

THE EFFECT OF MECHANICAL ACTIVATION ON THE CORDIERITE FORMATION IN B₂O₃ ADDED MAGNESITE WASTE-QUARTZ-KAOLIN-ALUMINA CERAMIC SYSTEM

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Abstract

The powder mixtures of B₂O₃ added Magnesite Waste-Quartz-Kaolin-Alumina were mechanically activated in a planetary ball mill for 1 hours. The structural alterations and thermal behaviour of the powder mixture were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis (TG-DTA). The results showed that the mechanical activation led to amorphization and decreased the temperature of cordierite formation.

Keyword: Amorphization, mechanical activation, cordierite

1. INTRODUCTION

Cordierite ceramics have been extensively studied in the last decades, due to their excellent properties, low thermal coefficient and dielectric constant, as well as high chemical and thermal stability. These ceramics are used in various industrial fields, in applications such as refractories, electrical, thermal or phonic insulation, filters, membranes, heating elements, microwaves absorbents, electromagnetic waves absorbents, etc [1].

The cordierite is characterized by a complex polymorphism:

- The α -cordierite with hexagonal symmetry (also well-known as indialite), takes place by a quick crystallization between 1000 and 1300 °C.
- The β -cordierite with orthorhombic structure is obtained by crystallization below 950 °C. This is most common phase is natural cordierite.
- The μ -cordierite - metastable rhomboedral phase is obtained by the crystallization of cordierite glass below 925 °C. This phase is also known just as an aluminum magnesium silicate [2].

The α -cordierite phase can be easily obtained by solid-state reaction, at temperatures between 1300 °C and 1400 °C. The usual precursors for the fabrication of synthetic cordierite are talc, kaolin, and alumina that have an acceptable cost-purity relation. To make the solid-state reaction method more cost effective, the temperature of the reaction needs be lowered. The use of an additive that assures the presence of a liquid phase during sintering favours the kinetics of formation of the cordierite and, consequently, lowers the temperatures needed for reaction to take place [3].

Mechanical activation of the starting materials is a promising method for the precursor's preparation. Particle size reduction, which increases the contact surfaces between the particles, is the direct consequence of milling. Also, the energy of the system increases and results in a decrease in the reaction temperature [4]. Different processes can remarkably influence the reactivity of the solids. Particularly, the mechanical treatments are important as long as they can help to make changes in the texture and structure of the solids. In many cases, these alterations in the structure cause certain modifications in the phases that formed by thermal treatment of the solids, which were mechano-chemically treated [5, 6].

Boron Oxide (B₂O₃) has been successfully used as a flux for the preparation of a cordierite precursor by a co-precipitation process [7]. In this study, by adding boric acid (HBO₃), and mechanical activation dense α -cordierite ceramics were obtained by firing at a low temperature, using a mixture of magnesite waste-quartz-

kaolin-alumina. The structural alterations and thermal behaviour of the powder mixture were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis (TG-DTA).

2. EXPERIMENTAL

Alumina, kaolin and quartz were supplied from Kale Ceramic and magnesite waste was supplied for KUMAŞ, Turkey. The chemical compositions of the raw materials are given in **Table 1**. Magnesite Waste-Quartz Kaolin-Alumina and addition 4.44 g H₃BO₃ (~2.5 wt.% B₂O₃) extra were mixed corresponding to stoichiometric according to chemical formula of cordierite (2MgO.2Al₂O₃.5SiO₂) in ashless rubber-lined ceramic jars for 2 h using zirconia balls and distilled water as the milling media. After drying, the mixture was carried out a high-energy planetary ball mill (Fritsch) with a rotation speed of 600 rpm. Ball-to-powder weight ratio was adjusted to 20. The precursor milling was carried out for 2 hours.

Table 1 Chemical composition of raw materials

	Raw materials (wt.%)				
	Kaolin	Alumina	Magnesite Waste	Quartz	Boric Acid
SiO ₂	48.0	-	35.61	99.1	-
Al ₂ O ₃	37.0	100	2.04	0.28	-
Fe ₂ O ₃	0.75	-	6.04	0.05	-
MgO	-	-	33.34	0.16	-
CaO	-	-	2.73		-
TiO ₂	0.02	-	0.22	0.05	-
Na ₂ O	-	-	0.08	0.17	-
K ₂ O	1.85	-	0.02		-
B ₂ O ₃	-	-	-	-	56.33
L.O.I ^a	12.20	-	19.77	0.19	43.67

^a Loss on ignition

X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and CuK α radiation. A Joel 6060 LV scanning electron microscope was used for morphological analysis of non-activated and activated mixed powders. The degree of amorphization (%A) mechanical activated was calculated from Equation (1) [8,9]:

$$\%A = [1 - (B_o I_x / B_x I_o)] \cdot 100, \quad (1)$$

where I_o is the integral intensity of the diffraction peak for non-activated mixture, B_o is the background of the diffraction peak for non-activated mixture and I_x and B_x are equivalent values for mechanically activated mixture. DTA was performed using TA Instruments SDTQ 600 at heating rate of 10 °C/min under atmospheric conditions.

3. RESULTS AND DISCUSSION

3.1 Structural changes in activated B₂O₃ added Magnesite Waste-Quartz-Kaolin-Alumina mixture powders

The XRD of non-activated and activated mixture powder is shown **Fig. 1**. Comparing the peak in the two diffraction peaks get shorter and/or disappear after mechanically activation. This reflects the partial amorphization and structural disordering in magnesite, kaolin, alumina, quartz and boric acid. Mechanical activation has already reported to amorphize materials [9].

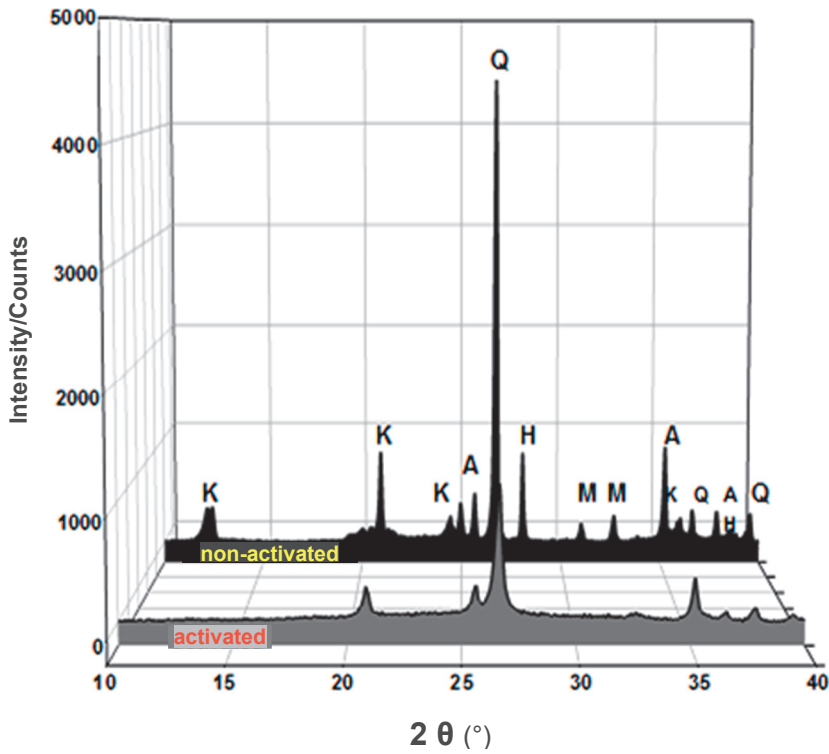
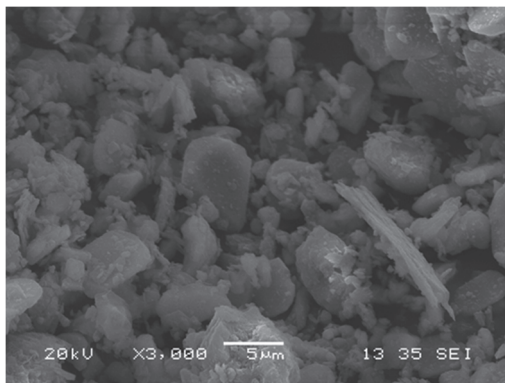
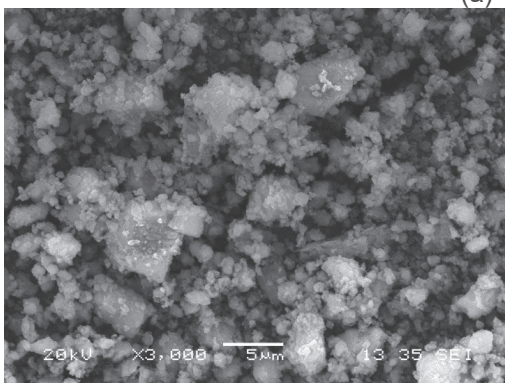
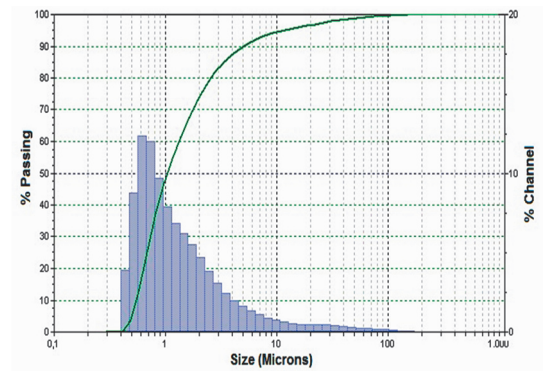


Fig. 1 XRD patterns of non-activated and activated B₂O₃ added Magnesite Waste-Quartz-Kaolin-Alumina [K: Kaolinite, A:Alumina, Q:Quartz, M: Magnesite, H: Boric Acid]



(a)



(b)

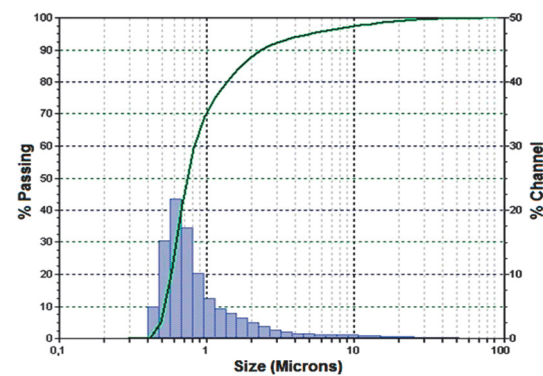


Fig. 2 SEM micrographs and particle size analysis of B₂O₃ added Magnesite Waste-Quartz-Kaolin-Alumina a) non-activated b) activated for 1 h

Tromans and Meech [10, 11] indicated that mechanical activation resulted in development of large numbers of dislocations and their associated strain fields which might lead to an overall decrease in long range lattice periodicity. This may be interpreted as the formation of a metastable “amorphous phase”, since line broadening and the disappearance of diffraction peaks takes place in the X-ray patterns after extended milling.

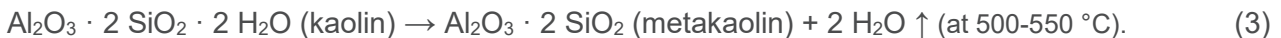
The scanning electron micrographs (SEM) of the non-activated and activated B₂O₃ added Magnesite Waste-Quartz-Kaolin-Alumina mixture powders can be observed in **Figs. 2a, 2b**. The particle size of non-activated mixture is over 5 μm (**Fig. 2a**). After mechanical activating, the mixture of powders is agglomerated. The degrees of amorphization of Magnesite Waste-Quartz-Kaolin-Alumina after mechanical activating were calculated by Equation (1). The degrees of amorphization of alumina, kaolin, quartz were founded approximately 75 %, 95 % and 85 %, respectively. Also, boric acid, magnesite were not calculated because of disappearing of their peaks.

3.2 Thermal behavior of non-activated and activated B₂O₃ added Magnesite Waste-Quartz-Kaolin-Alumina

In **Fig. 3** you can see the DTA analyses of non-activated and activated mixture powders. In the DTA analysis of non-activated mixture powders, the first endothermic peak (a) at round 140 °C is corresponded to the dehydration of kaolinite, according to the following reaction [12]:



The second endothermic peak (b) at round 530 °C is corresponded to the dehydration of kaolinite, according to the following reaction [13]:



And the third endothermic peak (c) at around 700 °C is corresponded to the decomposition of magnetite, according to the following reaction [14]:



These peaks are not present in the activated sample probably due to the occurrence of dehydration and decomposition reactions during the activation operation.

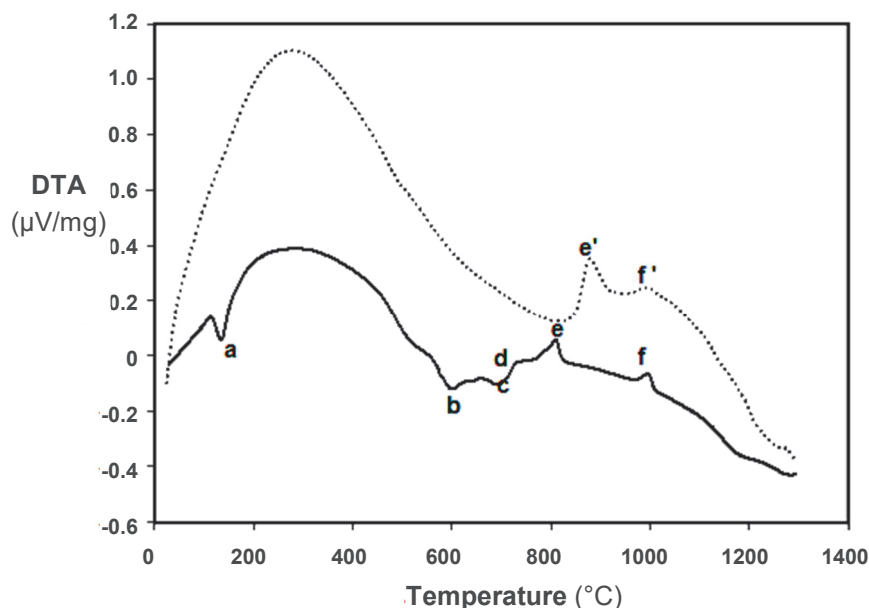


Fig. 3 DTA analyses of non-activated and activated B₂O₃ added magnesite waste-quartz-kaolin-alumina

The exothermic peak (d) indicates that the crystallization of μ -cordierite appeared at about 810 °C in non-activated mixture powder. The μ -cordierite formation (d') is increased to 870 °C after 1 h of mechanical activation. Furthermore, the second exothermic peak (e') at about 975 °C in activated mixture powders, corresponding to the transformation of μ - to α -cordierite, is lowered compared with that (at about 1005 °C) of none-activated mixture powders (e).

Hwang et al. [7] reported that the formation of μ -cordierite occurs at about 1005 °C B₂O₃ doped MgO-Al₂O₃-SiO₂ ceramics system. Hwang et al. [6] also stated that the transformation of μ - to α -cordierite develops in the B₂O₃ and P₂O₅ together doped ceramics system. Mechanical treatment in a high energy mill generates a stress field within the solids. Stress relaxation can occur via several channels: (1) heat release, (2) development of surface area as a result of brittle fracture of the particles, (3) generation of various sorts of structural defects and (4) stimulation of chemical reactions within the solids. All of the relaxation channels cause changes in the reactivity of the solid substance that is under treatment, which is resulting of mechanical activation [16]. The concentration of the mechanically induced defects and their spatial distribution depend upon the condition of the energy transfer in the mill. The creation of defects enhances the stored energy in the solids and consequently causes a decrease in the activation barrier for the process and/or subsequent processes [17].

CONCLUSIONS

The effects of the mechanical activation on the formation of cordierite in B₂O₃ added magnesite waste-quartz-kaolin-alumina mixture powders were studied by using XRD and SEM. The mechanical activation caused amorphization and structural disordering in B₂O₃ added Magnesite Waste-Quartz-Kaolin-Alumina mixture powders. The degrees of amorphization of alumina, kaolin, quartz were founded approximately 75 %, 95 % and 85 %, respectively. Also, boric acid, magnesite were not calculated because of disappearing of their peaks. The dehydroxylation reaction in kaolinite and boric acid, and decomposition reaction of magnesite occurred during milling. The application of high energy milling allowed a dramatic change in the structure and surface performance of solids. Therefore, the temperature of cordierite formation was lowered with mechanical activation.

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