Preparation and characterization of nano bismuth titanate powders with high reflectivity in near-infrared waveband

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Abstract. Nano powders with high reflectivity in near-infrared waveband have broad applications as thermal insulation materials. In this study, nano bismuth titanate powders with the reflectance to near-infrared of as high as 89.5% in average were prepared via a sol-gel method by using tetrabutyl titanate, bismuth nitrate as raw materials and citric acid, acetic acid as reaction adjuvant reagents. Furthermore, to control the reflectivity in the visible light waveband, the as-prepared nano bismuth titanate powders were further coated with nano-Ag by using NaBH4 as a reduction agent. The influence of different dispersants on reflectivity and on powder dispersibility has also been studied. SEM characterization demonstrates that PEG1000, worked as a dispersant, significantly enhances the dispersion of bismuth titanate powders comparing with non-dispersant system. UV-Vis-NIR spectra reveal that with addition amount of AgNO3 of 1.5 ml and PEG1000 as the dispersant, the Ag-coated bismuth titanate nano powders can reach about 60% of reflectance to near-infrared, while the reflectance of visible light can be controlled as low as around 14%. It is very promising for such nano powders to be used in thermal insulation glass materials.

Keywords: nano bismuth titanate powders, nano-Ag, dispersant, PEG1000

1. Introduction

Inorganic heat–reflective nano powders are hot–spot topics in studies on energy conservation and emission reduction of both automotive industry and construction industry. Among them, TiO2, a white pigment with a high solar reflectance of about 87%, is currently regarded as the best pigment for thermal insulation materials [1]. However, the very high reflectivity of TiO2 in visible band (as high as 68%), which leads to light pollution [2], is the technological roadblock for thermal insulation applications in glass materials. Therefore, the exploration of preparation technology of inorganic heat-reflective nano powders and application with a high reflectance in near-infrared while a low reflectance in visible light is still a challenge and a need.

Bismuth titanate (BiTi2O7, light yellow powder) can be prepared through a co-precipitation method [3], a hydrothermal method [4], an inverse-emulsion method[5] and so on. However, the investigation of solar radiation properties of BiTi2O7 nano powder has rarely been reported. In the present work, nano bismuth titanate powders with reflectivity to near-infrared of as high as 90% in average have been prepared via a sol-gel method. Furthermore, the as-prepared nano bismuth titanate powders have then been coated with nano Ag by using NaBH4 as a reduction agent, which leads to a decrease of reflectivity to visible light from 78% to 14%. It is a new approach of controlling the reflectivity in
2. Experimental

2.1. Preparation of Bismuth Titanate Nano Powders

The chemical reagents used were tetra-n-butyl titanate (Ti(C₄H₉O)₄), bismuth nitrate (Bi(NO₃)₃·5H₂O), nickel nitrate (Ni(NO₃)₂·6H₂O), acetic acid (CH₃COOH), ethanol (C₂H₅OH), citric acid (C₆H₈O₇), silver nitrate (AgNO₃), polyethylene glycol (PEG1000), polyvinyl ketone (PVP), sodium boron hydride (NaBH₄), and distilled water (H₂O). All reagents were analytical grade and used without further purification.

First, bismuth nitrate (0.01 mol) was dissolved in a mixed solvent (acetic acid : ethanol = 1 : 1 wt.%) by stirring and tetra-n-butyl titanate (0.01 mol) was added consequently and stirred for 30 min. Citric acid (0.01 mol) was then added and stirred for 4h. The sol was dried at 80 °C after cured for 24h. Finally, BiTi₂O₇ nano particles were obtained by grinding the dried precursor and then calcination in air at 540 °C for 3h.

BiTi₂O₇ nano particles with Ag-coated were prepared as follow. The as-prepared BiTi₂O₇ was dissolved in 30g mixed solvent (dispersant: ethanol = 0.08 : 99.92 wt ratio, PEG1000 and PVP used as dispersants, respectively). The mixed solution was put in a 100 ml polytetrafluoroethylene ball milling tank, and milled for 1h at a rotating speed of 400 r/min. 1.5 ml AgNO₃ solution (2 wt.%) was added to the above solution and stirred for hours. Then, 10ml NaBH₄ solution (2 wt.%) was also added and stirred for 5h. Finally, after centrifugation and washing for several times, the powders were dried at 80 °C.

2.2. Characterization

Bruker AXS (D8 advance) X-ray diffraction was used to analyze the phase structure of the samples. The XRD patterns were collected under the following conditions: Irradiated with graphite monochromatic copper (Cu, Kα) = 0.154 nm, at 40 kV and 40 mA, over a range of 20 ~ 80° with a step of 0.0167° for 0.1s. Scanning electron microscope (SEM, Hitachi SU-70, 10 kV) was used for particle size and morphology characterization. The optical properties were detected using a UV-Vis-NIR spectrophotometer (Varian, Cary 5000) with an integrating sphere. The reflection spectra were scanned in the range of 380 ~ 2500 nm with a step of 600 nm/min.

3. Results and discussion

Figure 1 shows XRD patterns: the bottom two are the standard patterns of Bi₂Ti₂O₇ and Ag; and Bi₂Ti₂O₇ samples (a) without Ag coated; and (b) with Ag coated and EG1000 as the dispersant, (c) with Ag coated and PVP as the dispersant and (d) with Ag coated without any dispersant. It can be seen that the main diffraction peak positions of these particles agree well with the reflection of Bi₂Ti₂O₇ phase (JCPDFS No. 320188). Since the Bi₂Ti₂O₇ (662) diffraction peak (2θ=38.100°) is very close with Ag (111) primary peak (2θ=38.116°), the XRD peak of Ag coating may not be determined directly. To determine the existence of Ag, NiTiO₃ coated with Ag was prepared by the same method with PEG1000 as a dispersant. In figure 2, the XRD pattern of (e)NiTiO₃ coated with Ag shows clearly the diffraction peaks corresponding to the Ag (111) plane and (200) plane, therefore the existence of Ag in the samples of Bi₂Ti₂O₇ with the same Ag coating method is reasonable.

Figure 3 shows the SEM images of different Bi₂Ti₂O₇ samples: (a) without Ag coated; and (b) with Ag coated without any dispersant, (c) with Ag coated and PVP as the dispersant and (d) with Ag coated and PEG1000 as the dispersant. The grain size of Bi₂Ti₂O₇ powders is 50 ~ 200 nm (figure 3 (a)). Before coated with Ag, Bi₂Ti₂O₇ powders have good dispersion. After coated with Ag, the particles agglomerated seriously in the case of without any dispersant (figure 3 (b)), but the dispersion is slightly improved when PVP was used as the dispersant (figure 3 (c)), and the dispersion is a lot better when PEG1000 was used as the dispersant figure 3 (d)). Both the PEG and the PVP are
non-ionic dispersants. In the solution, they could form a steric hindrance what reduce the agglomeration of particles. In the results, the dispersion is better when PEG was used as the dispersant, which may be due to PEG with larger molecular weight has better steric hindrance and better dispersion because of its higher degree of polymerization [6].

**Figure 1.** XRD patterns. From bottom, standard patterns of Bi$_2$Ti$_2$O$_7$ and Ag; Bi$_2$Ti$_2$O$_7$ samples (a) without Ag coated; and (b) with Ag coated and EG1000 as the dispersant, (c) with Ag coated and PVP as the dispersant and (d) with Ag coated without any dispersant.

**Figure 2.** XRD patterns. From bottom, standard patterns of Bi$_2$Ti$_2$O$_7$ and Ag; (e) NiTiO$_3$ coated with Ag.

**Figure 3.** SEM of different Bi$_2$Ti$_2$O$_7$ samples: (a) without Ag coated; and (b) with Ag coated without any dispersant, (c) with Ag coated and PVP as the dispersant and (d) with Ag coated and PEG1000 as the dispersant.
Figure 4 shows Vis-NIR reflection spectra of the Bi$_2$Ti$_2$O$_7$ samples: (a) without Ag coated; and (b) with Ag coated and EG1000 as the dispersant, (c) with Ag coated and PVP as the dispersant and (d) with Ag coated without any dispersant. Table 1 presents the reflectance data of Bi$_2$Ti$_2$O$_7$ samples at range of visible light and near infrared range before and after coated with Ag. The NIR reflectance of Bi$_2$Ti$_2$O$_7$ without coated Ag reaches 89.50 %, however, its visible light reflectance (78.37 %) is also very high. After coated with Ag, the reflectance decreases at both visible light and near infrared band. Among Bi$_2$Ti$_2$O$_7$ with coated Ag, the sample without dispersant and the sample with PVP as the dispersant have similar reflectance in above two bands (figure 4 (c)and(d)); noteworthy, reflection curve of the sample with PEG1000 as the dispersant is higher in the range of 1000 ~ 2500 nm with NIR reflectance of 60.24 %, while its visible light reflectance is the lowest, only being 13.88 %.

![Figure 4. Vis-NIR reflection spectra of Bi$_2$Ti$_2$O$_7$ samples: (a) without Ag coated; and (b) with Ag coated and PEG1000 as the dispersant, (c) with Ag coated and PVP as the dispersant and (d) with Ag coated without any dispersant.](image)

| Reflectance(%) | Blank Bi$_2$Ti$_2$O$_7$ | Bi$_2$Ti$_2$O$_7$ after Ag coated |
|---------------|-------------------------|----------------------------------|
|               | Without using dispersant | Using PVP as dispersant | Using PEG1000 as dispersant |
| Vis           | 78.37                   | 21.65                           | 19.78                           | 13.88                           |
| NIR           | 89.50                   | 51.29                           | 50.81                           | 60.24                           |

4. Summary
In this study, nano bismuth titanate powders with the reflectance of near-infrared as high as 90 % have been prepared via a sol-gel method. However, the reflectance in visible light is also very high (78 %). To decrease reflectance in visible light wave band, the as-prepared nano bismuth titanate powders have been coated with nano Ag, which leads to a significant decrease of reflectance in visible band. When PEG1000 is used as the dispersant, the Ag-coated bismuth titanate nano powders have good dispersion and their reflectance of near-infrared reaches up to 60%, while the reflectance of visible light is controlled to be merely 14%. Ag coating treatment is an effective method to keep the high infrared reflectivity of the thermal reflection nano powder materials as well as a reduced visible light reflectivity.

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