Mechanism of Nd2O3 in Optimizing the Properties of Bayan Obo Western Tailings Glass-Ceramics: Postprint

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Abstract

Using Bayan Obo west tailings as the primary raw material, CaO-Al2O3-MgO-SiO2 (CAMS) system glass-ceramics with Nd2O3 additions of (0-8.73)% (mass fraction, hereinafter) were prepared via the melt-casting method. The mechanism by which the addition of Nd2O3 optimizes the microstructure and properties of the prepared glass-ceramics was investigated by means of DTA, XRD, FEGSEM+EDS+EBSD, comprehensive mechanical property tester, and other techniques. The results demonstrate that: with increasing Nd2O3 content, the main crystal phase Ca(Mg, Al, Fe)Si2O6 (pyroxene) gradually refines, which is attributed to the hindering effect of the Ca2Nd8(SiO4)6O2 phase precipitated at the grain boundaries of the main crystal phase and the competition for Ca ions by this Nd-rich second phase during its growth. The sample with 2.21% Nd2O3 addition exhibits optimal comprehensive properties, with density, flexural strength, and acid-alkali resistance of 3.20 g/cm^3, 200 MPa, 95.22%, and 99.23%, respectively.

Full Text

Preamble

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Mechanism of Nd_2O_3 Optimization on the Properties of Glass-Ceramics Synthesized from Bayan Obo West Mine Tailings

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Abstract

Glass-ceramics of CaO-Al_2O_3-MgO-SiO_2 (CAMS) system with Nd_2O_3 additions of 0–8.73% (mass fraction) were synthesized primarily using tailings from Bayan Obo west mine via a melting-casting method. The mechanism by which Nd_2O_3 addition optimizes the microstructure and properties of these glass-ceramics was investigated using DTA, XRD, FEGSEM equipped with EDS & EBSD attachments, and universal mechanical property testers. Results demonstrate that increasing Nd_2O_3 content progressively refines the primary crystalline phase Ca(Mg, Al, Fe)Si_2O_6 (augite). This refinement arises from the hindering effect of $Ca_2Nd_8(SiO_4)_6O_2$ particles precipitated at grain boundaries and the competition for Ca ions during growth of this Nd-rich secondary phase. The sample with 2.21% Nd_2O_3 addition exhibits optimal comprehensive properties, with density, bending strength, acid resistance, and alkali resistance of 3.20 g/cm^3, 200 MPa, 95.22%, and 99.23%, respectively.

Keywords: inorganic non-metallic materials, glass-ceramics, Bayan Obo west mine tailing, Nd_2O_3

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1. Introduction

Glass-ceramics are composite materials formed when crystals precipitate from glass through specialized nucleation and crystallization heat treatments, with oxide glass-ceramics being the most widely applied [1-6]. Due to the substantial tolerance of oxide structures to raw material composition fluctuations, numerous silicate industrial solid wastes—including tailings, fly ash, steel slag, and red mud—can be utilized to prepare glass-ceramics [7-10]. This approach not only transforms land-consuming, polluting wastes into useful materials with high flexural strength, hardness, and acid-alkali corrosion resistance, but also significantly reduces raw material costs [11-14].

Previous research has shown that CaO-Al_2O_3-MgO-SiO_2 (CAMS) system glass-ceramics prepared from Bayan Obo west tailings containing trace rare earths (~1%) exhibit excellent performance, with flexural strength, acid resistance, and alkali resistance of 183 MPa, 76.27%, and 98.53%, respectively [11]. Pilot products (pipes and plates) manufactured from these materials have been used for wear-resistant and corrosion-resistant pipelines and scrapers, demonstrating service lives over five times longer than conventional wear-resistant steel or nylon materials.

Existing studies indicate that Nd^{3+} in B_2O_3-PbF_2-PbO-Al_2O_3-WO_3 system glass-ceramics promotes the precipitation of PbF_2 as elemental crystals. In Li_2O-Al_2O_3-SiO_2 system glass-ceramics, rare earth ions increase the crystallization activation energy and temperature of the primary phase (β-spodumene solid solution) while refining grain size [15]. Lanthanide (Ce, Nd, Eu, Gd, Yb) and actinide (Th) ions in SiO_2-Al_2O_3-CaO-ZrO_2-TiO_2 glass-ceramics exhibit strong field adsorption on surrounding anions, promoting phase separation in the base glass [16]. Masoud Eslami et al. [17] demonstrated that neodymium ions in SiO_2-CaO-MgO glass-ceramics function as both network formers and network modifiers: when content is below 5%, their network-forming role inhibits crystallization; above 5%, their network-modifying role becomes dominant, thereby promoting crystallization. These findings indicate that the specific effects of rare earth ions in glass-ceramics depend not only on the type and amount of rare earth but also on the material system.

Nd is a characteristic element in Bayan Obo rare earth resources. Although Bayan Obo west tailings containing trace Nd have been successfully used to manufacture glass-ceramic materials, the existing form of Nd and its influence mechanism on microstructure and properties remain unclear. Therefore, this study synthesized CAMS system glass-ceramics using Bayan Obo west tailings as the primary raw material via conventional melting-casting processes, and investigated the specific mechanism of action by adjusting Nd_2O_3 content in the base glass.

1.1 Experimental Materials and Base Glass Formulation

The base compositions and sample designations for glass-ceramics with (0-8.73)% Nd_2O_3 additions are shown in Table 1 . The primary raw materials were Bayan Obo west mine tailings and fly ash from a Baotou thermal power plant, with chemical reagents used to supplement any deficient components.

The six batches of raw materials were weighed, mixed, and ball-milled to homogeneity, then placed in corundum crucibles and melted at 1450°C for 2 hours to achieve clarification and homogenization. A small portion of the glass melt was water-quenched; the resulting glass particles were ground for DTA analysis to determine the heat treatment schedule. The remaining bulk melt was cast onto 40 mm × 60 mm × 8 mm steel molds, immediately transferred to a resistance furnace for annealing at 600°C for 4 hours, and furnace-cooled to room temperature. All six sample groups were subsequently heat-treated according to schedules determined from DTA results.

1.2 Structural and Property Characterization

After heat treatment, sample phases were identified using X-ray diffraction. Microstructural morphology, elemental composition, crystal structure, and growth orientation were analyzed using field emission scanning electron microscopy with integrated Nordlys EBSD system. Density and flexural strength were measured via Archimedes' principle and three-point bending method using a hydrostatic balance and electronic universal testing machine (CSS-88000), respectively. Acid and alkali resistance were evaluated according to JC/T258-1993 standard by immersing samples in 20% NaOH and 20% H_2SO_4 solutions at 100°C for 1 hour, with resistance characterized by mass loss before and after corrosion.

The average sample particle size ranged from 0.5–1.0 mm. The mass loss after corrosion in either acid or alkali solution was used to quantify acid/alkali resistance.

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2. Results and Discussion

2.1 DTA Analysis

Figure 1 [Figure 1: see original paper] presents DTA curves of water-quenched base glass samples doped with (0–8.73)% Nd_2O_3. All six samples exhibit only exothermic peaks resulting from crystallization, i.e., so-called crystallization peaks. As Nd_2O_3 content increases, the crystallization peak temperature rises from 861°C for the Nd_2O_3-free C1 sample to 899°C for the C6 sample with highest Nd_2O_3 content, indicating that increasing Nd_2O_3 addition delays precipitation of the primary crystalline phase. Since no distinct glass transition temperature (Tg) is observed, the nucleation temperature was determined to be 680°C and the crystallization temperature 880°C based on existing research group results and the current DTA data.

2.2 X-ray Diffraction Analysis

XRD patterns of glass-ceramics with (0–8.73)% Nd_2O_3 additions are shown in Figure 2 [Figure 2: see original paper]. Phase identification reveals that all samples consist of the primary phase augite ($Ca(Mg, Al, Fe)Si_2O_6$, PDF: 00-024-0202) and minor CaF_2. In Nd_2O_3-containing samples, a secondary $Ca_2Nd_8(SiO_4)_6O_2$ phase (PDF: 00-028-0228) also appears. M. Uo et al. [18] observed similar crystalline phases in their study of 10 mol% Nd_2O_3-doped 20 mol% CaO-10 mol% Al_2O_3-60 mol% SiO_2 glass-ceramics. With increasing Nd_2O_3 doping, the intensity of the main diffraction peak of the new $Ca_2Nd_8(SiO_4)_6O_2$ phase at approximately 31.43° gradually increases, while diffraction intensities of the augite and CaF_2 phases decrease. These intensity changes reflect that $Ca_2Nd_8(SiO_4)_6O_2$ suppresses formation of the other two Ca-containing phases through competition for Ca ions.

2.3 Microstructural Morphology

Backscattered electron (BSE) SEM images of the six heat-treated samples are shown in Figure 3 [Figure 3: see original paper]. The augite phase exhibits a chrysanthemum-like morphology with very large grain sizes, some exceeding 10 m. With Nd_2O_3 addition, the C2 sample shows reduced augite grain diameters while retaining the basic morphological characteristics. In C3–C5 samples, the chrysanthemum-like features of the primary augite phase disappear, transforming into an "island-like" morphology with progressively decreasing average size. Simultaneously, the quantity of secondary phases at primary phase grain boundaries gradually increases, with their morphology evolving from particulate in low-Nd_2O_3 samples (C1-C3) to "coral-like" in high-Nd_2O_3 samples (C4-C6).

To accurately determine the composition of these particulate secondary phases, EDS analysis was performed on grain boundary particles in the C6 sample, with results shown in Figure 4 [Figure 4: see original paper]. The analyzed microregion contains not only the main glass components Ca, Al, Mg, and Si, but also Nd and F. It should be noted that even with an electron beam spot size of ~10 nm, the microregion emitting characteristic X-rays extends to micrometer-scale areas around and beneath the analysis point, which explains the presence of Ca, Al, Mg, and Si in the results. Meanwhile, signals for Nd and F originate not only from the larger central particle but also from surrounding smaller grain boundary particles. Therefore, based on these results, the particulate secondary phases likely contain both CaF_2 particles and $Ca_2Nd_8(SiO_4)_6O_2$ particles. However, the secondary phases that grow into "coral-like" morphologies with increasing Nd_2O_3 content are definitively $Ca_2Nd_8(SiO_4)_6O_2$.

After completing EDS analysis and adjusting the sample-electron beam angle, EBSD patterns generated by backscattered electron diffraction from these grain boundary particles were collected [19], as shown in Figure 5a [Figure 5: see original paper]. In EBSD systems, crystal structure and orientation relationships are determined through Kikuchi bands diffracted from various crystal planes. Based on calibration of numerous Kikuchi bands in Figure 5a using the accompanying EBSD analysis software (Figure 5b) and referencing the composition from the EDS analysis of the same microregion, these Kikuchi bands are confirmed to originate from $Ca_2Nd_8(SiO_4)_6O_2$ secondary phase diffraction. This proves that most particulate phases in the EDS analysis region belong to the $Ca_2Nd_8(SiO_4)_6O_2$ secondary phase, with CaF_2 secondary phase particles being extremely rare.

After accurately identifying the grain boundary secondary phases, EBSD was used to analyze orientation distribution in a 15 × 20 m region of the augite primary phase in another polished C6 sample. Inverse pole figure results for the x, y, and z directions are shown in Figure 6 [Figure 6: see original paper]. In inverse pole figures, axis density line distribution indicates texture level: more concentrated distribution at a crystal direction pole signifies more severe oriented growth along that direction [20]. As shown, the x-direction inverse pole figure exhibits high x-axis density at the 100 and poles, indicating oriented growth of augite grains along the [100] crystal direction in the sample’ s x-axis. No similar phenomenon is observed in the y- and z-axis inverse pole figures.

2.4 Properties

The density, flexural strength, acid resistance, and alkali resistance of the six heat-treated samples are summarized in Table 2 . Data indicate that both density and flexural strength gradually increase with Nd_2O_3 content. Meanwhile, acid and alkali resistance initially increase then decrease, with sample C3 exhibiting extreme values. The density increase is attributed to Nd_2O_3 having higher density than other raw materials, while flexural strength improvement primarily relates to grain refinement of the primary phase with increasing Nd_2O_3 content. Grain refinement effects on mechanical properties such as flexural strength have been widely reported in other materials research [21, 22].

The variation in acid/alkali resistance primarily relates to microstructural changes. In glass-ceramics, interfaces between crystalline and residual glass phases represent weak links in corrosion resistance due to more disordered atomic arrangements. For the first two sample groups, although the primary phase grains are larger with smaller total outer interface area than the refined third group, these >10 m grains contain numerous residual glass phases internally. This results in chrysanthemum-like corrosion features and crystalline/residual glass phase interfaces not fewer than in the third group, explaining their inferior acid/alkali resistance. When primary phase grains transform to island-like morphology from the third group onward, increasing refinement with Nd_2O_3 content raises crystalline/residual glass phase interface area. Simultaneously, formation of Nd-containing secondary phases and their “competition” for primary phase-forming elements gradually suppresses primary phase formation in the latter three samples. These combined effects cause acid/alkali resistance to decline with increasing Nd_2O_3 content. Considering all performance indicators, the optimal Nd_2O_3 addition is determined to be 2%, with corresponding optimal sample C3 exhibiting density, flexural strength, acid resistance, and alkali resistance of 3.20 g/cm^3, 200 MPa, 95.22%, and 99.23%, respectively.

2.5 Discussion

Results confirm that in CAMS-based glass-ceramics prepared from Bayan Obo west tailings and Baotou power plant fly ash, progressively increasing Nd_2O_3 content not only gradually refines the primary augite phase $Ca(Mg, Al, Fe)Si_2O_6$ but also forms more $Ca_2Nd_8(SiO_4)_6O_2$ secondary phase. Correspondingly, comprehensive properties including density, flexural strength, and acid/alkali resistance are progressively optimized in the Nd_2O_3 content range of 0–2.21%. These property changes primarily relate to the gradual refinement of the augite primary phase caused by increasing Nd_2O_3 content.

Based on comprehensive results, the reasons for augite grain refinement with increasing Nd_2O_3 content are: (1) hindering effects of Nd-containing secondary phase particles distributed at grain boundaries on primary phase grain growth during heat treatment; and (2) Ca being a constituent element of the Nd-containing secondary phase, so formation of more Nd-rich secondary phases at primary phase boundaries inevitably leads to “competition” for Ca ions required for augite formation. Masoud Eslami et al. [17] found that Nd^{3+} can increase glass viscosity and hinder ion diffusion in Nd-doped SiO_2-CaO-MgO glass-ceramics, but Nd_2O_3 exists as an intermediate oxide functioning as both network former and network modifier without forming any Nd primary or secondary phases. M. Uo et al. [18] demonstrated that $Ca_2Nd_8(SiO_4)_6O_2$ grains exhibit oriented growth along the C-axis in 10 mol% Nd_2O_3-20 mol% CaO-10 mol% Al_2O_3-60 mol% SiO_2 glass-ceramics, but the high SiO_2 content in their system prevented precipitation of any primary phase similar to this study’ s results.

The maximum flexural strength of prepared samples reaches 223 MPa, with the optimally performing C3 sample exceeding 200 MPa. Such high comprehensive performance surpasses the maximum flexural strength of 122 MPa for CaO-Al_2O_3-SiO_2 glass-ceramics prepared from gold tailings by Chen Weiqian et al. [23] and the 197 MPa for glass-ceramic samples prepared from rare-earth tailings and fly ash by Zhang Xuefeng et al. [24] from this research group.

In summary, adding small amounts of Nd_2O_3 can significantly improve the microstructure and properties of CAMS glass-ceramics prepared from silicate solid wastes.

Conclusions

1. For CaO-MgO-SiO_2-Al_2O_3 glass-ceramics prepared primarily from Bayan Obo west tailings and Baotou power plant fly ash, increasing Nd_2O_3 content in the 0–8.73% range progressively refines primary augite (Ca(Mg, Al, Fe)Si_2O_6) grains while increasing $Ca_2Nd_8(SiO_4)_6O_2$ secondary phase quantity. The hindering effect of Nd-rich secondary phases on primary phase grain growth during heat treatment and their competition for Ca ions required for primary phase formation are the main causes of augite grain refinement.
2. The CAMS glass-ceramic exhibits optimal comprehensive properties at 2.21% Nd_2O_3 addition, achieving density, flexural strength, acid resistance, and alkali resistance of 3.20 g/cm^3, 200 MPa, 95.22%, and 99.23%, respectively.

References

1. A. A. Francis, Conversion of blast furnace slag into new glass-ceramic material, *Journal of the European Ceramic Society*, 24(9), 2819(2004)
2. Melo VARD, Lameiras F S, Tolentino E, Conversion of sandy tailing from banded iron formation exploitation into glass-ceramic materials, *Materials Research*, 15(1), 15(2012)
3. CHEN Hao, WU Yiwen, ZHANG Hong Z, Phase, magnetism and thermal conductivity of glass ceramics from iron ore tailings, *Journal of Central South University*, 21(9), 3456, (2014)
4. LI Bin, SUI Zhitong, Glass crystalline kinetics CaO-MgO-Fe_2O_3-Al_2O_3-SiO_2 of slags, *Chinese Journal of Materials Research*, 13(4), 412(2009)
5. LI Baowei, WANG Fang, CHEN Hua, Influence of Cr_2O_3 on the microstructure and properties of the glass-ceramics produced from bayan obo west mine tailing, *Journal of Synthetic Crystals*, 43(3), 642(2014)
6. T. Kehagias, P. H. Komninou, P. Kavouras, Crystal phase separation and microstructure of a thermally treated vitrified solid waste, *Journal of the European Ceramic Society*, 26(7), 1141(2006)
7. B. W. Li, Y. S. Du, X.F.Zhang, Effects of iron oxide on the crystallization kinetics of baiyunebo tailing glass-ceramics, *Transactions of the Indian Ceramic Society*, 72(2), 119(2013)
8. B. W. Li, L. B. Deng, X. F. Zhang. Structure and performance of glass-ceramics obtained by bayan obo tailing and fly ash, *Journal of Non-Crystalline Solids*, 380, 103(2013)
9. DONG Wei, LU Jinshan, LI Yaohui, Effect of cerium, neodymium based on industrial waste materials, *Journal of Non-Crystalline Solids*, 356(52), 3066(2010)
10. X. Z. Guo, W. Y. Li, H.Yang, Effect of neodymium on the crystallization, microstructure and colorization of Li_2O-Al_2O_3-SiO_2 glass ceramics, *New Journal of Glass and Ceramics*, 02(02), 98(2012)
11. FANG Yihang, YANG Qinghua, LI Hongwei, Low temperature sintering and performance of CBS/Al_2O_3 glass-ceramic doped with Li_2CO_3, *Chinese Journal of Materials Research*, 26(5), 515(2012)
12. Zunqi Xiao, Fatang Tan, Wei Wang, Hongfei Lu, Yuncheng Cai, Oxidation protection of commercial-purity titanium by Na_2O-CaO-SiO_2 and Na_2O-CaO-Al_2O_3-SiO_2 glass-ceramic coatings, *Ceramics International*, 41, 325(2015)
13. P. Loiseau, D. C. Caurant, N. Baffier, Glass-ceramic nuclear waste forms obtained from SiO_2-Al_2O_3-CaO-ZrO_2-TiO_2 glasses containing lanthanides

(Ce, Nd, Eu, Gd, Yb) and actinides (Th): study of internal crystallization, *Journal of Nuclear Materials*, 335(1), 14(2004)

14. M. Eslami, Z. Hamnabard, Synthesis and spectral properties of Nd-doped glass-ceramics in SiO_2-CaO-MgO system prepared by sol-gel method, *Journal of Rare Earths*, 31(6), 595(2013)
15. M. Uo, H. Seto, K. Morita, The effect of rare-earth oxides on the crystallization of CaO-Al_2O_3-SiO_2 glasses, *Journal of Materials Science*, 33(3), 749(1998)
16. A. J. Schwartz, M. Kumar, B. Adams, D. P. Field, *Electron backscatter diffraction in material science*, (New York, Plenum Publishers, 2001) p.406
17. V. Randle, O. Engler, *Introduction to texture analysis: macrotexture, microtexture, and orientation mapping*, (Boca Raton, CRC press, 2010) p.490
18. Nieh T G, Wadsworth J, Hall-petch relation in nanocrystalline solids, *Scripta Metallurgica et Materialia*, 25(4), 955(1991)
19. Chokshi A H, Rosen A, Karch J, On the validity of the hall-petch relationship in nanocrystalline materials, *Scripta Metallurgica*, 23(10), 1679(1989)
20. CHEN Weiqian, GAO Shuya, LIU Jie, Preparation and properties of glass-ceramics from gold tailings by melting method, *Journal of Synthetic Crystals*, 43(1), 217(2014)
21. ZHANG Xuefeng, DENG Leibo, LI Baowei, Effect of heating treatment temperature on mechanical properties of glass-ceramics preparation with rare-earth tailings and fly ash, *Nonferrous Metals (Mining Section)*, 63(4), 66(2011)

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