

DOLOMITE ADDITION IN NON-STOICHIOMETRIC CORDIERITE GLASS-CERAMIC: EFFECTS ON DIELECTRIC CONSTANT

M. Hasmaliza^a, A.A. Zainal^a and I. Norfadhulah^b

^a *Structural Materials Niche Area,
School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia Engineering Campus,
14300 Nibong Tebal, Penang, Malaysia.*

^b *Faculty of Earth Science, Universiti Malaysia Kelantan Kampus Jeli,
Karung Berkunci No.100, 17600 Jeli, Kelantan, Malaysia*

Corresponding author: hasmaliza@usm.my

ABSTRACT

Glass-ceramic was successfully synthesis using glass route by dolomite addition in cordierite ($\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$) using natural mineral kaolin and talc. The raw materials have been dictated due to their natural abundance (low price) and their beneficial properties. In this study, non-stoichiometric cordierite glass $x\text{CaO} \cdot (21-x)\text{MgO} \cdot 26\text{Al}_2\text{O}_3 \cdot 53\text{MgO}$ was melt at 1540°C followed by quenching process. The quenched glass was milled to $< 3 \mu\text{m}$ and was used to prepare glass ceramic. The phase evolution and physical properties of the samples sintered at 980°C for 2 hour was characterized. It is found that when dolomite addition ($x < 3$), the predominant phase in glass ceramics was found to be α -cordierite and the secondary crystalline phase to be forsterite. Anorthite start to appear when $x = 5$ and subsequently increased when $x = 10$. The dielectric constant of the samples increases by addition of dolomite. However, when $x = 10$, the dielectric constant decreases. The results shows that, a dense and low dielectric loss glass ceramic with predominant crystal phase of α -cordierite and some amount of anorthite was achieved using fine glass powders from talc and kaolin with an addition of dolomite.

Keywords: α -Cordierite; dolomite; rietveld quantitative; electrical properties

INTRODUCTION

Cordierite, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ is a ceramic material which has interesting properties ranging from very refractory materials to relatively low temperature eutectic in phase field [1]. Since cordierite possesses an excellent properties, such as high thermal shock resistance, low thermal expansion coefficient and dielectric constant, it has been widely used as a material in kiln furniture, filters for liquid at high temperature, carriers of purifying exhaust emission, glaze for tiles, partial electronic component and etc [2,3]. It is known that the ceramic containing cordierite phases have been synthesized from a starting powder base on the synthetic compounds-oxides, hydroxides, and mineral raw materials such as kaolin, talc. Often some additives-mineralizes are used to promote the reactions or to prevent the modification changes.

Dolomite $\text{CaMg}(\text{CO}_3)_2$ is the main source of CaO and MgO in commercial soda-silica flat, container, fiber, and consumer glasses. Dolomite normally used to assist melting, adjust melt viscosity, and impact qualities to the final glass such as increased durability, increase strength, and reduce devitrification. It was found that an addition of CaO in system glass ceramic can lower the melting temperature, glass transition temperature (T_g) and decrease dielectric loss [4]. One of the main advantages of dolomite as a raw material is that it is relatively inexpensive and is far more abundant in nature. The recent work also indicated that the dolomite addition has a positive effect on the porosity [5].

Various mixtures have been used to synthesize cordierite. The most commonly employed was a mixture of clay (kaolin), talc and alumina or silica, or mixture of clay, $\text{Mg}(\text{OH})_2$ and additives [6].

This study is an extension of previous research to see the possibility of using dolomite as one of the raw materials since dolomite not only contains MgO but also CaO. Dolomite is also recognized as an important material because it can be used for producing CaO-MgO composites. There has been no report on low temperature preparation of glass ceramics with the non-stoichiometric cordierite composition added with CaO from dolomite. Therefore, the use of dolomite in specific value for its MgO and CaO content will decrease the use of pure MgO in the composition. The aim of the present study was to investigate the effect of dolomite addition on the α -cordierite formation and properties of $\text{MgO}.\text{Al}_2\text{O}_3.\text{SiO}_2$ system glass-ceramics.

EXPERIMENTAL

The raw materials for the preparation of cordierite body with the formulation of $x\text{CaO}.(21-x\text{MgO}).32\text{Al}_2\text{O}_3.53\text{SiO}_2$ were kaolin (Associated Kaolin Industry, Tapah, Perak, Malaysia) and talc (Ipoh Ceramic Sdn. Bhd., Malaysia). Silica (Ipoh Ceramic Sdn. Bhd., Malaysia), dolomite (Ipoh Ceramic Sdn. Bhd., Malaysia, alumina (Metco) and magnesia (Merck) were used to compensate the formulation of the composition. The element composition of raw materials were characterized by XRF (Rigaku X-ray Spectrometer model RIX 3000) and XRD (Bruker D8 Advanced). The mixtures of raw materials were milled at 25 rpm for 6 hours. The mixture was placed on alumina crucibles and melted at 1540°C for 4 hours followed by quenching in distilled water to form glass. The glass was dried at 100°C prior to two milling stages. Firstly, the dried glass was pulverized in Fritsch planetary mono mill (300 rpm, 5 min). The resultant powders were then sieved and milled using at 300 rpm for 150 min. The obtained glass powders with particles size $\leq 3 \mu\text{m}$ were pelletized at 120 MPa and sintered for 2 hours at 980°C with $5^\circ\text{C}/\text{min}$ heating rate. The crystal structure of the samples was analyzed using (XRD Bruker D8 Advanced). Total wt % of metal oxide in accordance to the formulation was calculated to produce cordierite using non-stoichiometry $x\text{CaO}.(21-x\text{MgO}).26\text{Al}_2\text{O}_3.53\text{SiO}_2$. Table 1 shows the dolomite composition used for each sample.

Table 1: Amount of dolomite in the composition

Sample	D1	D2	D3	D4	D5	D6	D7	D8
x	0	1	3	5	6	7	8	10
Dolomite	0	1.64	5.85	10.97	13.54	16.1	18.68	23.79

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern for sintered pellet. Most of the amorphous phase has transformed to crystalline phase when the samples heat treated at 980°C for 2 hours. There are three crystalline phases that were observed in all samples which are α -cordierite (ICSD 98-001-6867), forsterite (ICSD 98-004-7032) and anorthite (ICSD 98-004-1925). No unknown peak was observed in the sample. Crystallization of glass involves the transition from the random structure of liquid to the more ordered regular lattice of a crystalline solid. Previous research reported that, the only crystalline phase observed was α -cordierite when the glass prepared by sol-gel method with the composition of MgO 5 wt%, CaO 19 wt%, Al₂O₃ 26 wt% and SiO₂ 50 wt% heated at 900°C for 2 hours [8]. While in another research using glass method and oxide materials with the same non-stoichiometry found that the predominant crystalline phase in sample with 0 and 1 wt% CaO was α -cordierite with μ -cordierite as a crystalline phase [9].

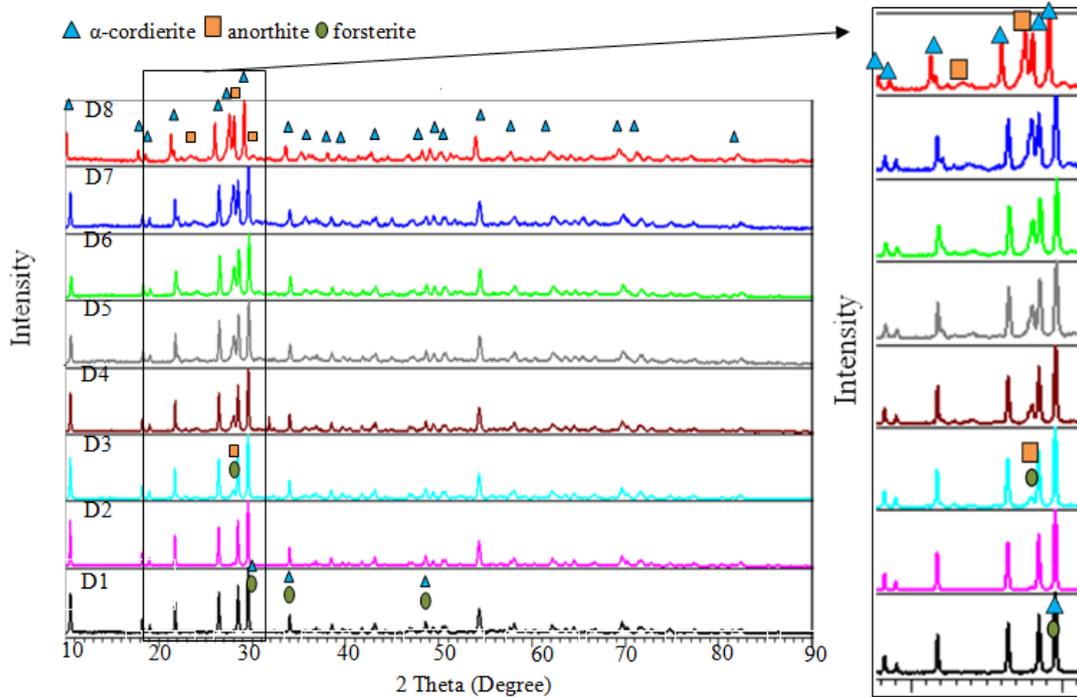


Figure 1: XRD pattern for glass powder after sintering at 980°C for 2 hours

The only phase occurred in sample with 3 wt% CaO was α -cordierite while at 5 wt% CaO, anorthite started to appear. Whereas sample with 10% CaO shows that anorthite phase was obviously increased with the decreasing of α -cordierite [8,9]. Results obtained in this study are in agreement with previous researchers and it

proved that the CaO from dolomite has a significant effect on the formation of anorthite phase.

Quantitative phase analysis of sintered samples was carried out using the Rietveld method and the results are tabulated in Table 2 which also demonstrates total weight percent of α -cordierite as a function of dolomite addition. The Rietveld results were normalized to 100 wt% of crystalline fraction, so the hypothetical amorphous content of samples was assumed to be negligible. It shows that more than 90 wt% of α -cordierite was observed in sample D1 and D2 but the amount of α -cordierite decreased with increasing of dolomite addition whereas forsterite phase increased. However, forsterite phase was disappeared due to crystallization of anorthite from D4 to D8.

Table 2: Percentage of phases present in sintered sample

Sample	Rxp	Rp	Gof	Rwp	α -Cordierite	Anorthite	Forsterite
D1	4.3344	7.675	5.1204	9.8079	95.7	-	4.3
D2	4.3132	7.2536	6.2207	10.8823	91.8	-	8.2
D3	4.3632	7.7745	6.2207	10.8823	88.7	-	11.3
D4	4.3967	7.4057	5.506	10.3168	85	15	-
D5	4.5145	9.0306	5.7963	10.8689	65.6	34.4	-
D6	4.5017	8.281	5.4368	10.4954	61.9	38.1	-
D7	4.6254	7.7264	4.891	10.2387	53	47	-
D8	4.4811	8.0873	5.1807	10.1995	52	48	-

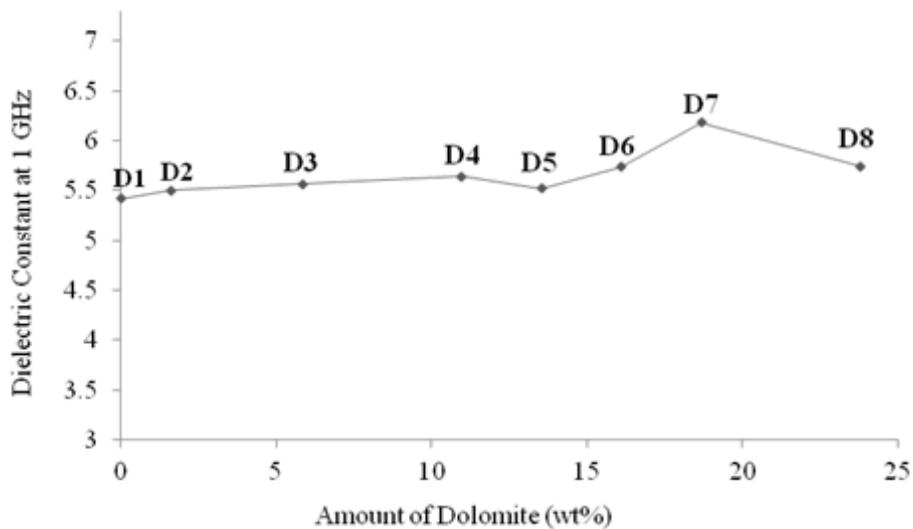


Figure 2: ϵ_r of all samples measured at frequency 1 GHz as a function of amount of dolomite

Figure 2 shows the ϵ_r of the samples with different amount of dolomite. It shows that ϵ_r increased when the dolomite content was increased but there is a sudden drop for D5. The sudden decrease at D5 was due to significant decrease (19.4%) of α -cordierite phase and increasing of anorthite phase at more than 15% (Table 2). The invisible forsterite phase in this sample also contributes to the sudden decrease. ϵ_r of

forsterite was about 7.1 which is higher, compared to α -cordierite and anorthite. ϵ_r is the relative permittivity of dielectric material. Many factors will affect the dielectric properties for glass-ceramic, including the content of the individual crystalline, glass phases and the degree of densification [10].

The increasing of ϵ_r may be due to the decreasing amount of α -cordierite in both sample and increasing of anorthite phase because the theoretical ϵ_r value of α -cordierite is about 5.5 which less than theoretical for anorthite (6.2). However, at the highest content of dolomite used (D8), the ϵ_r decreased. ϵ_r value depending on stoichiometric composition, initial raw material, processing parameter, particles size, phase content, level of porosity, degree of densification and etc [7]. However, in this research, ϵ_r value is more related to the non-stoichiometric used which effected by dolomite content and phases present. Non-stoichiometric used give effected ϵ_r because higher value of x in $x\text{CaO} \cdot (21-x)\text{MgO} \cdot 26\text{Al}_2\text{O}_3 \cdot 53\text{SiO}_2$ will required higher dolomite content as shown in Table 1. As in XRD quantitative analysis, the higher the dolomite content, the formation of α -cordierite will reduced as well as producing secondary phases such as anorthite and forsterite. Since each secondary phases present has their own theoretical dielectric value, it can contribute to the increase and decrease of ϵ_r . The value of dielectric is in the range of 5 - 6 which is similar to the theoretical range value of cordierite and are in close agreement with other published value [1]. In this research, it was found that dielectric properties were not only relied on the density of the material itself, but also the type of crystalline phase and its quantity.

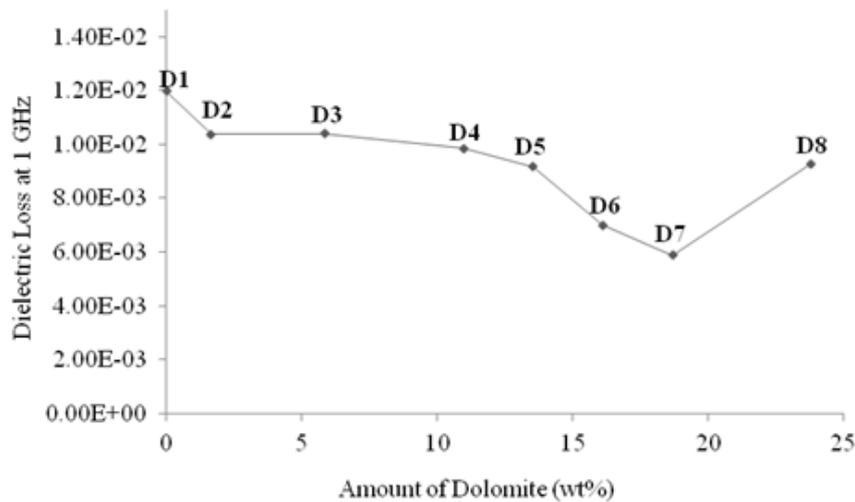


Figure 3: Tan δ of all samples measured at frequency 1 GHz as a function of dolomite addition

Figure 3 shows that the tan δ of samples significantly decreases with an increasing of dolomite content. The trend of tan δ of sample as a function of dolomite was similar to the total amount of α -cordierite and anorthite phase that existed in the sintered samples. However, sample D8 shows an increment with dielectric loss, which due to the higher anorthite phases. These was agreed with previous research where increasing of anorthite content contributed in decreasing the tan δ of the samples since anorthite itself having tan δ [8]. This is also in agreement with previous findings where an addition of CaO in glass ceramic system will decrease

tan δ . Increase of dolomite content will increase the CaO content. The tan δ values for all samples are within 2×10^{-3} - 1.2×10^{-2} throughout the frequency range [4].

CONCLUSION

The property for MgO-Al₂O₃-SiO₂ system glass-ceramic using talc and kaolin with the addition of dolomite was studied. The non-stoichiometric cordierite composition ($x\text{CaO} \cdot (21-x)\text{MgO} \cdot 31\text{Al}_2\text{O}_3 \cdot 53\text{MgO}$) used with dolomite addition has been proved that the sample could be melted at 1540°C without devitrification and become fully amorphous glass. Phases presence were influenced the characteristic of glass and glass-ceramic. The increasing of dolomite addition increased the anorthite phase and the density. The dielectric constant obtained were in the range of 5 to 6 and dielectric loss of sample was about 2×10^{-3} when $x = 7$ used.

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