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Comprehensively utilizing waste coal gangue to fabricate high strength glass-ceramics

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Waste coal gangue was utilized for the fabrication of strength glass-ceramics for environmental management. The optimal utilization rate of coal gangue is 55 wt.% when the utilization rate of another mineral material bauxite is 35 wt.%. The mullite showing high strength is the main crystal phase in the sintered glass-ceramics. The effect of various processing parameters on the microstructure and mechanical performances of the sintered glass-ceramics was systematically studied. Mineralization agent $BaCO_3$ and $MnCO_3$ resulted in remarkable enhancement of the mechanical properties of the sintered glass-ceramics. The strength of 148.36-156.12 MPa, water absorption of 0.17-0.02%, and a density of 2.66-2.68 g/cm^3 were achieved for the sintered glass-ceramics. The process of forming and sintering also showed a remarkable effect on the microstructural and mechanical properties. By optimization experiments, optimal processing parameters were also determined.

Keywords: Coal gangue; Glass-ceramics, Waste management, Maximal utilization ratio, Process optimization, Mechanics property.

Introduction

Glass-ceramics are attractive materials used in various applications such as building materials, cooking ceramics, machinable ceramics, bio-ceramics, electrical ceramics, glass semiconductors in thermal insulation, optical materials, etc. [1-6]. From a point of the raw material, utilizing the industrial solid wastes were widely used to fabricate the g;ass-ceramics and cecrents et al. [7-10].

Coal gangue is a category of solid industrial waste. This waste material is largely produced in coal production. The amount produced in China is reached above several million tonnes and increases by about one million tonnes per year. To prevent its pollution to air and river environments and save natural resource, the comprehensively utilizing the coal gangue are urgent for efficient environmental management. However, the ratio of utilizing coal gangue is greatly limited. The coal gangue contains a high alumina of ~30 wt.% and a high silica of ~62 wt.%, and so has been used to produce cement [11-13], cement [14], ceramics [15, 16], glass-ceramics [17, 18], brick [19, 20], zeolite [21], lightweight aggregate [22], and so on. The glass-ceramics mainly contains the crystals and amorphous phase that is composed of SiO_2, Al_2O_3, CaO, and/or MgO. The mullite and some other crystals composed of both alumina and silica are favorable for the high strength of the glass-ceramics. The high content of SiO_2 and Al_2O_3 makes the coal gangue is very suitable to fabricate the glass-ceramics having high mechanical properties.

For sintering high strength glass-ceramics, the crystal phase and its size and content are critical factors. In general, mullite and other crystals composed of both aluminium and silicon will be favorable for the high strength of the glass-ceramics. Meanwhile, the nucleating agent and some process parameters are the deterministic factors for the size and content of the formed crystal phase as well as the density of the sintered glass-ceramics.

This work focuses on the fabricating the glass-ceramics by utilizing waste material coal gangue and the optimizing coal gangue utilization ratio, nucleating agent, and processing parameters. The glass-ceramics with the mullite as main crystal phase were successfully obtained by selecting the reasonable prescriptions of the glass-ceramics in the condition of considering the maximal utilization rate of the coal gangue. The optimization of nucleating agent and process parameter were also focused to further realize the enhancement of property of the sintered glass-ceramics.

Experimental Procedures

Mullite ($Al_6Si_2O_{13}$) generally has high strength and so was designed as the main crystal phase. The mullite ($Al_6Si_2O_{13}$) contain higher alumina than the coal gangue (Table 1). Thus, the bauxite with high alumina content was utilized to be in favor of the formation of mullite crystal phase. Clay as an adhesive was utilized

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Table 1. The composition of the raw materials (wt%)

Raw material	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	K_2O	Na_2O	Ingition loss
Coal gangue	62.50	20.80	2.12	4.83	3.14	0.83	3.12	3.17	0.70
Bauxite	7.25	76.25	1.00	1.00	1.50	1.50	0.00	0.00	11.50
Clay	41.03	37.71	2.66	0.46	0.14	0.14	0.68	0.54	14.18
Limestone	1.51	0.00	55.28	0.00	0.00	0.00	0.00	0.00	43.22
Steatite	62.82	1.03	2.06	31.93	0.10	0.00	0.00	0.00	2.06

to enhance slurry formability. Besides, small amounts of steatite and limestone were used as additives; and $BaCO_3$, $MnCO_3$, and $MgCO_3$ were used as mineralizers. The sodium tripolyphosphate (STPP) and methylcellulose (CMC) as water reducers were utilized to decrease the slurry viscosity. The chemical composition of the bauxite and clay together with coal gangue and some mineral minerallizers is listed in Table 1. In consideration of the utilization ratio of the coal gangue, the basic prescriptions were designed as listed in Table 2.

Typical sintering processes of the designed glass-ceramics are mentioned below: the raw materials were first mixed according to the designed prescriptions. The mixtures were filtered through 10 mesh, wet-milled at the ratio of raw materials : ball : water = 1 : 2.5 : (0.3-0.5) for 15-25 min and then filtered through 120 mesh (Aperture: 0.045 mm, ASTM). As prepared mixtures were undergone a 3-5 h drying of 50-70 ºC. The 200 g each of the dried mixtures was mixed with 5 g STPP and 5 g CMC and ball-milled using the appropriate amount of water for 12 min. The formed slurries were sifted with a serve (80 mesh, aperture: 0.180 mm, ASTM). The ~0.1% residue above the sieve only remained. The slurries were dried at 50-70 ºC for 3-5 h. The formed powders underwent a pulverization and then sifted with a sieve (55 mesh, aperture: 0.280 mm, ASTM). The fine powders were sprayed by water and sintered to form prilled grains. The prilled grains were sifted with a sieve (20 mesh, aperture: 0.850 mm, ASTM). The fine grains were undergone re-spraying water and then processed to be the samples for the measurement of flexural strength. The formed samples were then pressed at 25-35 MPa and dried at 50-100 ºC for 24 h. The large grains on the sieve were dried at 80 ºC for 4 h. The dried samples and large grains were finally sintered at 1290-1430 ºC for 30-90 min at a heating rate of 5-10 ºC/ min.

Table 2. The basic prescriptions of samples (wt%)

No	Coal gangue	Bauxite	Clay	Steatite	Limestone
1#	60	30	5	3	2
2#	55	35	5	3	2
3#	50	40	5	3	2
4#	45	45	5	3	2
5#	40	50	5	3	2

The sintered glass-ceramics samples were characterized with D/Max-2200PC X-ray diffractometer (XRD, $CuK_{\alpha 1}$, λ=0.15406 nm), S-570 scanning electron microscopy (SEM), and the flexural strength measurement on 401/3 strength tester. The water absorbance (A_w) was measured on the sintered grain samples. On the measured W_d and W_h, the A_w was specified by the following relation:

$$A_w = \frac{W_h - W_d}{W_d}$$

In which, W_d is the weight of some grains that undergone the drying at 110 ºC for 3 h, W_h is the weight of the above-used grains undergone the soaking in the water for 36 h at room temperature followed by erasing the surface water with a wet towel. The density (d) was measured on the sintered grain samples, and specified with the following relation:

$$d = \frac{m_0}{m_1}$$

Where m_0 is the mass of some grain samples that undergone the 3 h drying at 105-110 ºC, m_1 is the mass of the above-used grain samples when immersed in the water at room temperature. The withdrawn grains underwent the erasion of the surface water with a wet towel.

All the property measurements were repeated three times to obtain accurate results.

Results and Discussion

The five samples with the basic prescriptions listed in Table 2 were first tested to determine optimal utilization ratio of the coal gangue. Fig. 1 shows the variations of flexural strength and water absorbance of glass-ceramics fabricated with basic prescriptions as a function of sintering temperature. The glass-ceramics fabricated with prescription 2# shown a maximal strength and minimal water absorbance in the sintering temperature range of 1290-1430 ºC. Therefore, the utilization ratio of 55% is determined for the coal gangue. The prescription 2# was further studied by adding various mineralizers. Table 3 lists the new prescriptions. Fig. 2, 3, and 4

Table 3. The prescriptions of samples containing various mineralizers (wt.%)

No	Coal gangue	Bauxite	Clay	Steatite	Limestone	$BaCO_3$	$MnCO_3$	$MgCO_3$
6#	55	35	5	3	2	3	0	0
7#	55	35	5	3	2	0	3	0
8#	55	35	5	3	2	0	0	3
9#	55	35	5	3	2	3	3	0
10#	55	35	5	3	2	3	0	3
11#	55	35	5	3	2	0	3	3
12#	51	33	5	3	2	3	3	

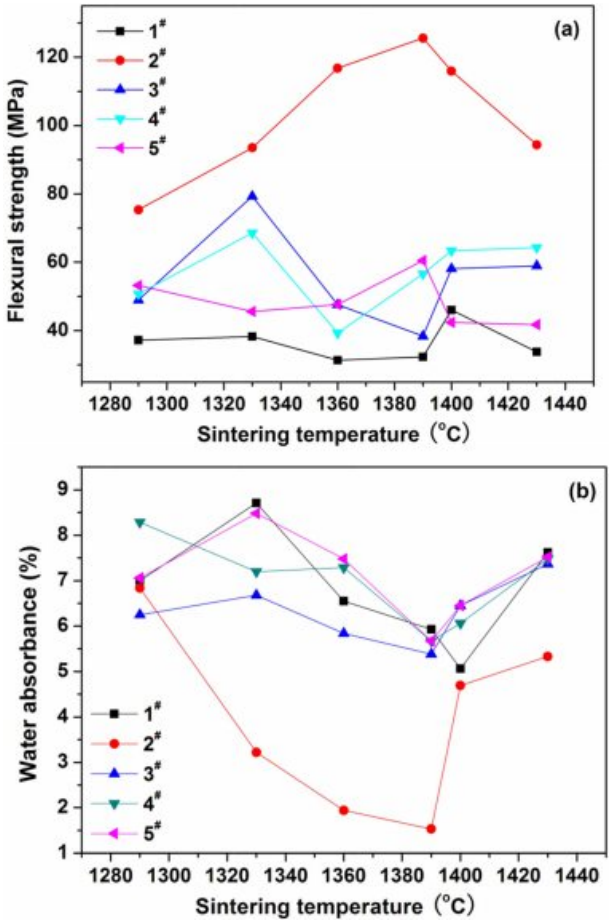

Fig. 1. Variations of (a) flexural strength and (b) water absorbance of the glass-ceramics fabricated with basic prescription 1-5# with sintering temperature (Sintering time: 30 min; milling time: 20 min; forming pressure: 30 MPa).

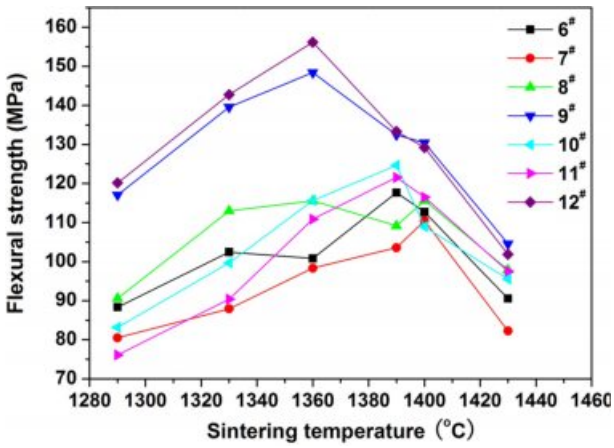

Fig. 2. Variations of flexural strength of the glass-ceramics fabricated with prescription 6-12# with sintering temperature (Sintering time: 30 min; milling time: 20 min; forming pressure: 30 MPa).

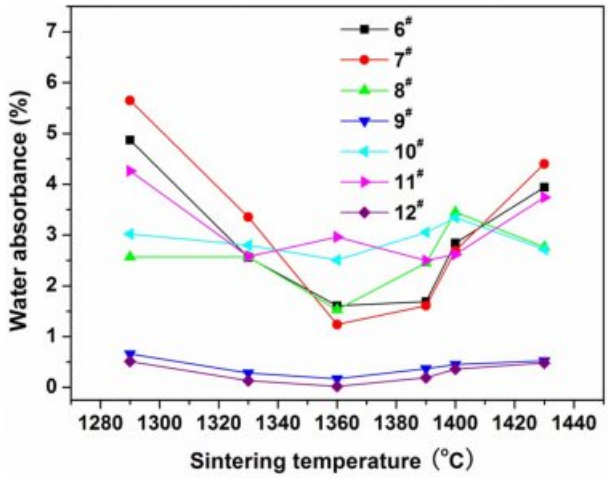

Fig. 3. Variations of water absorbance of the glass-ceramics fabricated with prescription 6-12# with sintering temperature (Sintering time: 30 min; milling time: 20 min; forming pressure: 30 MPa).

illustrate the properties of the glass-ceramics formed at the press of 30 MPa and sintered at different temperatures for 30 min. $BaCO_3$ and $MnCO_3$ co-adding (prescription 9#) lead to better effect, achieving a minimal water absorption (0.17%), maximal flexural strength (148.36 MPa), and maximal density (2.66 g/cm^3) at sintering temperature of 1360 °C. Whereas, the $BaCO_3$ and $MnCO_3$ co-substitution for the small amount of coal gangue (prescription 9#) lead to an optimal effect. That is, minimal water absorption (0.02%), maximal flexural strength (156.12 MPa) and density (2.68 g/cm^3) are

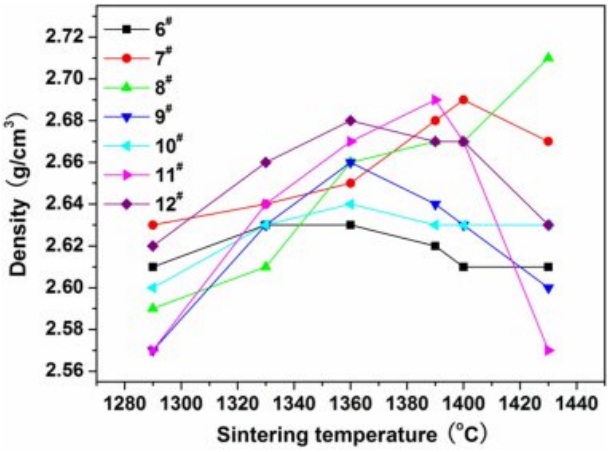

Fig. 4. Variations of the density of the glass-ceramics fabricated with prescription 6-12# with sintering temperature (Sintering time: 30 min; milling time: 20 min; forming pressure: 30 MPa).

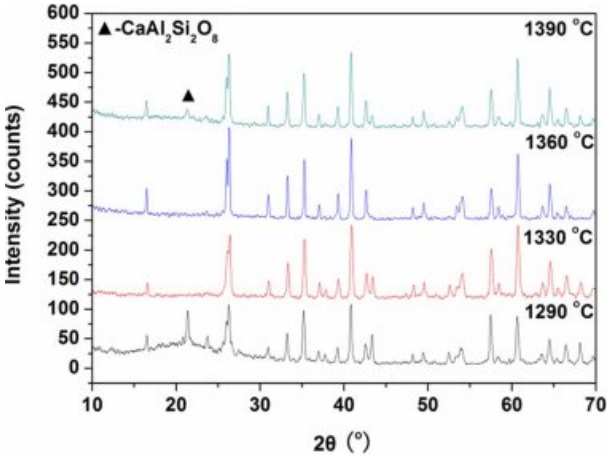

Fig. 5. XRD patterns of the glass-ceramics fabricated with prescription 12# at different sintering temperatures for 30 min (Milling time: 20 min; forming pressure: 30 MPa).

achieved at sintering temperature of 1360 °C. The optimal sintering temperature for these samples is 1360 °C. The chemical compositions of the prescription 9# and 12# are listed in Table 4.

Fig. 5 shows the XRD patterns of the samples fabricated with prescription 12#. The glass-ceramics sintered at 1330 °C and 1360 °C only contain mullite ($Al_6Si_2O_{13}$) (JCPDS: 15-0776). When sintered at 1290 °C and 1390 °C, second phase svyatoslavite ($CaAl_2Si_2O_8$) (JCPDS: 46-1266) appeared. The mullite is generally formed at the higher temperature, such as above 1320 °C as reported in previous literature [23]. The formation of mullite in the glass-ceramics at the sintering temperature of 1290 °C may be due to fine raw materials, fluxing actions of minerals additives and mineralizers, and nucleation of Fe_2O_3 and TiO_2 existing in the raw materials [24]. The mullite shows a compressive strength (0.69 GPa) larger than many other crystals including the cordierite (0.32 GPa), the boron nitrate (0.32 GPa), and the forsterite (0.55 GPa) [25]. This makes the glass-ceramics samples high-strength. Thus, the glass-ceramics sintered at 1330 °C and 1360 °C show better properties. Furthermore, the XRD peaks are enhanced as the increase in sintering temperature from 1330 °C to 1360 °C, indicating the increase in the content of the mullite crystal. This results in the optimal sintering temperature of 1360 °C.

Fig. 6 shows the SEM micrographs of the glass-ceramics fabricated with prescription 12# at sintering temperature of 1360 °C. The small and compact crystals

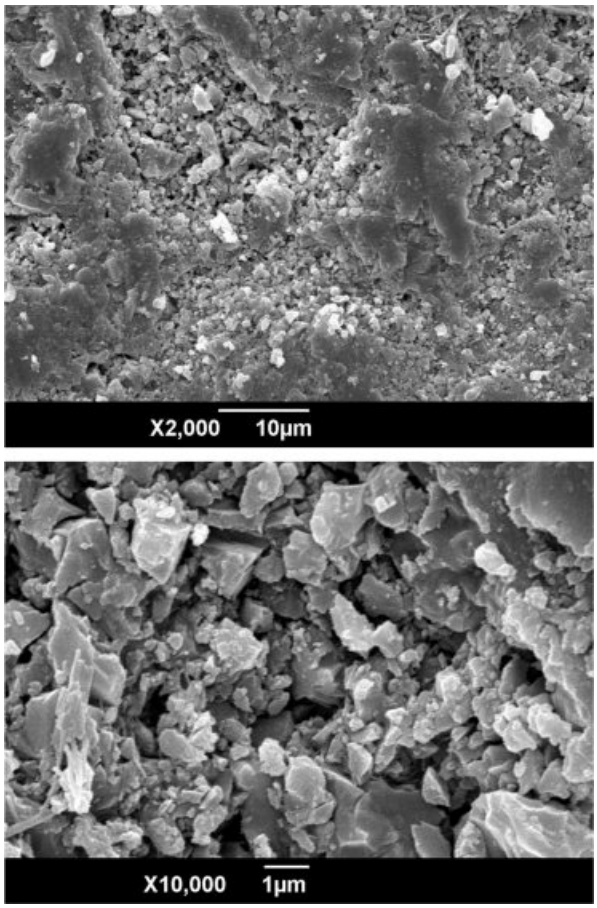

Fig. 6. SEM micrographs of the glass-ceramics fabricated with prescription 12# at sintering temperature of 1360 °C for 30 min (Milling time: 20 min; forming pressure: 30 MPa).

Table 4. Chemical composition of the samples (wt%?)

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	K_2O	Na_2O	MnO_2	BaO
9#	33.88	53.68	2.02	1.89	0.81	0.86	0.35	0.32	3.19	2.92
12#	33.73	54.00	2.03	1.76	0.71	0.81	0.25	0.21	3.38	3.10

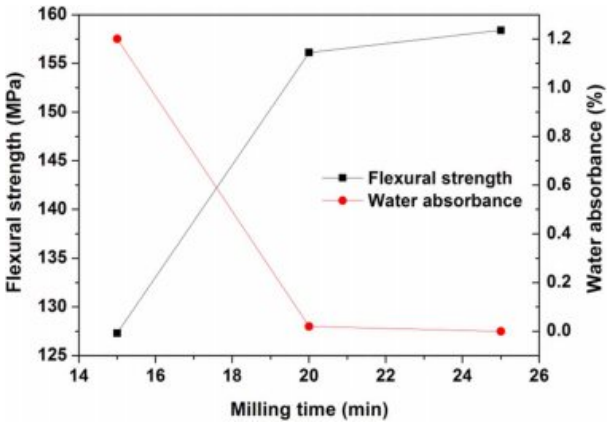

Fig. 7. Variations of flexural strength and water absorbance of the glass-ceramics fabricated with prescription 12# at sintering temperature of 1360 °C for 30 min with wet-milling time (Forming pressure: 30 MPa).

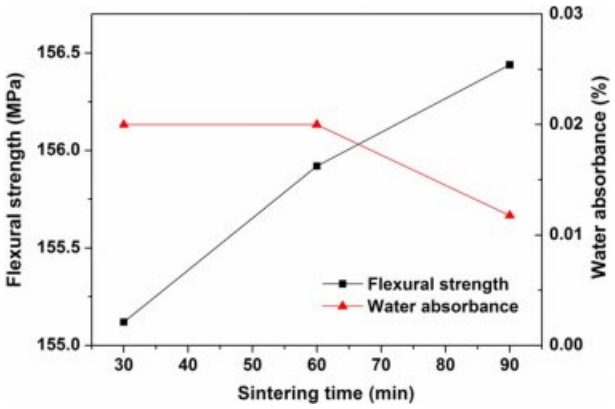

Fig. 9. Variations of flexural strength and water absorbance of the glass-ceramics fabricated with prescription 12# at sintering temperature of 1360 °C with sintering time (Milling time: 20 min; forming pressure: 30 MPa).

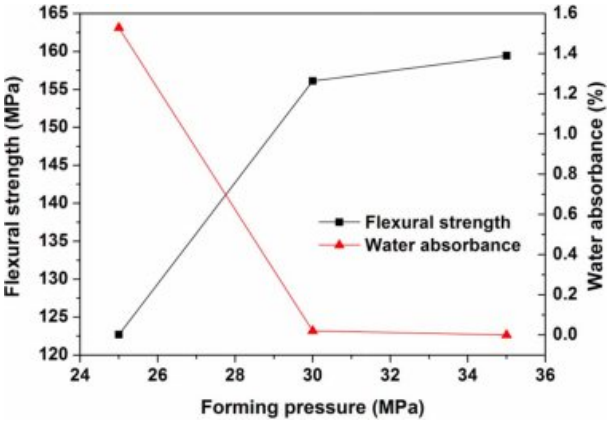

Fig. 8. Variations of flexural strength and water absorbance of the glass-ceramics fabricated with prescription 12# at sintering temperature of 1360 °C for 30 min with forming pressure (milling time: 20 min).

with polygonal morphology can be observed.

To optimize the processing parameter, the prescription 12# was further studied in various processing parameters including milling time, forming pressure, and sintering time. The results are shown in Fig. 7, 8, and 9. The increase of milling time from 15 to 20 min leads to great enhancement of the properties, however further increase of milling time only shows a slight effect on the properties. Similarly, the increase of forming pressure from 25 to 30 min leads to great enhancement of the properties of the glass-ceramics, however further increase of forming pressure only shows a slight effect. The increasing sintering time from 30 min to 90 min only results in slight increase (~1.4 MPa) of flexural strength and a slight decrease (0.01%) of water absorbance.

Many researchers have fabricated the glass-ceramics with various waste minerals [26-32]. Their glass-ceramics generally had the flexural strength in the range of 30-130 MPa [26-32] and the density in the range of ~1.8-3.0 g/cm^3 [26, 27, 30-32]. The glass-ceramics fabricated with coal gangue contained the gehlenite as a main crystal phase and nepheline as the next crystal phase [18]. The glass-ceramics only showed a bending strength of 28 MPa [18]. The mullite glass-ceramics fabricated with coal gangue and γ-Al_2O_3 showed the bending strength from 64 MPa to 218 MPa as adding the La_2O_3 from 0 mol% to 10 mol% [16]. The porous mullite ceramic fabricated from coal gangue and bauxite showed the flexural strength of 66.06 to 133.61 MPa varied with corn starch content [22]. The crystal phases different from mullite and their sizes and densities are the key factors. By comparison, our glass-ceramics have higher strength.

Conclusions

The waste coal gangue has been utilized for the fabrication of high-strength glass-ceramics. Optimal utilization ratio of coal gangue was first investigated. The effects of mineral additives, mineralizers, processing parameters of forming and sintering of glass-ceramics were also researched. The optimal utilization ratio of the coal gangue was determined to be 55 wt.% when the appropriate amounts of bauxite, clay, limestone, and steatite were used. The appropriate amounts of mineralizers $BaCO_3$, $MnCO_3$, $MgCO_3$ can improve the property of the glass-ceramics, in which $BaCO_3$ and $MnCO_3$ codoping and substitution show an optimal effect as their amounts are 3 wt.%, respectively. The process optimization showed that reasonable forming process parameters are milling time of 20 min and forming pressure of 30 MPa, while optimal sintering temperature and time are 1360 °C and 30 min, respectively. Further increases of the milling time, forming pressure and sintering time only lead to slight enhancements of the properties. In the condition of these reasonable process parameters, the sintered glass-ceramics were of high strength (156.12 MPa), low

density (2.68 g cm^{-3}), and low water absorption (0.02 %). This makes the sintered glass-ceramics an excellent glass-ceramics having potential superiority for the applications in proppant materials, building materials, cooking ceramics, et al..

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