS/LiOMe (Process II); ×:ZIP/TEOS/NaOAc (Process II).

1075 cm^{-1} for the Process I gels, and the peak position shows almost no change with the increase of heat-treatment temperature, while the peak is at 1040 cm^{-1} in the Process II gel and shifts once down to 1000 cm^{-1} and to about 1075 cm^{-1} when the tetragonal ZrO_2 is precipitated in the gel at around 800 °C. As well as Li^+-containing gels, the Na^+-containing gel exhibits the i.r. peak at 1000 cm^{-1} which is shifted to higher wavenumber at the crystallization of tetragonal ZrO_2 above 800 °C as do other Process II gels.

In the silicate glasses and crystals, it is known that the peak position of the IR absorption of Si–O–Si vibration is smoothly shifted from about 1100 cm^{-1} for SiO_2 to lower wavenumber position as the content of SiO_2 is decreased. Namely, the i.r. absorption peak around 1075 cm^{-1} corresponds roughly to the disilicate composition, and that at 950–1000 cm^{-1} to the metasilicate composition.

4. Discussion

4.1. Comparison of the formation process of zircon in the gels with that in the solid-state reaction

In the solid state reaction between quartz and monoclinic ZrO_2, it has been reported by Nurishi *et al.* [5] that prior to the formation of zircon, some lithium silicate compounds such as $Li_2Si_2O_5$ and Li_2SiO_3 were formed, and at 900 to 1000 °C quartz transformed to cristobalite. These facts may have led them to the speculation that $Li_2Si_2O_5$ crystal is an important intermediate and reacts with ZrO_2 to form zircon as follows

$$Li_2Si_2O_5 + ZrO_2 \rightarrow ZrSiO_4 + Li_2SiO_3 \qquad (2)$$

Li_2SiO_3 crystal observed during the solid-state reaction has been considered not to play any essential role in the zircon formation. However, in the present work, the formation of $Li_2Si_2O_5$ crystal as an intermediate was not clearly detected (Fig. 5). Although, as is generally accepted in other solid-state reactions, the transformation of quartz to cristobalite has been considered to enhance the zircon formation (Hedvall effect), the fraction of zircon formed at 1000 °C was still low as 10 to 20 wt %.

On the contrary, the process of zircon formation in the gels is very different from that in above-described solid-state reaction in a few important points. The only crystalline species present in the gels before zircon is developed around 800 °C is tetragonal ZrO_2, with the remaining part being amorphous. Any distinctive lithium silicate crystals such as $Li_2Si_2O_5$ and Li_2SiO_3 are not detected by X-ray diffraction in the heat-treatment temperature range adopted in the present sol–gel work. Therefore, it is considered that poorly crystallized tetragonal ZrO_2 reacts directly with the amorphous phase consisting mainly of Li_2O and SiO_2 (this phase should contain also ZrO_2 as will be mentioned below) to form zircon, although the temperature where zircon starts to be formed is slightly different among gels added with different lithium compounds and depends on the preparation scheme of the gel.

The i.r. spectra of as-prepared and heat-treated gels suggest that the structure of the gel made by Process I and heated to 600 °C is different from that made by Process II. Namely, the i.r. absorption band due to Si–O–Si stretching vibration is sited at 1075 cm^{-1} for the gels made by Process I, while that of the 600 °C-treated gels made by Process II is at lower wavenumber than ~ 1000 cm^{-1}. The former is rather similar to the pure SiO_2 gel derived from TEOS by the sol–gel method [18] or the glasses of disilicate composition, and the latter resembles the $0.4ZrO_2{\cdot}0.6SiO_2$ (mol %) gel [19] or the glasses of metasilicate composition. Such a different structure may be attributed to the different scheme of the gel preparation.

In Process I, highly hydrolysable ZOC (or ZIP) is pre-hydrolysed and then added to pre-hydrolysed TEOS, which may lead to the phase separation in the resultant gel, i.e. the resultant gel may consist of SiO_2-rich phase and ZrO_2-rich phase.

On the other hand, in process II, ZIP just diluted with absolute ethanol is added to the partially hydrolysed TEOS solution, followed by thorough mixing and co-hydrolysis of TEOS and ZIP, which may result in the mixing of two chemicals at the atomistic level or the formation of Zr–O–Si bonds even in the gel (although this has not been proved).

The difference in the microstructure between such two types of gels should have brought about the different crystallization behaviour. It may be natural that the precipitation of tetragonal ZrO_2 is caused in the Process I gels at lower temperature than in the Process II gels. However, even in the Process II gels, the precipitation or exsolution of ZrO_2 above 800 °C leaves the amorphous phase similar to that in Process I gels, in other words, the amorphous phase is rich in SiO_2 (and Li_2O), which can be easily imagined from the IR data shown in Figs 7 and 9. Anyhow, independently of the preparation scheme, both types of gels are considered to consist of poorly crystallized tetragonal ZrO_2 and the amorphous rich in SiO_2 (and Li_2O) at 700–800 °C. Furthermore, because the lithium silicate glass containing 10–20 wt % ZrO_2 can be easily realized by the conventional melting technique, the remaining amorphous phase above 800 °C should be in the Li_2O–ZrO_2–SiO_2 system. If the amorphous phase was in the Li_2O–SiO_2 system, it would be easily crystallized to lithium silicate compounds. In reality, in the present work, the separately prepared melt-derived Li_2O–ZrO_2–SiO_2 glass was confirmed to be very resistant toward crystallization up to above 900 °C. This is consistent with the fact that at 900 to 1000 °C, where the fraction of zircon among crystalline species estimated by Equation 1 reaches 90–95%, the weight fraction of zircon in the whole product is 40–50%, with the left part being still in amorphous state.

Eventually, we have now a following scheme of zircon formation in the gels made through hydrolysis and condensation (or sol–gel reaction) of the starting chemicals.

$$\begin{aligned}&\text{Amorphous gels} \rightarrow \\ &\quad \text{tetragonal } ZrO_2 + Li_2O{-}ZrO_2{-}SiO_2 \text{ amorphous} \\ &\quad \text{phase (at } 800\,^{\circ}\text{C)} \rightarrow \text{zircon} + \text{tetragonal} \\ &\quad ZrO_2,\ \text{monoclinic } ZrO_2 + Li_2O{-}ZrO_2{-}SiO_2 \\ &\quad \text{amorphous phase (at } 900{\sim}1000\,^{\circ}\text{C).} \qquad (3)\end{aligned}$$

4.2. Possible mechanism of zircon formation in the gels

As described in the introductory section, several plausible mechanisms have been proposed for the mineralizing effect of additives on the zircon formation by the solid-state reaction:

1. The additives form liquid phase in the voids between loosely contacted SiO_2 and ZrO_2 particles, through which Zr^{4+} and Si^{4+} ions counterdiffuse to form zircon more easily [2–4]. The best efficiency of LiCl has been ascribed to its low melting temperature.

2. Among additives, lithium compounds react with SiO_2 to produce $Li_2Si_2O_5$, with which ZrO_2 react to form zircon. In other words, $Li_2Si_2O_5$ is an important intermediate compounds to synthesize zircon [5].

3. Structure transformation of SiO_2 and/or ZrO_2 during the heattreatment process cooperates with above reactions and enhance the formation of zircon (Hedvall effect).

However, it has not been revealed yet whether these mechanisms work effectively in the sol–gel processing of zircon.

Generally, in the sol–gel processing, the mixing of raw chemicals at atomistic level can be easily attained and enables the low temperature synthesis of various ceramic materials, which is said to be one of the important advantages of the method. Unfortunately, in the case of zircon formation, such an advantage for other materials does not seem to work efficiently, because the sol–gel synthesis of pure zircon is known to require still very high heat-treatment temperature as ~ 1500 °C [8–10], unless the gel is seeded with zircon particles [11, 12]. It has been found in the previous and present works that the addition of lithium compounds is necessary to synthesize zircon at lower temperatures even in the sol–gel method. Other cations such as Na^+ and Mg^{2+} exhibited no mineralizing effect to the sol–gel synthesis of zircon below 1000 °C.

As can be seen in Fig. 3, the mineralizing effect is independent of the anions associated with Li^+ ion, i.e. no substantial difference in the zircon formation process is noted among the added lithium compounds. In the Process I gels made from the ZOC/TEOS/LiCl and ZIP/TEOS/LiOAc/HCl combinations, zircon starts to form at slightly lower heat-treatment temperature than in the Process II gels. Such a difference in the zircon formation in the Process I gels from other gels may not be ascribed to the co-existence of Cl^- ions but to their microstructure, because the Process II gel made from the ZIP/TEOS/LiCl combination starts to form zircon at almost the same or rather higher temperature where other Process II gels do.

This fact indicates that effective for the low temperature synthesis of zircon in the gel is not the anions such as Cl^-, OCH_3^- and CH_3COO^-, but the lithium ion itself, which is reasonable because those anions should be removed during the sol–gel process and/or calcination at 600 °C. Actually, any trace of those anions is not detected in i.r. spectra of the gels heat treated above 600 °C; in other words, lithium compounds do not remain in the heat-treated gels as their original forms any more, but have been changed to Li_2O. Consequently, the melting of the lithium compounds to form liquid phase does not explain the mineralizing effect of those compounds.

Instead of lithium compounds themselves, lithium ions are incorporated into ZrO_2–SiO_2 phase to form the amorphous phase, which undergoes glass transition around 600~700 °C [20] to give viscous liquid state. Then, it may be possible that the liquid phase acts to enhance the counterdiffusion of Zr^{4+} and Si^{4+} ions. On the other hand, the ZrO_2–SiO_2 gel added with Na^+ ions precipitates tetragonal ZrO_2 above 800 °C, leaving the amorphous phase consisting of Na_2O, SiO_2 and ZrO_2. Although the amorphous or glass phase becomes viscous above its glass transition temperature (~ 700 °C), no trace of zircon is detected in the XRD patterns of the gel heat treated up to 1000 °C (the glass in the Na_2O–ZrO_2–SiO_2 system is also very resistant toward crystallization to 900 °C or higher temperatures [21]). These facts noted in the ZrO_2–SiO_2 gels added with Li^+ and/or Na^+ ions suggest that the presence of the liquid phase during heat treatment may not be a determinative factor for the formation of zircon in the gels below 1000 °C.

$Li_2Si_2O_5$, which has been considered as an important intermediate material for zircon in the solid-state reaction, is not encountered in the sol–gel processing. However, instead of $Li_2Si_2O_5$ crystal, we may have $Si_2O_5^{2-}$ structure units in the amorphous phase as Li_2O to SiO_2 molar ratio is between 0 to 0.33 and the amorphous state gives an i.r. absorption peak of Si–O–Si bonds around 1075 cm^{-1}. The disilicate ions may mineralize (or catalyse) zircon formation. However, no zircon formation in the Na^+ added gel which should also contain $Si_2O_5^{2-}$ units implies that such units do not have a significant role in the sol–gel zircon formation, either.

The Hedvall effect also does not work in the sol–gel processing of zircon, as no crystallization of the amorphous phase and no transformation of tetragonal ZrO_2 occur prior to the formation of zircon.

Then, the problem is: what is the mineralizing effect of Li^+ ions in the sol–gel synthesis of zircon? In the above, nothing has been mentioned about a crystalline species which starts to precipitate almost along with zircon around 800 °C. The XRD peak due to this crystalline species is sited at $2\theta = 21.5°/CuK_\alpha$, as seen in Fig. 2a,b and its magnification (Fig. 10). The peak position is clearly different from that of cristobalite ($2\theta = 22.0°/CuK_\alpha$). Furthermore, it seems that the species is in the transient state, as its XRD intensity is decreased with the increase of heat treatment temperature. This XRD peak is not detected in the Na^+-containing gel heat treated at any temperature. Therefore, it is assumed that the formation of this intermediate crystalline compound is related to the formation of zircon in the Li^+-containing gels. Among the known crystalline compounds which are made up by Li^+, Zr^{4+}, Si^{4+} and oxide ions, only a high temperature form of Li_4SiO_4 (JCPDS Card No. 24-650) gives a XRD peak at about 21.5° in 2θ. The high temperature form of Li_4SiO_4 is known to be quenched with ease [22].

Eventually, the following mineralizing effect of Li^+ ions is proposed: The Li^+ ions form lithium orthosilicate, Li_4SiO_4, in the Li_2O–ZrO_2–SiO_2 amorphous phase, which is analogous to the Li_2O–SiO_2–ZnO system in which orthosilicates such as Li_4SiO_4 and Zn_2SiO_4 can coexist with SiO_2 [22]. Then, Zr^{4+} ions substitute for Li^+ ions to form $ZrSiO_4$. This replacement of the cation is reasonable because the size of

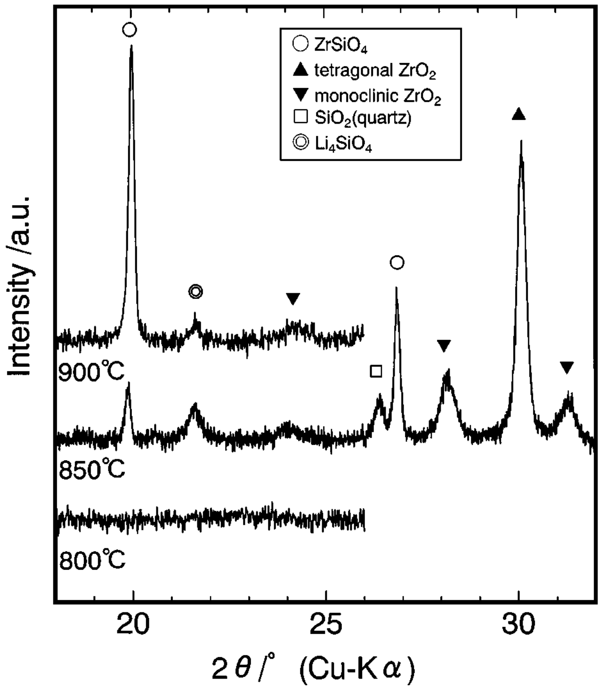


Figure 10 Enlarged XRD patterns covering 2θ from 18 to 32° for the gels made from ZIP/TEOS/LiCl combination by Process II and heat-treated at 850 and 900 °C.

Zr^{4+} ($r = 0.072$ nm in the sixfold coordination state) is very similar to that of Li^+ ($r = 0.074$ nm) in sixfold coordination state [23].

5. Summary

The sol–gel method using zirconium oxychloride hydrate, $ZrOCl_2 \cdot 8H_2O$ (ZOC) and zirconium tetra-iso-propoxide, $Zr(OC_3H_7)_4$ (ZIP), and tetraethylorthosilicate, $Si(OC_2H_5)_4$ (TEOS) as starting materials has been applied to the synthesis of zircon. In the present work, the zircon formation process of the $ZrO_2 \cdot SiO_2$ (in molar ratio) gels added with different lithium compounds was examined, and the mineralizing effect of the lithium compounds was discussed, comparing with the solid-state reaction. The results obtained are summarized as follows.

1. Zircon, $ZrSiO_4$ started to form above 800 °C, when the gels were added with lithium compounds, although the zircon formation temperature was slightly changed if the order of adding chemicals was changed.
2. The mineralizing effect was independent from the anions associated with Li^+ ion, in other words, it is Li^+ ion itself that is effective for the zircon formation.
3. The formation of $Li_2Si_2O_5$ crystal which has been considered to play an important role to trigger the zircon formation in the solid-state reaction method was not encountered in the sol–gel method, indicating that $Li_2Si_2O_5$ may not be a key intermediate compound for the formation of zircon. The disilicate $Si_2O_5^{2-}$ units in the amorphous of Li_2O–ZrO_2–SiO_2 system which should occur during heat-treating the gels seemed not to work to form zircon, either.
4. A metastable compound which showed a weak XRD peak at 21.5° in 2θ was found to form just before the precipitation of zircon. This peak was temporarily assigned as a high temperature form of Li_4SiO_4. The zircon formation process via such metastable Li_4SiO_4 crystal through the replacement of Li^+ ions by Zr^{4+} ions was proposed.

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