



## Feature Article

## Ex situ Raman mapping study of mechanism of cordierite formation from stoichiometric oxide precursors

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Available online 15 November 2013**Abstract**

Ex situ Raman spectroscopy and Raman mapping showed that at temperatures below 1300 °C, magnesia reacted with either alumina or silica to form magnesium aluminate (spinel) or magnesium silicate. At 1300 °C or higher, the reaction between magnesium silicate and alumina, or spinel and silica, led to cordierite formation. Moreover, the presence of silica and spinel, and the disappearance of magnesium silicate at 1400 °C, indicated that cordierite formation was more favored by the reaction between alumina and magnesium silicate than by that between silica and spinel. © 2013 Elsevier Ltd. All rights reserved.

**Keywords:** Cordierite; Raman mapping; Raman spectroscopy; Solid-state reaction

**1. Introduction**

Cordierite, an aluminosilicate ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ) with a ring framework, has attracted much attention because of its low thermal expansion coefficient and dielectric constant. Its synthesis and characterization have therefore been well studied, especially synthesis via solid-state reactions.<sup>1–7</sup> Cordierite undergoes a phase transition from hexagonal to orthorhombic with increasing annealing time and temperature, and reverts to a highly disordered hexagonal phase after further sintering. This phase transition has been described in many papers and investigated using powder X-ray diffraction, infrared spectroscopy, and Raman spectroscopy.<sup>8–14</sup> Raman spectroscopy clearly showed the phase transition, with a gradual splitting of the peak located at about  $568\text{ cm}^{-1}$  into peaks at  $557$  and  $578\text{ cm}^{-1}$ .

The precursor used for cordierite phase-transition kinetics and mechanism studies was cordierite glass prepared by melting and quenching a mixture of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{MgO}$ .<sup>8,9,11,15,16</sup> The phase transition from cordierite glass to hexagonal, modulated, and orthorhombic cordierite has been well studied and well established, but the mechanism of the solid-state reaction

among the oxide precursors to form cordierite has not yet been thoroughly studied. The aim of this study was to investigate the pathway of cordierite formation from stoichiometric oxides, using ex situ Raman spectroscopy and Raman mapping.

**2. Experimental**

Alumina, magnesia, and silica of reagent grade were purchased from Wako Pure Chemical Industries Ltd., and used without purification. In a typical batch, silica (10 g), magnesia (2.68 g), and alumina (6.8 g) were mixed with ceria balls (100 g). The mixture was milled in ethanol (100 mL) for 24 h, and then the ethanol was evaporated using a hot plate. The obtained powder (0.5 g) was then pressed into a pellet (diameter 13 mm) at 200 MPa. The green bodies were sintered at 1250–1450 °C for different times. The sintered bodies were then mechanically polished prior to Raman spectroscopy measurement in an ambient environment (NRS-7100, JASCO). An  $800\text{ }\mu\text{m} \times 800\text{ }\mu\text{m}$  square was divided into 1600 points ( $40 \times 40$ ) and Raman spectra were recorded using  $20\times$  lenses, with a laser spot of diameter  $8\text{ }\mu\text{m}$ . Fluorescent subtraction was also performed during all measurements and all spectra underwent baseline correction before mapping calculations. Mixtures of alumina–silica, silica–magnesia, and magnesia–alumina, with 1:1 molar ratios, were also prepared and sintered at 1200 and 1300 °C for 2 h to

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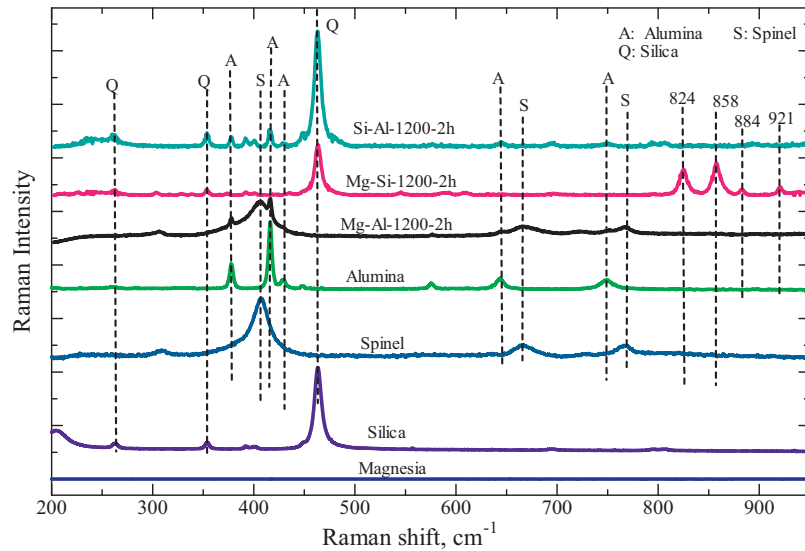


Fig. 1. Raman spectra of raw materials and standard samples.

investigate new peak evolution compared with cordierite and the raw materials.

### 3. Results and discussion

The Raman spectra of standard materials are shown in Fig. 1. Silica, alumina, and magnesium aluminate (spinel) were characterized by intense peaks located at 463, 406, and 417  $\text{cm}^{-1}$ , respectively, but magnesia gave no peak in the observation range. The mixture of magnesia and alumina after sintering at 1200  $^{\circ}\text{C}$  for 2 h showed a peak at  $\approx 406 \text{ cm}^{-1}$ , indicating the presence of spinel as a result of reaction between the two components. The formation of new peaks at 824, 858, 884, and 921  $\text{cm}^{-1}$  in the spectrum of the mixture of magnesia and silica also showed that interactions took place between magnesia and silica, and these peaks are attributed to magnesium silicate. The mixture of silica and alumina sintered at 1200  $^{\circ}\text{C}$  for 2 h showed no change in the Raman spectrum, which meant that diffusion did not occur between these two materials.

The spectrum of the sample sintered at 1250  $^{\circ}\text{C}$  for 2 h had Raman peaks at 411, 473, 680, 768, 831, 860, 924, and 972  $\text{cm}^{-1}$  (Fig. 2). The peak at 411  $\text{cm}^{-1}$  is assigned to alumina, that at 473  $\text{cm}^{-1}$  is from silica, and those at 680 and 768  $\text{cm}^{-1}$  are contributed by spinel resulting from the reaction between alumina and magnesia. The peaks at 831, 860, 924, and 972  $\text{cm}^{-1}$  are attributed to magnesium silicate. The peaks were assigned by comparison with the spectra of the standard materials, shown in Fig. 1. The peaks at 411, 473, 680, and 830  $\text{cm}^{-1}$  were used to map the distributions of alumina, silica, spinel, and magnesium silicate, respectively. The mapping results for silica and magnesium silicate show that they are alternately distributed over the measured surface; the spot with high magnesium silicate intensity has no silica, as shown in Fig. 2. Spinel and alumina were also well distributed over the entire mapping area. These mapping images also indicate that the raw materials were well mixed in the experiments. After sintering at 1250  $^{\circ}\text{C}$  for 2 h, we observed diffusion of the raw

materials, resulting in the formation of spinel and magnesium silicate, but not cordierite. This may be because the temperature was not high enough to activate the raw materials and overcome cordierite's formation energy barrier.

The sample sintered at 1300  $^{\circ}\text{C}$  for 2 h had Raman peaks at 413, 472, 570, 680, 830, and 861  $\text{cm}^{-1}$ , which were assigned to alumina, silica, cordierite, spinel, and magnesium silicate, respectively (Fig. 3). At this temperature, although spinel and magnesium silicate still remained, cordierite formation was observed, with finger peaks at 570, 978, and 1040  $\text{cm}^{-1}$ .<sup>8,11–13</sup> The peaks at 413, 472, 570, 680, and 830 were used to map the distributions of alumina, silica, cordierite, spinel, and magnesium silicate, as shown in Fig. 3. The mapping results show that all the substances present alternately covered the selected area; however, the peak intensities of silica and alumina were much smaller than those in the sample sintered at 1250  $^{\circ}\text{C}$ . These results show that cordierite was formed via the reaction between spinel and silica, or magnesium silicate and alumina. These results confirm that cordierite was not directly formed from the three raw materials.

The sample sintered at 1400  $^{\circ}\text{C}$  for 2 h showed peaks at 296, 366, 430, 465, 486, 570, 671, 900, 973, 1010, and 1190  $\text{cm}^{-1}$  (Fig. 4). Except for the peaks at 430 and 465  $\text{cm}^{-1}$ , attributed to spinel and silica, respectively, the peaks were all attributed to cordierite.<sup>13,15,16</sup> Magnesium silicate disappeared from the spectrum, proving that it was completely consumed in cordierite formation. The detection of spinel may indicate that cordierite was formed from magnesium silicate and alumina faster than from spinel and silica. The intensities of the peaks at 430, 465, and 570  $\text{cm}^{-1}$  were used to map the presence and positions of spinel, silica, and cordierite (Fig. 4b). The intensity of the silica peak, only about 200 compared with 9000 of sample sintered at 1250  $^{\circ}\text{C}$  (Fig. 2b), shown by the mapping results, proves that silica was disappearing as a result of taking part in the reaction to form cordierite. The mapping results also show that silica was still present in the places where no cordierite was present. As shown in Fig. 4a, the peak at 570  $\text{cm}^{-1}$  observed in the sample

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