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Synthesis of α-cordierite based glass-ceramic from Bayan Obo tailing and fly ash through volume crystallization

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Abstract. The α -cordierite glass-ceramics samples were synthesized from Bayan Obo mine tailing and fly ash through volume crystallization as a result of using (NH₄) H₂PO₄ and MgF₂ as the nucleating and glass network relaxing agents, respectively. The application of some natural impurities within above wastes, i.e., CaO, Na₂O, and K₂O, as the flux to lower the viscosity of the base glass, also contributed to this successful synthesis. The density, bending strength, Vickers hardness, dielectric constant and loss within the 1-10 MHz testing frequency range, and the average coefficient of thermal expansion of the glass-ceramic were characterized at 2.56 g cm⁻³, 113.5±15.87 MPa, 7.04±0.26 GPa, ~7.3, ~10⁻² and 1.86×10⁻⁶ °C⁻¹ respectively. These properties make this solid waste-derived material a lucrative candidate for replacing the industrial cordierite in metallurgy and construction. The results of this study may serve as a useful example of the re-utilization of solid wastes similar to Bayan Obo tailing with high added value.

1. Introduction

The α -cordierite (Mg₂Al₄Si₅O₁₈) glass-ceramic is a material of outstanding commercial and technical importance because of its low dielectric permittivity and loss, high mechanical strength, and excellent thermal stability and strong resistance to thermal shock [1-2]. However, it contains more than 50 wt% of SiO₂ in its starting materials [3]. This characteristic makes its parent glass very resistant to crystallization. Therefore, α -cordierite glass-ceramics are not easy to produce by the mechanism of volume-crystallization [4]. As one of the counteracting measures to this problem, the sintering fabrication process has widely been used, in which surface defects of the starting material powders can be employed as the hetero-nucleating sites to enhance the crystallization of α -cordierite grains[3, 5-6]. The glass-ceramics fabricated by this process have inherent pores that may inevitably deteriorate both the mechanical and dielectric property of the final product. Alternatively, the high-temperature (e.g., 1150°C) volume crystallization method can also be used to produce α -cordierite glass-ceramics, wherein some expensive nucleating agents [7], such as TiO₂, ZrO₂, and flux materials, for example, CeO₂, were used. Recently, the ever-escalating scarcity of resources has been calling for better use of different natural resources and industrial solid wastes. The R&D of the cordierite based material should not be an exception. As an answer to this calling, drift sand [8], kaolin [9], fly ash [10], gold tailing [11] and ferrochromium slag [12] were successfully adapted as the starting materials to fabricate cordierite glass-ceramics. However, to the best of our knowledge, no attempt has ever been made on Bayan Obo tailing. The accumulation of this specific industrial solid waste has reached 170

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million tons in the dam for its reservation at Bao Tou and posed as a constant threat to the environment and people nearby.

In this paper, we report the successful fabrication of an $(NH_4)H_2PO_4$ and MgF₂ co-doped α cordierite glass-ceramic from Bayan Obo tailing and fly ash through the volume crystallization process without using TiO₂ or ZrO₂, the more commonly applied nucleating agents with high values. The factors affecting the fabrication was analyzed using techniques, such as DTA, XRD, and SEM orientation imaging techniques and discussed with the relevant works of peers.

2. Experimental

The compositions of Bayan Obo tailing and the fly ash were decided using the XRF and the traditional chemical analysis method, respectively, and their results are listed in table 1. Referencing to this table and the composition of cordierite glass, the starting constituents of our cordierite glass-ceramic were designed as (all in weight ratios): 13.57% Bayan Obo tailing, 29.32% fly ash, 25% industrial grade silica sand, 11.58% Al₂O₃, 7.48% MgO, 6.81% borax, 4.84 % MgF₂, and 0.81% (NH₄)H₂PO₄.

Table 1. Constituents of Bayan Obo tailing and the fly ash used in this study.

					0	5			
Constituents	MgO	Al_2O_3	SiO ₂	CaO	Fe_2O_3	R_2O^*	P_2O_5	Loss	Other
Tailings	11.76	1.89	14.21	15.87	16.56	2.71	1.65	25.59	9.76
Fly ash	0.78	30.71	51.68	3.90	8.60	2.28	-	-	-
* R ₂ O: Na ₂ O and K ₂ O in total									

The well-mixed raw materials (200g) were melted in a corundum crucible in air at 1580 °C for four hours. The obtained glass melt was cast in a preheated (600 °C) steel mold. The obtained glass plate was transferred immediately to an electric furnace also preheated to 600 °C, wherein it was further annealed for three hours to release the internal stress generated in the process of casting. A small fraction of the aforementioned melt was directly quenched into cold water to create some frit particles. Then those particles were ground and measured in the differential thermal analysis (DSC- NETZSCH STA 449C) with pure Al₂O₃ as the reference standard within the temperature range of the ambient air to 1200 °C at a heating rate of 10 °C min⁻¹. Based on the endothermic inflection and the exothermic peak temperature on the DSC curve, the glass transition point (Tg) and crystallization point (Tc) were assessed and used as the reference to determine the temperatures for the final nucleating and crystallizing heat-treatments respectively. The soaking time for these two heat-treatments was equally set at 2.5 hours with a heating rate of 2.5 K min⁻¹. The crystalline phase assemblage of the heattreated sample was identified by a Panalytical X'pert powder XRD. Based on this result, the crystallinity of the sample was calculated according to the Rietveld method. The surface morphology was examined on a field emission scanning electron microscope (FESEM-Zeiss Supra 55) operating in both second electron (SE) and orientation imaging (OIM) modes. According to the standard JT/T 263-93, bending strength was determined by the three-point method with spans of 15 mm at a cross-head speed of 0.5 mm min⁻¹ on a Universal Testing Machine (CSS-88000) using samples with dimensions of 3×4×40 mm. For each measurement, the reported value was the average of six samples. The hardness was determined on a Vickers hardness tester (HV-SOA) with a load of 3 N and a dwell time of 10 s. Testing results of six samples were averaged and reported as the Vickers hardness. The coefficient of thermal expansion (CTE) was measured by a thermal expansion tester (ZRPY-1400) within the temperature range of 100-600 °C using 5×5×50 mm samples. The heating rate of the CTE test was 10 K min⁻¹. The classic parallel plate method was used to determine the dielectric constant and loss tangent of the final material on a Keysight 4294 A RLC meter at the frequency range of 1-10 MHz.

3. Results

DSC results on the cordierite melt frit powder are depicted in figure 1. It shows $T_g = 720^{\circ}$ C and $T_c = 1000.4^{\circ}$ C. The only exothermal peak marked by T_c is apparently a result of the formation of α -

cordierite, the single main crystalline phase confirmed by of the XRD pattern of the obtained cordierite glass-ceramic depicted in figure 2.

Referencing to the as measured T_g , T_c and also our experience, the temperature for the nucleating and crystallization heat-treatment were set at 760 and 1050 °C respectively to finalize the fabrication of our cordierite glass-ceramic. As shown in figure 2, α -cordierite (JCPDS: 01-082-1884) is the main crystalline phase. Besides, figure 2 also confirms the formation of just a small amount of CaFeO₄ (JCPDS: 00-003-0804) as the secondary phase. The crystallinity of the whole sample was calculated at around 85% with a residual error value of <14.89%, while the crystallinity of α -cordierite alone was determined at over 83%.





Figure 1. DSC result of the frit powder obtained by pouring a fraction of the melt into water.

Figure 2. XRD pattern of the cordierite glassceramic fabricated mainly from Bayan Obo mine and fly ash.

The SEM photo shown in figure 3 exhibits that there are some darker blocks embedded within the light gray matrix of the sample. These blocks resemble those α -cordierite crystals closely in the cordierite based glaze for conventional floor tile [13]. Therefore, they should be the α -cordierite main phase identified in our XRD result.



Figure 3. SEM photo of the cross-section surface of the as studied cordierite glass-ceramic.



Figure 4. Orientation imaging (OIM) photo of the as studied cordierite glass-ceramic.

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The OIM-SEM photo of the sample material using the lattice parameters of α -cordierite as the precondition is presented in figure 4. The color contrast in such picture was generated by the electrons diffracted by different crystalline planes of the crystals on the sample surface. Thus the shape of a colored area represents the shape of a crystal. It is obvious the colored regions in figure 4 strongly resemble the α -cordierite crystals in figure 3. Therefore, this result further confirms the above identification of those darker blocks as α -cordierite crystals, and their different color in figure 4 suggests a random distribution of those α -cordierite crystals within the matrix.

Another thing worth noticing here is the surface of the gray matrix area in figure 3 should be much rougher than the surface of α -cordierite crystals, since only rougher surface can generate more SE signals, thereby resulting in a stronger contrast (being whiter in color) in an SEM picture. This fact suggests the matrix should also contain some cordierite crystals, whose size was too small to generate detectable diffracted electron signals in the OIM photo shown in figure 4. Because the phase boundaries between small cordierite crystals and residual glass were less resistant to acid erosion and could have been etched out by light HF solution in the sample preparation process for SEM observation, yielding a rough surface as observed in the aforementioned matrix areas. This deduction is following the above XRD result which shows the crystallinity of this sample is more than 80%.





Figure 5. Variation of the Coefficient of thermal expansion (CTE) of the as studied cordierite glass ceramic.

Figure 6. Variations of the dielectric constant and loss of the as studied cordierite glass.

The variation of the coefficient of thermal expansion (CTE) of the as-prepared cordierite glass over the temperature range of 100-600 °C is illustrated by figure 5. The recorded CTE value increased continuously from 0.25×10^{-6} to 3×10^{-6} °C⁻¹ and averaged at 1.86×10^{-6} °C⁻¹. This result is comparable with the earlier reported CTE values for the cordierite glass-ceramics fabricated from pure chemicals [14]. An opposite trend can be observed in the variation of the dielectric constant with the increase of frequency in figure 6, which exhibits the dielectric constant decreased slowly from about 7.8 to slightly over 7 within the tested frequency range of 1 to 10 MHz. Meanwhile, the dielectric loss varies between 0.1 and 0.0024. Both dielectric parameters were somewhat larger than the commonly reported ones [5]. This is a result of the decrease in the network connectivity introduced by those natural impurities within the raw materials, so ions within the network of the final material can be more flexible under the alternative electrical field, thereby yielding a higher dielectric constant and loss [15].

Table 2. Summary table of some physical properties of the as-fabricated α -cordierite glass-ceramic (GC) and those reported in peer study.

Reference	Density I (g/cm ³)	Bending strength (MPa)	Vickers hardness (GPa)	Averaged CTE over 100~600°C (×10 ⁻⁶ / °C)
α-cordierite GC	2.56	113.5±15.87	7.04 ± 0.26	1.86
Industrial cordierite [16]	2.5	110	-	2.5

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Moreover, the additional tests showed that the density of this solid-waste derived material was 2.56 g/cm⁻³, the bending strength was about 113MPa, and the Vickers hardness was about 7 GPa. These results, together with the obtained averaged CTE values, are listed in table 2. The corresponding values of the industrial cordierite are also listed in this table for comparison. It shows the mechanical and thermal properties of our waste derived α -cordierite glass-ceramic are generally comparable to those of industrial cordierite. Therefore, this glass-ceramic can be a feasible candidate to replace the industrial cordierite.

4. Discussion

As it has been revealed, the T_c in this study was 1000.4 °C, considerably lower than those commonly reported ones at around 1150 °C [4], suggesting the crystallization of α -cordierite from this wastederived material has become relatively easier. The reason should be related to those chemical ingredients within the raw materials other than forming the basic crystalline structure of cordierite. Numerous studies have shown CaO [17], Fe₂O₃[18] and R₂O [19] (Na₂O and K₂O), the natural residing impurities within Baiyan Obo tailing and the locally collected fly ash can all be used as a flux to reduce the viscosity of cordierite melt, therefore benefiting the crystallization of α -cordierite. Meanwhile, P₂O₅, one of the decomposing products of (NH₄)H₂PO₄, can be applied as the nucleating agent and flux at the same time [20]. On the other hand, MgF₂ may decrease the connectivity of the silicate glass network by substituting O with F [15]. These three factors can all contribute to our success in fabricating α -cordierite glass-ceramic through volume crystallization at 1050 °C without using TiO₂, the commonly applied nucleating agent of much higher value than P₂O₅.

Noteworthy is that no trace of μ -cordierite could detected in this sample. Peer study has shown μ cordierite may deteriorate the mechanical properties of cordierite based material through creating internal micro-fractures during the process of its crystalline structure transforming into that of α cordierite [21]. Therefore, our result indicates the formation of this harmful secondary phase has been completely suppressed in the context of as a designed composition of raw materials. This could be a contributing factor to the observed good mechanical property of the as investigated material.

5. Conclusions

Bayan Obo tailing and fly ash, together with a small fraction of (NH₄) H₂PO₄ and MgF₂ were used to fabricate α -cordierite glass-ceramic using the volume crystallization process characterized by a 2.5-hour nucleating process at 760 °C followed by a crystallizing treatment at 1050 °C for 2.5 hours. The glass transition temperature (T_g) and the crystallization temperature (T_c) of α -cordierite were determined at 720 and 1000.4 °C. Block-alike α -cordierite grains were observed to be randomly distributed within the bulk of the material. The density, bending strength and Vickers hardness of this solid wastes derived material were determined as 2.56 g cm⁻³, 113.5±15.87 MPa, and 7.04±0.26 GPa respectively. Meanwhile, the dielectric constant and loss within the 1-10 MHz frequency range were found out to be at around 7.3 and 10⁻² respectively, and the average coefficient of thermal expansion over the 100-600 °C temperature range was at around 1.86×10⁻⁶ °C⁻¹.

Acknowledgments

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