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The preparation of cordierite from talc, fly ash, fused silica and alumina mixtures

R. Goren [*], C. Ozgur, H. Gocmez

Dumlupinar University, Department of Ceramic Engineering, Engineering Faculty, Kutahya, Turkey

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Abstract

In this study, cordierite ceramic was synthesized using a composition prepared by the mixture of four different materials: a talc, fly ash, fused silica and alumina. The formation of cordierite was achieved with the solid-state sintering reactions at 1350 °C for 1 h. The synthesized powder has been characterized by X-ray diffractometer (XRD), differential thermal analyzer (DTA), and the Rietveld analysis. The XRD analysis results showed the hexagonal or α-cordierite (indialite) as a major phase along with $MgAl_2O_4$ spinel and cristobalite as a secondary phase in the pressed mixture that sintered at 1300 °C for 3 h, while the only indialite phase was observed at 1350 °C for 3 h as well as 1375 °C for 1 h.

Keywords: D. Cordierite; Fly ash; Talc; Rietveld

1. Introduction

Natural cordierite having a chemical composition of $(Mg,Fe)_2Al_4Si_5O_{18}$ is a magnesium aluminosilicate mineral, occurring very rare in nature. The cordierite ceramics due to its low thermal expansion coefficient, high chemical durability, low dielectric constant, high resistance to thermal shock and high refractoriness are a promising candidate in many applications. Some examples of the applications are electrical porcelains, catalytic converter substrates for exhaust gas control in automobiles, heat exchanger for gas turbine engines, industrial furnaces, packing materials in electronic packing, refractory coating on metals, integrated circuit substrates, etc. [1–6].

Normally, the conventional methods for the synthesis of cordierite ceramics include the solid-state sintering of individual oxides of magnesium, aluminum and silicon corresponding to the chemical composition of cordierite, crystallizing the glasses or the sintering of the natural raw materials having MgO, Al_2O_3 and SiO_2 content, such as talc and china clay with low silicon content [6,7].

The cordierite occurs in three polymorphic forms: (i) the stable high-temperature disorder form, also known as indialite (α- or hexagonal-cordierite), stable below 1450 °C, (ii) β-cordierite called as orthorhombic cordierite, stable between 1450 °C and its melting point (1460 °C), and (iii) μ-cordierite called as metastable cordierite phase, which can be prepared only under special conditions, the low-temperature ordered orthorhombic form [6–10]. Indialite consists of the six-membered rings formed by five silicon and aluminum tetrahedral that share corners. Other aluminum tetrahedral and magnesium octahedral network connect the alternate six-membered (hexagonal) rings in such a manner that two structural cavities or channels per formula unit parallel to the *c*-axis are formed. Natural cordierites usually have intermediate Mg–Fe composition and contain small amount of other substitutional cations (Na, K, Be, Ca, Mn, etc.) and a variety of volatile components at elevated temperatures (H_2O, CO_2, Ar, etc.) [11,12].

The channel cations are generally monovalent ions and achieve the electrical neutrality in the structure for trivalent cations in the tetrahedral units. Geiger et al. [2] give a

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[*] Corresponding author.
E-mail address: remz_tr1968@hotmail.com (R. Goren).

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modified structural formula for natural cordierite as [^{ch}(Na, K)$_{0-1}$ ^{VI}(Mg, Fe^{2+}, Mn^{2+}, Li)$_2$ ^{IV}(Si, Al, Be, Fe^{2+}, Fe^{3+})$_9$ O$_{18}x^{Ch}$(H$_2$O, CO$_2$, Ar, . . .]. The symbols in the formula were ch, IV and VI for channel, tetrahedral and octahedral region cations, respectively.

The main purpose of the present study was to produce cordierite phase only without secondary crystalline or amorphous phases. Talc, fly ash, fused silica and alumina were selected as the starting materials to achieve this purpose.

2. Experimental

The starting raw materials used in this study were talc (Egypt), fused silica, α-alumina (Merck, Germany) and fly ash having a chemical composition (wt.%) of 56.49 SiO_2, 21.04 Al_2O_3, 4.85 MgO, 10.69 Fe_2O_3, 1.86 CaO, 0.91 TiO_2, 2.87 K_2O and 0.42 Na_2O, a waste product that is generated in thermal power station during the combustion of coal (Kutahya, Turkey). The prepared cordierite, determined by X-ray fluorescence, has a chemical composition (wt.%) of 12.19 MgO, 34.77 Al_2O_3 and 50.92 SiO_2 with some other constituents such as 0.46 CaO, 0.3 K_2O, 0.04 Na_2O and 1.22 iron oxide. The composition was formulated as the general structural formula of cordierite and the molecular formula was calculated on the basis of 18 oxygen atoms per anhydrous formula unit.

$$[^{ch}(\mathrm{Na}_{0.06}\mathrm{K}_{0.03}\mathrm{Ca}_{0.05})_{\overset{VI}{\sum}0.14}(\mathrm{Mg}_{1.82})_{\overset{IV}{\sum}1.82}(\mathrm{Al}_{4.03}\mathrm{Fe}^{3+}\mathrm{Si}_{5.04})_{\sum 9.16}x\mathrm{O}_{18}]$$

After the talc, fly ash, fused silica and alumina were weighed in terms of mole ratio of 2MgO. $2Al_2O_35SiO_2$, mixtures were dispersed in de-ionized water and milled as wet with alumina balls of 10 mm Ø for 8 h. The average particle size of ground powder was around 13.5 μm, which was determined by particle size analyzer (Malvern Inst., Mastersizer 2000). The green compacts were prepared by uniaxial press to form a disk, 1 cm Ø, 0.5 cm height and ~0.51 g weight. The green disks were placed in an alumina cylinder and then sintered in air up to 1200, 1300, 1350 and 1375 °C at a rate of 5 °C min^{-1}. The formed phases were analyzed by X-ray powder diffractometer (Rigaku, miniflex) using Cu Kα radiation with Ni filter. The Rietveld analysis for cordierite sintered at 1375 °C was performed by the Rietveld (DBWS) module of Cerius^2 (Accelrys Inc., USA) software Highly Filled Materials Institute of SIT (USA).

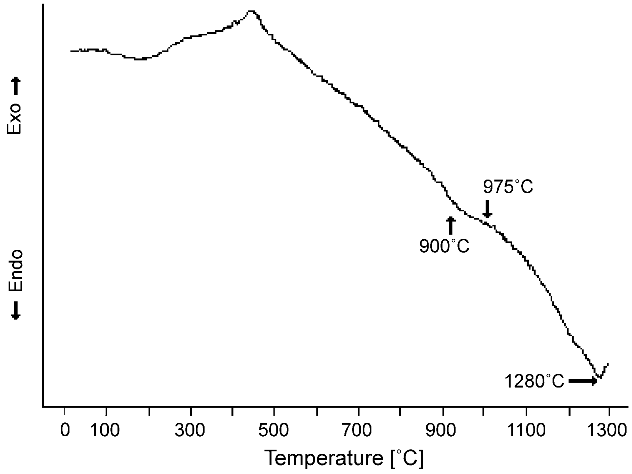

Fig. 1. The DTA patterns of the physical raw materials mixtures.

3. Result and discussions

The thermal behavior of the cordierite composition was characterized by differential thermal analyzer (DTA; Linseis, Thermowaage L81) in air up to 1300 °C at heating rate of 10 °C min^{-1} (Fig. 1). The endothermic peak at 900–975 °C might be attributed to the decomposition of talc to amorphous magnesium metasilicate (enstatite), amorphous

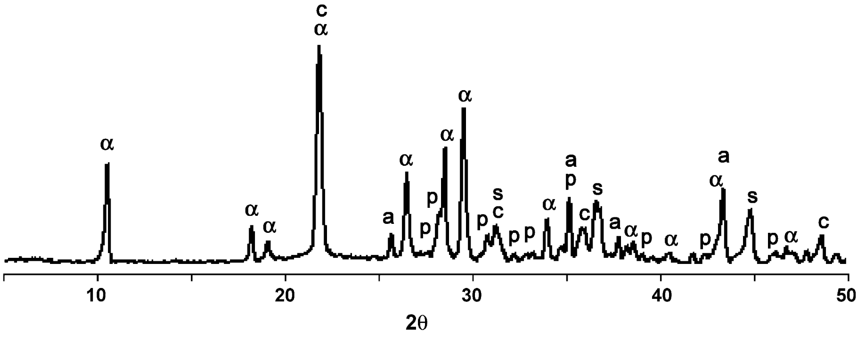

Fig. 2. XRD pattern of the cordierite sintered at 1200 °C for 1 h. Observed phases: (α) α-cordierite, (s) spinel, (a) corundum, (c) cristobalite and (p) protoenstatite.

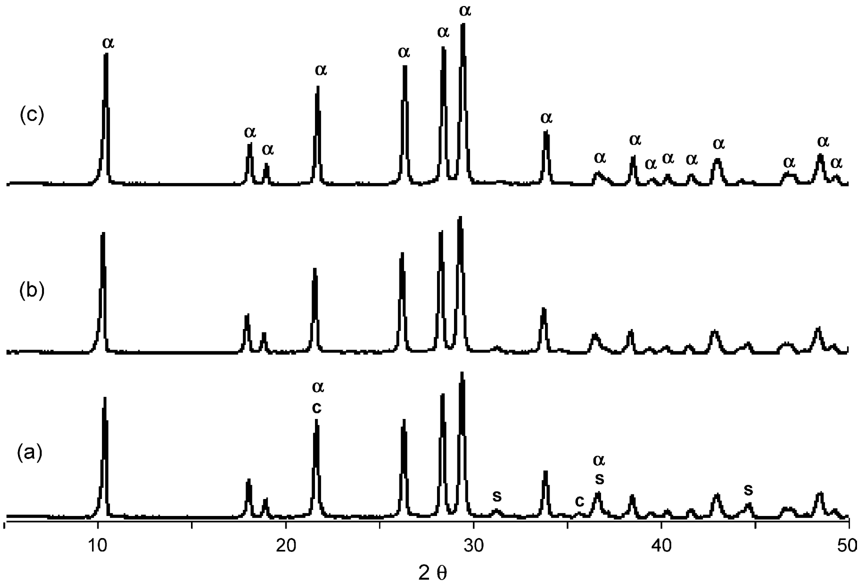

Fig. 3. XRD pattern of the cordierite sintered at different temperatures: (a) 1300 °C for 3 h, (b) 1350 °C for 3 h and (c) 1375 °C for 1 h. Observed phases: (α) α-cordierite, (s) spinel and (c) cristobalite.

silica and water vapor. As a result of the decomposition of the talc and the solid-state reactions up to 1280 °C, $MgAl_2O_4$ spinel formed with the interaction of $[AlO_6]$ and $[MgO_6]$ octahedral, enstatite turned to protoenstatite, amorphous silica was crystallized to cristobalite, and the transformation of μ- to α-cordierite had occurred. The peak after 1280 °C corresponded to the solid-state reaction of the cordierite formation with the interaction of spinel and cristobalite, noticeable in the XRD patterns obtained at 1200 °C (Fig. 2) and 1300 °C (Fig. 3a).

The X-ray diffraction measurements on the sintered samples at 1300 °C for 1 h (Fig. 3a) clearly indicate the indialite (hexagonal or α-cordierite) (PDF #48-1600) as the prevailing phase along with a significant amount of $MgAl_2O_4$ spinel (PDF #21-1152) and a very small amount of cristobalite (PDF #27-0605). The intensity of the diffraction peak for α-cordierite at 4.06 Å is higher than expected for pure α-cordierite phase. This peak can overlap with the 100% peaks for cristobalite at 4.0397 Å. The cristobalite and spinel phases disappeared completely at 1350 °C for 3 h. According to Naskar et al. [12], the spinel ($MgAl_2O_4$) forms at about 1040 °C with the interaction of $[AlO_6]$ and $[MgO_6]$ octahedral, and then the transformation of spinel to cordierite at 1365 °C occurs due to the interaction with cristobalite. The compositions sintered at 1375 °C for 1 h exhibit the same XRD pattern compared with the composition at sintered 1350 °C for 3 h (Fig. 3b and c).

The natural resources used for the production of cordierite contain generally impurities such as the alkaline metal, iron and calcium oxides. According to Geiger et al. [2], Fe^{3+} ions can replace with Si^{4+} in tetrahedral region. Al^{3+} ions can adopt tetrahedral and octahedral co-ordinations. Insertion of K^+ cations, in the cordierite hexagonal channels, leads to a local positive charge excess which favors the enrichment of the nearest tetrahedral with the lower-charged cations (Al^{3+}, Fe^{3+}, etc.) [10]. When a cation having trivalent charge is replaced with Si^{4+}, a change imbalance results that can be corrected by the substitution of an alkaline metal ions.

The Rietveld analysis for cordierite sintered at 1375 °C was performed by the Rietveld (DBWS) module of Cerius^2 (Accelrys Inc., USA) software. Rietveld refinement occurs by improving the parameters of the trial structure so that the simulated diffraction pattern can match an experimental one. In Rietveld (DBWS) analysis and refinement, a simulated powder diffraction pattern is calculated from a trial structure and this is compared with X-ray powder diffraction data obtained experimentally. Fig. 4 shows the simulated

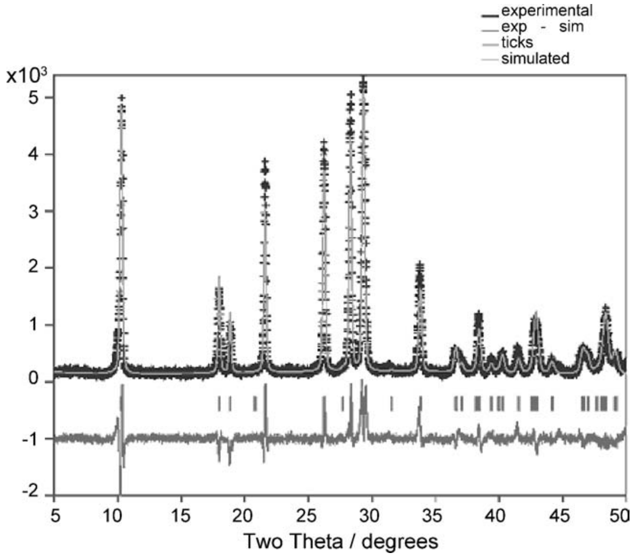

Fig. 4. Observed, calculated and differential pattern for the cordierite.

refinement pattern with experimental pattern. The value of the agreement factor was $R_P = 14.6\%$ (P is for pattern), which shows good fit. The Rietveld refinement has shown that cell parameters of the synthesized cordierite is the same as reference cell parameter of α-cordierite ($a = b = 9.764$ Å and $c = 9.360$ Å).

4. Conclusions

The cordierite has been successfully synthesized by using standard raw materials including talc, fly ash, fused silica and alumina. The XRD results showed that the synthesized material sintered at 1350 °C for 3 h is formed of only indialite phase (high temperature form of cordierite) and no secondary crystalline or amorphous phase can be detected. The comparison of the samples sintered at 1350 °C for 3 h with 1375 °C for 1 h indicates that sintering time is as important as sintering temperature to improve the recrystallization of cordierite.

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