



Sol-gel synthesis and structure of cordierite/tialite glass-ceramics

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Abstract

In the present work the results of the research on the sol-gel synthesis and structure of cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$), tialite ($\text{Al}_2\text{O}_3\cdot \text{TiO}_2$) and cordierite/tialite glass-ceramics as well cordierite containing 2 wt.% of Co and Co+Cu have been described and discussed. The sol-gel synthesis was carried out using different kind of precursors as follows: $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, chlorides or nitrates of corresponding metals, H_2O , $\text{C}_2\text{H}_5\text{OH}$, Aqua Regia, NH_4F and PEG. The synthesized gels were dried and thermally treated in the temperature range from 800°C to 1200°C . The sol-gel processes and structure of the cordierite, tialite and cordierite/tialite glass-ceramics have been investigated by means of XRD, FTIR, TEM, SEM and EPMA.

Keywords: sol-gel, cordierite/tialite, glass-ceramics, electroceramics

I. Introduction

It is well known that the cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and tialite (Al_2TiO_5) ceramics are excellent insulators and high-thermal resistant materials possessing low dielectric constants and thermal expansion coefficient. The cordierite ceramics is a promising material for the barrier rib in plasma display panels [1], high integral circuits, microchips [2] and multilayer chip indicators [3]. The cordierite and tialite ceramics are very attractive supports of catalysts for the conversion of combustion gases from engines and for treatment of diesel exhaust [4–9].

Considerable research has been devoted to advanced methods of powder synthesis from solutions. One of these wide used techniques is alkoxide sol-gel method. Disadvantages of this method are the relatively high price of starting compounds and solvents, as well as the great difference between the rates of hydrolysis of alkoxides, making powder synthesis more difficult and expensive [10–18]. However, this method is very promising for synthesis of different type of composites. Thus, some authors prepared cordierite/zirconia composites doped with CeO_2 [4,16,17], CeO_2 - ZrO_2 and Y_2O_3 - CeO_2 - ZrO_2 [18] via sol-gel technique. Composite mullite/cordierite powders were also synthesized

using sol-gel method by Ismail et al. [19]. Maxata et al. investigated the formation of tialite/mullite composite form bauxite red mud [20].

In our previous investigations the glass-ceramic materials, in the $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ - Al_2TiO_5 system, have been synthesized by solid-state reactions and some of their characteristics have been determined [21]. Sol-gel technology has been used for investigation the synthesis and structure of gels in the Al_2O_3 - TiO_2 - SiO_2 - MgO system [22].

Taking into account that the main advantages of sol-gel method can contribute to improve the properties and applications of cordierite/tialite glass-ceramics, this method has been used for their synthesis, as well as for obtaining of cordierite ceramics containing 2 wt.% Co, Co+Cu. In the present article the phase formation and structure evolution in cordierite/tialite glass-ceramics, after thermal treatment at 1200°C have been studied, discussed and described below.

II. Experimental procedure

Cordierite ceramic (sample denoted by C) was prepared by the sol-gel method using three metal compounds: $\text{Si}(\text{OC}_2\text{H}_5)_4$ i.e. TEOS (Aldrich), $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Merck) and $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Merck). Initially, TEOS (34.17 g) was used for preparing of SiO_2 sol, after being partially hydrolyzed in the presence of $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}:\text{Aqua Regia}$ at molar ratio 1.2:6:0.01 and at room temperature for 30 min. The obtained mixture was transferred into partially

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hydrolyzed TEOS, followed by refluxing at 25°C until clear sol formed. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (49.00 g) and PEG as a chelating agent was dissolved in water for 15 min. The molar amount of chelating agent was equal to the total molar amount of metal nitrates in solution. It was necessary, because chelating agent may form ion associated “inner- and outer-sphere complex” with “clathrate coordination”. On the one hand, this complex could prevent the aggregation of particles in the obtained mixed sol after adding cobalt salt. On the other hand, the presence of NO_3^- , with its preference for bidentate coordination and its hard oxygen donors, has the greatest effect on the conformations of organic molecules used as chelating agent. Moreover nitrate ions may act as an oxidizing agent for the decomposition of PEG [23].

Subsequently, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (16.81 g) dissolved in water was added “drop to drop” into the mixture of partially hydrolyzed TEOS, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and PEG, refluxed for 6 h to obtain a clear cordierite sol. The obtained cordierite sol was dried at 70°C for several days and then at 120°C for 6 h. Dried cordierite sol was annealed at 1100 and 1200°C for 2 h. Cordierite ceramics, containing 2 wt.% Co and Co+Cu were prepared by mixing of cordierite gel with corresponding metal salts solved in $\text{CH}_3\text{COCH}_3:\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}=1$.

Aluminum titanate (tialite sample denoted by T) gel was prepared from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (68.82 g) and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (31.18 g) in 50 ml $n\text{-C}_4\text{H}_9\text{OH}$. Each mixture was stirred to complete dissolution and then they were mixed together under intensively stirring for 3 h. The obtained yellow tialite gel was dried under vacuum at 25°C for 3 h and then at 120°C for 6 h. The dried tialite gel was thermally treated at 1200°C/2h in tubular furnace.

Cordierite-tialite glass-ceramics were obtained by mixing of cordierite and tialite sols in different volume ratio, i.e. C:T=70:30, 50:50 and 30:70 (samples denoted by CT-x, where x represents vol% of cordierite). The obtained mixed sols were dried at 120°C for 6 h and then annealed at 1200°C for 2 h.

After thermal treatment, ceramic powders were analyzed by XRD using Rigaki XDMAX-X-ray diffractometer (Cu K_α -radiation). The IRS of calcined powders was recorded over MATSON 7000-FTIR. The microstructure analysis was carried out by TEM (EM Philips-400), EPMA (EDAX 9900, Philips) and SEM (Philips-525). The electrical resistance was measured using circular specimens of 20 mm in diameter and 1.5 mm thickness at 20°C.

III. Results and discussion

The XRD diffraction patterns for cordierite gels in the presence of aqua regia, thermally treated at different temperatures are given in Fig. 1.

It is shown that XRD of the cordierite gel (sample C) in the presence of aqua regia remained amorphous up to 800°C. With further heating at 1000°C, μ -cordierite

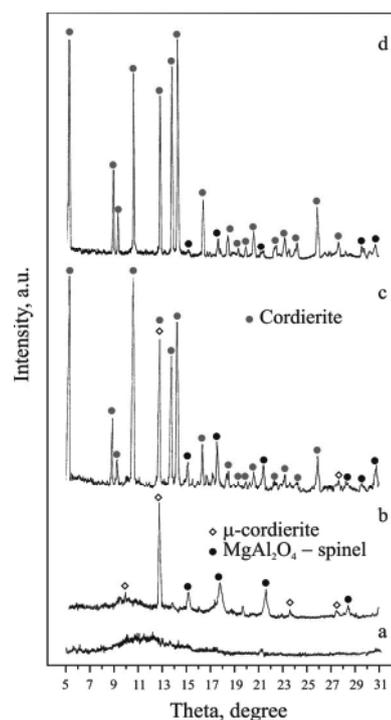


Figure 1. XRD patterns of cordierite-aqua regia gel after thermal treatment for 2 h at: a) 800°C, b) 1000°C, c) 1110°C and d) 1200°C

peaks (PDF 14-0249) appeared together with smaller peaks of spinel (PDF 21-1152). At 1100°C, the α -cordierite (PDF 13-0293) was the primary phase, but other phases were present too: μ -cordierite, spinel and probably a small amount of forsterite, enstatite and mullite [14]. The presence of μ -cordierite has been supposed

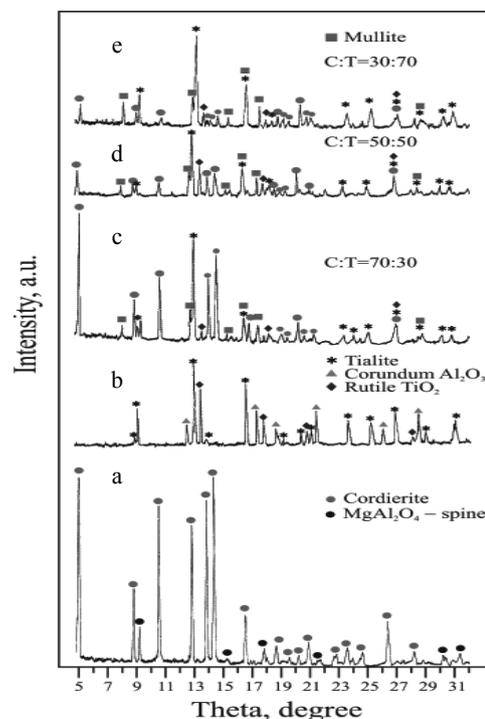


Figure 2. XRD of: a) cordierite, b) tialite and c) cordierite-tialite glass-ceramics CT-70, CT-50 and CT-30, treated at 1200°C/2h

because of the intensity increasing at $\theta=13.28$. The sample C heated at $1200^{\circ}\text{C}/2\text{h}$ consists of α -cordierite as a main phase and small amount of spinel.

XRD patterns for cordierite gels in the presence of aqua regia, containing PEG and thermally treated at $1200^{\circ}\text{C}/2\text{h}$ show that in all cases, only α -cordierite and spinel phases were observed. In the presence of PEG, the intensity of spinel peak increases.

The XRD diffraction patterns of cordierite, tialite and cordierite-tialite composite powders are given in Fig. 2. Analysis of the XRD pattern of tialite gel annealed at 1200°C for 2 h (Fig. 2a) shows the formation of tialite phase (PDF 41-0258) with two other phases, rutile (PDF 21-1276) and corundum (PDF 88-826) [24]. Fig. 2b,c,d show XRD patterns obtained of composite samples containing different quantity of cordierite and tialite (CT-70, CT-50 and CT-30). It has been established that in cordierite-tialite composites cordierite, tialite and rutile crystalline phases are presented, but spinel and corundum are not registered. The mullite new phase has been appeared. It can be noted that the presence of tialite in the composites reduces the crystallization ability of cordierite (Fig. 2d).

The results of FTIR spectroscopy for the synthesized and thermally treated at different temperatures for 2 h samples are illustrated in Fig. 3.

As it is known a broad absorption bands with the minimum posited at ~ 1060 and ~ 1070 cm^{-1} correspond

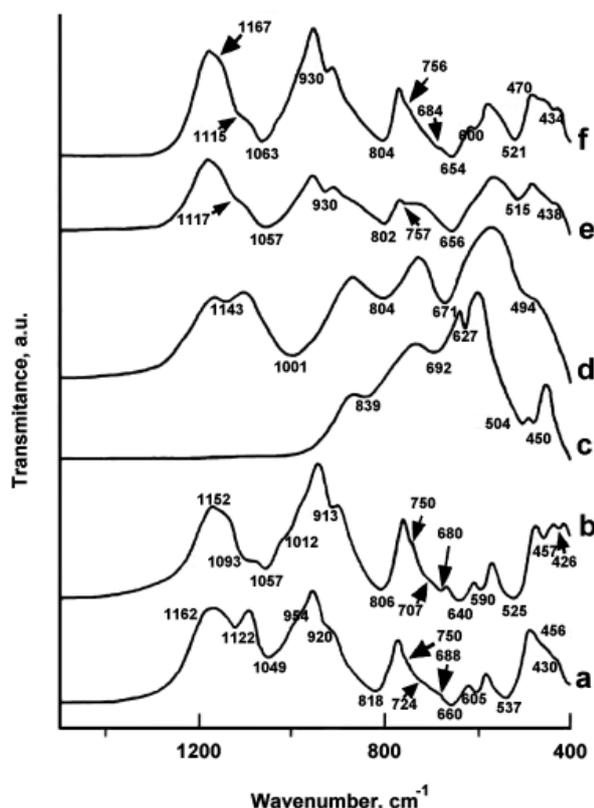


Figure 3. FTIR spectra of thermal treated samples at $1100^{\circ}\text{C}/2\text{h}$: a) C and at $1200^{\circ}\text{C}/2\text{h}$: b) C, c) T, d) CT-30, e) CT-50 and f) CT-70

to the presence of Si-O bonds of amorphous SiO_2 powder [25]. The shift of these bands towards lower values than those of amorphous SiO_2 indicates the formation of Si-O-Me bonds in the structure of μ -cordierite (curves a, b, d, e and f), where Me=Al, Mg [11,15]. The band centered at 700 cm^{-1} probably corresponds to the vibration of Al-O or Mg-O bonds [15] indicating the presence of Si-O-Me bonding [2]. Other authors reported that the band centered at ~ 750 cm^{-1} (curves a, b, e and f) is associated with the formation of a ring structure of SiO_4 tetrahedra and with Si-O-Me bond formation [26]. At the same time the reaction of ions which form spinel also occurs, which can explain the appearance of absorption bands, centered at 700 cm^{-1} and 530 cm^{-1} , corresponding to MgAl_2O_4 , registered by X-ray diffraction [2,15,19,27–29]. Bands around 640 (660) cm^{-1} (curves a and b), 525 cm^{-1} (curve b), 521 cm^{-1} (curve b and f) and 514 cm^{-1} (curve e) are found, and also correspond to the presence of MgAl_2O_4 [30]. The presented FTIR spectra of the prepared cordierite powders obtained by calcinations at 1100 and 1200°C for 2 h (curves a and b) are typical for the presence of μ -cordierite: bands at ~ 1100 cm^{-1} , ~ 920 cm^{-1} , ~ 720 cm^{-1} and ~ 460 (430) cm^{-1} are presented [2,12,19,31,32]. In the depicted spectra, there are the bands, characteristic to α -cordierite and a band centered at ~ 590 cm^{-1} corresponds to MgO_6 octahedra and a band at ~ 920 cm^{-1} corresponds to the AlO_4 tetrahedra [15]. On the other hand, a wide band from 1100 to 1200 cm^{-1} corresponds to the presence of SiO_4 tetrahedra in both α -cordierite as well as in μ -cordierite. The minimum of this band for μ -cordierite is at 1122 cm^{-1} (curve a) while for α -cordierite at ~ 1160 cm^{-1} (curves a and b) [15]. In addition the bands centered at ~ 680 cm^{-1} (curves a, b, d and f) and ~ 800 – 810 cm^{-1} (curves a, b, d, e and f) can be assigned to the symmetric stretching mode of the Si-O-Si bond [14,33]. The IR bands of the calcinated at 1200°C for 2 h tialite dried gel (Fig. 3, curve c) at 504 cm^{-1} , 640 cm^{-1} and 692 cm^{-1} could be related to the presence of Al-O octahedral and a weak band at 839 cm^{-1} to Al-O tetrahedral stretching vibration. Ti-O stretching mode appears at 480 cm^{-1} [22,34].

The microstructural characterization of all synthesized materials was made using a combination of TEM, SEM and EPMA (Fig. 4). For the TEM observations powdered samples were prepared and bright field (BF) and dark field (DF) mode with SAED analysis was applied. The SEM investigations were performed at SE and BSE mode so that topological (Topo) and compositional (Compo) informations were received. In order to trace the oxides and elements distribution EPMA was applied on specially prepared pallets with polish surface.

The SEM observations of cordierite samples show monodispersed microstructure containing uniformly distributed elongated crystals which average sizes are from 0.1 – 0.2 μm to 0.5 – 1 μm (Fig. 4a). These results

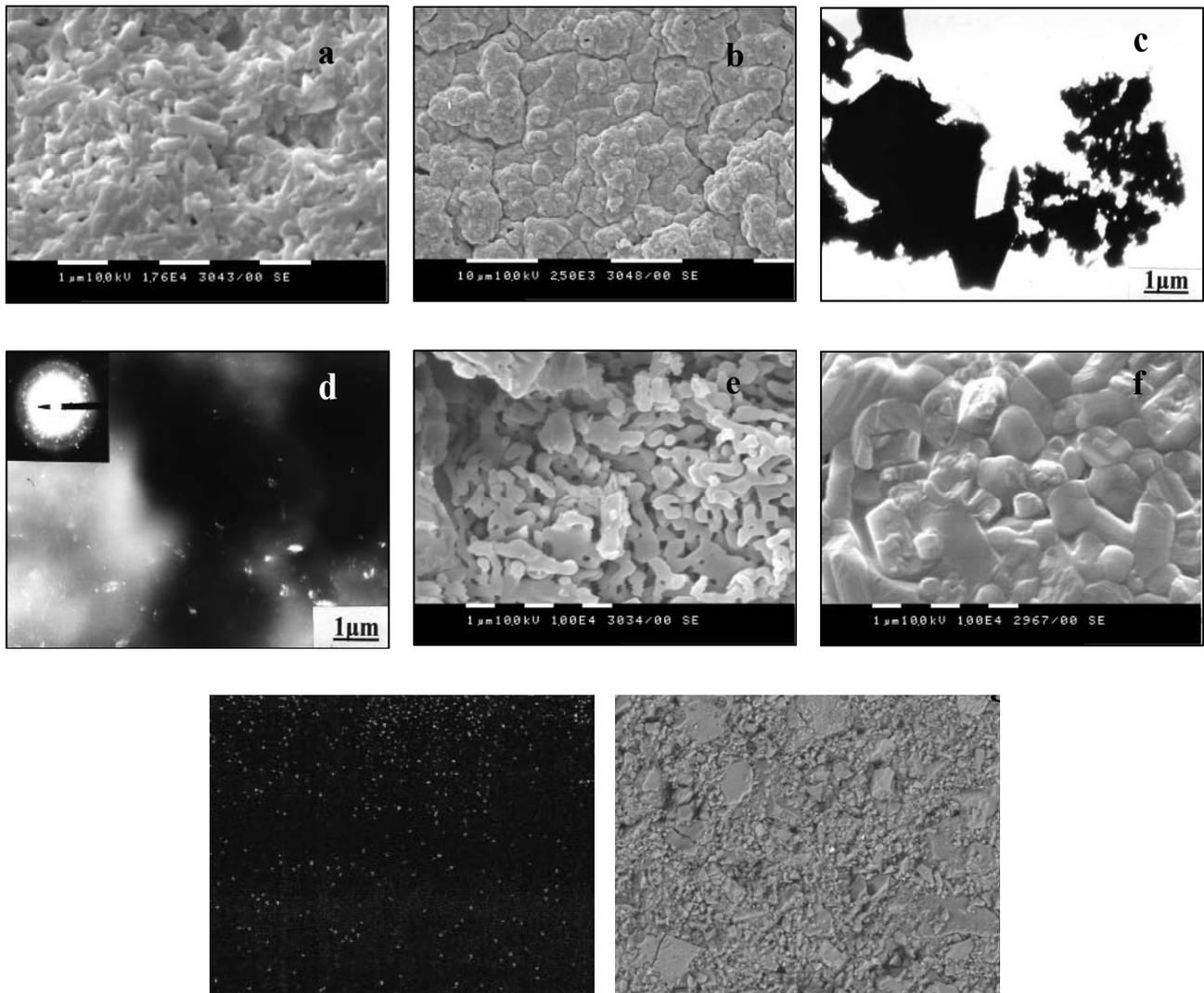


Figure 4. Micrographs of synthesized samples: a) SEM of cordierite – C, b) SEM of cordierite/talite glass ceramics - CT-70, c) TEM - BF of cordierite – C, d) TEM – DF+SAED of cordierite – C, e) SEM of tialite – T, f) SEM of cordierite/talite glass ceramics - CT-30, g) SEM of cordierite+2 wt.% Co, h) EPMA – Co X-ray mapping of cordierite+2 wt.% Co

are confirmed by the TEM data in BF mode presenting clearly formed polygonal crystals (Fig. 4c). The combination of TEM - DF mode and SAED (Fig. 4d) allows illustration of several amount of nano-scaled crystalline phase located on the surface and boundaries of grains at BF mode. The tialite samples possess also monodispersed microstructure (Fig. 4e) but their elongated crystals are relatively larger (from 0.3–0.4 μm to 1.5–2 μm) with habitus not so clearly pronounced as in the cordierite. Complex microstructure (Fig. 4b,f) corresponding to the XRD data (Fig. 2) is found in the samples with both combinations from cordierite and tialite (C:T) with composition ratio 70:30 and 30:70. In the sample CT-70 the crystal size being about 0.1–0.5 μm is influenced by the cordierite presence and an aggregation trend with formation of compact microstructure is found (Fig. 4b). At higher tialite content (the sample CT-30) the grain sizes increase up to 1–1.5 μm (Fig. 4f). In the cordierite samples with participation of Co the microstructure

remains its character (Fig. 4g). By EPMA using the X-ray mapping mode the uniform Co distribution in the cordierite + Co sample is illustrated (Fig. 4h).

The electrical resistance (ρ) of selected samples containing cordierite and 2 wt.% Co and Co+Cu was measured at 20°C. The obtained results show that the materials studied have isolator behavior. The ρ values vary in relatively narrow limits - from $1.50 \times 10^{10} \Omega$ to $6.54 \times 10^{10} \Omega$.

IV. Conclusions

Nanocomposites in the cordierite-tialite system, as well as the cordierite containing different metals have been synthesized via sol-gel method with the present of aqua regia. The structure evolution of gels treated from 800°C to 1200°C has been studied. It has been established that in cordierite-tialite nanocomposites cordierite, tialite and rutile crystalline phases are present. The new phase - mullite has been appeared. It can be noted that the presence of tialite in the composites reduces

the crystallization ability of cordierite. In the gels containing PEG, the intensity of spinel peak increases. Depending on the composition the samples show uniformly distributed monodispersed crystal phases or more complex microstructures with pronounced aggregation trend of the structural formations.

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