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Preparation of $BaPbO_3$ functional ceramics from leaded waste

**Bin Li, Shen-Gen Zhang*, Kun Zhang,
De-An Pan, Jian-Jun Tian, Hu Liu,
Alex A. Volinsky**

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Abstract In this study, Pb was separated and used to prepare $BaPbO_3$ conductive ceramics from leaded waste. The experimental results show that $BaPbO_3$ powder synthesized at 700 °C has particle size of 2–5 μm. The powders were densified by sintering at 1,000 °C for 2 h in the air. Synthesized $BaPbO_3$ ceramics have high Curie temperature and high-temperature positive temperature coefficient (PTC) resistivity characteristics. Electrical resistivity of $BaPbO_3$ compact increases from 5×10^{-6} Ω·m at room temperature to 4×10^{-4} Ω·m at 750 °C. Compared with the one prepared by pure chemical reagents, the $BaPbO_3$ prepared from leaded waste has the similar characteristics of high Curie temperature and PTC resistivity.

Keywords $BaPbO_3$; Leaded waste; Positive temperature coefficient (PTC)

1 Introduction

Owing to the depletion of the primary mineral resources for valuable metals extraction, more efforts should be made to process secondary sources, such as waste rare earth products [1], tailings [2], and anode slime [3]. The anode slime from printed circuit boards (PCB) waste recycled by copper electrolysis contains many valuable metals, including a lot of Pb and Sn, and some noble metals (Au, Ag, Pt, Pd, etc.). It is particularly important that the Pb content could be up to 20 wt% in the form of $PbSO_4$. Consequently, the leaded waste of anode slime from PCB waste is an important secondary lead resource and can lead to serious environmental pollution without being recycled.

There are several investigations on recycling Pb from different kinds of leaded waste [4–6]. Currently, the main technical process of extracting Pb from PCB waste is pyrometallurgical technology. Zhan et al. [7] researched the method of separating and recovering Pb by evaporation and condensation. This method was suitable for the treatment of Pb and leaded alloys rather than leaded salts. Amer [3] recycled Pb and Sn in the form of Pb–Sn alloy from the copper anode slime. In the study, the amount of carbon and Na_2CO_3 added was necessary, and the mixtures needed to be smelted at a high temperature of above 1,100 °C. The disadvantages of pyrometallurgical technologies were of high-energy consumption and emission of much CO_2 and SO_2. However, the hydrometallurgical process could solve these problems.

In many special fields, such as ceramic electrode materials, positive temperature coefficient (PTC) thermal resistors, and anti-corrosion conductive coatings, $BaPbO_3$ was widely studied as a ceramic material with good electrical conductivity, high Curie temperature, and PTC of resistance. Over the years, many studies were about the

B. Li, S.-G. Zhang*, D.-A. Pan, J.-J. Tian, H. Liu
Institute for Advanced Materials and Technology, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China
e-mail: zhangshengen@mater.ustb.edu.cn

B. Li
e-mail: thlibin@sina.com

K. Zhang
Beijing Nonferrous Metals and Rare Earth Research Institute, Beijing 100012, China

A. A. Volinsky
Department of Mechanical Engineering, University of South Florida, Tampa 33620, FL, USA

preparation methods and performance of $BaPbO_3$. Nitta et al. [8] prepared $BaPbO_3$ by firing a mixture of $BaCO_3$, Pb_3O_4, and PbO in oxygen at 980 °C. The solid reaction process needed an increase in the partial pressure of O_2, which was provided by decomposing Pb_3O_4 into PbO. Yamanaka et al. [9] reported that $BaPbO_3$ was prepared by co-precipitation from the mixed analytical pure $BaCO_3$ and analytical pure PbO. The advantages of co-precipitation were low synthesis temperature, high-production efficiency, and low-energy consumption.

Leaded waste is an important secondary lead resource. $BaPbO_3$ is an important PTC ceramic, which needs to consume a large amount of Pb. Therefore, it has important significance to prepare $BaPbO_3$ by leaded waste. In this study, $BaPbO_3$ ceramic was prepared by co-precipitation from leaded waste, and presented in electrolytic copper anode slime from PCB waste. The material compositions and PTC resistivity characteristics of the $BaPbO_3$ prepared from leaded waste were similar with the results obtained from the pure chemical reagents. Pb was not only recycled but also reused directly to prepare functional $BaPbO_3$ ceramic material. It was helpful to reduce the pollution of Pb, and improved the high-value utilization of leaded waste as well.

2 Experimental

2.1 Source of leaded waste and pretreatment

After Cu and noble metal were recycled, the anode slime slag forming from PCB waste mainly contained large amounts of Pb (about 20 wt%), named leaded waste. The source material was the slag of leaded waste from PCB waste without Cu and noble metals, which contained about 23.71 wt% Pb and about 26.74 wt% Sn. The content of leaded waste is shown in Table 1.

2.2 Preparation of $BaPbO_3$ ceramic by co-precipitation

$BaPbO_3$ ceramic was obtained through a multi-step process including carbonating, acid leaching, mixing barium, co-precipitation, and roasting. The experimental flow chart is given in Fig. 1. All experiments were performed in a 2 L glass reactor immersed in a thermostatically controlled water bath. Na_2CO_3 was added to water until the concentration reached 1 $mol \cdot L^{-1}$; then water bath was heated to 60 °C. The slag of leaded waste was added to the solution, and the solid–liquid ratio was adjusted to 0.05 $g \cdot ml^{-1}$. Mixed Na_2CO_3 solution was mechanically stirred for 1 h. After filtering the mixed solution, the residue was dissolved by HAc water solution with the concentration of 1 $mol \cdot L^{-1}$, resulting in 0.1 $g \cdot ml^{-1}$ solid–liquid ratio. Mixed HAc solution was mechanically stirred for 1 h. After filtering the mixed solution, Pb content was analyzed in the solution. $BaCO_3$ was added to the mixed solution, including HAc and $Pb(Ac)_2$, until the Pb/Ba molar ratio of 1.05 was achieved. An excess of $H_2C_2O_4$ solution was added to the mixed solution, forming a white $BaPbO_3$ precursor powder deposit. The precursor powder was dried at 100 °C for 2 h, and then heated at 700 °C for 2 h in air to synthesize fine $BaPbO_3$ powder. $BaPbO_3$ powder was pressed into ceramic body under 200 MPa pressure, and sintered at 1,000 °C for 2 h in air.

Table 1 Content of leaded waste (wt%)

Pb	Sn	Bi	Ag	Others (O, S, Cl, etc.)
23.7100	26.7400	0.0021	0.3430	49.2000

2.3 Characterization

The chemical composition was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS). The phase analysis of $BaPbO_3$ powder was characterized by X-ray diffraction (XRD). The morphology of $BaPbO_3$ powder and compact $BaPbO_3$ ceramic was observed by scanning electron microscopy (SEM). $BaPbO_3$ ceramic electrical resistivity was measured by the four wires probe.

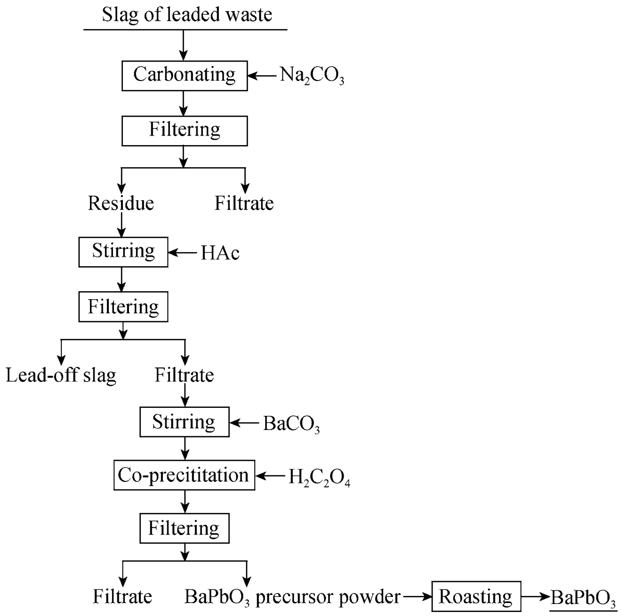

Fig. 1 Preparation flow chart of $BaPbO_3$ ceramic obtained from leaded waste

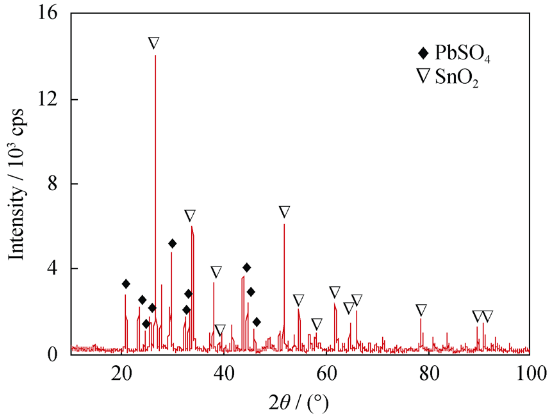

Fig. 2 XRD pattern of leaded waste

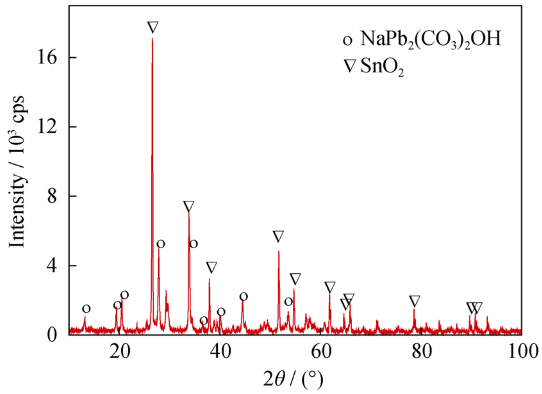

Fig. 3 XRD pattern of slag transformed by solution of Na_2CO_3

3 Results and discussion

3.1 Principle analysis

3.1.1 Carbonation reaction

The main phase composition of source material obtained by XRD is shown in Fig. 2. In the slag of leaded waste, tin and lead are in the form of SnO_2 and $PbSO_4$. In the process of recycling precious metals, silver is residual in the form of AgCl. However, the diffraction of AgCl is not obvious, because the amount of silver is small. SnO_2 and AgCl are stable, which do not react with Na_2CO_3 and acids. Therefore, the tin and silver do not affect the synthesis of $BaPbO_3$. The lead is in the form of $PbSO_4$ in the leaded waste.

Mixed with Na_2CO_3 solution for 1 h, the phase composition of the slag is shown in Fig. 3. The basic reaction between $PbSO_4$ and Na_2CO_3 could be summarized as follows:

$$4PbSO_4(s) + 5Na_2CO_3(aq) + H_2O(aq) \rightarrow 2NaPb_2(CO_3)_2OH(s) + 4Na_2SO_4(aq) + CO_2(g) \quad (1)$$

The $PbSO_4$ transforms into $PbCO_3$ with a little alkali in the form of $NaPb_2(CO_3)_2OH$. The alkali mainly comes from the carbonation process. The solubility product constant of $PbCO_3$ is 7.4×10^{-14} at room temperature, which is much smaller than that of $PbSO_4$ (1.6×10^{-8}), the $PbCO_3$ is usually more stable. It is not obvious that the solubility product constant of insoluble substance is affected by the temperature. In the solution, the ionization of $PbCO_3$ is more difficult, and the chemical reaction tends to produce a more stable product. The Gibbs free energy of Reaction (1) could be represented by Eq. (2).

$$\Delta G = \Delta H - T \times \Delta S \quad (2)$$

where ΔG is the change of gibbs free energy ($J \cdot mol^{-1}$); ΔH is the change of enthalpy ($J \cdot mol^{-1}$); T is the reaction temperature (K); and ΔS is the change of entropy ($J \cdot mol^{-1} \cdot K^{-1}$). According to the calculation result of Eq. (2), ΔG of Reaction (1) is $-8.135\ J \cdot mol^{-1}$at 60 °C. Therefore, the carbonation reaction was to happen positively. The experimental results put out that, under optimal working conditions, the conversion rate of $PbSO_4$ is 95 %, and the confidence level can be 97 % approximately.

3.1.2 Synthesis process of precursor

The synthetic process of precursor powders mainly included the following reactions.

$$NaPb_2(CO_3)_2OH(s) + 3HAc(aq) \rightarrow 2Pb(Ac)_2(aq) + NaAc(aq) + 2H_2O + 2CO_2(g) \quad (3)$$

$$BaCO_3(s) + 2HAc(aq) \rightarrow Ba(Ac)_2(aq) + H_2O + CO_2(g) \quad (4)$$

$$Pb(Ac)_2(aq) + H_2C_2O_4(aq) \rightarrow PbC_2O_4(s) + 2HAc(aq) \quad (5)$$

$$Ba(Ac)_2(aq) + H_2C_2O_4(aq) \rightarrow BaC_2O_4(s) + 2HAc(aq) \quad (6)$$

The formed alkaline $PbCO_3$ could be dissolved by HAc as Reaction (3) shows. $PbSO_4$ transforms into $Pb(Ac)_2$, which is separated from the leaded waste by the carbonation reaction and acid dissolution. By this method, Pb is separated and purified in the form of ions in the solution. $BaCO_3$ could also be dissolved by the HAc as shown in Reaction (4). When the appropriate amount of Ba^{2+} was dissolved in the solution, $BaPbO_3$ precursor powders could be co-precipitated by adding $H_2C_2O_4$ as shown in Reactions (5) and (6), because PbC_2O_4 and BaC_2O_4 are insoluble substances. Therefore, the major

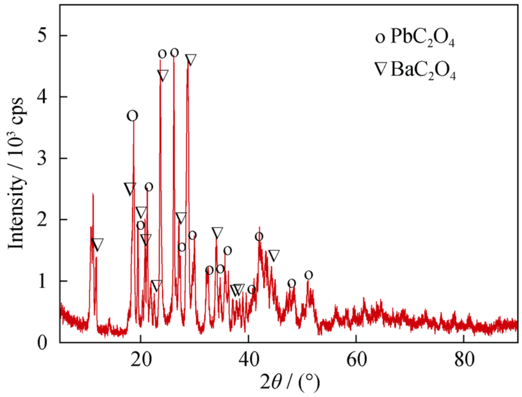

Fig. 4 XRD pattern of $BaPbO_3$ precursor powder

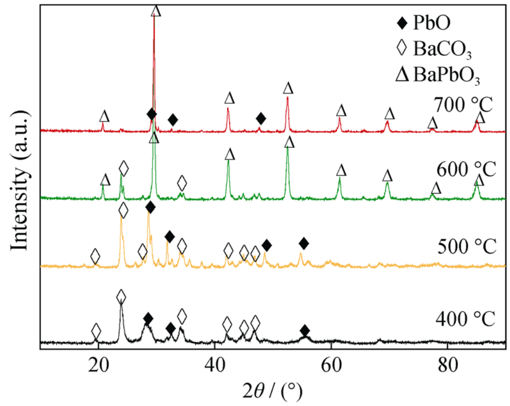

Fig. 5 XRD patterns of precursor powders heated to 400, 500, 600, and 700 °C

components of $BaPbO_3$ precursor powders are PbC_2O_4 and BaC_2O_4.

Phase composition of precursor powder obtained by XRD is shown in Fig. 4. After oxalic acid is added in the solution of acetate, PbC_2O_4 and BaC_2O_4 co-precipitate as the $BaPbO_3$ precursor powder. PbC_2O_4 and BaC_2O_4 exist in separated phase.

3.1.3 *Synthesis process of $BaPbO_3$*

The synthetic process of $BaPbO_3$ could be summarized as Reaction (7).

$$2PbC_2O_4(s) + 2BaC_2O_4(s) + 3O_2 \rightarrow 2BaPbO_3(s) + 8CO_2(g) \tag{7}$$

The precursor was heated to 400, 500, 600, and 700 °C for 2 h in air to synthesize the fine $BaPbO_3$ powder, and Fig. 5 shows the corresponding XRD data. Most of BaC_2O_4 convert to $BaCO_3$ at 400 °C, and PbO phase forms at 500 °C. At 600 °C, the $BaPbO_3$ phase forms from $BaCO_3$ and PbO. When temperature increases to 700 °C, $BaCO_3$ phase disappears, leaving trace amounts of PbO as a surplus, and $BaPbO_3$ powder was synthesized. The content of $BaPbO_3$ powder analyzed by energy spectrum is given in Table 2. According to the XRD data, $BaCO_3$ and PbO form first from $Ba(AC)_2$ and $Pb(AC)_2$ decomposition at a lower temperature. Since $BaCO_3$ and PbO powders prepared by co-precipitation have small particle size and are uniformly mixed, they have high surface reactivity and can be synthesized at 600–700 °C. Yamanaka et al. [9] reported that BaC_2O_4 and PbC_2O_4 changed to $BaCO_3$ at 397 °C and PbO at 447 °C, respectively. The formation of $BaPbO_3$ started at 567 °C from the PbO and $BaCO_3$ mixture. Results obtained in this paper are similar.

Table 2 Content of $BaPbO_3$ powder analyzed by EDS (wt%)

Pb	Ba	O	Totals
56.05	36.52	7.43	100.00

3.2 SEM analysis

Figure 6 shows the SEM image of $BaPbO_3$ precursor powder. Figure 7 shows the SEM image of $BaPbO_3$ powder heated to 700 °C. By co-precipitation synthesis, the morphology of $BaPbO_3$ precursor powder is massive structure with the size of 1–3 μm. After heated at 700 °C, $BaPbO_3$ precursor powder is decomposed and agglomerated to 2–5 μm particles. Because of CO_2 produced by precursor powder decomposition, the massive structure is dissociated to fine particles with the size of 400–600 nm. However, the fine particles are easier to agglomerate. Compared with the $BaPbO_3$ powder synthesized by solid reaction process, the powder size by co-precipitation is much smaller, which could contribute to reducing the sintering temperature of ceramic body.

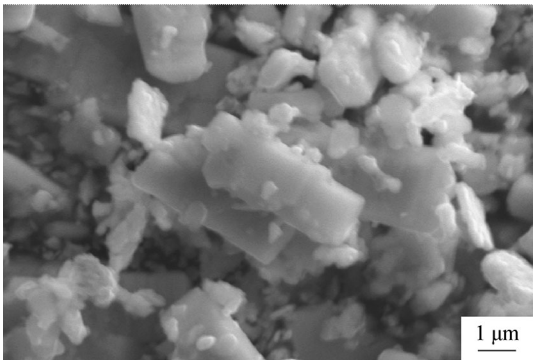

Fig. 6 SEM image of $BaPbO_3$ precursor powder

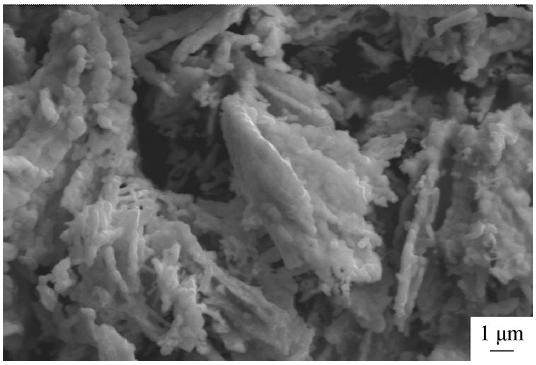

Fig. 7 SEM image of $BaPbO_3$ powder heated to 700 °C

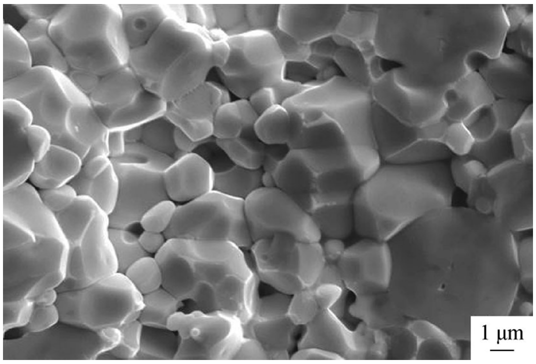

Fig. 8 SEM image of fracture surface of sintered $BaPbO_3$ ceramic

$BaPbO_3$ powder was pressed into the ceramic body under 200 MPa pressure, and sintered at 1,000 °C for 2 h in air. The fracture surface of $BaPbO_3$ ceramic is shown in Fig. 8. $BaPbO_3$ powder was sintered to 2–5 μm polyhedron particles with perovskite structure. Owing to Pb volatilization at 1,000 °C, there are a few 1 μm holes between the $BaPbO_3$ particles. Yasukawa et al. [10] prepared dense $BaPbO_3$ ceramic with different Pb/Ba ratios by co-precipitation, and studied its influence on electrical conductivity. They indicated that only 5 mol% excess of Pb content was enough for the densification in the preparation method, and the relative density of $BaPbO_3$ ceramic was 93 % when the Pb/Ba molar ratio was 1.05. The results obtained in this paper are similar with it.

3.3 Electrical properties

The resistivity measurements were done in the muffle furnace with the temperature increasing. $BaPbO_3$ ceramic electrical resistivity is 5×10^{-6} Ω·m at room temperature (Fig. 9). $BaPbO_3$ ceramic electrical resistivity does not change significantly until 650 °C, after which it rapidly increases. At 750 °C, electrical resistivity reaches 4×10^{-4} Ω·m. Synthesized $BaPbO_3$ ceramics have high-temperature PTC resistivity characteristics. The phenomenon is the same for the one synthesized by pure $BaCO_3$, PbO or Pb_3O_4, which was reported in Refs. [11, 12].

The reason that the $BaPbO_3$ ceramic has conductive properties is explained by different methods [13–15]. Because of the perovskite structure of $BaPbO_3$ [14, 15], the PTC characteristic of $BaPbO_3$ could be speculated by the Heywang model [16]. The electrons from oxygen vacancies could act as charge carriers. At room temperature, the electrons move freely. However, above the Curie temperature, the potential barrier on the grain boundary increases rapidly. The increase of potential barrier is greater than that of electronic activity. The electrons are difficult to cross the barrier. That is the reason for the PTC phenomenon.

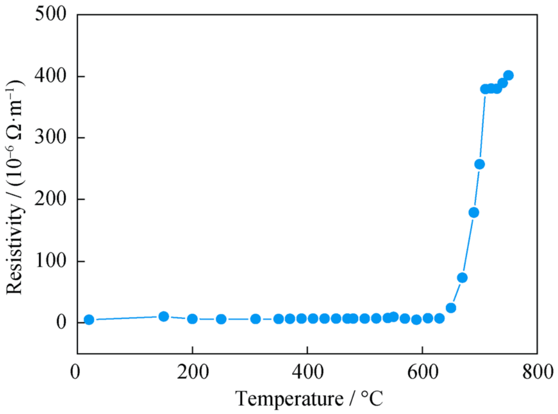

Fig. 9 Electrical resistivity of $BaPbO_3$ ceramic at different temperatures

4 Conclusion

In short, $BaPbO_3$ ceramic was synthesized by the co-precipitation from the slag of leaded waste, obtained by PCB waste with Cu and noble metals previously removed. Pb in the waste was recycled and reused. $BaPbO_3$ powder synthesized at 700 °C was 2–5 μm in particle size. Powder was densified by sintering at 1,000 °C for 2 h in the air. Electrical resistivity of $BaPbO_3$ compact increases from 5×10^{-6} Ω·m at room temperature to 4×10^{-4} Ω·m at 750 °C. The material compositions and PTC resistivity characteristics of the $BaPbO_3$ prepared from leaded waste are similar with the results obtained from the pure chemical reagents, which can be utilized in ceramic electrode, high-temperature PTC thermal resistors, anti-corrosion conductive coatings, as well as many special fields.

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