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Effect of cerium addition on phase transformation and microstructure of cordierite ceramics prepared by sol-gel method

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Low-temperature sintering of cordierite ceramic depends on the phase transformation into cordierite and the properties depend on its microstructure. In the present work, the effect of cerium on the phase transformation and microstructure of cordierite ceramics prepared by sol-gel method is studied by X-ray diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM) in order to lower the sintering temperature and improve the properties of cordierite ceramic with the addition of cerium. It is observed that the cerium addition obviously lowers the crystallization temperature of α-cordierite while slightly raises that of μ-cordierite. The lowest temperature for $\mu \rightarrow \alpha$ cordierite transformation, which approaches the crystallization temperature of μ-cordierite, is achieved in the sample containing 4 wt% of cerium, implying a possibility to lower the sintering temperature of cordierite ceramics. The Ce-contained ceramics show a biphasic microstructure that is dependent on sintering temperature. Sintered below 1300°C, a cordierite-CeO_2 microstructure is present; while sintered at the temperature above 1300°C, appears a cordierite-glass microstructure, of which the amount of glass phase is limited to a small extent. Since the addition of 4 wt% cerium to this MgO-Al_2O_3-SiO_2 system substantially enhances the densification of cordierite ceramics and lowers the sintering temperature to the level of around 1000°C, it makes the ceramics suitable for such applications, where the low-temperature sintering is required, as the substrates for electronic circuit and the catalytic supports (with oxygen storage capacity) for cleaning of automotive exhaust emissions.

1. Instruction

Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) ceramics are generally used for preparing the substrates for electronic circuit and the catalytic supports for cleaning of automotive exhaust emissions due to their low thermal expansion and low dielectric constant [1–3]. However, the high density is difficult to be achieved for the ceramic with a stoichiometric cordierite composition, because of its relatively high sintering temperature, narrow sintering temperature range and slow transformation. By the sol-gel technique and the addition of some flux, the sintering temperature of the ceramic can be suppressed to a relatively low level, and good properties can be achieved.

Although such substances with low melting point as P_2O_5, K_2O and B_2O_3 enhance the densification and lower the sintering temperature, they spoil the thermal expansion property of cordierite ceramic by yielding a large amount of glass phase. Thus, it is necessary to choose a flux, which is able to promote sintering without producing much glass, to obtain ceramics with high cordierite content and high densification.

The positive influence of added CeO_2 on promoting the sintering, stabilizing the microstructure and improving the properties of ZrO_2, AlN and $BaTiO_3$ ceramics has been reported in previous works [4–6]. It also promotes phase transformation and sintering in the preparation of cordierite-based glass ceramics by glass-crystallization method [7, 8]. Besides, the effect of CeO_2 on the phase transformation was found to be significant in the preparation of cordierite ceramic by oxide powder sintering [9].

However, Glahkov *et al.* [10] pointed that CeO_2 played no important role in the phase transformation in preparing cordierite ceramics by sol-gel technique.

The keys to the preparation of substrates for electronic circuit are the low-temperature sintering and densification of cordierite ceramics, which are determined by the characteristic of phase transformation into cordierite. Therefore, further study on the effect

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of cerium on the phase transformation and microstructure will help improve the sinterability of cordierite ceramics.

2. Experimental procedures

The sol-gel method was employed using TEOS ($Si(OC_2H_5)_4$), $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ as the starting materials (all AR grade). Samples based on the stoichiometric composition of cordierite are prepared with different amount of Ce added. The hydrolyzed TEOS and nitrate solution were mixed and intensively stirred, and then HCl and NH_3OH were added as catalysts to perform the solution–gelatin process. The resulting gels were dried up, calcinated at 450°C in order to remove the volatile species, finally ground into fine powders.

The crystallization sequences of the samples were determined by a differential thermal analyzer (SETARAM-DTA92), using a crucible of α-Al_2O_3 as reference sample, at a heating rate of 10°C/min. Crystalline phase were identified by an X-ray powder diffractimeter (Rigaku D/max-2400X) using Cu-K_α radiation with 40 kV, 120 mA, at a scanning rate of 4°/min. The samples for XRD analysis were uniaxially pressed with a pressure of 50 MPa into partially (half-) dried bodies and then sintered at different temperatures. The surface morphology and microstructure of ceramics were performed by a scanning electron microscope (Model: CSM950). The mechanically polished samples are sputtered with a film of gold to avoid electron aggregation.

3. Results and discussion

3.1. Crystallization behavior

Figs 1 and 2 show the DTA curves of the samples and the X-ray patterns of samples sintered at different temperatures respectively. By comparing the two results (Figs 1 and 2), it can be concluded that the exothermic peak at around 980°C corresponds to the crystallization of μ-cordierite. The addition of cerium slightly raises the crystallization temperature of μ-cordierite.

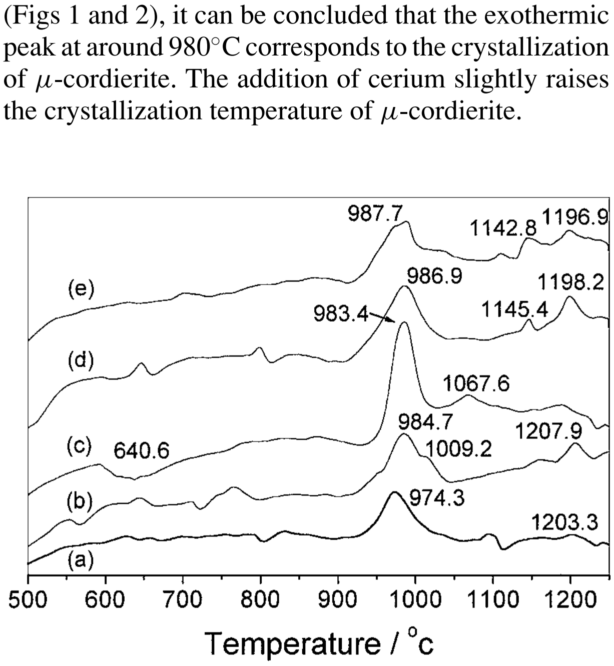


Figure 1 DTA curves of samples with different amount of Ce (a) Ce-free, (b) 2 wt%Ce, (c) 4 wt%Ce, (d) 6 wt%Ce, (e) 10 wt%Ce.

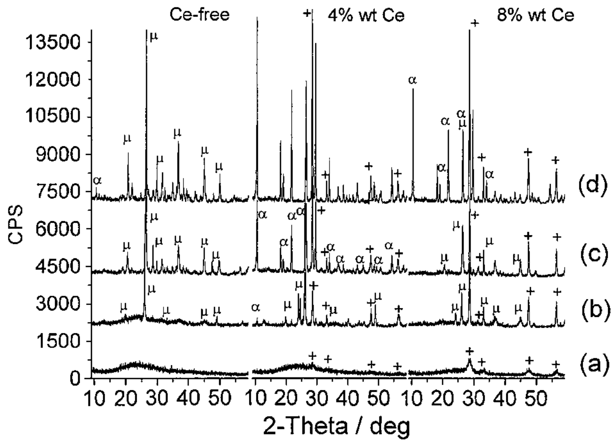


Figure 2 XRD patterns of samples sintered at (a) 450°C, (b) 1000°C, (c) 1100°C and (d) 1200°C for thirty minutes respectively, the marks μ, α and + represent μ-cordierite, α-cordierite and CeO_2.

With the increase of Ce content, the height of exothermic peak presents a movement of increasing first and then decreasing, the highest of which occurring when adding 4 wt% of Ce. Sintered at 1000°C, the sample containing 4 wt% of Ce is determined to contain both μ- and α-cordierite, while no characteristic peak of α-cordierite is detected in other samples even sintered at 1100°C. This implies that the peak next to the one at around 980°C is certain to be the result of the transformation from μ- to α-cordierite, which shifts to lower temperature first and then comes back to high-temperature side with increasing cerium content. The lowest temperature for the transformation (983.4°C) is observed at 4 wt% cerium content. Therefore the widening and sharpening of the exothermic peak in this case is attributed to the overlapping of two peaks corresponding to the crystallization of μ-cordierite and the transformation from μ- to α-cordierite respectively. An addition of cerium over 4 wt% tends to suppress the transformation again.

Besides, the last minor exothermic peak in the temperature range of 1190–1210°C in Fig. 1 may be caused by the direct transformation from amorphous phase to α-cordierite.

Moreover, cerium is known to act as a network modifier in the glass (or amorphous) with high valence (+4) and large coordination number [11], consequently compacting the glass network [12]. So, compared with the Ce-free amorphous phase, the Ce-contained amorphous phase gets more stable for the crystallization of μ-cordierite. As a result, the crystallization of the Ce-contained amorphous phase is suppressed.

However, it can be drawn that a complete inhibition of the crystallization of μ-cordierite is not achieved as shown is Figs 1 and 2. This is because the precipitation of CeO_2 in the period prior to the formation of μ-cordierite reduces the concentration of cerium in the amorphous phase. The lowest temperature for $\mu \rightarrow \alpha$ cordierite transformation at 4 wt% cerium is due to a small amount of cerium decreasing the activation energy for crystallization of α-cordierite [7].

It was reported by Montanaro [13] and Montorsi [14] that the solubility of cerium in cordierite crystalline is insignificant and there occurs no reaction between cerium and cordierite to form other crystalline. The present work proves that cerium exists in the form of CeO_2 or Ce-rich glass phase in the ceramics.

Since cordierite crystallizes from the amorphous phase, the concentration of cerium in the amorphous phase increases along with the crystallization of cordierite due to its low solubility in cordierite. Consequently, the crystallization of cordierite in these Ce-riched areas is suppressed and the temperature for crystallization is raised. The more cerium is added, the greater is the effect. The increasing resistance of cerium to ion diffusion in amorphous phase results in a wide range of temperature for crystallization of cordierite and the coarsening of its particles.

In conclusion, the addition of 4 wt% cerium promotes the $\mu \rightarrow \alpha$ cordierite transformation and is favorable to lowering sintering temperature.

3.2. Density of ceramics

Fig. 3 shows the surface morphology of samples sintered at 1100°C. There appears a good densification in the sample containing 4 wt% of cerium, while high porosity is still present in other samples sintered even at temperature up to 1350°C. This indicates the densification of ceramics depends on the phase transformation in sintering process.

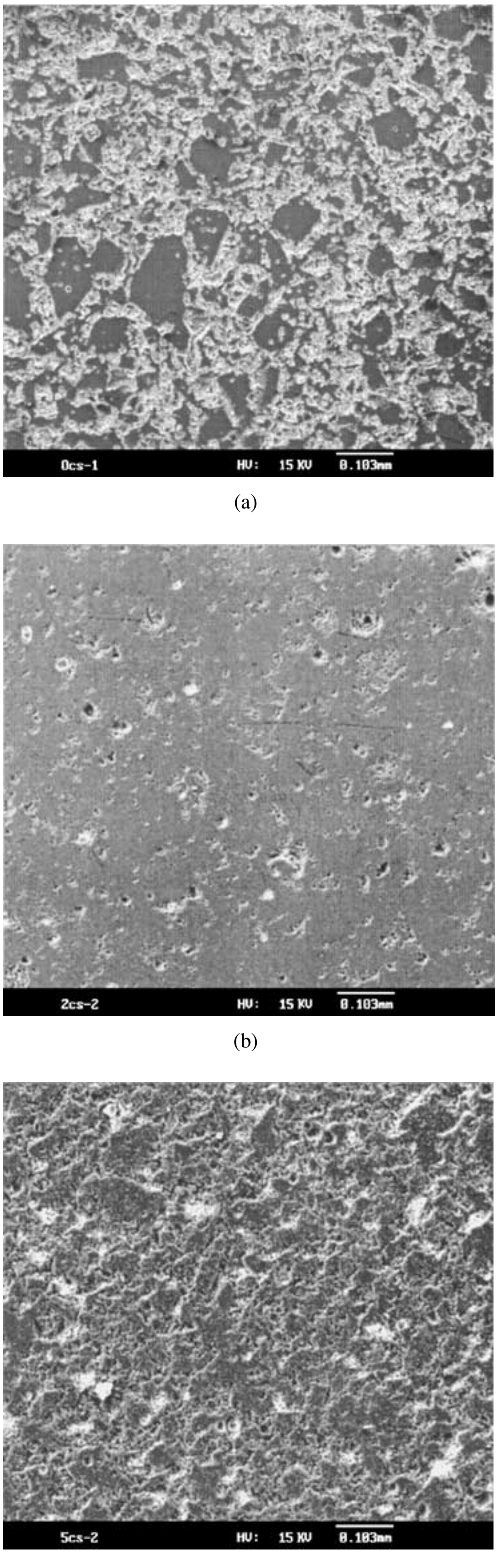
The reason affecting the densification of the sintered bodies is proposed as follow.

As is shown in the DTA curve of the sample containing 4 wt% of cerium (Fig. 1), there is an obvious endothermic peak close to 640°C, signifying the softening of amorphous phase occurred at glass transition temperature, which leads to the viscous flow at relatively low temperature and consequently an improvement of densification of ceramic body. On the contrary, The DTA curves of other samples present no similar endothermic peak, instead of some minor exothermic peaks. They may be resulted from the precipitation of the crystals such as CeO_2, SiO_2 or spinel, which retard the viscous flow of amorphous phase and consequently, prevent the attainment of high densification. So it can be concluded that the addition of 4 wt% cerium lowers the softening temperature of amorphous and promotes the densification of ceramic body.

3.3. The effect of cerium on microstructure of ceramics

Fig. 4 shows backscattered electron morphology of the samples sintered at different temperatures. The matrix of the ceramics is α-cordierite, but the secondary phase of Ce-contained samples depends on the sintering temperature. When sintered below 1300°C, CeO_2 crystal presents; and when sintered above 1300°C, the Ce-riched glass phase presents, both phases dispersed separately in the matrix. This is because Ce addition results in the melting of the compound of Mg-Al-Si-Ce-O system at about 1300°C.

As is observed from Fig. 2, CeO_2 can precipitate during the gelatin and the subsequent heating process. Thus the content of cerium added, the sintering temperature and the speed of cordierite crystallization all are responsible for the amount and size of CeO_2 particles. Obviously, the more the content of cerium and the lower the speed of crystallization of cordierite, the larger the amount and size of CeO_2 particles will be. On comparison between samples with 4 wt% and 10 wt% cerium added respectively, the amount and size of CeO_2 particles in the latter sample are relatively larger.

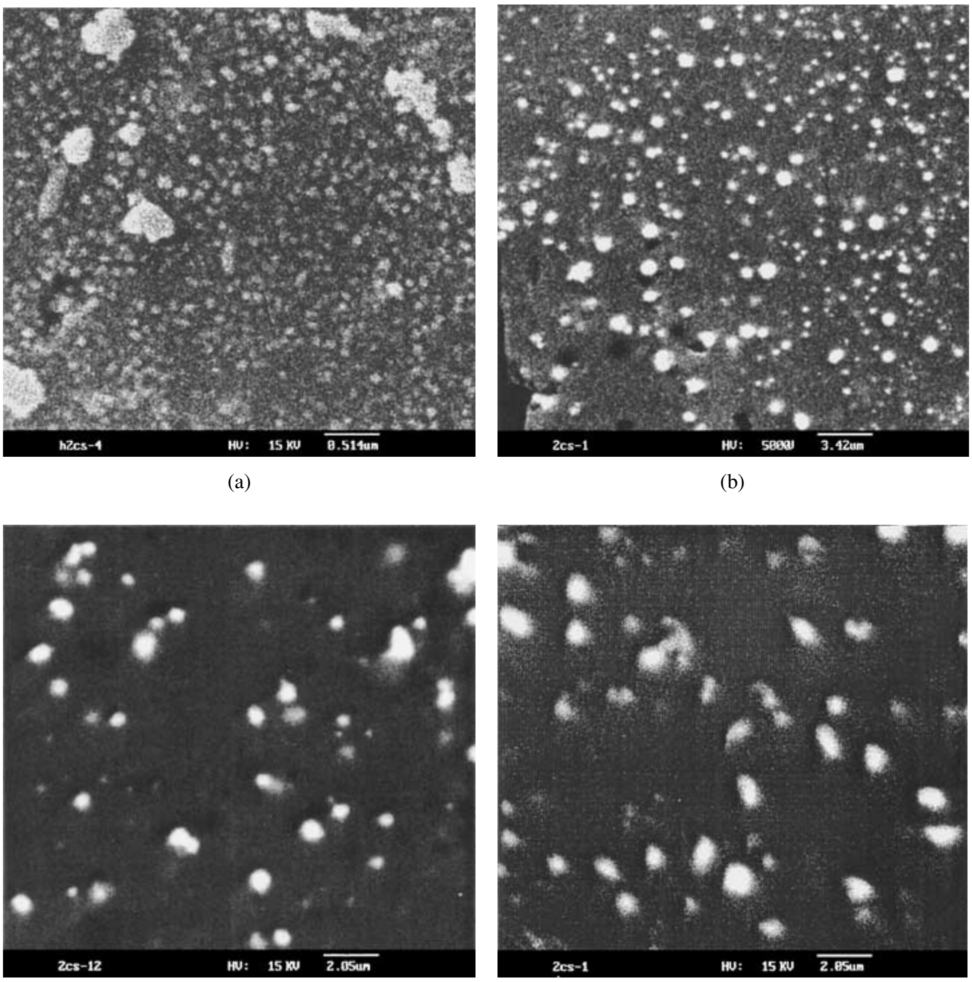


(a)

(b)

(c)

Figure 3 Surface morphology of samples sintered at 1100°C for one hour, (a) Ce-free, (b) 4 wt%Ce, (c) 10 wt%Ce.



(a) (b) (c) (d)

Figure 4 Microstructure of sample containing 4%wt of Ce (backscattered electron image) (a) 1100°C, (b) 1200°C, (c) 1300°C, (d) 1350°C.

4. Conclusions

1. The addition of cerium increases the temperature for crystallization of μ-cordierite and lowers that of the transformation from μ- to α-cordierite.

2. With 4 wt% of cerium added, the lowest temperature for $\mu \rightarrow \alpha$ cordierite transformation is achieved, which approaches the crystallization temperature of μ-cordierite, making it possible to lower the sintering temperature of cordierite ceramics to about 1000°C.

3. When sintered below 1300°C, the α-cordierite –CeO_2 microstructure is present; while sintered above 1300°C, it turns to be the microstructure composed of α-cordierite and cerium-rich glass phase.

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