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Optical properties of polycrystalline and amorphous cordierite

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Cathodoluminescence and infrared absorption studies were made on polycrystalline as well as amorphous cordierite, either in the as-received state or after different thermal treatments. Emission bands centred at about 400 nm were observed in all the samples studied. Red emission bands around 650 nm were also found in samples irradiated with ionizing radiation or annealed in different atmospheres. Infrared absorption measurements were performed to estimate the glass phase and to monitor the presence of OH^- ions.

1. Introduction

Cathodoluminescence (CL) is the scanning electron microscope is a sensitive tool to detect, with high spatial resolution, the intrinsic luminescence as well as the luminescence associated with impurities. The important $MgO-Al_2O_3-SiO_2$ system, in which we are primarily interested, offers good examples of CL emission due to electronic transitions within lattice defects or impurities. In MgO the CL blue-green emission, centred at about 410 nm, is associated with lattice defects and particularly with anion vacancies [1–4]. Emission in the red region is attributed to impurities [5]. Recently two CL emission bands (blue-green and red) have been reported [6] in spinel ($MgO \cdot Al_2O_3$) and associated with V^{3+} and Cr^{3+} respectively. In this paper results on CL emission from natural polycrystalline Spanish cordierite and synthetic amorphous cordierite are reported.

Cordierite (ideal formula $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) possesses high strength, corrosion resistance and low thermal expansion that make it suitable for different industrial applications such as automotive and gas-turbine heat exchangers [7–9]. Natural cordierite occurs [10] in a number of structural states related to order–disorder changes among Si_5Al and $Al_3(Mg, Fe^{+2})_2$ groups. These different structural states are dependent on the thermal history of individual rocks. Nearly all natural specimens of composition $Al_3(Mg, Fe^{+2})_2\ Si_5Al\ O_{18}$ are orthorhombic [10].

The infrared (IR) spectrum of cordierite gives information on the glass concentration in the sample [11], thus providing an easy method of following the changes in the amorphous samples after different thermal treatments.

2. Experimental methods

Most of the natural cordierite samples used in this work are pegmatitic, exhibiting in the as-received state a characteristic greyish colouration. The typical chemical analysis is given in Table I.

Amorphous cordierite frit, in the form of flakes, was developed by the Ferro Corporation (Independence, Ohio). The sample number was 5G–226–M. The frit composition was reported by Nielsen [8] to be 13.3% MgO, 32.0% Al_2O_3, 52.7% SiO_2 and 2.00% BaO (all in wt %). Chemical analyses of impurities have been reported previously [12].

Cathodoluminescence images were obtained with a scanning electron microscope (Cambridge S4–10) operating in the cathodoluminescence mode at 30 kV and a beam current ranging from 10^{-9} to 10^{-5} A. For spectral analysis a light-pipe which feeds the light into a 0.25 m Ebert–Jarrell–Ash monochromator was attached to the microscope. The emitted light was detected with an EMI 9558QB photomultiplier tube. The relative intensity of the system as a function of wavelength was calibrated against a standard lamp. The cathodoluminescence emission spectra were recorded between 350 and 700 nm.

IR absorption measurements were performed with a Perkin-Elmer Spectrophotometer Model 781. For some of the IR measurements the samples were pulverized and mixed with KBr powder. X-ray irradiation was performed using a Philips PW 1008 X-ray diffraction generator with a molybdenum tube operating at 40 kV and 20 mA. Heat treatments in a reducing atmosphere were made with the samples resting in a graphite container, surrounded by flowing nitrogen gas, in a mullite tube inserted in a horizontal Chesa (Madrid, Spain) furnace (Model 50/152). Oxidizing treatments were made in flowing oxygen gas.

3. Results and discussion

3.1. Natural cordierite

The as-received samples of natural cordierite were chemically analysed and the results are shown in Table I. The composition was found to be $Al_3(Mg, Fe^{2+})_2\ Si_5AlO_{18}$. The Fe/Mg ratio is 22.5% which corresponds to a cordierite that occurs in pegmatite (i.e. it is not a metamorphic cordierite) and is practically unaltered [10]. As mentioned before the IR spectrum of pulverized cordierite mixed with KBr powder gives information on the glass content of the sample [11]. The glassy samples exhibit a maximum at about

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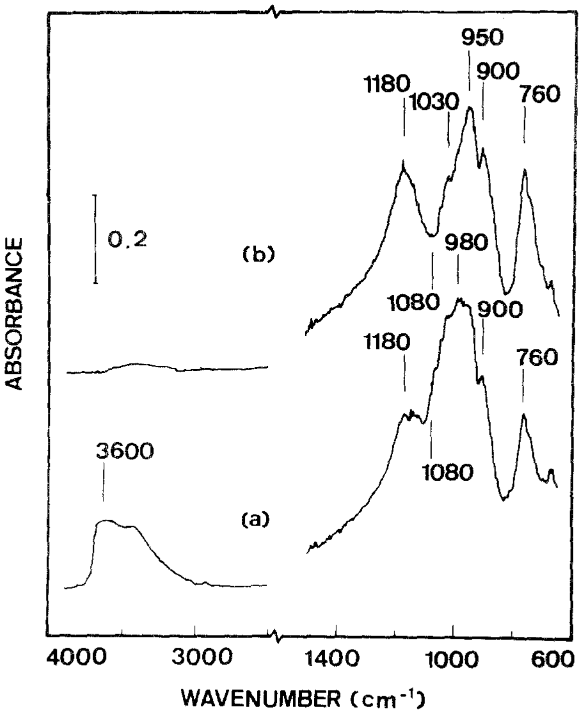

Figure 1 IR absorption of natural cordierite (a) as-received and (b) after annealing at 1373 K for 2 h.

$1080\,cm^{-1}$ that is absent in our samples (Fig. 1a) indicating that the samples are crystalline. Furthermore, the spectrum shape and the presence of peaks at about 1180, 980 and $900\,cm^{-1}$ indicates that the sample crystallized in the orthorhombic system [11], which agrees with the fact that nearly all natural specimens with the above composition are orthorhombic [10].

A very broad band centred at about $3600\,cm^{-1}$ also appears. In this region a broad band centred at about $3550\,cm^{-1}$ has been observed in as-grown amorphous cordierite [12]. After heat treatments in H_2O vapour at 1344 K a resolved peak appears at $3577\,cm^{-1}$ that has been attributed to the OH^- stretching frequency [12]. Thus we conclude that the $3600\,cm^{-1}$ band is also associated with the presence of hydrogen in OH^- configurations in the sample.

Heat treatments of 2 h duration in reducing or oxidizing atmospheres produce several changes in the IR spectrum. Fig. 1b corresponds to the IR spectrum of the samples after annealing in graphite for 2 h at about 1373 K. In the region between 1300 and $800\,cm^{-1}$ peaks at about 900, 950, 1030 and 1180 are now better resolved; the minimum at about 1080 is more pronounced. This spectrum clearly corresponds to an orthorhombic sample [11].

TABLE I Chemical analyses of cordierite (obtained by wet chemistry)

Compound	Content (%)	Number of ions (taking 18 oxygens as reference)	
SiO_2	49.4	Si 4.994	6.000
Al_2O_3	33.6	Al 1.006	
FeO	5.3	Al 2.997	
MgO	10.2	Mg 1.536	1.983
H_2O	1.5	Fe 0.447	
Total	100.0		

$$\frac{Fe^{2+} + Mn}{Mg^{2+} + Fe^{2+} + Mn} \times 100 = 22.5$$

Another important feature of this spectrum is the dramatic decrease of the broad band centred at about $3600\,cm^{-1}$, indicating that H^+ out-diffusion probably occurs during the heat treatment. H^+ or D^+ out-diffusion have previously been observed in other oxides when the samples are heated at sufficiently high temperatures in reducing or oxidizing atmospheres [13–16]. On the other hand, as the chemical analyses reveal, our samples contain approximately 1.5% of H_2O molecules that, as in the beryl structure, are probably located in the large channels parallel to the *z* axis [10, 17–19]. In most examples the water content is related to the degree of alteration [10]. When the samples are heated at temperatures above 1150 K these molecules are irreversibly removed and the IR part of the spectrum between 1300 and $800\,cm^{-1}$ becomes better defined. No significant changes were observed in the IR spectrum between a reduced or oxidized sample. However, after oxidation the sample turns to a brownish colouration while the reduced sample keeps its initial grey colour.

Prior to imaging the samples in the scanning

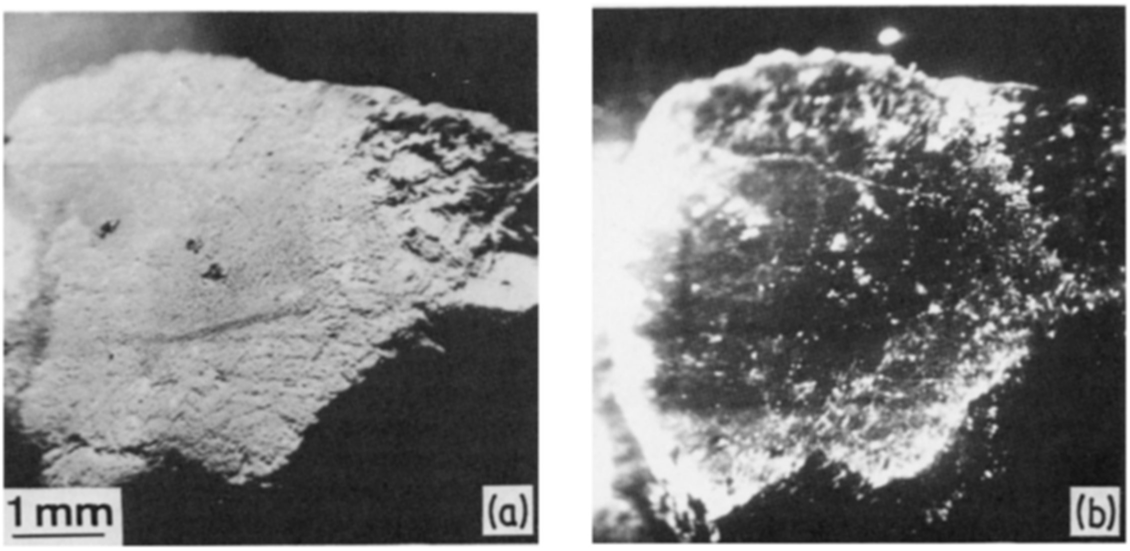

Figure 2 Scanning electron microscope images of the same natural cordierite sample: (a) emissive mode, (b) CL mode.

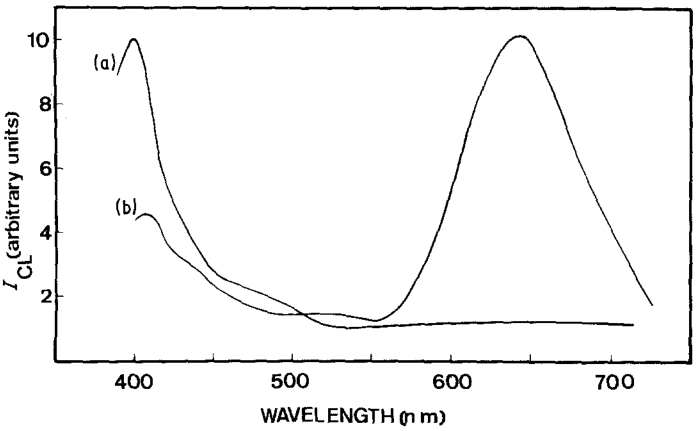

Figure 3 CL spectra of as-received natural cordierite sample.

electron microscope, the samples were carefully polished with progressively finer grades of emery paper. The detection of CL in natural cordierite requires a much higher electron excitation current than that used in MgO or MgO • Al_2O_3 spinel. Beam currents of 10^{-5} A are necessary to produce a luminescence intensity high enough to record the spectra. Fig. 2a shows the image of a sample using the emissive electron mode. Fig. 2b shows the CL panchromatic image of the same sample. The CL intensity distribution is very inhomogeneous and a clear correlation between the damage at the sample surface and the CL emission intensity could not be established.

Fig. 3 shows two CL spectra and both are characteristic of the as-received samples. In Fig. 3a there is only one emission band located at about 400 nm. In Fig. 3b the blue emission is less intense and a much stronger emission band emerges at about 640 nm. It appears that the red emission is induced after long electron excitation times.

Annealing for 2 h at 1373 K in graphite decreases the 410 nm band without affecting the band at 640 nm (Fig. 4a). Heat treatment in flowing oxygen also decreases the blue emission. The red emission is shifted to 680 nm and the intensity is enhanced, as Fig. 4b shows. In a metamorphic cordierite, very altered and with a high content of SiO_2, the CL spectrum of the as-received sample is very similar to that presented in Fig. 3a. The CL spectra after annealing in graphite or oxygen are shown in Fig. 5. After the former annealing, besides the band at 400 nm another small band at about 600 nm appears in the CL spectrum. The oxidized sample exhibits the band at 400 nm, a bump around 490 nm and a sharp band at about 660 nm.

3.2. Synthetic amorphous cordierite

The as-grown samples of amorphous cordierite were transparent and had typically an area of roughly 1 cm^2 and a thickness of 0.06 cm. The IR spectrum of pulverized cordierite mixed with KBr indicates that the samples are indeed amorphous [11]: in Fig. 6a an absorption maximum occurs at 1080 cm^{-1}. Resolidification of the samples can be visually observed after heating for 2 h at about 1373 K in reducing or oxidizing atmospheres. The samples are characterized by cloudiness and a slight but unmistakable shrinkage of the samples. Changes on the surface topology are shown in Fig. 7. Also several changes occur in the IR spectrum (Fig. 6b) indicating that a crystallization process has been undergone by the samples. Bands at 760, 950 and 1160 cm^{-1} emerge that correspond to samples crystallized in the hexagonal system [11]. After annealing at 1573 K for 2 h the samples were

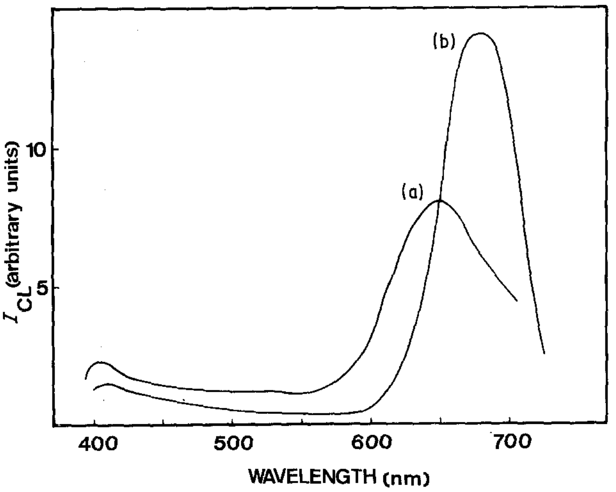

Figure 4 CL spectra of natural cordierite samples annealed at 1173 K for 2 h in (a) graphite and (b) flowing oxygen.

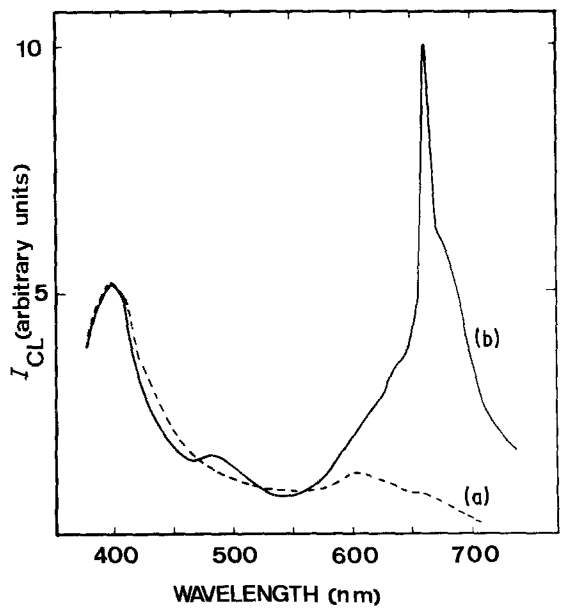

Figure 5 CL spectra of metamorphic cordierite samples after annealing at 1373 K for 2 h in (a) graphite and (b) flowing oxygen.

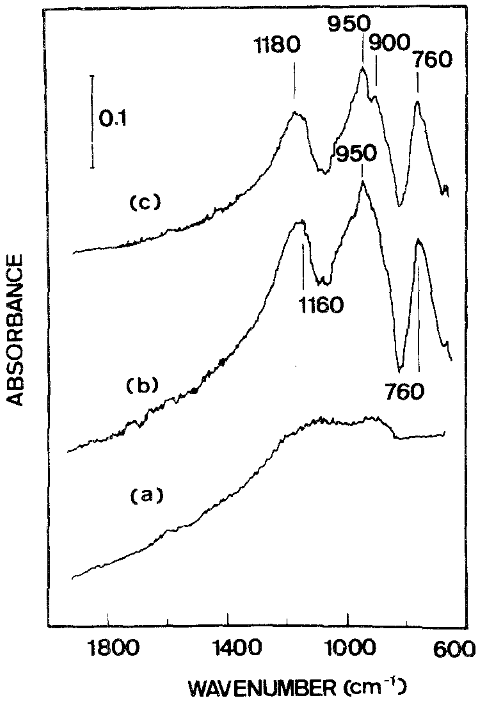

Figure 6 IR absorption of amorphous cordierite (a) as-grown, (b) annealed at 1373 K and (c) annealed at 1573 K.

crystallized in the orthorhombic system, as shown in Fig. 6c [11].

No band has been observed in the region around 3600 cm^{-1} for the pulverized sample (Fig. 8a) although, as has been mentioned before, a broad band centred at about 3550 cm^{-1} is observed when the IR spectrum is made using an unpulverized sample 0.06 cm thick (Fig. 8b). A comparison of Figs. 1a and 8a indicates that the concentration of hydrogen in the OH$^-$ configuration is much lower in a synthetic sample than in a natural one (both in the as-grown state). In order to be able to detect the OH$^-$ absorption band in amorphous cordierite it is necessary to use thicker samples (Fig. 8b) than those of natural cordierite. The different OH$^-$ concentrations could be due to the different environments in which the samples were during the growing process.

Synthetic cordierite is a cathodoluminescent material more efficient than the natural samples used here. Intermediate currents of the order of 10^{-7} A were used to detect the CL emission. In contrast to the latter samples the emission intensity of the former is quite uniform. Fig. 9a shows the CL spectrum of an as-grown sample. The structureless broad band has its maximum at about 400 nm. X-ray irradiation for 3 h gives the sample a yellowish colouration and changes the CL emission as shown in Fig. 9b. The band at 400 nm is shifted to 410 nm and a broad band emerges at about 620 nm. As in the natural samples, thermal treatments also modified the CL emission. The CL spectra of samples annealed for 2 h at 1373 K in graphite or oxygen are shown, respectively, in Figs. 10a and b. After the former treatment the blue emission decreases and a small bump emerges at about 490 nm. When the sample is heated in oxygen the emission at 400 nm also decreases and a band around 660 nm appears.

4. Summary

1. IR absorption bands at about 3600 cm^{-1} have been observed in natural cordierite as well as in amorphous cordierite. The bands are attributed to the OH$^-$ stretching frequency. After heat treatment, at high temperature these bands disappear, indicating that H$^+$ out-diffusion probably occurs.

2. The IR spectrum between 800 and 1300 cm^{-1} can be used to estimate the glass phase. As-grown samples of amorphous cordierite crystallize in the hexagonal system after annealing at 1373 K. At temperatures higher than 1573 K they crystallize in the orthorhombic system.

3. CL emission bands in natural cordierite appear at about 400 and 640 nm. Amorphous cordierite is a cathodoluminescent material more efficient than the natural form; in the as-grown state only the emission band at 400 nm is observed. Heat treatment at 1373 K

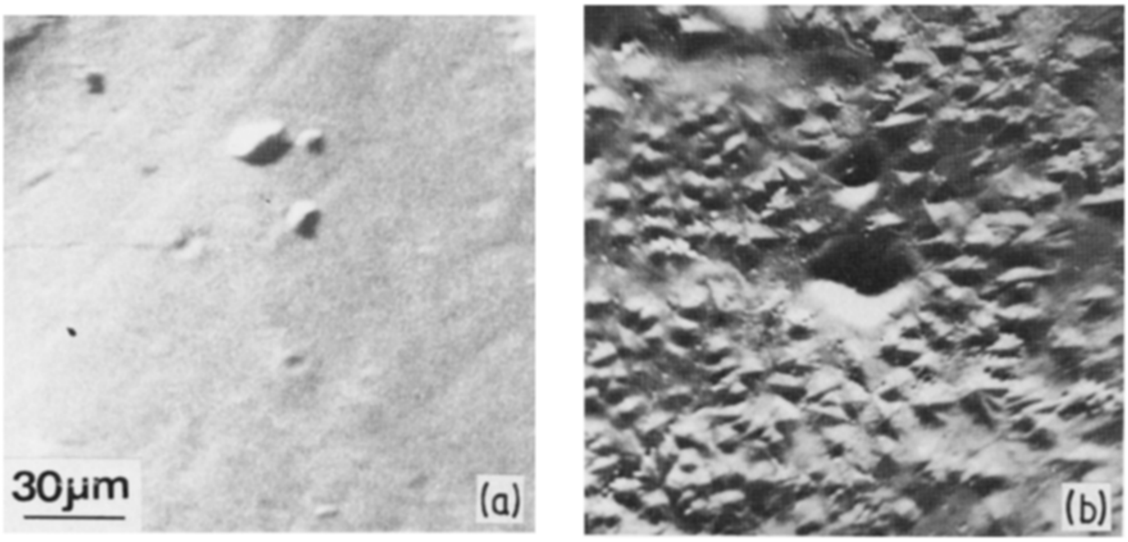

Figure 7 Scanning electron microscope images in the emissive mode of an amorphous cordierite sample (a) as-grown and (b) after heat treatment at 1373 K.

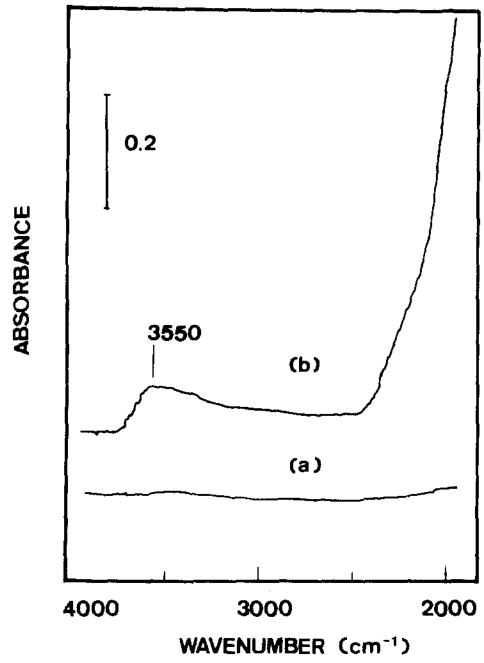

Figure 8 IR absorption of amorphous cordierite: (a) pulverized and mixed with K Br, (b) sample 0.06 cm thick.

enhances the red emission and decreases the blue one. In general the intensity of the former is higher than that of the latter. One may speculate that, as in MgO, the blue emission could be associated with the presence of some defects in the sample, while the red emission could probably be related to different impurities.

Acknowledgments

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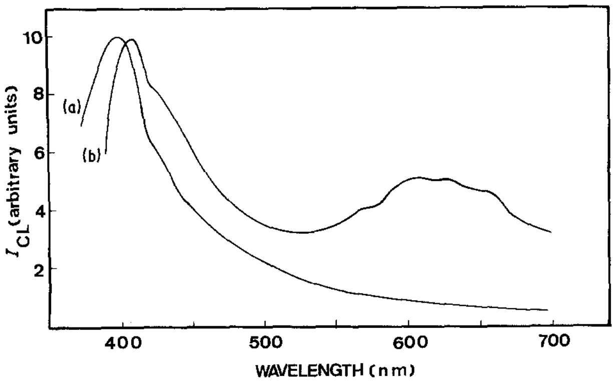

Figure 9 CL spectra of amorphous cordierite (a) as-grown and (b) after X-ray irradiation.

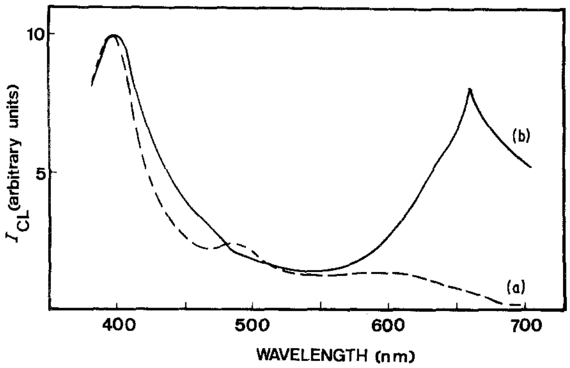

Figure 10 CL spectra of amorphous cordierite (a) annealed in graphite and (b) annealed in oxygen.

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