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**Influence of B$_2$O$_3$ doping on synthesis of MgTiO$_3$ ceramics from recycled magnesia-hercynite materials**

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**Abstract**

Herein, magnesium metatitanate (MgTiO$_3$) ceramics were synthesised using recycled magnesia-hercynite (MH) bricks as the raw materials to achieve solid waste reusing of cement kiln refractories. The recycled MH materials were mixed with anatase TiO$_2$ to investigate the effect of addition of doped B$_2$O$_3$ during the synthesis of MgTiO$_3$ ceramics at 1400 °C. Phase compositions and microstructural studies were performed using x-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. In addition, energy-dispersive spectroscopy (EDS) was conducted and the dielectric properties of the samples were studied. Results show that the addition of B$_2$O$_3$ can promote sintering, improve shrinkage, promote densification, stabilise MgTiO$_3$ lattice, and inhibit the formation of MgTi$_2$O$_5$. In addition, the presence of appropriate amount of B$_2$O$_3$ can accelerate the material diffusion and result in grain growth through the formation of intercrystalline liquid phase. Results also suggest that an increase in dielectric constant results in a decrease in dielectric loss. It was concluded that 2 wt% was the optimum amount of B$_2$O$_3$ required to obtain the most favourable synthesis rate of MgTiO$_3$ (98.2%). The samples exhibited a maximum density of 3.69 g·cm$^{-3}$ and excellent microwave dielectric properties at $\varepsilon_r = 18.28$ and $\tan\delta = 0.086$.

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**1. Introduction**

China, as one of the largest cement producing countries, consumes a large number of refractories in the cement production process. However, the used refractories are discarded as industrial waste [1–3], which results in waste accumulation and loss of non-renewable resources, thereby polluting the environment. To address this concern, recycling and reusing these spent refractories has attracted significant attention [4–7]. Magnesia-hercynite (MH) bricks have excellent performance and are widely used refractories in firing zone of cement kilns [8–10]. However, the MH bricks contain a certain amount of Fe$_2$O$_3$ (about 5%) and CaO (about 2%), which limits their reuse [1]. Therefore, it is imperative to study how the recycled MH bricks can be reused.

MgO-TiO$_2$ ceramics have shown excellent dielectric materials [11, 12], with excellent electrical, optical, and chemical properties, and thus, they play an important role in the field of functional materials [13, 14]. Among them, pure magnesium metatitanate (MgTiO$_3$) has the good microwave dielectric properties [12, 15–17]. Doping of Fe$_2$O$_3$ during the synthesis of MgTiO$_3$ could inhibit the synthesis of intermediate phase magnesium dititanate (MgTi$_2$O$_5$) [18–20]. Furthermore CaTiO$_3$ can be synthesised by doping with CaO that improves the denseness of MgTiO$_3$ grains [21, 22]. It can therefore be deduced that MgTiO$_3$ can be synthesised by using recycled MH bricks. The proposed study also showed that the formation of MgTi$_2$O$_5$ can be inhibited by impurity Fe$_2$O$_3$ and the densification of MgTiO$_3$ can be promoted by the formation of CaTiO$_3$. In conclusion, the synthesis of MgTiO$_3$ is feasible when recycled MH bricks with good economic benefits are used. This provides a theoretical basis for reusing the recycled MH bricks.

The poor dielectric properties of Mg$_2$Ti$_4$O$_9$ significantly affect the dielectric properties of MgTiO$_3$ [15–17]. In this paper, we discuss the influence of B$_2$O$_3$ doping during the synthesis of MgTiO$_3$ ceramics at 1400 °C using pre-treated MH bricks as recycled materials and TiO$_2$ as raw materials.
2. Materials and methods

A large amount of waste refractories is produced during cement production. Currently, the main method of disposing of spent refractories is to damp them in landfills, which not only pollutes the environment but also wastes the non-renewable resources, such as magnesia, found in these refractories. Therefore, this research focuses on the reuse of the recycled MH bricks.

The recycled MH bricks were crushed, ground to 0.043 mm, and soaked in water to remove harmful impurities. The recycled materials of pre-treated MH bricks (see Table 1 for chemical composition) and anatase TiO$_2$ (Aladdin’s reagent, TiO$_2$ ≥ 99%) were used as raw materials. These powders were weighed according to the molecular ratio of MgO:TiO$_2$ = 1.13:1, which were placed in ethanol and subsequently ball-milled using zirconium dioxide (ZrO$_2$) grinding media for 24 h. The mixed materials were then divided into five different samples. B$_2$O$_3$ (Sinopharm, China, analytical pure, B$_2$O$_3$ ≥ 98.0%) was added separately at 0%, 1%, 2%, 3%, and 4% in the five samples. Cylindrical samples (Φ15 mm × 2 mm) were produced by pressing isostatically at 200 MPa and sintered at 1400 °C for 3 h in a high-temperature furnace.

The shrinkages in the sintered samples were tested. Archimedes’ method was used to measure the bulk densities of samples. The oxide content of raw material was analysed by x-ray fluorescence spectrometer (XRF) using S8 TIGER, Bruker, Germany. The crystalline phases of the sintered ceramics were identified by x-ray diffraction (XRD) using X’Pert Powder, Panaco, Netherlands. The Rietveld Refinement module of the high

![Figure 1. XRD diffractions pattern of the samples. (a) 0 wt% B$_2$O$_3$; (b) 1 wt% B$_2$O$_3$; (c) 2 wt% B$_2$O$_3$; (d) 3 wt% B$_2$O$_3$; (e) 4 wt% B$_2$O$_3$.](image1)

![Table 1. Chemical composition of recycled materials by pretreated (%).](image2)

| Component | MgO | Al$_2$O$_3$ | SiO$_2$ | Fe$_2$O$_3$ | CaO |
|-----------|-----|------------|--------|-------------|-----|
| Content   | 89.35 | 2.84 | 2.06 | 3.64 | 2.11 |

![Figure 2. Yield of MgTiO$_3$ and Mg$_2$TiO$_4$ of the samples doped with different content B$_2$O$_3$.](image3)
score software was used to calculate the content of the mineral phase of the sintered ceramics. The microstructural studies and composition analysis of sintered samples were performed through field emission scanning electron microscopy (FESEM, SIGMA/HD, Carl Zeiss, Germany). The built-in energy-dispersive spectroscopy (EDS) system of the FESEM was used to detect oxides in micro areas of each sample. The dielectric constant and dielectric loss of samples were tested using LCR meter AT610, Anbo, China, at 200 kHz and the dielectric constant of the materials was calculated using the capacitance.

3. Results and discussion

3.1. Phases and compositions
XRD patterns of MgTiO₃ ceramics doped with B₂O₃ and sintered at 1400 °C are shown in figure 1. Figure 2 showed the effect of B₂O₃ addition on the yield of MgTiO₃ and Mg₂TiO₄ in the samples. As shown in figure 1, the main crystal phase of the sintered sample was MgTiO₃, and the secondary phases were Mg₂TiO₄ and CaTiO₃. The diffraction peaks at 17°–31° were amplified. With an increase in the doping amount of B₂O₃, the peak intensities of Mg₂TiO₄ at 18.5° and 30° initially increased and then decreased. The phase elements, such as aluminium, iron and silicon, were not detected in the XRD because the elements were in solid solution in the
crystal of magnesium metasilicate. Specifically, $\text{Al}^{3+}$ and $\text{Si}^{4+}$ replaced $\text{Ti}^{4+}$ and $\text{Fe}^{2+}$ replaced $\text{Mg}^{2+}$, resulting in a magnesium metasilicate crystal with defective structure. The strongest peak lattice of magnesium metasilicate increased and diffraction angle moved to the small angle direction.

Doping with 1 wt% $\text{B}_2\text{O}_3$ produced the highest yield of $\text{Mg}_2\text{TiO}_4$, as shown in Figure 2. With a further increase in $\text{B}_2\text{O}_3$, $\text{Mg}_2\text{TiO}_4$ did not synthesise, suggesting that the addition of $\text{B}_2\text{O}_3 \geq 2\%$ inhibited the synthesis of $\text{Mg}_2\text{TiO}_4$. Doping $\text{MgTiO}_3$ with 2 wt% of $\text{B}_2\text{O}_3$ produced the highest yield at 98.2%. The added $\text{B}_2\text{O}_3$ not only worked as an additive for combustion but also increased the density of the Magnesium metasilicate. However, it prevented the generation of $\text{Mg}_2\text{TiO}_4$. When $\text{Fe}^{2+}$ replaced $\text{Mg}^{2+}$, some parts of raw materials would full of $\text{Mg}^{2+}$, causing more effective precipitation of $\text{Mg}_2\text{TiO}_4$. When the $\text{B}_2\text{O}_3$ content was greater than 1%, it preferentially reacted with $\text{Mg}^{2+}$ to produce $\text{Mg}_3\text{B}_2\text{O}_6$ ceramic due to its low melting point and high reactivity with $\text{MgO}$. Under this condition, the generation of $\text{Mg}_2\text{TiO}_4$ would be precluded for the lack of $\text{Mg}^{2+}$.

### 3.2. Sintering property

Figures 3 and 4 demonstrated that with an increase in $\text{B}_2\text{O}_3$, the shrinkage and density of the samples first increased and then decreased at 1400 °C. The synthesis of $\text{MgTiO}_3$ from $\text{TiO}_2$ and the recycled MH materials was a solid-state reaction. So when the appropriate amount of $\text{B}_2\text{O}_3$ was added, $\text{B}_2\text{O}_3$ melted to form a liquid phase at 450 °C, which promoted the diffusion and transfer of materials. Addition of $\text{B}_2\text{O}_3$ can effectively reduce the sintering temperature of ceramics, promote sintering, improve the shrinkage and increase ceramics density.

![Figure 5](image1)

**Figure 5.** SEM micrographs of samples with different amounts of $\text{B}_2\text{O}_3$: (a) No $\text{B}_2\text{O}_3$; (b) 1 wt% $\text{B}_2\text{O}_3$; (c) 2 wt% $\text{B}_2\text{O}_3$; (d) 3 wt% $\text{B}_2\text{O}_3$; and (e) 4 wt% $\text{B}_2\text{O}_3$.

| Points | Mg  | Ti  | Ca  | Fe  | Si  | O    |
|--------|-----|-----|-----|-----|-----|------|
| A      | 18.42 | 20.63 | —   | 0.51 | —   | 60.44 |
| B      |      | 20.52 | 19.23 | —   | —   | 60.26 |
| C      | 7.93 | 14.34 | 13.32 | —   | 4.83 | 59.58 |

Table 2. EDS results for each point in Figure 5.

Crystal of magnesium metasilicate. Specifically, $\text{Al}^{3+}$ and $\text{Si}^{4+}$ replaced $\text{Ti}^{4+}$ and $\text{Fe}^{2+}$ replaced $\text{Mg}^{2+}$, resulting in a magnesium metasilicate crystal with defective structure. The strongest peak lattice of magnesium metasilicate increased and diffraction angle moved to the small angle direction.
In addition, it promotes shorter distances between particles, accelerates the chemical reaction of particles, promotes the growth of grain particles [23, 24], and finally enhances the process of sample densification. The density of the samples was observed to have increased and the maximum density recorded was 3.69 g·cm$^{-3}$.

3.3. Microstructure
The SEM morphology of samples with different amounts of B$_2$O$_3$ at 1400 °C was shown in figure 5. In the figure, pores were black, MgTiO$_3$ was grey-black, and glass phase was bright grey-white. Table 2 shows the EDS result of each point in figure 5. From the figure, it can be deduced that an increase in the addition of B$_2$O$_3$ resulted in the phase transition from pure solid-state sintering to liquid-phase sintering. The addition of B$_2$O$_3$ increased the intercrystalline liquid-phase content between grains. The glass phase liquid film (point C) was formed between MgTiO$_3$ grains, and the neck region was formed between the adjacent MgTiO$_3$ grains. The material transfer was rapid, and the grains were continuously pulled closer due to the capillary effect. To achieve the continuous and close accumulation of grain particles, the grain size of MgTiO$_3$ increased from ~20 to ~55 μm, and the grains were gradually transformed from granular to lamellar. At 0 wt% of B$_2$O$_3$, the grain size of MgTiO$_3$ was small (point A), the CaTiO$_3$ phase was observed on all the grain boundary (point B in figure 5(a)). Figure 5(b) shows that addition of 1 wt% B$_2$O$_3$ resulted in reduced pores of the samples, promoted grain growth of the MgTiO$_3$ grains, encouraged precipitation of glass phase between the grains, and enhanced the formation of liquid film.
(point C in figure 5(b)). It was observed that, after adding 2 wt% B$_2$O$_3$, the driving force for liquid-phase sintering continued to increase, and the liquid film on the grain boundary became thinner after grain rearrangement, as shown in figure 5(c). The glass-liquid-phase film became thinner and the pressure increased between the MgTiO$_3$ grains, which continued to shorten the distance between the centres of the two adjacent Mg$_2$TiO$_4$ grains. The grains continued to grow, and the sample continued to shrink, which was consistent with the experimental results in figure 3. With increase in B$_2$O$_3$ greater than 2 wt%, more glass phases were formed resulting in higher grain boundary energy of the MgTiO$_3$. With rapid migration of grain boundary, there was an increase in grains size and the grain boundary was blurred. Therefore, the addition of B$_2$O$_3$ made CaTiO$_3$ and other ions form glass phase materials fill between grain boundaries, which promoted sintering and increased grain size.

The B$_2$O$_3$ formed a liquid phase at the grain boundaries, which promoted sintering. The resistance to diffusion was less in the glass phase and the movement rate of the grain boundaries was accelerated. Consequently the growth rate of the grains was accelerated, and the promotion of sample shrinkage. However, excessive addition of B$_2$O$_3$ resulted in the grain boundary blurring and lower shrinkage. It should be noted that when the recycled raw materials were used to synthesise MgTiO$_3$ ceramics, the optimal addition amount of B$_2$O$_3$ was 2 wt%, which prevented the formation MgTiO$_3$ ceramics from Mg$_2$TiO$_4$ thereby resulting in the appropriate shrinkage and grain size.

3.4. Dielectric properties

Figures 6 and 7 show the dielectric constant and dielectric loss of the samples doped with different content of B$_2$O$_3$. The graph shows that as the amount of B$_2$O$_3$ increased, the dielectric constant of the samples first increased and then decreased. However, an opposite behaviour was observed for the dielectric loss: it initially decreased and then slowly increased.

Further, at B$_2$O$_3$ < 2 wt%, the dielectric constant of the samples was increased, and the dielectric loss decreased significantly. This was because the Mg$_2$TiO$_4$ synthesis was inhibited, and the density of the samples increased [12, 15, 25]. This was consistent with the variation in the XRD and the density studies. At 2 wt% B$_2$O$_3$, the maximum dielectric constant was 18.28, and the dielectric loss was 0.086. The excess addition of B$_2$O$_3$ (≥3 wt%) resulted in the generation of considerable amount of liquid phases resulting in a reduction in density, a decrease in dielectric constant and a slow increase in dielectric loss for the samples. In general, the dielectric constant of MgTiO$_3$ ceramics is ~17 [26, 27], and thus, the samples considered in this study met the requirements. To reduce heat loss and energy consumption, the dielectric loss of the dielectric ceramic material should be reduced [25]. Therefore, it is important to prepare dielectric ceramic materials with high dielectric constant and low dielectric loss by the addition of B$_2$O$_3$ to MgTiO$_3$ ceramics.

4. Conclusions

B$_2$O$_3$ could accelerate the sintering process and promote densification of sintering, and transform the MgTiO$_3$ synthesis from pure solid-state reaction to liquid-solid reaction. The intercrystalline liquid phase accelerated elemental diffusion, stabilised the grain lattice of MgTiO$_3$, accelerated grain growth, and inhibited Mg$_2$TiO$_4$ synthesis.

At B$_2$O$_3$ content less than 2 wt%, the sample shrinkage gradually increased, thereby increasing the densification of the sample. At 2 wt% B$_2$O$_3$, the Mg$_2$TiO$_4$ was not formed in MgTiO$_3$ ceramics. The maximum synthesis rate of MgTiO$_3$ was 98.2%, and the sample exhibited the maximum density at 3.69 g·cm$^{-3}$. Further increase in B$_2$O$_3$ ≥ 3 wt% accelerated the growth of MgTiO$_3$ grain but led to grain boundary blurring, which was not conducive to the densification of the sample. In conclusion, the optimum amount of B$_2$O$_3$ was 2 wt%. Addition of B$_2$O$_3$ led to a reduction in Mg$_2$TiO$_4$ phases, increased sample density, increased the dielectric constant, and subsequent decrease in dielectric loss for the samples. It was further observed that 2 wt% of B$_2$O$_3$ produced excellent microwave dielectric properties at $\varepsilon_r = 18.28$ and tan$\delta = 0.086$.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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