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Effects of mechanochemical processing and doping of functional oxides on phase development in synthesis of cordierite

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Abstract

Mechanochemical activation of cordierite precursors (using laboratory planetary milling equipment) was applied as an intentional way of creating defects in the structure in order to affect the sinterability of the material. Effects of doping certain functional oxides on the sinterability and structural development of the resultant composites were also investigated. The microstructure of the sintered samples was considerably modified by intensive milling (even when applied at short times); at the same time, phase transformation of the mechanically milled material resulted in an almost single-phase cordierite ceramic when sintered at 1300 °C/2 h. In cases where the ratio of oxide dopants, ceria/yttria-stabilised zirconia was either 4 or 1/4, the influence of longer activation on the XRD peak intensities of the sintered samples was considerable. Destabilisation of zirconia and formation of zircon were observed in the activated material. Intensive milling also resulted in increased bulk density and shrinkage, and decreased pore content in the sintered composite samples.

Keywords: Mechanochemical activation; Sintering; Cordierite ceramics; Microstructure; Doping; Ceramic composites

1. Introduction

Mechanochemistry, a term which was first defined by Ostwald[1] in the late 19th century, is considered as a branch of solid state chemistry dealing with intentional formation of defects in the structure of solid substances by application of mechanical forces. These defects are often created using intensive milling processes.[2,3] The formation of defects in solids during intense milling action is characterised by non-equilibrium conditions; therefore, solids after mechanical treatment are regarded as metastable or in an *active* state.[4] Thermodynamically, such a state is defined by the difference in Gibbs free energy (ΔG) between the activated and equilibrium states such that[5]:

$$\Delta G_T = G_T^* - G_T = (H_T^* - H_T) - T(S_T^* - S_T) \xrightarrow{\text{at room temperature}} \Delta G_T \cong H_T \qquad (1)$$

wherein the G_T^*, H_T^* and S_T^* are the free energy, enthalpy and entropy respectively in the activated state.

There is often accompanying plastic deformation, amorphisation and agglomeration during such intensive grinding (or size reduction) processes.

The mechanochemical activation process is one of the most efficient ways to overcome the kinetic/diffusion constraints, arising from separation of particles in a dry powder mixture. These limitations are common in conventional solid-state synthesis methods and necessitate high processing temperatures. In those applications, mechanochemical preparation of the precursor material could help to increase the diffusion rates of the reactants across phase boundaries, leading to an increase in the kinetics of the solid-state reactions.[6,7]

Cordierite ceramics are widely used as glass–ceramic compositions for manufacturing multilayer circuit boards, catalytic converters, filters, kiln furniture and thermal insulation materials, to name a few. In all these applications the physical and chemical (sometimes unique) properties of cordierite are considered to be advantageous, of particular interest are the low thermal expansion coefficient (low degree of volumetric expansion at high temperatures and therefore resistant to thermal shock), and low dielectric constant (therefore low polarizability) at high

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frequencies. Recently it has been found that mechanochemical processing of kaolin, talc and gibbsite (as cordierite precursors) can significantly affect the thermal behaviour of the mixture during heat treatment of the activated material and modify the sequence and/or directions of the reaction in a way that ultimately result in a reduction in synthesis temperature of cordierite ceramics.[8,9] Other researchers also emphasise the efficiency of mechanochemical milling of precursors on densification and final amount of cordierite formed in the sintered bodies.[10,11] The toughening of the cordierite system by zirconia is particularly attractive; however, it has also been shown that fine zirconia dispersions in ceramic matrices can affect the sinterability.[12–14] There has been research[15,16] on the toughening of cordierite ceramics by ZrO_2 where the focus was on evaluation of thermal and mechanical properties of the sintered bodies. Moreover, rare earth elements such as Ce are considered to be highly active substances the oxides of which could be used to enhance the sintering of ceramics. This doping results in greater stability and a desirable modification of the microstructure.[17,18] Further, Shi et al. in their series of studies[15,19,20] on ceria-doped cordierite ceramics, showed that small amounts (2–4 wt%) of CeO_2 can improve the ionic diffusion in solid state, consequently promoting the conversion towards cordierite composition.

In synthesis of cordierite from natural silicates, no previous research was found to have investigated the combined effects of mechanochemical processing and doping of functional oxides. Therefore, this study is devoted to investigating possible effects of such treatments on sintering behaviour as well as microstructural development of the emerging cordierite ceramics.

2. Materials and methods

The precursor powders were used as-received, and they included high purity talc (10 μm, Sigma–Aldrich), ultrafine kaolinite (77% <1 μm Polsperse™ 10, Imerys Minerals Ltd.), and boehmite powder (SSA ~260 m²/g, Pural SB1®, Condea Chemie GmbH). Appropriate proportions of the three constituent powders were mixed based on the stoichiometric cordierite composition ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), and according to the reaction:

$$\underset{\text{Talc}}{4[Mg_3Si_4O_{10}(OH)_2]} + \underset{\text{Kaolinite}}{7[Al_2Si_2O_5(OH)_4]} + \underset{\text{Boehmite}}{10[AlO(OH)]} \rightarrow \underset{\text{Cordierite}}{6[Mg_2Al_4Si_5O_{18}]} + 23[H_2O] \qquad (2)$$

Functional additives applied during activation process included two oxide powders: yttria-stabilised zirconia (YSZ, ~3 mol% yttria, Unitec Ceramics Ltd.), and ceria (<50 nm, >99.95% purity, Sigma–Aldrich Co.).

Mechanochemical milling experiments in a non-contaminating environment were performed using a planetary mill consisted of two alumina pots and 5 mm diameter zirconia balls. In combination this allowed 100 g of the precursor powder blend to be milled at any one time. The planetary mill pots rotated at about 265 rpm around the common axis. Powder mixtures (±functional additives) were ground for two different times of 10 and 50 min, which respectively were considered to represent low and high degrees of grinding and/or activation.

Table 1
BET specific surface area values for the ground material.

Sample	Activation time (min)/sample code	BET surface area, m²/g (calculated)
Unmilled	0/MIX	43.73
Planetary-milled	10/PM10	52.88
	50/PM50	57.29

The as-milled powders were uniaxially compacted in a steel die without additives/binders at a compression of 1 kN (~20 MPa) using an Instron Universal Testing Machine. The cylindrical compacts (Ø8 mm) were later sintered at 1300 °C for 2 h in a furnace programmed with heating and cooling ramps of 10 °C/min. Characterisation of powders and sintered samples was carried out using laser diffraction size analysis (Mastersizer 2000), scanning electron microscopy (Philips XL30 SEM-Oxford EDX), X-ray diffraction analysis (Philips X'Pert), BET specific surface area measurement (Micromeritics ASAP 2010), bulk density (dimension measurements) and mercury porosimetry (Micromeritics WIN9400).

3. Results and discussion

3.1. As-milled samples

Although laser diffraction size analysis was used for size distribution measurements in this study, due to several factors such as significant difference in particle shapes, sizes and densities among different precursor powders, and further, due to high degree of agglomeration of nano-sized kaolinite and boehmite dispersion problems were encountered, scanning electron microscopy was used as a method to evaluate the size and shape variations in the ground samples. Fig. 1 shows that milling time up to 10 min (sample PM10) apparently not have caused significant size reductions, however, longer milling in sample PM50 have resulted in size reductions, while generating significantly more fines and consequently more agglomerations.

Larger talc particles (>1 μm flakes in sample PM10, Fig. 1) frequently had smaller particles (mostly kaolinite) attached to the surface (this would potentially give rise to the 'shielding effect' which commonly occurs in ultrafine grinding systems[21]). BET surface area measurements showed an increase in the specific surface area of the as-milled powders relative to the unmilled sample MIX (Table 1).

3.2. Sintering experiments

The XRD data given in Fig. 2 shows that the mechanical activation of the precursor powders resulted in formation of a near single-phase cordierite material containing minor proportions of spinel (samples PM10 and PM50). However, sintering of the unmilled sample resulted in a material (MIX) which still contained considerable amounts of corundum; this indicates that an incomplete phase development occurred prior to

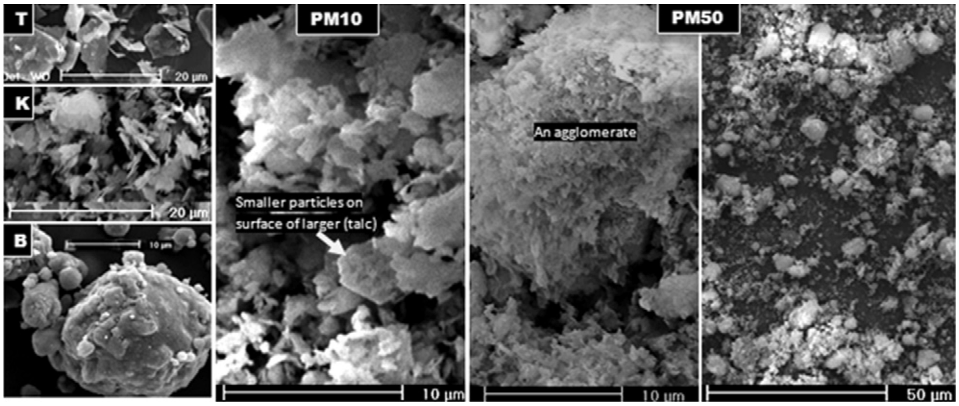

Fig. 1. SEM secondary electron images of the individual precursors (T: talc; K: kaolinite; B: boehmite), as well as planetary milled mixtures: shielding effect (PM1O), and agglomeration (PM5O) in ultra-fine intensive grinding.

sintering at 1300 °C. Significantly greater densification was observed after sintering at 1300 °C/2 h, when high intensity milling was applied. The bulk densities measured were 1730, 2130 and 2330 kg/m^3 for the MIX, PM10 and PM50 respectively (the theoretical density of cordierite is 2600 kg/m^3). The effect of mechanical milling on reduction of pore content and pore size is evident in the SEM images given in Fig. 2. The activated material (PM50) contained 10.4% residual porosity (considering pure cordierite composition for the theoretical density value).

The amounts of functional oxides added to cordierite precursor powders in these experiments are given in Table 2, and were selected based on the data reported in the literature.[13,16] Results of studying the effects of zirconia and ceria (added during activation process) on the sintered bodies are presented in Fig. 3a–d.

Formation of zircon ($ZrSiO_4$), indicated with "*Z*" in the XRD patterns, was the most important phase transformation within the samples which contained only yttria-stabilised zirconia (PZ) as dopant. Such a reaction, when promoted by activation (Fig. 3a), suppresses the availability of SiO_2 for the formation of cordierite. However, as observed in Fig. 3b, the zircon diffraction peaks in PZC50 are reduced (by almost 40%) compared to PZ50; this could be attributed to the ceria addition, giving partial stabilisation through formation of cerium zirconium oxide 'CZ', in combination with mechanochemical activation.

Table 2
Coding of the doped samples.

Sample code (numbers are milling time in minutes)	Additive types and amounts (wt%)	
	Yttria-stabilised zirconia, YSZ (Y_2O_3–ZrO_2)	Ceria (CeO_2)
PZ10	15	Nil
PZ50	15	Nil
PZC10	12	3
PZC50	12	3
PC10	Nil	4
PC50	Nil	4
PCZ10	3	12
PCZ50	3	12

It is assumed that the mechanical stress applied to precursor oxides in the activation process, could have affected the destabilisation of YSZ by the diffusion of yttria into the glassy phase during subsequent heat treatment. In a study by Travitzky and Claussen,[22] where no mechanochemical activation was applied, similar results were obtained only when the material was sintered at a higher temperature (~1400 °C) and for a longer retention time (48 h).

In samples where ceria is added in relatively high volumes, the product becomes glassier in nature with the cerium oxide

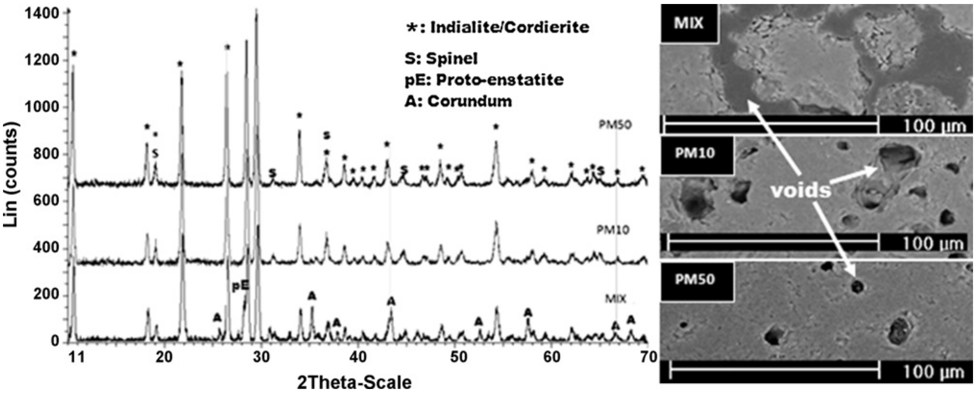

Fig. 2. Effect of activation on the phase composition (XRD graph, left), and microstructure (SEM images, right) of the cordierite material after sintering at 1300 °C.

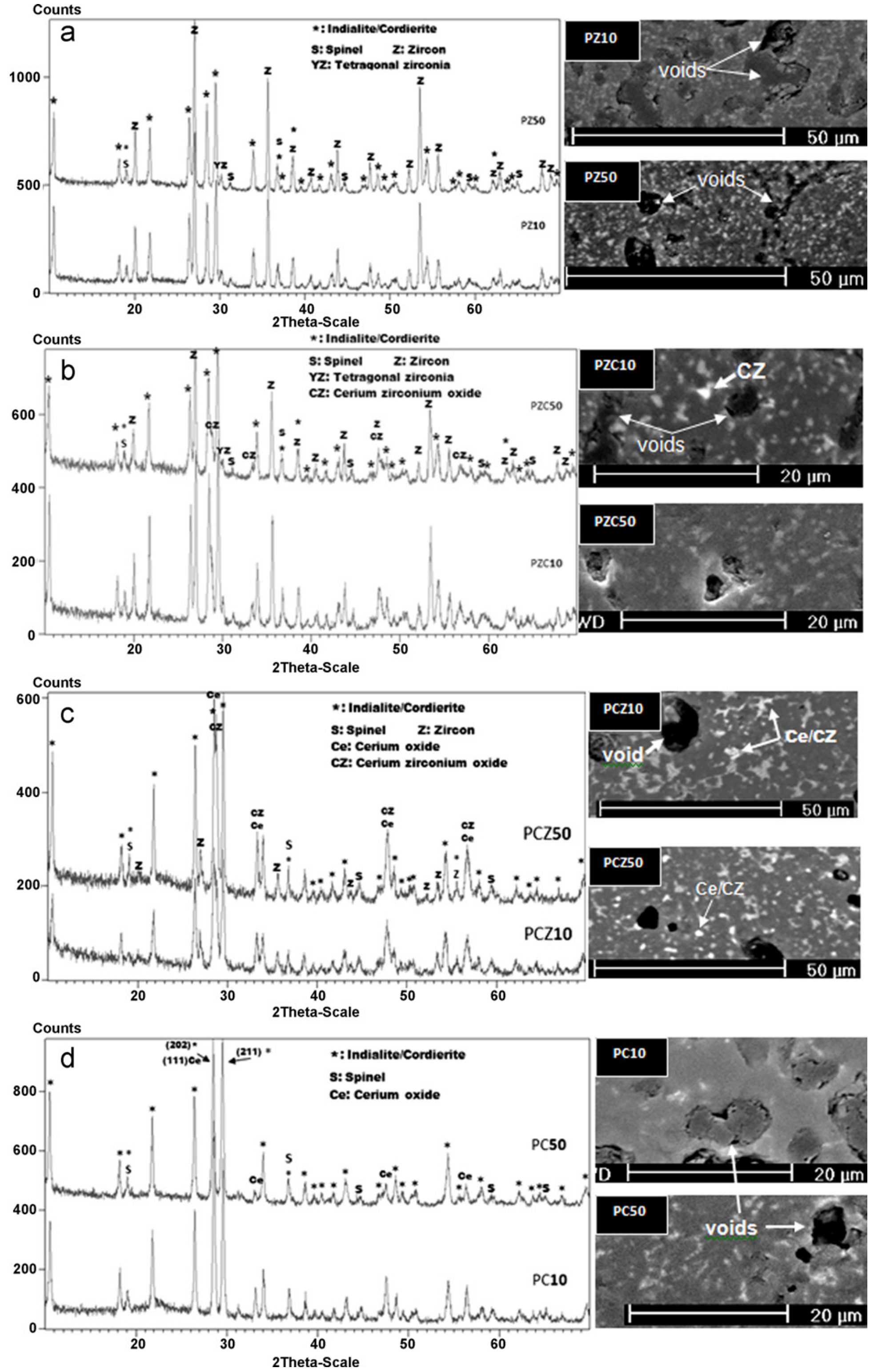

Fig. 3. XRD graphs (left) and SEM images (right) showing effect of milling on phase transformations and microstructure of the composite cordierite samples sintered at 1300 °C/2 h.

acting as a fluxing agent. This is shown by low XRD peak intensities in sample PCZ10 (Fig. 3c). However, with longer milling (in sample PCZ50), improved crystallinity was observed compared to shorter milling time in PCZ10. The process limited the formation of zircon, apparently due to formation of stable cubic cerium zirconium oxide ‘CZ’. When ceria was added alone in low amounts, increased mechanical activation (PC50) seems to have improved slightly the phase transformation to cordierite

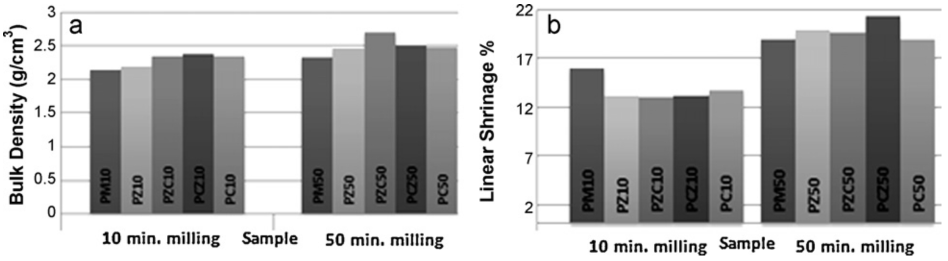

Fig. 4. Comparative bulk density (a) and shrinkage (b) data for the activated sintered samples with/without additives.

which is reflected in an increase in the relevant XRD peak heights (Fig. 3d).

Distribution of zirconia and ceria through the matrix appeared homogenous in all the sintered composites, and the homogeneity of additives' distribution in the matrix was increased with activation time. Addition of doping oxides to the cordierite matrix during milling generally improved the densification of the sintered materials, which significantly reduced the porosity when activation was prolonged (as observed in SEM images in Fig. 3). The densest sintered material was sample PZC50 (bulk density: 2690 kg/m^3, with about 15% porosity based on theoretical density of the composition) as observed in Fig. 4a. It is also found from the shrinkage data (Fig. 4b) that the oxide additives have generally reduced the shrinkage in the sintered material when milling time has been short. The influence of the zirconium and cerium oxide additions changes with intensive grinding as the pining mechanisms are lost and enhanced densification occurs.

4. Conclusion

Mechanochemical activation of the precursor powders in solid-state synthesis of cordierite ceramics was found influential with respect to the preparation of the powders for subsequent sintering. When dealing with sheet-like crystalline structures such as the precursor silicates used in these experiments, planetary milling (grinding basically through impact and attrition effects) is an appropriate method for achieving high densification in the final sintered material. There have been general improvements obtained by mechanochemical milling in this study, when compared to non-activating mixing/milling. Formation of almost pure indialite (hexagonal cordierite) at 1300 °C in the mechanically activated material due to enhanced particle contacts and increased reactivity of the powders resulted from the milling process. Good mixing of the precursors due to intensive milling has been considered as a significant factor in achieving homogeneous phase distributions in the sintered bodies. EDX analysis indicates zirconium silicate (zircon) formed in those samples that contained yttria-stabilised zirconia (particularly in samples with 15 wt% YSZ, and samples with 12 wt% YSZ and 3 wt% CeO_2). However, in samples containing 3 wt% YSZ, formation of a combined cerium zirconium oxide considered as an inhibitor for such transformation. When ceria was added in small amounts (3 wt%) to 12 wt% YSZ-doped cordierite mixtures, extended intensive milling (sample PZC50) resulted in more glassy structure in the sintered bodies.

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