

APPLICATION OF DIOPSIDE MINERAL IN LOW TEMPERATURE PORCELAIN PRODUCTION

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ABSTRACT

The ceramic wall tile, tableware and sanitary ware industries have constantly been searching for new raw materials. The diopside mineral ($\text{CaMgSi}_2\text{O}_6$) has been presented as excellent option. In this study, the applications of this phase to obtain porcelain products with low firing temperatures were analyzed. Ceramic compositions were studied with diopside and boron frit (B_2O_3) as raw materials. The interactions between the frit and the other compounds were verified and its ideal percentage determined. The results show products can be obtained in the 1150-1200°C temperature range, with water absorption between 0.1 and 0.8 %. The samples showed good dimensional stability (5-7% shrinkage range). The physical properties of samples were measured at different firing temperatures. Density, deep abrasion and bending strength values were shown to be compatible with standard ISO 10545.

1. INTRODUCTION

The market continuously demands new products for wall tile, tableware and sanitary ware applications. Functional properties have stimulated research into new materials with low costs in finished products. Following this tendency, the research carried out in ceramic materials in the last 50 years can be distinguished in two lines: i) synthesis of ceramics from new raw materials; and ii) decrease of the firing temperature^[1, 2]. A further line of research is certainly based on the availability and quality of the raw materials. The second line is has its origins in technical and economic reasons. Recently, some natural occurrences of diopside (calcium magnesium silicate) have provided a good alternative for study in the respective lines. The advantages of diopside include a low melting point, low coefficient of thermal expansion, absence of polymorphism and crystallization precursors^[3, 4, 5]. This phase has also been used in the production of biomaterials because of its hydroxyapatite affinity^[6]. However, for industrial applications, diopside has been obtained by silica and magnesium synthesis^[7]. According to Vereshchagin and Abakumov^[8] it is possible to fire and produce porcelain materials, based on natural diopside, at temperatures between 950 and 1050 °C, with water absorption between 1 and 3%. However, to reach these results the addition of a flux is necessary. In the Russian studies the B₂O₃ frit compounds are indicated as the best option for flux applications, because they promote sintering by viscous flow and also enable controlling system viscosity. This study presents the initial results on the use of natural diopside, in partial substitution of feldspar, for porcelain production, especially for porcelainized stoneware tiles. Thus, different ceramic compositions were formulated based on a natural diopside, a sodium-potassium feldspar and a transparent boron frit. Samples were fired at several temperatures and their mechanical properties were evaluated.

2. EXPERIMENTAL PROCEDURE

2.1. RAW MATERIAL CHARACTERIZATION

The studied compositions were prepared from three different raw materials: sodium-potassium feldspar (F-1), supplied by Mining Tabatinga, a boron frit supplied by Esmalglass do Brazil and a natural diopside, supplied by Mining São Judas Ltda.

Oxides (% by weight)	Raw materials		
	Diopside	Frit *	Feldspar *
SiO ₂	56.0	61.0	71.8
Al ₂ O ₃	1.62	8.0	17.0
Fe ₂ O ₃	0.62	---	0.20
CaO	18.0	---	0.75
Na ₂ O	0.04	---	5.30
K ₂ O	0.17	---	3.20
MnO	0.03	---	---
TiO ₂	0.05	---	0.01
MgO	20.0	---	0.04
P ₂ O ₅	0.01	---	0.8
BaO	---	1.0	---
B ₂ O ₃	---	10.0	---
CaO + MgO	38.0	6.0	---
Na ₂ O + K ₂ O	0.21	10.0	---
ZnO	---	2.0	---
L.O.I.	3.45	---	1.02

*Chemical composition supplied by the manufacturer

Table 1: Chemical composition of raw materials.

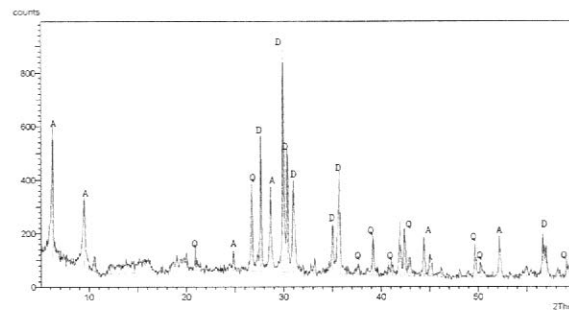


Figure 1: XRD of diopside powder: D-diopside; Q-quartz and A-tremolite.

2.2. SAMPLE PREPARATION

Raw Materials	Formulations (% weight)			
	C1A	C2A	C3A	C6A
Diopside	35.7	35.7	35.7	37.6
Frit	13.7	8.2	2.8	-----
Feldspar	5.6	11.10	16.5	17.4
*Clay	45.0	45.0	45.0	45.0

* Ball clay

Table 2 : Samples composition.

3. RESULTS AND DISCUSSION

The results of this work demonstrate the potential use of diopside in commercial porcelain production. The samples exhibited a decrease in water absorption in the 0.1-3 % range at temperatures of between 1150-1200°C. The results presented in Table 3 show that water absorption values lie around 0.1 % at 1150 and 1200°C for C1A, C2A and C3A compositions. Shrinkage values are found ranging from 5.9 to 7.1 %, respectively.

Frit addition in the compositions had a great influence on sintering behavior compared with the C6A composition without frit. Even when 2.8% of frit was added, a significant reduction in water absorption was observed.

Sample/Firing temperature	Water absorption (%)	Linear shrinkage (%)	MOR (N/mm ²)	
C1A	1150°	0.1	6.4	62.0
	1200°	0.1	6.3	53.5
C2A	1150°	2.7	5.9	53.0
	1200°	0.1	6.5	51.1
C3A	1150°	5.1	5.9	45.7
	1200°	0.1	7.1	56.4
C6A	1150°	6.8	5.6	45.4
	1200°	0.8	6.9	55.4

Table 3: Physical and mechanical properties of samples.

4. CONCLUSIONS

- The porcelain tile composition obtained from diopside mineral presented compatible properties with standard ISO 10545 in the presence of boron frits.
- Diopside phase presented an interesting option for porcelain compositions, mainly in feldspar substitution.
- The availability natural diopside occurrences can improve the development of new ceramic products due to chemical and structural properties, this includes glass and glass-ceramics applications.
- It was shown that compositions with diopside mineral enable producing porcelainized stoneware tiles at low firing temperatures, with good dimensional control.

REFERENCES

- [1] OLIVEIRA, A. P. Novaes de; **Gres porcelanato: Aspectos mercadológicos e tecnológicos**. Cerâmica Industrial, 3 (3) May/June, 1998.
- [2] BALDI, G.; GENERALI, E.; LEONELLI, C.; MANFREDINI, T.; PELLACANI, G. C.; SILIGARDI, C.; **Effects of nucleating agents on diopside crystallization in new glass-ceramics for tile-glaze application**. Journal of Materials Science 30 (1995) 3251-3255.
- [3] LEONELLI, C.; MANFREDINI, T.; M. PAGANELLI, P. POZZI, G. C. PELLACANI; **Crystallization of some anorthite-diopside glass precursors**. Journal of Materials Science 26 (1991) 5041-5046
- [4] BARBIERI, L.; LANCELLOTTI, I.; PELLACANI, G. C.; OLIVEIRA, A. P. Novaes de; **Nucleation and Crystallisation Studies on Silicate Glass-Ceramics**. Proceedings of the ICG Annual Meeting 2000 – Glass in the New Millennium - Challenges and Break-through Technologies - Amsterdam May 15-17, 2000.
- [5] OLIVEIRA, A. P. Novaes de; ALARCON, O. E.; BARBIERI, L.; LANCELLOTTI, I.; **A Preliminary Crystallization Study of a MgO-CaO-Al₂O₃-SiO₂ Glass Composition With Added Steel Fly Ash**. Ninth International Conference on the Physics of Non-Crystalline Solids, October 17-21, 1999 Tucson-Arizona, USA.
- [6] NONAMI, Toru; TSUTSUMI, Sadami; **Study of diopside ceramics for biomaterials**, Journal of materials science: materials in medicine 10, 1999, p. 475-479, Japan.
- [7] HAUSHIS, S.; **Sintering behavior of diopside, CaO.MgO.2SiO₂ from various powder preparation methods**. Master. Sci. Leti, n°4, 382 – 385, 1990.
- [8] VERESHCHANGIN, V. I.; ABAKUMOV, A. E.; **Diopside porcelain produced by low-temperature firing**. Glass and Ceramics, Vol. 55 Nos. 7-8, 1998.