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ESR study of CuO-doped cordierite

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The reactivity of cordierite precursor with CuO powder was studied by means of X-ray diffraction measurements and electron spin resonance spectroscopy. Two concentrations of CuO were used: 10 and 20 mol %. An ESR signal was detected after heating the mixture of cordierite precursor–CuO at 500 °C showing that CuO begins to dissolve with the cordierite precursor. The reactivity strongly increased between 700 and 800 °C, in relation to the transition amorphous →μ-cordierite. However, the crystallization of α-cordierite prevented the dissolution. Cu^{2+} was located in the amorphous phase and characterized by $g_{\parallel} = 2.35$ and $g_{\perp} = 2.08$.

1. Introduction

Cordierite ($Mg_2Al_4Si_5O_{18}$) has been extensively studied because of its particular physical properties, such as its relatively low polycrystalline linear thermal expansion coefficient, $\alpha_p(1\times10^{-6}–4\times10^{-6}\,°C^{-1})$, low dielectric constant (4–6) and high volume resistivity ($> 10^4\,\Omega$ cm) which make it attractive for use as catalyst carriers and applications in electronic packaging. Magnesium cordierite exists under three polymorphic forms: a hexagonal high-temperature form, named indialite or α-cordierite (space group P6/mmc), an orthorhombic low-temperature form designated β-cordierite (space group Cccm) and a metastable form μ-cordierite, isostructural with β-SiO_2 [1–3].

The use of cordierite in electronic packaging becomes very interesting when copper can be taken as a conductive element, i.e. when it is possible to sinter cordierite below the melting temperature of copper 1080 °C [4]. Such a cordierite is obtained by sol–gel synthesis. However, a satisfactory copper–cordierite cosintering, with a sufficiently strong metal-to-ceramic adhesion, occurs only in an oxidizing atmosphere, showing the major role of oxygen and copper oxides.

A previous study of the reaction of the metal oxides MnO, CoO, NiO, CuO, ZnO and Cu_2O with indialite has shown that CuO has a particular behaviour towards indialite [5]. Indeed, MnO, CoO, NiO and ZnO strongly react with indialite: the first three compounds give the metal silicate M_2SiO_4 (M = Mn, Co, Ni) of olivine structure and $MgAl_2O_4$ and, the latter leads to α-SiO_2, $ZnAl_2O_4$ and $MgSiO_3$. When CuO is involved, a spinel phase, identified as $Cu_xMg_{1-x}Al_2O_4$, appears but no silicate phase is formed. However, the most noteworthy reaction is observed at low concentrations of CuO, < 25 mol % and between 900 and 1040 °C. The diffraction lines of CuO disappear in the X-ray diffraction pattern recorded on a sample heated at 1000 °C and appear again when this sample is heated at 1040 °C. While Cu^{2+} ions of CuO are coupled and do not give any signal by standard ESR measurements, the samples heated at 1000 and 1040 °C do give a signal. Preliminary measurements of intensities indicate that very few Cu^{2+} participate in it, while the Curie constant calculated from susceptibility measurements corresponds to all copper ions introduced. However, before studying the reaction between CuO and indialite, it is more interesting to determine the mechanism of interaction between cordierite precursor and CuO. We present here the observations made on samples of cordierite precursor–CuO heated in air between 500 and 1000 °C for different annealing times.

2. Experimental procedure

In order to be close to the system copper–cordierite multilayers, the samples were made up of a mixture cordierite precursor–CuO. The cordierite powder was a sol–gel precursor which was previously dried at 700 °C for 3 h [6]. This first thermal treatment led to an amorphous cordierite with a specific area of 225 $m^2\,g^{-1}$. CuO was obtained by oxidation at 300 °C of a copper powder whose grain size was 1 μm. CuO and cordierite were ground together in alcohol for 10 h. After all the alcohol had been evolved by heating at 100 °C, the powders were pressed into pellets at 200 bar pressure. Two concentrations of CuO in cordierite were studied: 10 and 20 mol %. The different thermal treatments are reported in Table I. For every temperature, several annealing times were used, from 5 min to 40 h. At the end of short heating times, the samples were quenched into liquid nitrogen in order to stop the reaction quickly. Samples of powder were then thrown into ammonia or water in order to dissolve copper oxide or hydrated copper ions within the sample.

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TABLE I Thermal treatments and crystallographic structures of precursor cordierite–CuO samples. The major phase is written first

CuO (mol %)	T(°C)	Time		Crystallographic structure
		(min)	(h)	
10	700		40	Amorphous + CuO
	800		1	Amorphous + CuO
			4	Amorphous + μ-cordierite
			25	μ-cordierite + amorphous
	900	5		μ-cordierite + amorphous
		10		μ-cordierite
		30		μ-cordierite
			15½	μ-cordierite
	1000	5		μ-cordierite + α-cordierite
		45		μ-cordierite + α-cordierite
			2½	α-cordierite + μ-cordierite
20	500		24	Amorphous + CuO
	600		24	Amorphous + CuO
	700		24	Amorphous + CuO
	800		24	μ-cordierite + CuO
	900		24	α-cordierite
	1000		24	α-cordierite
	1040		24	α-cordierite

The samples were investigated by X-ray diffraction and electron spin resonance measurements. X-ray diffraction patterns were taken at room temperature using a Kristalloflex Siemens diffractometer and cobalt radiation. Electron spin resonance measurements were recorded between 4.2 and 300 K using a Brucker ER 100 X-band spectrometer. The signal intensities were related to Cu^{2+} concentration using $CuSO_4 \cdot 5H_2O$ as standard.

3. Results

From examination of the X-ray diffraction patterns recorded at room temperature on the sample cordierite precursor–10 mol % CuO presented in Fig. 1, it can be noted that the precursor is amorphous at 700 °C and that CuO is always detected at this temperature. At 800 °C, the precursor slowly crystallizes into μ-cordierite while the X-ray diffraction lines of CuO disappear. Nevertheless, the quantity of μ-cordierite seems to be very low after 25 h annealing. The crystallization rate into μ-cordierite is strongly increased at 900 °C because a pure μ-cordierite phase is observed after 30 min annealing. The transition μ-cordierite → α-cordierite occurs after 5 min heating at 1000 °C.

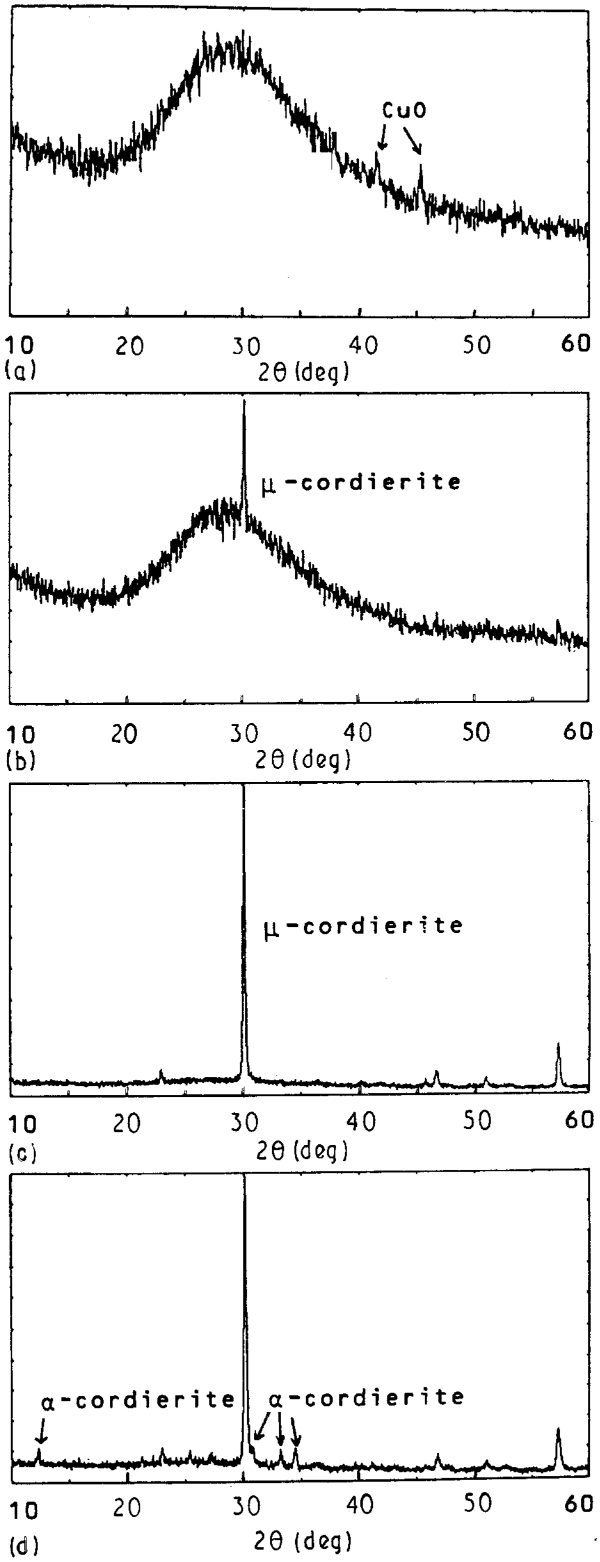

Figure 1 X-ray diffraction patterns of sample of cordierite precursor–10 mol % CuO after annealing at (a) 700 °C, 40 h, (b) 800 °C, 25 h, (c) 900 °C, 30 min, (d) 1000 °C, 5 min.

The thermal treatments on samples of cordierite precursor–20 mol % CuO performed for a constant annealing time (24 h) but at different temperatures, show that the crystallization temperature decreased when the concentration of CuO increased. Indeed, a pure α-cordierite structure was observed at 900 °C and no CuO was detected, while undoped cordierite gave μ-cordierite at this temperature [6]. A further heating to 1040 °C did not destroy the α-cordierite phase which crystallizes as previously observed on the CuO-doped α-cordierite [5].

Undoped cordierite produces no ESR signals, with the exception of a low-intensity hump at $g = 4.0$, which is probably due to Fe^{3+} impurities. CuO-doped cordierite samples gave no signal due to Cu^{2+} before annealing. The ESR spectra recorded at room temperature on 10 mol % CuO-doped cordierite, annealed at 700, 800 and 1000 °C are presented in Fig. 2. The hyperfine structure is discernible at low concentrations of Cu^{2+} and at $T < 700$ °C, but is absent for the other samples. However, their intensities which are related to the amounts of isolated Cu^{2+} in the samples are different. The intensities are shown in Fig. 3 as ratios of ESR active Cu^{2+} ions to total CuO content versus log *t*, where *t* is the heating time for the samples precursor cordierite–10 mol % CuO. Although the precision of the values is poor (about 10%), some general features of the behaviour of the samples CuO–cordierite precursor can be drawn.

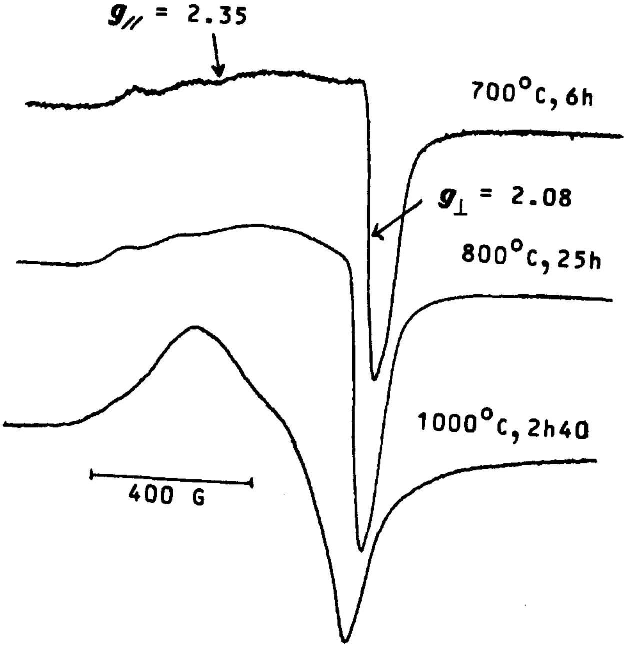

Figure 2 ESR spectra of samples of cordierite precursor–10 mol % CuO recorded at room temperature.

1. The speed of the reaction of CuO with the cordierite precursor increases with increasing temperature. Indeed, 5 min are necessary at 1000 °C to obtain a relative amount of Cu^{2+} detectable by ESR spectroscopy higher than 50%, while 2 h are needed at 800 °C.

2. The amount of Cu^{2+} seems to reach a level of about 45% at 700 °C. As CuO is still detected by X-ray diffraction measurements, it can be concluded that 0.8 wt % CuO is visible by X-ray diffraction measurements.

3. The reactivity strongly increases between 700 and 800 °C, the temperature range for which the transition amorphous → μ-cordierite occurs.

4. The amount of Cu^{2+} detected by ESR does not increase when the α-cordierite structure appears, whatever is the annealing time.

The evolution of signal intensities versus annealing temperature for the samples of cordierite precursor–20 mol % CuO are reported in Fig. 4. A small signal is obtained for a sample heated at 500 °C showing that the reaction between CuO and the cordierite precursor has begun at this temperature. The reactivity increases at the transition amorphous → μ-cordierite and stops when α-cordierite appears. It should be noted that the maximal amount of Cu^{2+} detected by ESR corresponds to 10 mol % in both cases studied. Such a measurement performed on the samples of α-cordierite–20 mol % CuO show that few Cu^{2+} are detected, while all Cu^{2+} contribute to the magnetic susceptibility [5].

The intensities do not change when the powder is put into ammonia for several days showing that the isolated copper cannot be reached easily. Moreover, the shape of the signal does not change when the powder is hydrated.

The shape of the ESR spectra recorded on CuO-doped cordierite precursor does not change when the samples are cooled to 4.2 K, only a light improvement of the resolution of the hyperfine structure for low concentrations is observed. The signal intensities follow a Curie law between 4.2 and 300 K.

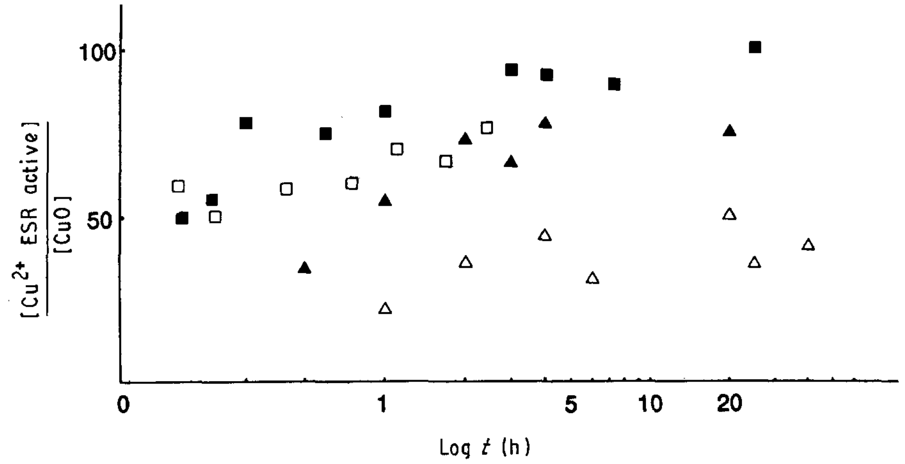

Figure 3 Ratios of ESR-active Cu^{2+} ions to total CuO content versus log *t* (heating time) for samples of cordierite precursor–10 mol % CuO annealed at (△) 700 °C, (▲) 800 °C, (■) 900 °C and (□) 1000 °C.

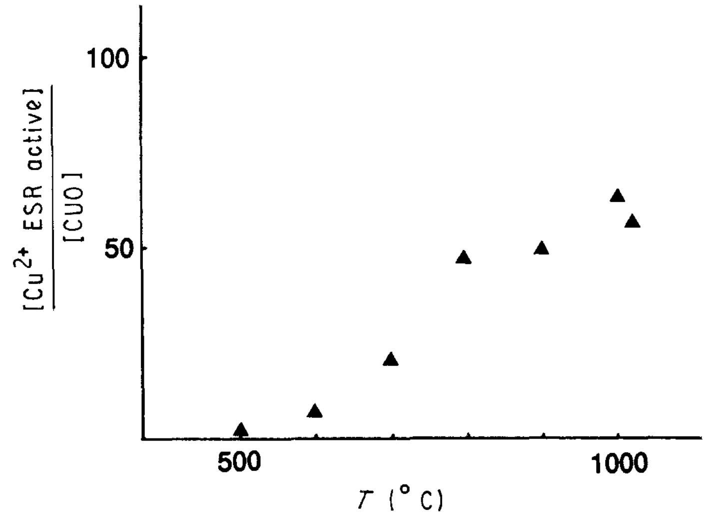

Figure 4 Ratios of ESR-active Cu^{2+} ions to total content versus annealing temperature for samples of cordierite precursor–20 mol % CuO.

4. Discussion

ESR technique is well adapted to follow the reaction between CuO and the cordierite precursor because before reaction, no signal can be detected, contrary to after annealing. A recent study of CuO showed that no resonance was found in CuO when the standard ESR spectrometer was used [7, 8]. Thus, the signals we observe are due to isolated Cu^{2+} within the sample. Therefore, the result of reaction between CuO and cordierite is the dissolution of CuO in the cordierite. The shape of the signals, the variation of the shape and the intensities are the three characteristics which can provide information about the site of copper, the phase in which it is located and the intensity of reaction due to the annealing temperature and time.

The solubility of CuO is directly measured by the signal intensity. CuO begins to dissolve at 500 °C. This phenomenon increases slowly up to 600–700 °C, then rapidly between 700 and 800 °C in relation to the transition amorphous phase → μ-cordierite and in agreement with Hedvall's studies which show that the reactivity between solids is strong at structural transition points [9]. For a constant concentration of starting CuO, [Cu^{2+} ESR active]/[CuO] is greater at 900 °C than at 1000 °C, indicating that α-cordierite crystallization prevents CuO dissolution.

The observed lineshape is typical for a polycrystalline sample containing Cu^{2+} in a site of axial symmetry, similar to that observed in $Cu(NO_3)_2 6H_2O$ impregnated silica gels, copper oxide-doped alumina and silica alumina catalysts [10–14]. As the shape does not change, whatever the thermal treatment, it can be concluded that the host phase is always the same and it can be only the amorphous one. The lack of hyperfine structure for the sample heated at 1000 °C compared to those annealed at 700 and 800 °C indicates that the Cu^{2+} concentration in the host phase is lower for samples heated at 700 and 800 °C. Because the samples annealed at 800 and 1000 °C for a time of about 5 h show the same amount of Cu^{2+} ESR active, it can be deduced that the quantity of host phase is lower at 1000 °C, so that Cu^{2+} ions are closer together. At 1000 °C, part of the sample crystallizes and does not accommodate isolated Cu^{2+}, which stay in the amorphous matrix. This explains why the absolute amount of Cu^{2+} observed by ESR is even lower at 1000 °C than at 900 °C annealing temperature. The increase in Cu^{2+} dissolution due to increasing temperature is compensated by the decrease of the host matrix quantity. Then, the g is constant, but the hyperfine structure is smeared out by the exchange interaction occurring between the copper ions. Attempts to dissolve Cu^{2+} in ammonia and to hydrate it in water failed, because no change in the shape or intensity was observed, showing that copper ions are strongly protected within the host matrix.

5. Conclusion

It can be concluded that the dissolution of CuO begins at 500 °C and strongly increases between 700 and 800 °C in relation to the transition amorphous phase → μ-cordierite. Dissolution is prevented by α-cordierite crystallization. The dissolved Cu^{2+} is located within the amorphous phase.

It would now be of great interest to study the localization of Cu^{2+} when the starting cordierite is a well-crystallized α-cordierite. It may be that a type of amorphous phase is formed accommodating some Cu^{2+}-isolated ions and ESR non-active CuO clusters. Such an amorphous phase may serve as an interface between the indialite support and the metallic copper.

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