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# GLASS FORMATION AND PROPERTIES OF CORDIERITE COMPOSITIONS FROM TALC-BASED NATURAL RAW MATERIALS WITH BORON OXIDE ADDITION

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## *ABSTRACT*

In this study, the glass forming behaviour of cordierite compositions in MAS ($MgO-Al_2O_3-SiO_2$) system with added $B_2O_3$ content up to 3% were studied by melting the natural raw materials such as; talc, kaolin, alumina and boric acid as the source of MgO, $SiO_2$, $Al_2O_3$ and $B_2O_3$ respectively. XRD analysis revealed the glass formation. Optical properties of the glasses were measured using UV-VIS spectrophotometer and structural changes were monitored by using FT-IR spectrometer. Physical properties such as density, colour, thermal expansion coefficients and hardness were measured according to the standard test methods. Glasses with a green colour were produced and this was attributed to the Fe content in the glass up to 0.5% coming from talc and kaolin. The addition of $B_2O_3$ to the glasses increased the glass transition temperatures ($T_g$) values and reduced the thermal expansion coefficient values of the glasses from 5.2226 to 5.0072ºCx$10^{-6}$, for MAS-T-0 and MAS-T-3, respectively.

**Keywords:** Green glass, Colour, Glass-formation, Natural raw materials, Optical properties.

# BOR OKSİT İLAVESİ İLE TALK-ESASLI DOĞAL HAMMADDELERDEN KORDİYERİT CAMI OLUŞUMU VE ÖZELLİKLERİ

## *ÖZ*

Bu çalışmada, $SiO_2$, MgO, $Al_2O_3$ ve $B_2O_3$ kaynağı olarak sırasıyla kaolin, talk, alumina ve borik asit gibi doğal malzemelerin eritilmesi ve %3'e kadar $B_2O_3$ ilavesi ile MAS ($MgO-Al_2O_3-SiO_2$) sistemindeki kordiyerit kompozisyonlarının cam oluşturma davranışı incelenmiştir. Camların optik özellikleri UV-VIS spektrofotometre ve yapısal analizler FT-IR ile belirlenmiştir. Yoğunluk, renk, termal genleşme katsayısı ve sertlik gibi fiziksel özellikler standart test metotlarına göre ölçülmüştür. Talk ve kaolendeki %0.5'e kadar olan Fe içeriği nedeniyle, yeşil renkli camlar elde edilmiş ve $B_2O_3$ ilavesi cam geçiş sıcaklığı ($T_g$) değerlerini yükseltmiştir ve MAS-T-0'dan MAS-T-3'e doğru termal genleşme katsayısını 5.2226'dan 5.0072ºCx$10^{-6}$'ye düşürmüştür.

**Anahtar Kelimeler:** Yeşil cam, Renk, Cam oluşumu, Doğal hammaddeler, Optik özellikler.

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# 1. INTRODUCTION

The market for glass bottles has enormous potential because glass containers are high quality packaging materials, the demand will increase together with the population. Glass containers have a number of indisputable qualitative advantages over other forms of packaging, such as; transparency, chemical inertness, safety, the possibility of recycling and salvaging of wastes, and wide selection. Brown and green glass containers have another important characteristic; strong absorption of ultraviolet and short-wavelength visible light, thereby providing long-term biological protection of the contents.

It is known that when exposed to ultraviolet light, many beverages (principally, beer) containing carbonic acid loose the aroma, taste and health qualities for which they are valued. Figure 1, shows the optical transmission spectra for commercial green and brown glasses which were produced in Russia by Rusdzham LLC (Turkey-Russia). According to the technical requirements of the company, the dominant wavelength of green and brown glass must fall within the ranges of 552-558 nm and 578-586 nm, respectively. This guarantees that the bottles will have protective qualities (Zhernovaya et al., 2007)

There is a conflicting trend which appeared in the last few years, in glass container industry. In one hand the glass quality requirements are becoming more stringent while on the other hand ecological and economical norms dictate that the secondary products with unstable compositions, such as glass scrap, slags, fly-ashes, be used in glass making. Also, in economical sense it is interesting to use some abundant and less pure natural raw materials, such as perlite (Arutyunyan et al, 1997), sepiolite, talk and kaolin, especially in coloured container glasses, i.e; bottles. Glass scrap, often with mixed colours, is already being used in amounts up to 85% to make container glass (Papadopoulas and Moutsatsou, 2003).

Opera et al. (1999) studied the cordierite glass from kaolinite, calcined alumina and talc, and added some nucleating agents such as $TiO_2$, $ZrO_2$, $CeO_2$ or mixtures of them. They showed that the glasses were all coloured, the shade strength increased as the concentration of the nucleating agent was increased. Also they showed that the additives decreased the thermal expansion coefficient (α) values.

In the present work, the glass forming behaviour of cordierite compositions in MAS ($MgO$-$Al_2O_3$-$SiO_2$) system with added $B_2O_3$ content up to 3% were studied by melting the natural raw materials such as; kaolin, talc, alumina and boric acid as the source of $SiO_2$, $MgO$, $Al_2O_3$ and $B_2O_3$. Cordierite glasses with a green colour were easily produced and optical and physical properties were reported.

# 2. EXPERIMENTAL PROCEDURE

The $MgO$-$Al_2O_3$-$SiO_2$ glass was melted from natural raw materials of talc, kaolin and alumina. The chemical analysis of the starting raw materials are given in Table1.

$B_2O_3$ were added to every 100 g of batch material. $B_2O_3$ was added in the form of $H_3BO_3$. The calculated batch was melted in platinum 2 % rhodium crucible. The melting was carried out at 1520°C for 2 hrs using a programmable electrical furnace (Protherm Elv160/8). Following this, melt was cast into a preheated graphite mould with the dimensions of 5cm x 5cm and 0,5cm depth. In order to remove thermal residual stresses of the glass samples, they were annealed in a regulated Carbolite HTF3 furnace at 600°C for 1 h. The muffle furnace was left to cool to room temperature. The composition of the resultant MAS-T-0 glass sample is given in Table 2, and it was shown in $MgO$-$Al_2O_3$-$SiO_2$ phase diagram, in Figure 2 (http://serc.carleton.edu).

X-ray powder diffraction (XRD) analysis of the glass samples were determined by PANalytical X'Pert Pro MPD diffractometer using Cu $K_\alpha$ radiation with wavelength of 1.5418 Å. The chemical analysis of the starting raw materials and the glass samples were carried out by Philips PW 2404 X-ray spectrometer.

Thermal behaviour of glasses were determined by DTA method which was performed in Seiko Exstar 6300 model DTA/TG instrument using 200 mg powdered samples employing heating rate of 10°C $min^{-1}$. All DTA experiments were performed in static air atmosphere with $Al_2O_3$ powder as reference material.

Thermal expansion coefficients (α) of the glasses were measured by using Netzsch Dilatometer (DIL 402C/ 3/ F) up to 500ºC with a heating rate of 10ºC $min^{-1}$.

Vickers hardness measurements were carried out using Zwick ZHV10 micro hardness equipment on polished glass samples and at least

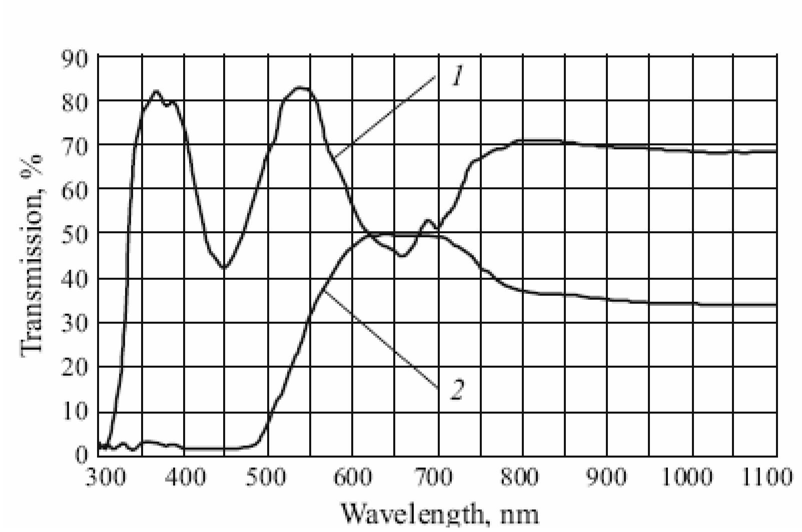



Figure 1. Transmission spectra of green (1) and brown (2) container glasses (Zhernovaya et al, 2007)

Table 1. Chemical analysis of all the starting raw materials

| | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **CaO** | **$Fe_2O_3$** | **$TiO_2$** | **$Na_2O$** | **$K_2O$** | **$B_2O_3$** | **LOI** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Talc** | 34.4 | 0.78 | 62.1 | 1.36 | 0.36 | - | - | - | - | 1.0 |
| **Kaolin** | - | 36.92 | 47.80 | 0.31 | 0.62 | 0.31 | 0.01 | 0.73 | - | 13.3 |
| **Boric Acid** | - | - | - | - | - | - | - | - | 56.25 | 43.75 |
| **Alumina** | - | 100.00 | - | - | - | - | - | - | - | - |

Table 2. Composition of MAS-T-0 base glass (as wt%)

| Oxide | Amount (as wt%) |
|---|---|
| MgO | 22.403 |
| $Al_2O_3$ | 28.136 |
| $SiO_2$ | 47.357 |
| CaO | 0.935 |
| $Fe_2O_3$ | 0.429 |

5 measurements were taken and the mean values were reported. The applied load during the hardness measurements was 300 g.

Apparent densities were measured by the Archimedes water displacement technique using small glass pieces.

The optical measurements were performed with Perkin-Elmer EZ 201 UV-VIS spectrophotometer and FT-IR spectra were obtained by employing a Shimadzu IRPrestige-21 model Fourier Transform Infrared Spectrometry (FT-IR).

X-rite Portative SP64 Sphere Spectrophotometer was used for determining the colour of the MAS-T glasses, commercial green wine glass and commercial green mineral water glass.

## 3. RESULTS AND DISCUSSIONS

### 3.1 X-ray Diffraction Analysis

Figure 3 shows XRD analysis of glass samples and as seen that all MAS-T compositions showed amorphous structure which indicates the glass formation abilities of the cordierite compositions.

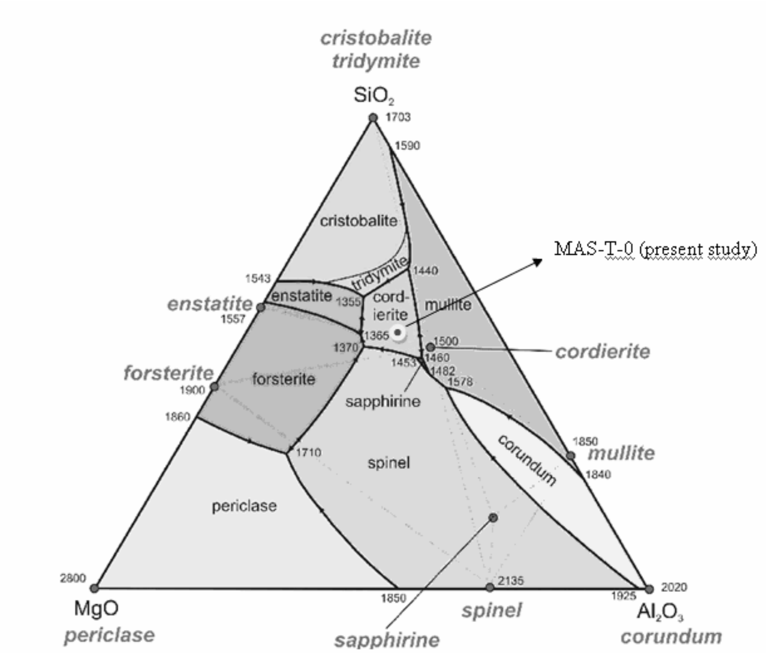



Figure 2. $MgO$-$Al_2O_3$-$SiO_2$ phase diagram (http://serc.carleton.edu)

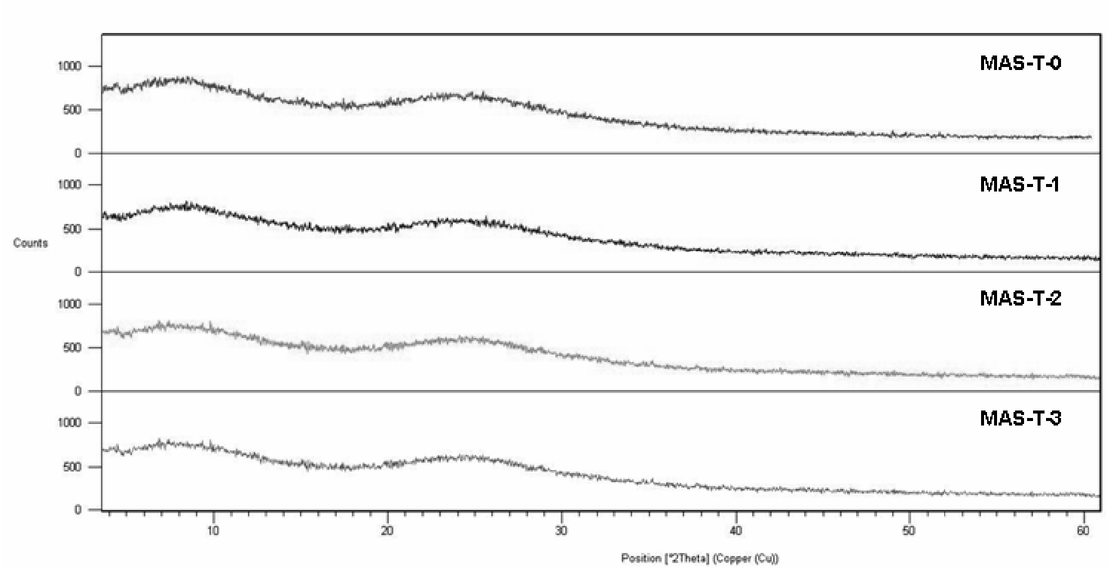



Figure 3. XRD paterns of the MAS-T glasses

The resultant glasses have green colour. In the present study, only natural raw materials were used in order to see the glass forming abilities of the cordierite compositions. In commercial glass production, usually some additives were added to the glass batches in order to control the quality of the glass such as; refining agents, oxidizing or reducing agents, and colouring agents.

## 3.2 Differential Thermal Analysis

DTA traces were recorded at heating rate of 10ºC $min^{-1}$ up to 1000ºC for each cordierite glasses. Endothermic reactions at the temperatures 776, 780, 786 and 788ºC were recorded respectively for MAS-T-0, 1, 2 and 3 glasses (Figure 4). These endothermic peaks are attributed to the glass transition temperature ($T_g$) of the MAS-T glasses. $B_2O_3$ addition affected the glass transition temperature ($T_g$) of the cordierite glasses.

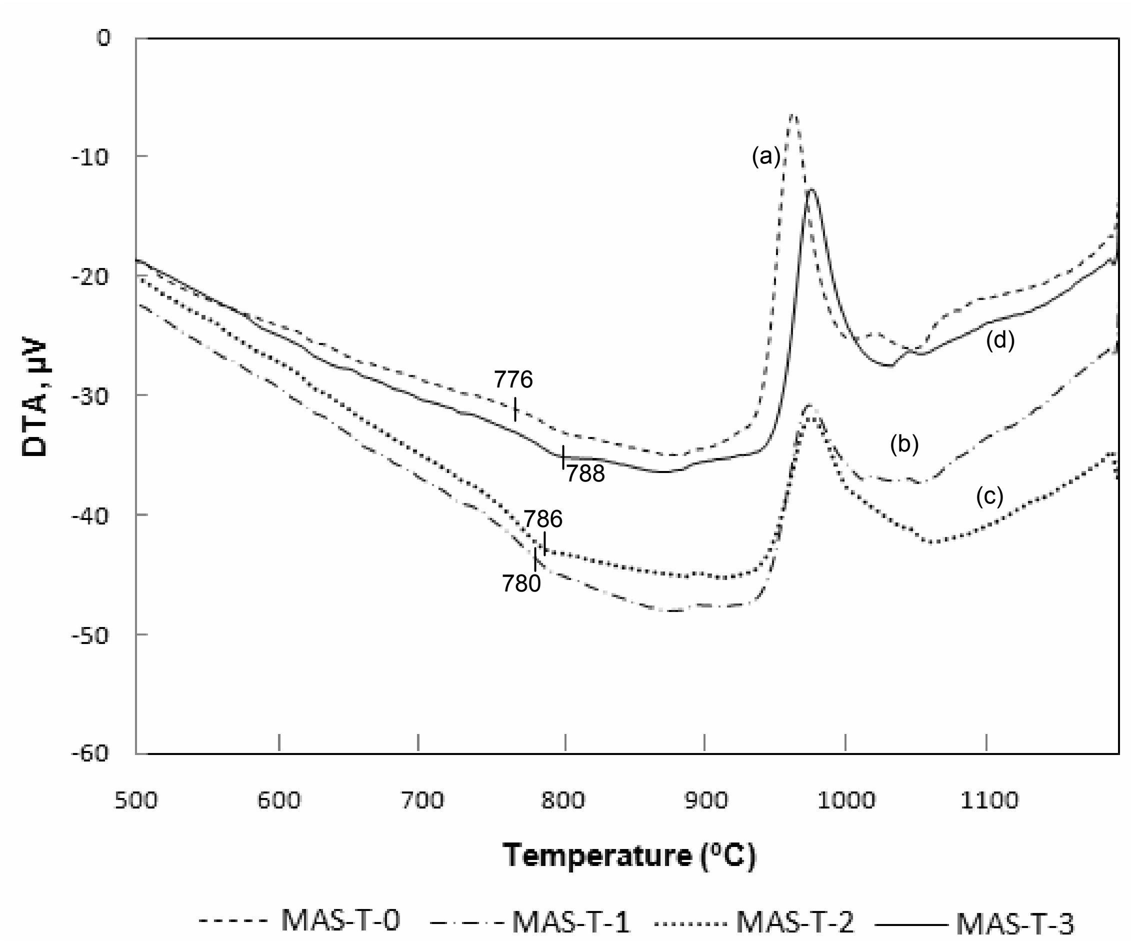



Figure 4. DTA curves of (a) pure, (b) 1%, (c) 2% and (d) 3% $B_2O_3$-doped cordierite glasses

As seen in the results that, with increasing boron oxide content in the glasses, the glass transition and crystallization temperatures were also increased. This behaviour is attributed to the glass forming ability of $B_2O_3$ and with increasing boron oxide in the glass composition, the bonds are stronger and as very well known that, glasses with stronger bonds are more resistant to crystallization on heat-treatments.

### 3.3 Physical Properties of the Glasses

The thermal expansion behaviour of the undoped sample (MAS-T-0) and all the doped samples (MAS-T-1, MAS-T-2, MAS-T-3) show a normal, linear increase in Δl/l up to a temperature of 500ºC. The undoped sample, MAS-T-0, shows the maximum expansion in the temperature range of 32-500ºC. As the $B_2O_3$ addition increases from 1 to 3%, the thermal expansion values decreased within the same temperature range as given in Table 3. TEC values were changed from 5.2226 to 5.0072ºC x $10^{-6}$, for MAS-T-0 and MAS-T-3 glasses respectively. This is an expected result because $B_2O_3$ is a glass former and its increase in the glasses resulted with stronger B-O-Si or B-O-B bonds in the MAS-T glasses, in turn the stronger the bonds in glasses, the lower the TEC values.

Vickers hardness of the MAS-T glasses with increasing $B_2O_3$ content, are given in Table 4. The hardness values for all the glasses were very close to each other as 7.879 to 7.502 GPa.

Density of the MAS-T glasses are given in Table 5 and it can be seen that the density values of the glasses show small increases with the increasing $B_2O_3$ content in the glasses. The highest density value was 2.71 and the lowest density value was 2.63 g/cm$^3$, for MAS-T-3 and MAS-T-0 glasses respectively. This behaviour could be attributed to the glass-forming ability of $B_2O_3$ with $SiO_2$, which resulted with a denser glass structures with increasing $B_2O_3$ content in the glasses.

Table 3. Thermal expansion coefficients (TEC) between 30-500ºC.

| Sample Code | TEC ($x10^{-6}$) |
|---|---|
| MAS-T-0 | 5.2226 |
| MAS-T-1 | 5.1989 |
| MAS-T-2 | 5.0653 |
| MAS-T-3 | 5.0072 |

Table 4. Vickers hardness values for 300gr load.

| Sample code | Vickers hardness **(GPa)** |
|---|---|
| MAS-T-0 | **7.875** |
| MAS-T-1 | **7.591** |
| MAS-T-2 | **7.551** |
| MAS-T-3 | **7.502** |

Table 5. Density values of glasses with increasing $B_2O_3$ content

| Sample code | Density ($g/cm^3$) |
|---|---|
| MAS-T-0 | 2.63 |
| MAS-T-1 | 2.65 |
| MAS-T-2 | 2.68 |
| MAS-T-3 | 2.71 |

## 3.4 Optical Properties of the Glasses

The results of the colour measurements of MAS-T glasses, a commercial green wine bottle and a commercial green mineral water bottle, were given in Table 6, as the CIE L*a*b* values. In Figure 5, the reference material is "commercial green mineral water bottle glass". All the MAS-T glasses are in the intersection of red and blue zone. The wine bottle glass is in the intersection region of red and yellow region with respect to reference glass.

L* value of mineral water bottle glass is 70.33. The L* values of the MAS-T glasses and green wine bottle glass were 42.91, 49.98, 50.19, 53.02 and 48.85, respectively. All the L* values of the MAS-T glasses are smaller than the green mineral water bottle. Since the L* refers to the lightness of the material (as it increases, the material gets whiter), mineral water bottle is whiter than all the MAS-T glasses. The results show that $B_2O_3$ addition increased the L* value. a* value of mineral water bottle and the MAS-T glasses are in negative values that means all of them are green but the mineral water bottle glass is greener than both MAS-T and green wine bottle glasses. Positive b* values mark to yellow and in this study, the reference, the MAS-T and wine bottle glasses are all have positive b* values. Mineral water bottle has a b* value of 34.47 and b* values of MAS-T-0 to MAS-T-3 glasses were 18.95, 23.03, 23.09 and 26.60. All MAS-T glasses are less yellow (more blue) than the green mineral water bottle glass, but the wine bottle glass is more yellow than mineral water bottle glass. Also, the $B_2O_3$ addition increased the yellowness of the MAS-T glasses.

The infra-red transmission spectra of glasses could provide some information about the structural changes. The infra-red transmission spectra of MAS-T glasses were generated over the 4000-450 $cm^{-1}$ range and shown in Figure 6.

The absorption peaks and their assignments were given in Table 7 and from these peaks structural changes in MAS-T glasses are observed. The peak at around 700 $cm^{-1}$ is assigned to ring structures of the $SiO_4$ tetrahedra or to a network Si-O-Si symmetric bond stretch (Ardelen et al., 2000).

Table 6. CIE L*a*b* values of MAS-T glasses, commercial green wine bottle and commercial green mineral water bottle

| Samples | Colouring parameters | | |
|---|---|---|---|
| | L* | a* | b* |
| Commercial green mineral water bottle | 70.33 | -26.63 | 34.47 |
| Commercial green wine bottle | 48.45 | -4.53 | 35.68 |
| MAS-T-0 | 42.91 | -3.13 | 18.95 |
| MAS-T-1 | 49.98 | -5.33 | 23.03 |
| MAS-T-2 | 50.19 | -4.64 | 23.09 |
| MAS-T-3 | 53.02 | -3.84 | 26.60 |

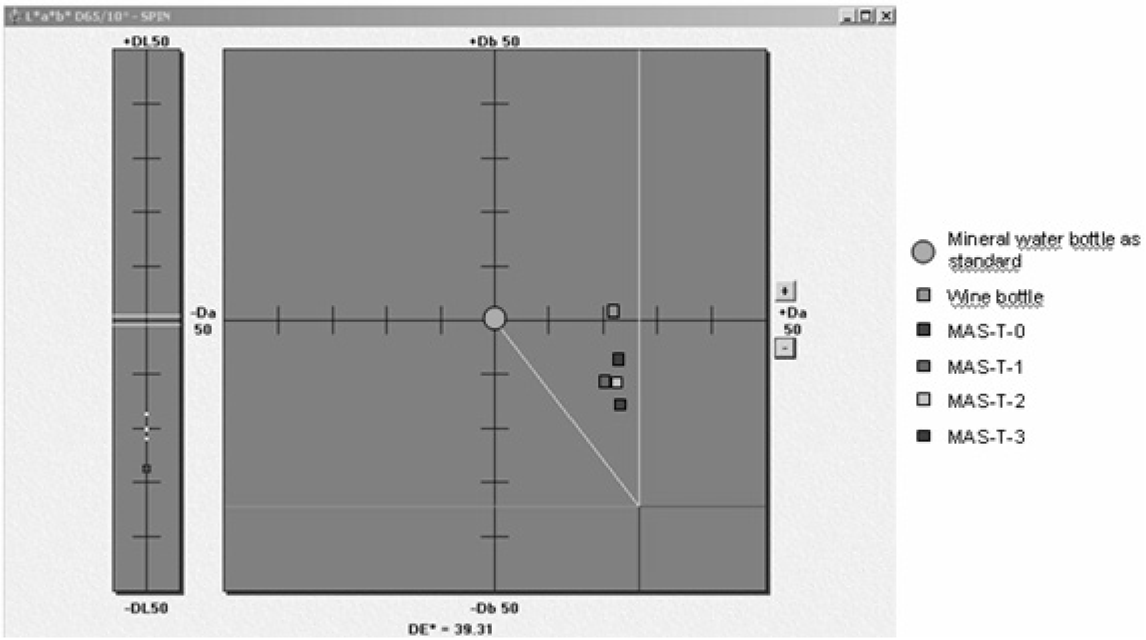



Figure 5. L*a*b* D65/10º-spin values of MAS-T glasses and commercial green wine bottle (mineral water bottle as standard)

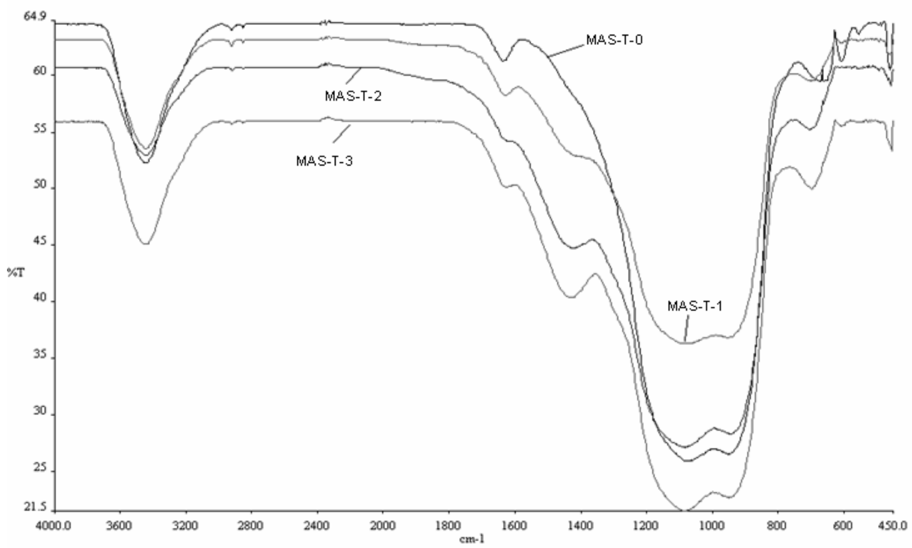


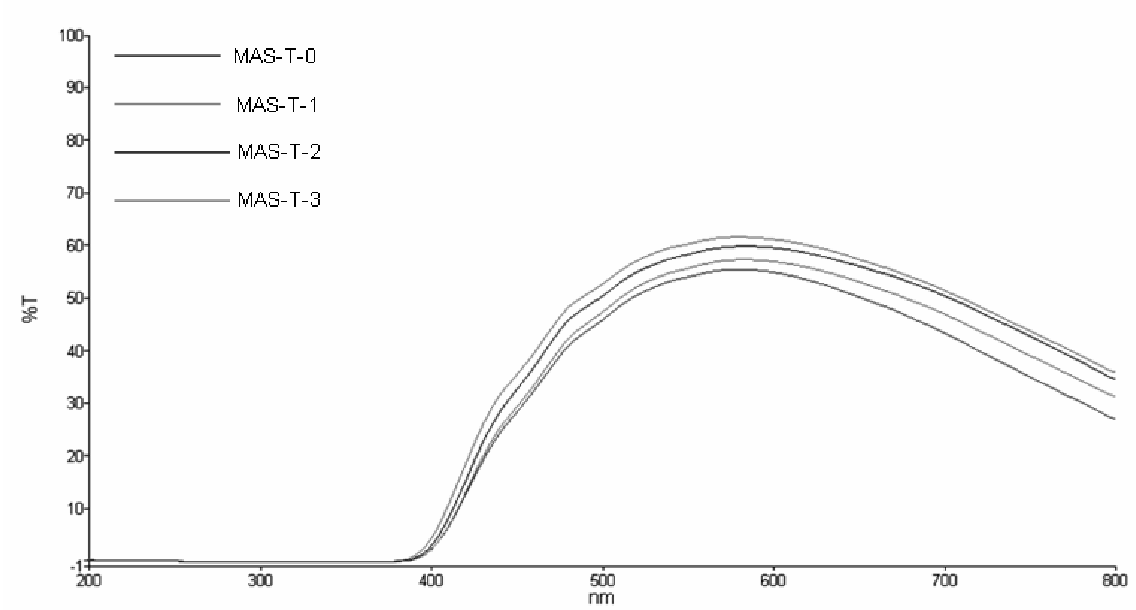

Figure 6. FT-IR curves of the MAS-T glasses

Table 7. Frequencies and their assignments for FT-IR spectra of the MAS-T glasses

| **Wave-length (nm)** | **Assignment** | **Ref.** |
|---|---|---|
| ≈ 700 | B-O-B bending vibrations | Ardelen et al (2000) |
| ≈ 770 | $O_3B$-O-$BO_4$ bending vibrations | Kamitsos et al, (1987) |
| ≈ 930 and 1060 | B-O stretching vibration of $BO_4$ units in tri, tetra and penta borate groups | Kamitsos et al, (1987) |
| ≈ 1370 | B-O stretching vibration of $BO_3$ units in meta-borate, pyroborate and orthoborate groups | Kamitsos and Chryssikos, (1991) |
| ≈ 1630 and 3450 | Stretching of OH groups and stretching and de-formation of free water | Gunay (1990) |

The absorption peak at around 930 and 1060 $cm^{-1}$ is attributed to the stretching of the Si-O bonds (Kamitsos et al, 1987). This peak is associated with the peak at about 455 $cm^{-1}$, attributed to the bending of the O-Si-O group. The absorption peak around 770 $cm^{-1}$ is assigned to the B-O-B bending vibrations (Kamitsos et al, 1987). The absorption peaks at 3450 and 1630 $cm^{-1}$ are associated with water and attributed to the stretching mode of OH groups, i. e. bonded water and the stretching and deformation modes of $H_2O$, i. e. free water, respectively (Gunay, 1990). B-O stretching vibrations of $BO_3$ units in metaborate, pyroborate and orthoborate groups have been observed at around 1370-1400 $cm^{-1}$ by Kamitsos and Chryssikos, (1991) and by Boroica et al., (2008). In the present study, it can be clearly seen in Figure 6, that at around 1400 $cm^{-1}$, B-O stretching peaks were clear for $B_2O_3$ containing MAS-T glasses (MAS-T-1, MAS-T-2 and MAS-T-3) but there is no peak for MAS-T-0 glass.

Transmission properties of MAS-T glasses in UV-VIS region were shown in Figure 7. As seen in the figure that, there is no transmission in the UV region up to 400 nm wave-length. In the VIS range (around 400 to 700 nm), the transmission is very low at lower wave-lengths and there is are around 50 to 60% transmission in MAS-T glasses around 580 nm wave-length. In MAS-T glasses, it can be seen that, there is an increase in transmittance with increasing $B_2O_3$ content. The low transmission of UV and VIS regions is a desirable property in packaging glasses (bottles) for biological protection as explained in the earlier sections. This is a comparable result to that of reported by Zhernovaya et




al (2007) for brown bottles.

Figure 7. Transmission UV-VIS spectras of the MAS-T glasses

## 4. CONCLUSIONS

The glass formation and properties of cordierite compositions from talc-based natural raw materials with boron oxide addition was studied and it was seen that cordierite glasses with green colour was produced. The addition of $B_2O_3$ to the glasses did not affect the colour of the glasses but increased the glass transition ($T_g$) values and also reduced the thermal expansion coefficient values of the glasses from 5.2226 to 5.0072ºCx$10^{-6}$, for MAS-T-0 and MAS-T-3, respectively.

Density values of the glasses showed small but linear increase with increasing $B_2O_3$ content.

Vickers hardness of the MAS-T glasses were similar even there was a very small decrease with increasing $B_2O_3$ addition.

According to colour measurements, a* value of mineral water bottle and the MAS-T glasses are in negative values that means all of them are green but the mineral water bottle glass is greener than both MAS-T and green wine bottle glasses. All MAS-T glasses are less yellow (more blue) than the green mineral water bottle glass, but the wine bottle glass is more yellow than mineral water bottle glass. By that of this result, it is observed that the $B_2O_3$ addition increased the yellowness of the MAS-T glasses.

All the MAS-T glasses showed similar green colour and no transmission in the UV region and very small transmission in shorter wave-lengths in the VIS region. The maximum transmission in VIS region was around 60% around the wave-length of 580 nm. This is an important point especially in glass packaging for biological protection of the content in the bottles, such as beverages.

Present study showed that it is possible to produce green coloured glasses with the cordierite compositions from less pure natural raw materials.

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