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Article

Effect of Bi_2O_3 doping on the mechanical properties of PbO ceramic pellets used in lead-cooled fast reactors

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Abstract: In this paper, the effect of Bi_2O_3 doping on the mechanical properties of PbO ceramic pellets was studied. For this purpose, different ratios of Bi_2O_3/PbO (i.e., $x$$Bi_2O_3$–(1-$x$)PbO, where x is 0, 1, 3, 5, 7 wt%) were fabricated and sintered at 570, 620, and 670°C. Mechanical properties including density, hardness, flexural strength, and sintering of PbO were studied for the aforementioned compositions. Phase compositions, microstructures, and worn surfaces of the composites were characterized by scanning electron microscopy and X-ray diffraction (XRD). The XRD analysis revealed that a solid solution formed in the composite ceramic. The best suited conditions of temperature and doping of Bi_2O_3 for optimal sintering are 620°C and 3 wt%, respectively. The hardness of the 3 wt% Bi_2O_3–97 wt% PbO ceramic was 717 MPa, which is about four times higher than the hardness of pure PbO; in addition, the strength of the composites was 43 MPa, which is two times higher than that of pure PbO. The integrity of the composites was verified using the lead–bismuth eutectic alloy flushing experiment. Results of this research paper are important for future studies of oxygen control in the lead–bismuth eutectic alloy of lead-cooled fast reactors.

Keywords: Bi_2O_3; PbO; sintering temperature; mechanical properties; lead–bismuth eutectic alloy.

1. Introduction

Lead oxide (PbO) ceramic pellets are used in solid-phase oxygen control systems, which are an important constituent of lead-cooled fast reactors (LFRs). In LFRs, the lead–bismuth eutectic (LBE) alloy was chosen as a coolant material [1]. However, LBE can cause severe corrosion of structural materials [2], including pipes and other components. To prevent such corrosion, it is important to consider appropriate protective methods. Studies in the past have shown that oxygen is the most critical element in the corrosion caused by LBE alloys. When oxide layers of a certain thickness get coated on the internal surface of the steel pipes, forming a film of magnetite ferroferric oxide and iron chrome spinel-$[Fe_{(3-x)}Cr_x]O_4$, it prevents the further penetration of LBEs. The thickness of the oxide layer varies at different levels of oxygen concentration; an oxide layer that is too thick or too thin cannot protect the steel well [3]. Many research studies have shown that solid-phase oxygen control is a promising anti-corrosion method [4]. In this approach, the PbO ceramic pellets are set inside and liquid metal and oxygen ions are released from the ceramic pellets into the liquid metal. The concentration of oxygen ions in the liquid metal can be adjusted by the low rate and temperature of the coolant. To keep the coolant pure and to protect the steel pipe, high-strength PbO ceramic pellets are required, which have fast oxygen concentration regulation and crack resistance during operation.

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Currently, experiments on solid-phase control systems are being carried out in the LBE test loop CRAFT at SCK•CEN in Mol, Belgium [5], in the Pb–Bi forced convection loop in Ibaraki, Japan [6], and as part of the DEMETRA project by CEA, Saclay in Gif-sur-Yvette, France [7]. Though several studies have been done theoretically and practically on solid-phase control systems, only a few have reported on the mechanical properties and microstructures of PbO. Hence, research on developing sintering techniques of PbO ceramic pellets that will have excellent performance during operation has become a hot topic in this area.

Some studies have reported that the PbO ceramic pellets tested in CRAFT loop were cracked in the area of equator during the experiment (Fig. 1). PbO ceramic pellets broken in the loop can result in debris being formed in the coolant, eventually blocking the pipeline in extreme cases [5]. Kondo et al. found that PbO powder was sintered in the form of lumps at 800°C, following which the lumps were mechanically broken into small pieces [6]. The relative density of the PbO ceramic pellets in the above loop was 72.82%. Brissonneau reported that the PbO pellets were generated from PbO powder and water under a force of 45 kN at the pellet for 2 min, and then the pellets were sintered at 620°C for 2h at a slow temperature ramp (2°C•min^{-1}) [7]. The ceramic pellets discussed above are used as PbO pellets in oxygen concentration control experiments, but there is no detailed literature on the properties of PbO ceramic pellets. It can be seen from Fig. 1 that the PbO ceramic pellets used in the experiment were not high in strength and could be easily cracked along the equatorial plane because of their spherical shape.

We have enhanced our scope of research to improve the mechanical properties and avoid the cracking of PbO ceramic pellets in the LBE alloy. Doping by Pb powder using liquid-phase sintering improved the mechanical properties of the ceramic pellets [8]. The mechanical properties and microstructures of the Pb, PbO, and Pb_3O_4 ceramic pellets were also studied in detail, and the results showed that the addition of lead powder facilitates sintering and increases the strength of the ceramic. We also used the microwave sintering technique to improve the strength of the PbO ceramic pellets [9]. However, there was no significant improvement in the mechanical properties and the technique resulted in the occurrence of cracks.

In this study, Bi_2O_3 powder as the sintering aid was added to the PbO precursor. Bi_2O_3 powder was chosen as the sintering agent for two reasons: (1) the raw material of the ceramic pellets will not cause pollute the coolant or make it impure and (2) the diameter of Bi^{3+} is similar to the diameter of Pb^{2+} and their chemical properties are very similar, which is beneficial in the sintering process. In this paper, the mechanical properties and microstructures of Bi_2O_3/PbO with different compositions (i.e., xBi_2O_3-(1-x) PbO, where x is 0, 1, 3, 5, 7 wt%) were investigated in terms of their strength, hardness, and scanning electron microscopy (SEM) data to arrive at the optimal value of x and the sintering temperature. Flushing experiments were then performed to verify the integrity of PbO ceramic pellets.

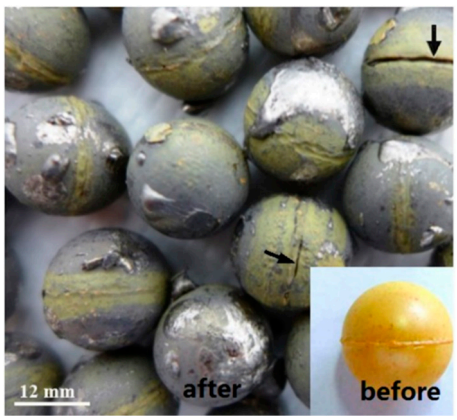

Figure 1. PbO ceramic pellets tested in the CRAFT loop and MEXICO loop [5].

2. Materials and Methods

The chemical composition of the ceramic was chosen to be xBi_2O_3–(1-x)PbO (the value of x is 0, 1, 3, 5, 7 wt%) for conventional sintering. The initial Bi_2O_3 and PbO powders (A.R. 99% purity) were purchased from Sinopharm Chemical Reagent Co. Ltd., Beijing, China. The powders were mixed and ground using a planetary ball mill with 2 wt% deionized water for 24 h. The green compact was fabricated using a cold steel die at a uniaxial pressure of 40 MPa. The rate of pressure during compression and depression was kept controlled below 0.5 MPa/s, in order to reduce the elastic aftereffect and avoid the splitting of the compact. The specimens were then sintered at 570°C, 620°C, and 670°C for 2h at a heating rate of 10°C•min^{-1}, and cooled to room temperature [8].

During sintering, the compacts were covered by the PbO powder to further minimize PbO volatilization [10]. It was noticed that the loss of PbO leads to a decrease in density and affects the mechanical properties of PbO ceramic pellets [11]. Disc samples (diameter, 13 mm) and bar samples (4 mm ×3 mm ×35 mm) were fabricated for mechanical property testing. The tablet-like pellets of PbO ceramic pellets (diameter, 6 mm; height, 5 mm) were fabricated to test their integrity using the flushing experiment.

Microstructures were observed using a Quanta 200F field emission scanning electron microscope. The crystalline phases were analyzed using a D8 Focus X-ray diffraction with Cu Kα radiation. Hardness was estimated on polished samples by the indentation method using a Micro Vickers Hardness Tester. The indentation test was conducted with a load of 0.98 N held for 15 s. The hardness (Hv) was calculated according to ASTM C1327-15 [12] as below:

$$Hv = \frac{1.8544F}{d^2}, \quad (1)$$

where F is the applied load and d is the mean value of the diagonal length of the indentation. A flexural strength test was conducted by the three-point flexural method (span, 35 mm; crosshead speed, 0.5 mm•min^{-1}) using a WDW-100E computer control electronic universal testing machine. The densities of the specimens were estimated using the Archimedes method by weighing them in air and water. Data were collected for 6–8 samples to obtain an average of results.

3. Results

3.1 Mechanical properties of Bi_2O_3-PbO ceramic pellets

Figure 2(a) shows the relative densities versus sintering temperatures for PbO ceramic pellets as a function of Bi_2O_3 wt%. The effect of sintering temperature on the density did not show a specific increasing or decreasing trend. The peak value of 92.01% is achieved at 670°C with 1 wt% Bi_2O_3. Excluding the effects of errors, the best density is achieved at a sintering temperature of 620°C as a whole. From Fig. 2(a), we observe that with the increase in the sintering temperature and the Bi_2O_3 content, the sintering process is prolonged, creating more pores and reducing the relative density of the ceramic pellets.

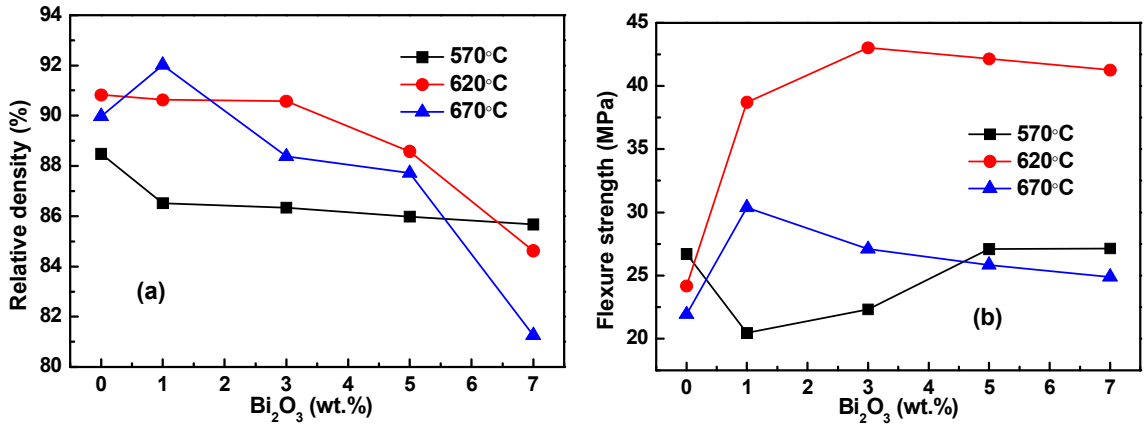

Figure 2. (a) Relative density and (b) flexure strength versus sintering temperature for PbO ceramics with different Bi_2O_3 wt.%.

At every sintering temperature, the relative density of the ceramic pellets decreases with the increase in the Bi_2O_3 content. At a sintering temperature of 620°C and an optimum doping value of 3 wt% Bi_2O_3, a high relative density of 90.57% is achieved. Kondo and Takahashi [6] found that the relative density is 72.82% for pure PbO ceramic pellets sintered at 800°C, which is lower than that found in this study. The results indicate that doping by a small amount of Bi_2O_3 significantly improved the density of PbO ceramic pellets.

Figure 2(b) shows the graph of flexural strength with content of Bi_2O_3 wt% at different sintering temperatures for PbO ceramic pellets. The effect of sintering temperature on the flexural strength is very prominent and changes significantly with changing temperature. The flexural strength of the PbO ceramic pellets sintered at 620°C is much higher than that of the samples sintered at 570°C and 670°C.

It is well known that pure PbO ceramic pellets are not tough enough to flush in LBE [5]. After doping with 1 wt% Bi_2O_3 at 620°C, the flexural strength of the PbO ceramic pellets increased by 75%. It reached the peak value of 43 MPa at 3 wt% Bi_2O_3 and then tended to decrease slightly with further increase in the Bi_2O_3 content. At 570°C, the strength of the ceramic pellets decreased abruptly when the Bi_2O_3 increased to 1 wt%, but as the Bi_2O_3 content continued to increase, the strength also increased and attained a constant value of flexural strength. However, the strength at 670°C was just the opposite. It increased linearly at 1 wt% Bi_2O_3 and then started to decrease and continued to decrease. The relationship between strength and porosity is defined by the Griffith equation [13] as shown below:

$$\sigma_f = \frac{(1-\frac{P}{P_0})^n}{Y\sqrt{c}}, \quad (2)$$

$$c = c_0\left[1-\frac{(P_0-P)}{3(1-P)}\right], \quad (3)$$

where P_0 and n are constants, P is the porosity, Y is the shape factor, and c_0 is the initial crack length. Thus, it may be concluded that the strength of the sample is inversely proportional to its porosity and directly proportional to its density. The strength of the material is also inversely proportional to its grain size according to the Hall–Petch equation [14] as shown below:

$$\sigma_f = \sigma_0 + kd^{-\frac{1}{2}}, \quad (4)$$

where k is a constant, σ_0 is the strength of the infinite single crystal, and d is the grain size. The porosity becomes a dominant factor in decreasing the strength when the Bi_2O_3 content is increased from 3 to 7 wt% at 620°C or at a higher sintering temperature of 670°C, which was consistent with the results shown in Fig. 2(a).

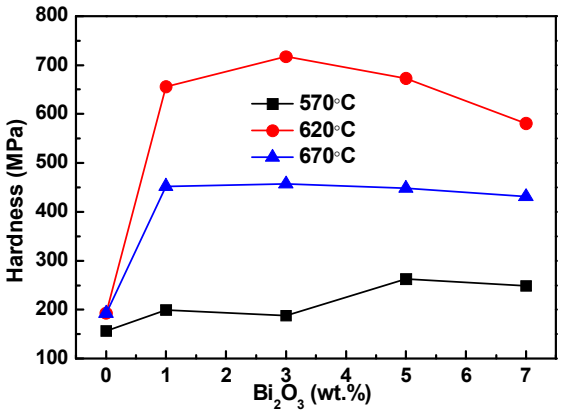

Figure 3. Hardness versus sintering temperature of PbO ceramic pellets with different wt% of Bi_2O_3.

The hardness of the PbO ceramic pellets at different wt% of Bi_2O_3 as a function of temperature is plotted in Fig. 3. It is obvious that the hardness of Bi_2O_3–PbO sintered at 620°C is higher than that at temperatures 570°C and 670°C. At 620°C, the change in hardness is very steep, which increases gradually until the content of Bi_2O_3 is 3 wt%. After reaching its peak, the hardness starts to decline. The optimum hardness of 717 MPa was achieved with 3 wt% Bi_2O_3 at temperature 620°C, which is about four times higher than that of pure PbO.

3.2 Flushing test

Suitable fabricated samples were obtained with a composition of 3 wt% Bi_2O_3–97 wt% PbO, sintered at 620°C. They were then tested in an experimental apparatus for a solid-phase oxygen control system at Beijing Key Laboratory of Passive Safety Technology for Nuclear Energy of North China Electric Power University (Fig. 4).

Figure 4. The experiment bench of the oxygen control system.

In the flushing experiment, 135 ceramic samples of 3 wt% Bi_2O_3–97 wt% PbO were placed in the middle of the mass exchanger. LBE flowed through the PbO ceramic pellets at a speed of 110 L/h for 100 h. The flushing test was carried out at 450℃ and the oxygen concentration is 3.14×10^{-4} wt%.

Figure 5 shows the images of the PbO pellets before and after testing. None of the ceramic pellets cracked, which indicated that the strength of the 3 wt% Bi_2O_3–97 wt% PbO ceramic pellets sintered at 620°C is promising to meet the needs of engineering strength requirements.

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Figure 5. The 3 wt% Bi_2O_3–97 wt% PbO pellets before and after the flushing experiment.

4. Discussion

To understand the toughness mechanisms of doping Bi_2O_3, XRD was used to get the patterns of the PbO ceramic pellets sintered at 620°C with different wt% of Bi_2O_3 (Fig. 6). The formation of massicot (PbO, PDF No. 72-0094) was identified as the main crystalline phase, with a small amount of litharge (PbO, PDF No.85-0711). The litharge phase disappeared when the doping was done with more than 5 wt% Bi_2O_3 and the intensity of massicot peaks became stronger. The crystals in the massicot phase were orthogonal (a=5.489, b=4.775, c=5.891) and those in the litharge phase were tetragonal (a=3.973, b=3.973, c=5.022). They are two forms of PbO in nature, and the phase transition temperature is 500°C. The addition of aid promotes the phase transition process, so at high aid content, the main component is massicot. Lead bismuth oxide and Bi_2O_3 phases were not detected in the XRD patterns for the fabricated samples.

Figure 6 indicates that the peaks of the PbO phase are shifted to a large angle, which is attributed to the formation of a solid solution between Bi_2O_3 and PbO. The radius of Bi^{3+} (1.03 Å) is smaller than that of Pb^{2+} (1.19 Å). When Bi^{3+} ions are substituted with Pb^{2+} ions, there is a lattice distortion and the resistance to dislocation increases. Therefore, the enhancement of mechanical properties is due to the strengthening of the solid solution of Bi^{3+} ions.

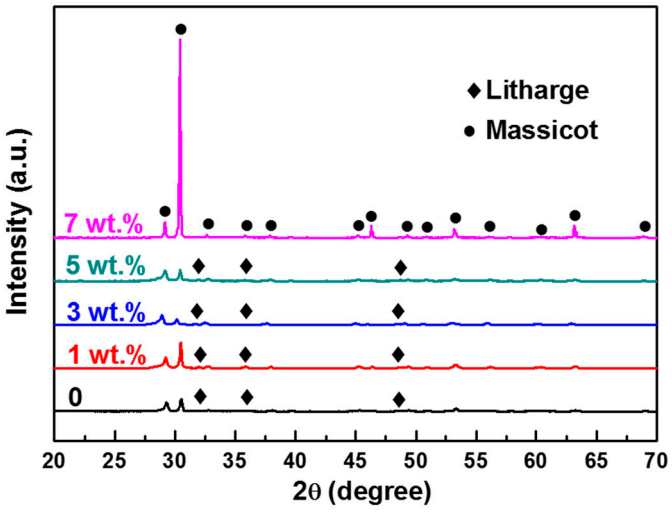

Figure 6. XRD patterns of PbO ceramic pellets sintered at 620°C with different wt% of Bi_2O_3.

Figure 7 (a)–(j) shows the SEM micrographs and fracture images of PbO ceramic pellets sintered at 620°C with different wt% of Bi_2O_3. First, with the addition of Bi_2O_3, the grain size of PbO ceramic pellets increases as compared with the pure PbO ceramic pellets. The grain boundaries cannot be seen clearly, which indicates that the sample is at the initial stage of sintering and metallurgical binding has not yet occurred between the powders.

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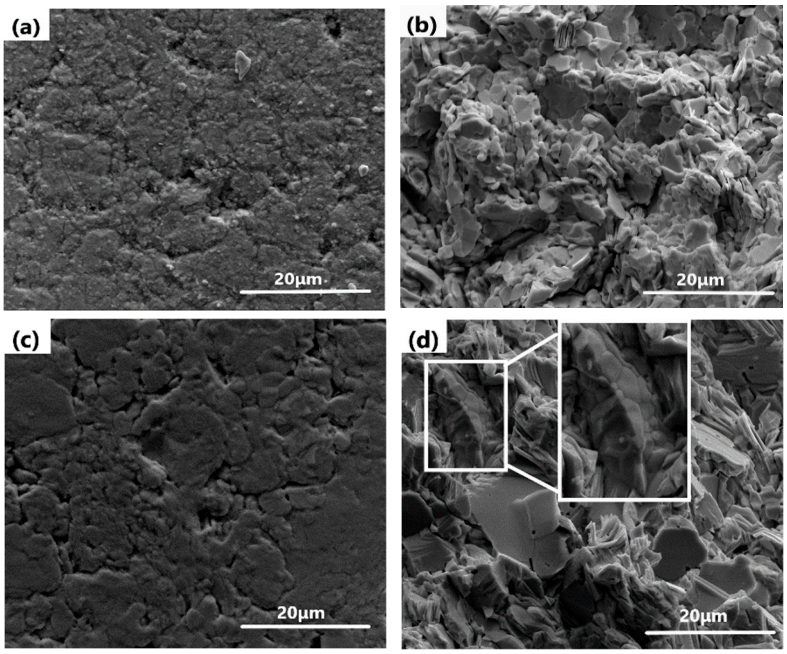
When doping is done with 1 wt% Bi_2O_3, the crystals are observed to start growing (Fig. 7(d), indicated by frame). When the Bi_2O_3 content increases to 3 wt%, grains are seen to aggregate to form with distinct grain boundaries (Fig. 7(e)). When the Bi_2O_3 content continues to increase, the solid solution is formed, wherein the solute ions Bi^{3+} replace the host ions Pb^{2+}, resulting in the formation of positive ion vacancies, which is beneficial to the sintering process and metallurgical binding [15,16].

Based on the results shown in Fig. 2, xBi_2O_3-(1-x) PbO (x being 0–3 wt%) can be considered to have the same relative density of ~90.6%. Thus, doping of Bi_2O_3 intensifies the sintering process by grain growth at 620°C as the amount of Bi_2O_3 is increased from 0 to 3 wt%. There is almost no change in the size of the grains for 3–7 wt% Bi_2O_3 ceramic pellets as observed by SEM (Fig. 7(e)–(j)). According to Eqs. (2) and (3), it is seen that the effect of porosity on the performance of ceramic pellets is dominant. It can be seen from Fig. 7(i) that pores are wrapped in grains, indicating that the grain boundaries move rapidly with 7 wt% Bi_2O_3 at 620°C, which leads to a decline in its mechanical properties. In addition, it can be seen from Fig. 2 that the density of Bi_2O_3–PbO ceramic pellets drops sharply when the Bi_2O_3 content exceeds 3 wt%, with almost the same grain size.

Figure 8 presents the SEM micrographs and fracture images of 3 wt% Bi_2O_3–97 wt% PbO sintered at 570°C and 670°C. Also, obvious powder agglomeration is observed in Fig. 8(a) and (b), indicating that sintering is not complete at this low temperature (570°C). Thus, grain growth plays a leading role in enhancing hardness and flexural strength at lower temperature (570°C). However, at 670°C, microcracks are observed on the surface of 3 wt% Bi_2O_3–97 wt% PbO ceramic pellets (Fig. 8(c)). They are apt to appear at the interface of two ceramic grains and readily propagate through the grains, which causes their hardness and strength to be lower than those of the ceramic pellets at 620°C. Thus, the optimum sintering temperature and doping amount of Bi_2O_3 for Bi_2O_3–PbO ceramic pellets are determined to be 620°C and 3 wt%, respectively.



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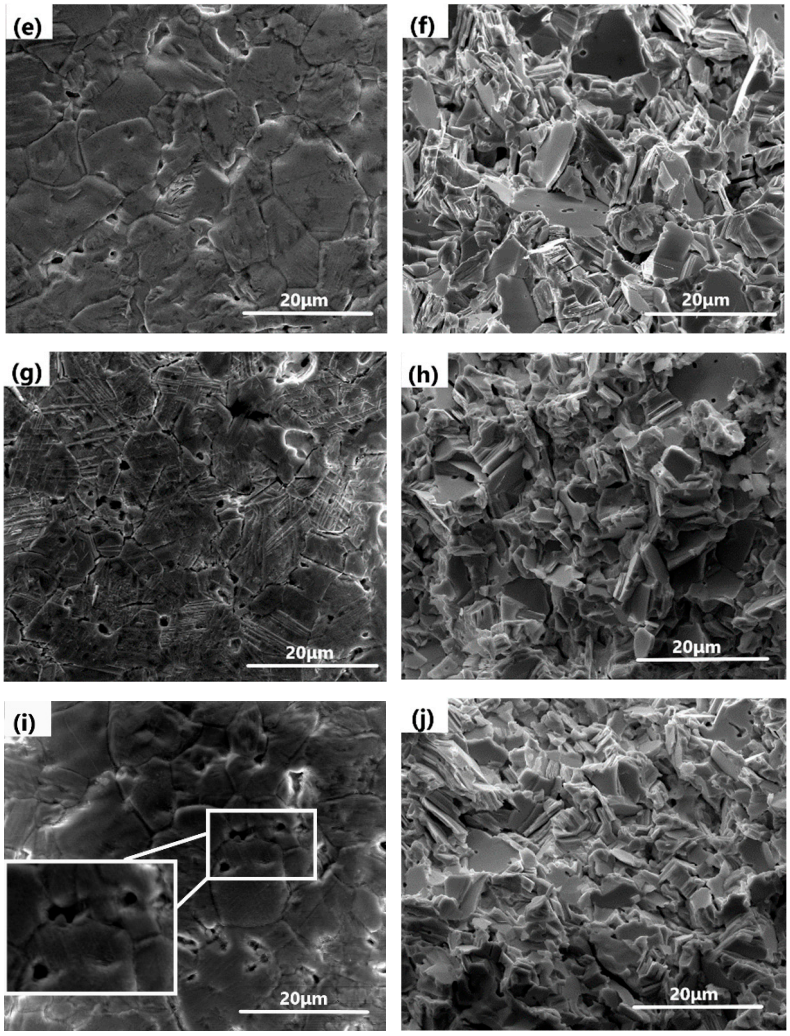

Figure 7. SEM micrograph and fracture images of PbO ceramic pellets sintered at 620°C with different Bi_2O_3 content (a, b) 0 wt%, (c, d) 1 wt%, (e, f) 3 wt%, (g, h) 5 wt%, (i, j) 7 wt%.

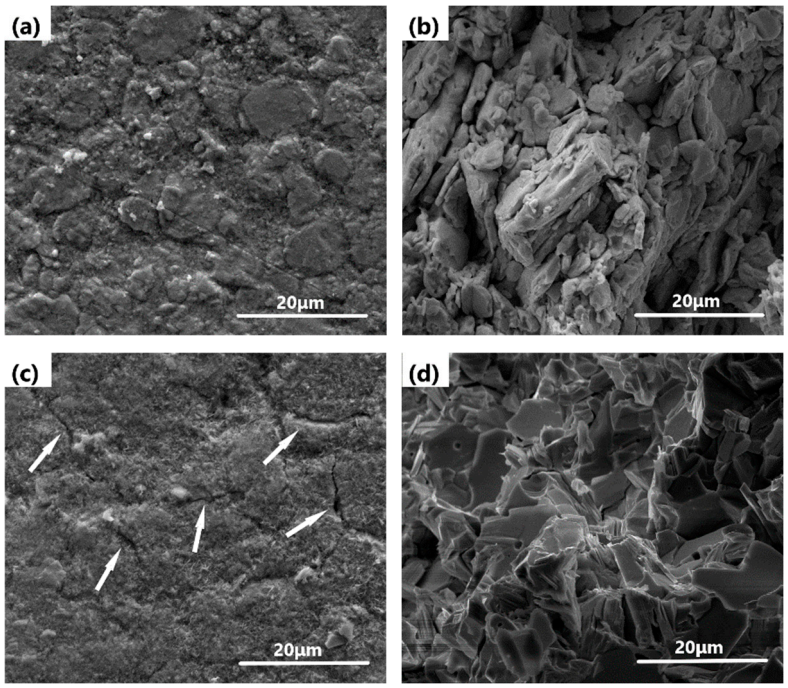

Figure 8. SEM micrographs and fracture images of 3 wt% Bi_2O_3–97 wt% PbO

sintered at (a, b) 570°C, and (c, d) 670°C.

5. Conclusions

In this paper, the effects of doping of Bi_2O_3 and sintering temperatures on the mechanical properties of PbO ceramic pellets were investigated. It was found that doping with a moderate amount of Bi_2O_3 could significantly enhance the mechanical properties of PbO ceramic pellets. The enhancement is attributed to the formation of solid solution of Bi^{3+} ions. The optimal sintering temperature and doping amount of Bi_2O_3 are 620°C and 3 wt%, respectively, for PbO. The hardness increased four times and the strength increased two times as compared with pure PbO. The ceramic pellets showed good performance in the LBE flushing experiment.

6. Patents

The method of bismuth oxide reinforced lead oxide ceramics introduced in this paper has been applied to China Patent Office for an invention paten.

Author Contributions: Conceptualization, Yan Ma; Funding acquisition, Huiping Zhu; Investigation, Anxia Yang; Methodology, Yan Ma and Anxia Yang; Project administration, Fenglei Niu; Writing – original draft, Yan Ma and Anxia Yang; Writing – review & editing, Yan Ma, Anxia Yang, Huiping Zhu, Arslan Muhammad, Pengwei Yang and Bokun Huang.

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Conflicts of Interest: The authors declare no conflict of interest.

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