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A study of the factors affecting dielectric properties of sol-gel derived cordierite to be used in a plasma display panel

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The effects of firing temperature and test frequency on dielectric properties such as dielectric constant, dielectric loss of three conductor-dielectric (combination) samples, namely nickel-cordierite, silver-cordierite and titanium cordierite samples have been studied after firing.The results showed that the value of dielectric constant and dielectric loss decreased with increasing test frequencies and increasing firing temperature such as 700°C at 1 MHz. A dielectric constant as low as 2.2 was obtained for the nickel-cordierite samples. In addition, the samples were also analyzed for phase purity and phase transformation with an X-ray diffractometer (XRD). Though XRD can detect presence of a phase only beyond 1%, it was used to determine the extent of diffusion of conductor ions across the interface. There could have been a small diffusion of the conductor ions, namely nickel, silver and titanium into the cordierite during firing, but it was not detectable, so presumably the diffusion had produced less than 1% of the total amount of phases in the fired samples. © *2003 Kluwer Academic Publishers*

1. Introduction

Cordierite based ceramics are promising materials for various technological applications due to its low thermal expansion properties and low dielectric constant ($\approx$5 at 1 MHz) coupled with high chemical and mechanical stability [1, 2].

One of the difficulties encountered with the preparation of cordierite ceramics using standard conventional processes, i.e., via direct crystallization of the melt is the narrow temperature band for sintering which is located just below the incongruent melting point of pure cordierite [3, 4]. The narrow temperature interval demands reasonably well-controlled temperature conditions during densification. Hence, to overcome this problem, sol-gel process has become a very attractive synthesis technique for processing cordierite. This is mainly because of its ability to generate stoichiometric materials of high purity with good control over particle size.

Knowledge of the dielectric properties such as dielectric constant, dielectric loss of cordierite is very important to find its use as a dielectric material for the barrier rib in Plasma display panels (PDP). In PDPs, the barrier rib structure maintains a separation between the glass substrate in order to prevent optical and electrical cross talk between the cells. In addition, the plasma display utilizes frequencies ranging from 50 to 200 kHz [5, 6]. Hence it is of utmost importance to use dielectric materials with low permittivity and low loss to fabricate the ribs. As such, the requirements for the barrier rib materials are stringent.

In this paper, the effects of firing temperature and test frequency on dielectric properties of three conductor-dielectric (combination) samples, namely nickel-cordierite, silver-cordierite and titanium-cordierite samples were studied after firing.

2. Experimental

Powders were synthesized by sol-gel process. Magnesium nitrate hexahydrate (E3530 GCE Laboratory Chemicals, Goodrich Chemical Enterprise) and aluminium nitrate non-hydrate (E0280 GCE Laboratory Chemicals, Goodrich Chemical Enterprise) were mixed together and colloidal silica (Aldrich Chemical Company, Inc. E. I. Du Pont de Nemours & Co.) was added to the solution. Bismuth ions derived from bismuth nitrate (Merck) in nitric acid was used to form the cordierite matrix phase. Bismuth oxide is known to decrease the viscosity of the glass-ceramics during sintering and thereby improves the sinterability and also lowers the sintering temperature of the compound. To form the sol, the precursors were mixed with a solution

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of deionized water and concentrated nitric acid (69.0–70%, J. T. Baker) with continuous stirring. The subsequent addition of ammonium hydroxide (25%, Ashland Chemical) resulted in gelation due to the precipitation of bismuth, magnesium and [1]aluminium hydroxide. The solid were collected by filtration and calcined at 300°C for 1 hour in an electric furnace. The resulting material called cordierite precursor, was a white, free flowing powder.

After calcination, the white cordierite powder was sifted to less than 106 μm, followed by uniaxial pressing at 25 MPa using a manual handpress. The cordierite pellets of diameter 20 mm were obtained after pressing. Pellets were subsequently fired by heating in air from 25°C to 900°C, followed by a 12 hours hold at 900°C. It is followed by the sputtering conductors. After sputtering, the conductor-cordierite samples were annealed at 300°C, 500°C and 700°C for 3 hours each in an electric furnace. After firing, capacitance and dielectric loss were measured using an Impedance Analyser. (Model 4192 LF Impedance Analyser, Hewlett-Packard Co.) Dielectric constants were calculated from capacitance measurements. Densities were determined using Archimedes method.

The samples were also analyzed for phase purity and crystallinity with an X-ray diffractometer (Shimadzu Lab X XRD).

3. Results and discussion

3.1. Dielectric constant

The capacitances of the conductor-cordierite samples after firing were determined at 1 kHz, 100 kHz and 1 MHz using an Impedance Analyzer. The dielectric constants were obtained via indirect methods; by calculating the thickness of the compact and the capacitance between two metal electrodes. Hence the dielectric constant, ε was calculated using the following formula:

$$\varepsilon = 5.75 \times 10^{12} \times \text{Capacitance} \times \text{thickness} \quad (1)$$

Figs 1, 2 and 3 show the variation of dielectric constant with test frequencies and firing temperatures for nickel-cordierite, silver-cordierie and titanium-cordierite samples respectively after firing those for 3 hours each. It is observed that the value of dielectric constant decreased with increasing test frequencies (from 1 kHz to 1 MHz) and increasing firing temperatures. A likely explanation for the observed decreasing dielectric constant of the samples could be explained by the following factors. Firstly, increasing firing temperatures might have resulted in phase transformation and or increase in the fraction of the phases present that might have affected the polarizability of the ions more than the mobility of the cation species, hence decreasing the dielectric constant. Secondly, the change in mechanism from interfacial to dipole polarization might have also contributed to the decrease in dielectric constant values [7].

It was also noted that all 3 samples showed more stable dielectric constant value at higher test frequency regardless of firing temperature. This is because electronic polarization contributes more significantly to dielectric constant at higher frequency such as 1 MHz.

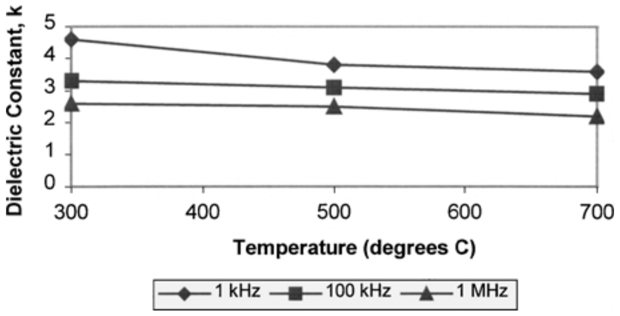

Figure 1 Dielectric constant as a function of frequency for nickel-cordierite samples fired at 300, 500, 700°C for 3 hours.

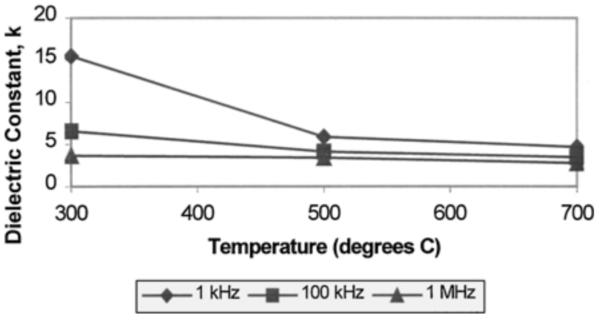

Figure 3 Dielectric constant as a function of frequency for titanium-cordierite samples fired at 300, 500, 700°C for 3 hours.

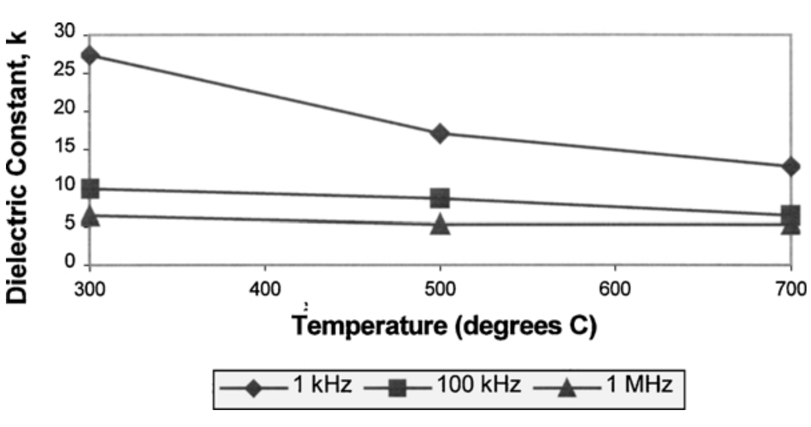

Figure 2 Dielectric constant as a function of frequency for silver-cordierite samples fired at 300, 500, 700°C for 3 hours.

TABLE I Variation of dielectric constant as a function of frequency for conductor-cordierite samples fired at 300, 500, 700°C for 3 hours

	Nickel			Silver			Titanium		
Temp (°C)	1 KHz	100 KHz	1 MHz	1 KHz	100 KHz	1 MHz	1 KHz	100 KHz	1 MHz
300	4.6	3.3	2.6	27.4	9.9	6.4	15.5	6.6	3.7
500	3.8	3.1	2.5	17.1	8.6	5.3	5.9	4.1	3.4
700	3.6	2.9	2.2	12.8	6.4	5.3	4.7	3.5	2.8

In comparison of the three conductor-cordierite samples, nickel-cordierite sample had achieved a dielectric constant value of 2.2 at 1 MHz (see Table I) that is lower than the silver-cordierite and titanium-cordierite samples after firing at 700°C for 3 hours at 1 MHz. And this can be explained by the fact that nickel-cordierite samples contained the largest amount of porosity. The amount of porosity in the samples was determined by the percentage densification of the samples (see Table II) after firing. As the pores that may contain air has dielectric constant about 1, so a porous body will have significantly lower dielectric constant compared to solid body. In other words, the dielectric constant decreases with increasing porosity [8].

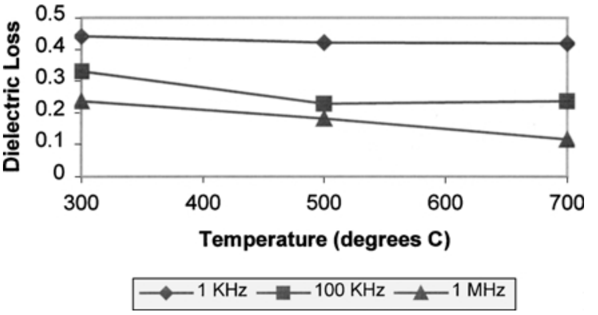

Figure 5 Dielectric loss as a function of frequency for silver-cordierite samples fired at 300°C, 500°C, 700°C for 3 hours.

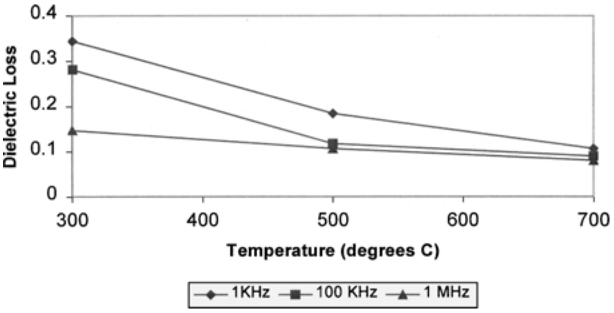

Figure 6 Dielectric loss as a function of frequency for titanium-cordierite samples fired at 300°C, 500°C, 700°C for 3 hours.

3.2. Dielectric loss

Similarly, the Impedance Analyzer that was previously employed to determine the dielectric constant, was also used to obtain the dielectric loss values of the samples. Fig. 4 depicts the effect of test frequency and firing temperature on dielectric loss of nickel-corderite samples. It can be observed that the value of dielectric loss also increased with increasing firing temperature and test frequency. This observation is evident in silver and titanium-cordierite samples (see Figs 5 and 6). The decrease in dielectric loss was more significant at lower test frequency and at lower firing temperature. Loss mechanism is typically due to ion migration process. And the total loss by ion migration is due to DC conductivity and ion jumping [8, 9]. DC conductivity dominates at low test frequencies, while ion jumping occurs at moderate frequencies. Hence this explains the high loss tangent values at low frequencies but low values at higher frequencies.

TABLE II Percentage densification of nickel, silver, titanium-cordierite samples after sintering at 300°C, 500°C, 700°C for 3 hours

	Percentage densification (%)		
Temp (°C)	Nickel-cordierite	Silver-cordierite	Titanium-cordierite
300	84.45	81.26	82.63
500	86.19	86.51	84.24
700	87.25	88.01	88.57

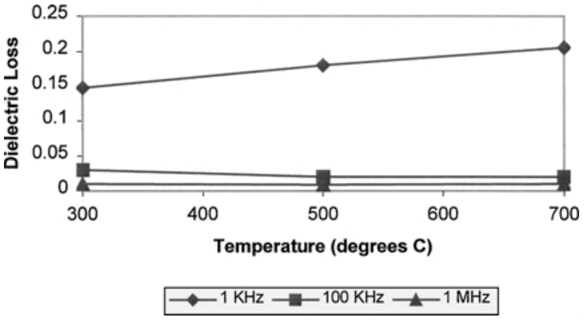

Figure 4 Dielectric loss as a function of frequency for nickel-cordierite samples fired at 300°C, 500°C, 700°C for 3 hours.

3.3. XRD analysis

X-ray diffraction studies revealed some important information regarding phase evolution at the interfaces of the nickel-cordierite, silver-cordierite and titanium-cordierite samples.

Fig. 7a shows the X-ray diffraction pattern obtained on nickel-cordierite samples after firing at 300°C for 3 hours. It should be noted that no additional new peaks were formed after firing at 500°C and 700°C (see Fig. 7b and c respectively), hence it indicates that no new phases were formed except μ-cordierite, cristobalite and indialite phases. No nickel peak was observed in the figures, therefore it could also be deduced that diffusion of nickel-ions across the nickel-cordierite interface was minimal (must have produced less than 1 vol% of phase resulting from the compound

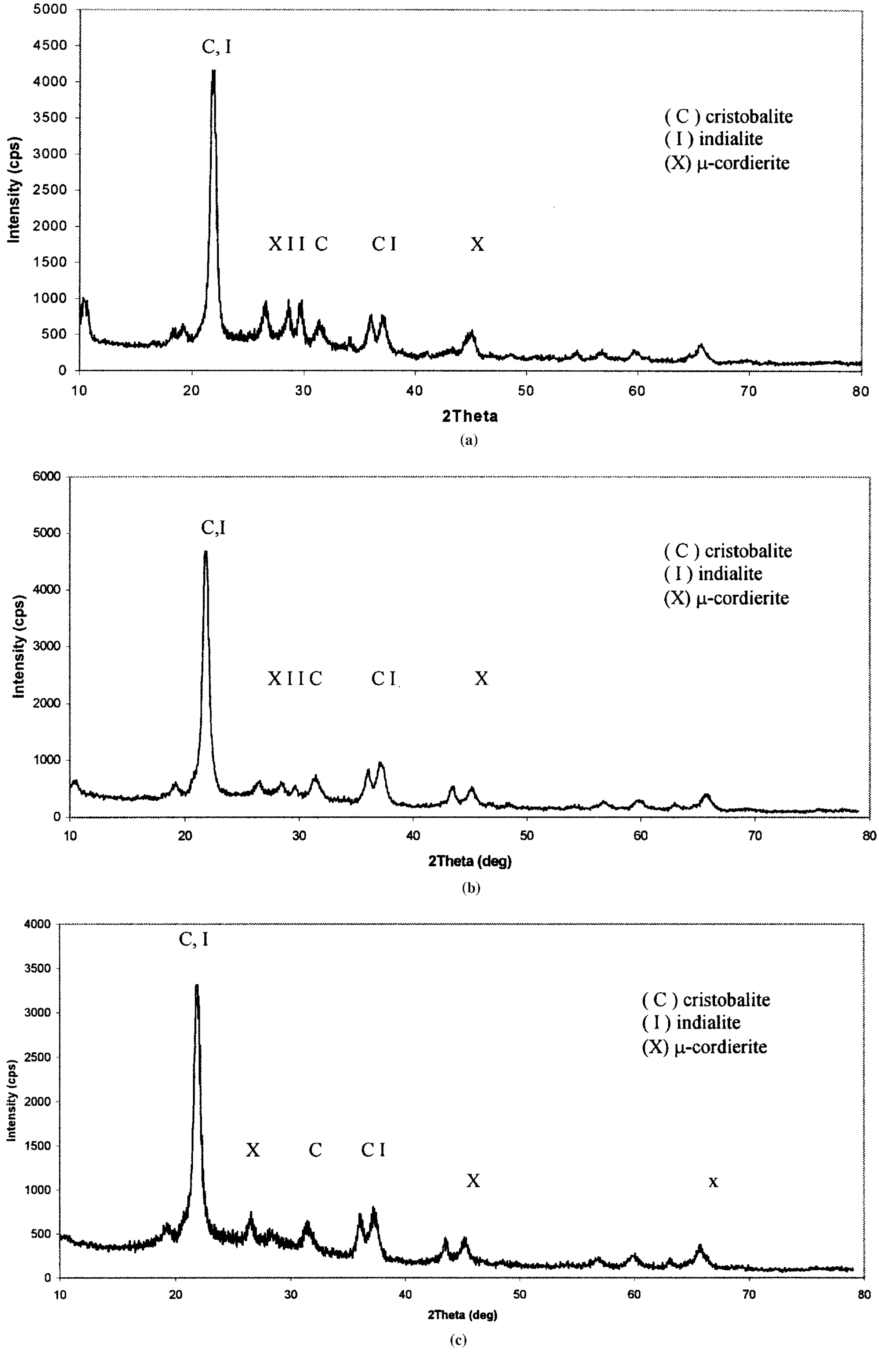

Figure 7 (a) XRD spectra of nickel-cordierite samples annealed at 300°C for 3 hours. (b) XRD spectra of nickel-cordierite samples annealed at 500°C for 3 hours. (c) XRD spectra of nickel-cordierite samples annealed at 700°C for 3 hours.

formation of Ni with cordierite) during the firing at 300°C, 500°C and 700°C. The presence of the phases was ascertained by matching the pattern to the JCPDS powder patterns.

The X-ray diffraction patterns for silver and titanium-cordierite samples fired at 300°C, 500°C and 700°C for 3 hours were similar to the X-ray spectra obtained in the nickel-cordierite samples, with major peaks at the same 2-theta angles. Similarly, μ-cordierite phase was observed at 2θ angle of 26.5, 45.0 and 65.6 degrees. In addition, cristobalite and indialite phases were also present in the samples. It was also noted that no additional new peak was formed with increased firing temperature in the silver-cordierite and titanium-cordierite samples as well, which indicates that no new phases were formed. Therefore it can also be said that diffusion of silver and titanium ions across interface were not significant when the samples were fired at 300°C, 500°C and 700°C.

4. Conclusion

By adopting sol-gel synthesis technique, cordierite can be processed at temperature of approximately 900°C. The dielectric properties of the nickel-cordierite, silver-cordierite and titanium-cordierite samples are found to be dependent on test frequency and firing temperature. In order to obtain low loss and permittivity, the cordierite samples should be fired at slightly higher firing temperature in order to reduce porosity and tested at frequencies of 1 MHz and beyond. In addition, diffusion of nickel, silver and titanium ions across the interface was not significant when the sintered samples were heat treated upto 700°C.

References

1. MEI SEN, YANG JUAN and F. JOSE M F, *Materials Letters* **47** (2001) 205.
2. LU GUO-QUAN and C. J. NOEL, *J. Mater. Res.* **15** (2000) 2857.
3. R. W. DUPON, R. L. MCCONVILLE, D. J. MUSOLF, A. C. TANOUS and M. S. THOMPSON, *J. Amer. Ceram. Soc.* **73** (1990) 335.
4. M. A. EINARSRUD, S. PEDERSEN, E. LARSEN and T. GRANDE, *J. Euro Ceram. Soc.* **19** (1999) 389.
5. U. KOGELSCHATZ, B. ELIASON and W. EGLI, *J. Phys. IV* **C4** (1997) C4.
6. YOUNG-GUON KIM, YOUNG SAM KIM, DAI-GEUN JOH, JAE-JUN KO, DAE IL KIM, EUN HA CHOI, YOON HO SEO and GUANGUP CHO, *Jpn. J. Appl. Phys.* Part 2 Letters **37** (1998) L1548.
7. L. L. HENCH and J. L. WEST, "Principle of Electronic Ceramics" (John Wiley and Sons, New York, 1990) p. 123.
8. T. OTA, J. TAKAHASHI and I. YAMAI, *Key Engineering Materials* **66/67** (1992) 185.
9. MINORU TOMOZAWA, in "Dielectric Characteristic of Glass, Treatise on Materials Science and Technology, Glass I: Interaction with Electromagnetic Radiation," edited by M. Tomozawa and R. H. Doremus (Academic Press, 1997) p. 282.

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