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ARTICLE

Synthesis of Amorphous BaO-TiO_2 and La_2O_3-Nb_2O_5 Glass Microspheres Using Containerless Flame-Spraying Technique and Their Properties

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Abstract: The $BaTi_2O_5$ (BTO) and $35La_2O_3$-$65Nb_2O_5$ (LNO) amorphous microspheres without conventional network-forming oxides were fabricated by a containerless flame-spraying technique. The results show that transparent BTO and LNO glass microspheres were successfully prepared. All the BTO glass microspheres have smooth surfaces and no crystalline traces, indicating they are amorphous glass. Their diameters range from 8 μm to 40 μm. And their amorphous forming ability is low. Most of the LNO glass microspheres have diameters of 10 μm to 40 μm, which are amorphous glass with smooth surfaces. And a small number of LNO microspheres have large particle diameters, which possess micron-sized grains on their surfaces. The BTO and LNO glass microspheres have high refractive index of 2.20 and 2.23, respectively, which are very promising to be applied as window, lens and reflection film materials.

Key words: flame spraying-water quenching; glass microspheres; TiO_2-based glass; Nb_2O_5-based glass

Conventional glasses must contain sufficient network-forming oxides such as SiO_2, P_2O_5 and B_2O_3, which result in a disordered three-dimensional (3D) glass-forming network over a long range. However, the refractive index of these conventional glasses is usually lower. Recently, a series of glass systems lacking network-former (LNF) have emerged. Among them, TiO_2-based[1-4] and Nb_2O_5-based[5-9] glasses have attracted extensive attention owing to their outstanding optical and dielectric properties. For example, $BaTi_2O_5$ (BTO) glass presents a super high refractive index exceeding 2.1 and is found to have a wide transmittance window from 340 to 7700 nm[2], and it exhibits anomalous permittivity (even greater than 10^7) near the glass transition temperature T_g[1]. The currently reported $0.3La_2O_3$-$0.7Nb_2O_5$ glass exhibits an ultrahigh refractive index greater than 2.3 in the visible range[5].

Since LNF glasses do not contain network formers, they have deficient glass-forming ability and are highly susceptible to crystallize. Thus, the LNF glasses cannot be obtained through conventional industrial techniques (e.g. float process). By now, the TiO_2-based and Nb_2O_5-based LNF glasses have been mainly prepared by aerodynamic levitation (ADL) technique, which could eliminate inhomogeneous nucleation caused by the container wall and promote deep undercooling in molten materials[1-10]. Unfortunately, the products obtained by ADL technique are generally 0.1~10 mm in diameter, so that it is difficult to reach the requirements of the preparation and mass production of micron-sized glass spheres. Containerless flame-spraying technique is recognized as a promising method for industrial large-scale glass microspheres production[11]. Many kinds of Al_2O_3-based glass microspheres, such as Al_2O_3-Y_2O_3 system[12,13], Al_2O_3-La_2O_3 system[14-16] and Yb_2O_3-Al_2O_3 system[17], have been successfully prepared using this method. Glass microspheres with high refractive indexes are important materials for making reflective films and are widely used in

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safety reflective signs. In addition, a bulky full-density amorphous glass can be further obtained by viscous sintered glass microspheres[18,19].

However, to the best of our knowledge, the synthesis of transparent micrometer-sized BaO-TiO_2 and La_2O_3-Nb_2O_5 LNF glass spheres has been rarely reported. In this work, transparent $BaTi_2O_5$ (BTO) and 35La_2O_3-65Nb_2O_5 (LNO) glass microspheres were fabricated by the containerless flame-spraying technique. The prepared transparent microspheres are amorphous glassy state, and they have high reflective indexes. They have the potential to be used in the applications of window, lens and reflection film materials.

1 Experiment

The high-pure commercial powders of La_2O_3 (Rare-Chem. Hi-Tech. Co., Ltd), Nb_2O_5 (Rare-Chem. Hi-Tech. Co., Ltd), BaO (Sinopharm Chemical Reagent, China) and TiO_2 (Sinopharm Chemical Reagent, China) were mixed according to the stoichiometric ratio of $BaTi_2O_5$ and 35La_2O_3-65Nb_2O_5. The mixtures were homogeneously mixed with ethanol by using wet ball milling for 12 h according to the ratio of powders:ethanol:milling ball=1:2:2, and then sintered at 1200 K for 2 h. The above powders were added into the water with 0.5 wt% PVA (purity 99.0%, Tianjin Fuchen Chemical Reagent Factory, China), 0.5 wt% PAA (purity 30%, Sinopharm Chemical Reagent, China) and 0.5 wt% n-octyl alcohol (purity 99.0%, Sinopharm Chemical Reagent, China). The slurry of mixtures was spray-dried through a spray dryer (Buchidryer B-290). The feed rate was set as 10 mL/min. The spray-dried powders were then fed into a C_2H_2-O_2 flame (>3000 °C) and quenched in water. The N_2 gas was selected to be carrier gas. The flame-sprayed microspheres were washed with deionized water at least 5 times, and then thermally annealed at 500 °C for 12 h, and named as BTO and LNO.

2 Results and Discussion

2.1 Preparation and characterization of BTO

The morphologies of mixed BaO and TiO_2 powders after ball milling and spray-dried porous microspheres are shown in Fig.1. The particle size of raw powers has become uniform submicron-sized after ball milling for 12 h. Further, after spray drying, the uniform submicron-sized raw powers agglomerate into microspheres with porous surfaces (Fig. 1b) and the diameter of porous microspheres has a distribution of 5~25 μm.

Fig.2 shows the morphologies of the prepared BTO microspheres. The optical microscopy photograph (Fig.2a) shows that the microspheres are transparent in the visible wavelength region. Fig.2a and 2b show that the BTO microspheres exhibit a perfectly spherical shape, and have smooth surfaces without any traces of crystallization which further confirms its amorphous feature. The diameter of the BTO microspheres ranges from 8 μm to 40 μm, which is slightly larger than that of spray-dried porous microspheres. This result matches the size distribution curve measured by laser particle size analyzer, as shown in Fig.3. It indicates that the small porous microspheres melt and coalesce together to form larger solid microspheres during flame-spraying process. The coalescence process can be confirmed by Fig.2c. Fig.2d shows the EDS spectrum and the results of the element analysis of the BTO microspheres of Fig.2b. All the compositional elements Ba, Ti, and O are detected and the semi-quantitative results are consistent with the stoichiometric ratio of BaO and TiO_2 crystalline raw powders.

Fig.4 shows the XRD patterns of the spray-dried porous microspheres and the BTO microspheres. It can be seen that the spray-dried porous microspheres are obvious crystalline consisting of three crystal phases, i.e., $BaTiO_3$, $BaTi_2O_5$ and $Ba_6Ti_{17}O_{40}$, while the BTO microspheres exhibit a broad amorphous peak, indicating that the cooling rate achieved by the containerless flame-spraying process is fast enough to prevent the crystallization of BTO melt droplets, and the BTO melt droplets are completely quenched into amorphous state.

Fig.5 illustrates the thermal stability of the BTO glass microspheres measured by DSC. The DSC curve shows a glass transition at 693 °C followed by two strong exothermic peaks T_{px} at 733 and 789 °C. The two exothermic peaks

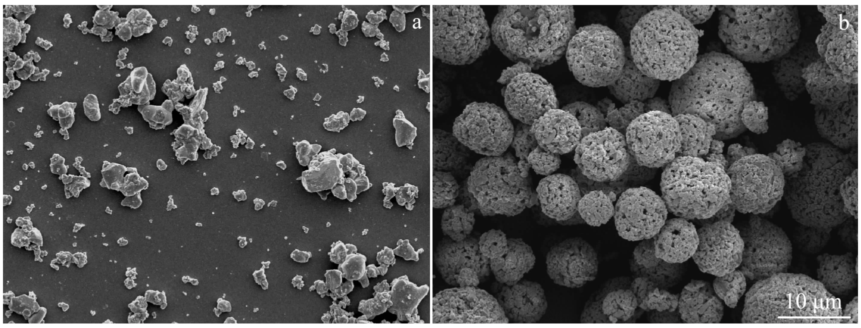

Fig.1 SEM images of BaO and TiO_2 mixed powders after ball milling (a), and the spray-dried porous microspheres (b)

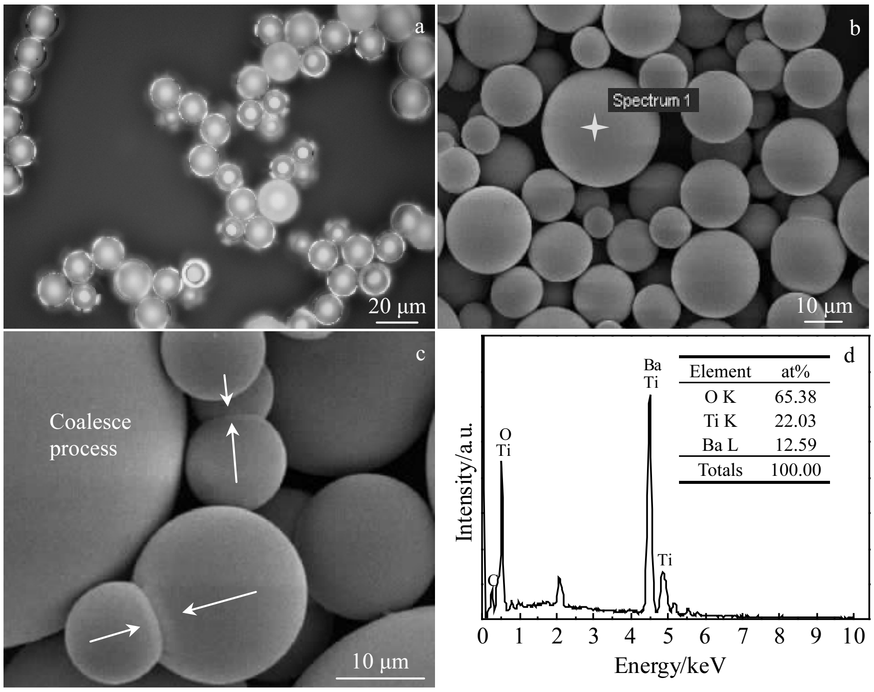

Fig.2 Optical microscopy photograph (a), SEM image (b), high magnification SEM image of the coalescence process (c), and EDS result of BTO microspheres of Fig.2b (d)

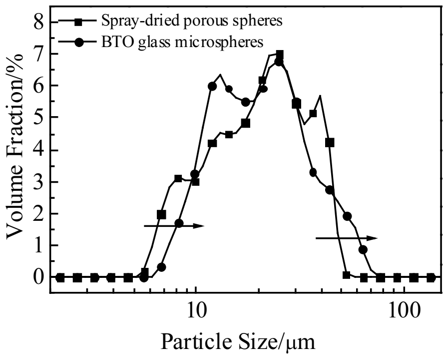

Fig.3 Size distributions of the spray-dried porous microspheres and the BTO microspheres

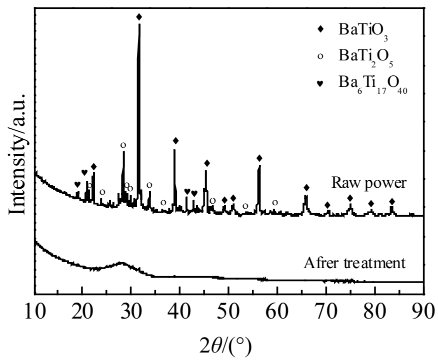

Fig.4 XRD patterns of the spray-dried porous microspheres and BTO microspheres

are attributed to the crystallization of α and β phases from the glassy matrix, respectively. The Kinetic window ΔT ($\Delta T = T_{p1} - T_g$) is a reference of the glass-forming ability. The maximum size of the obtained glasses would increase with the increase of ΔT. Typically, ΔT of conventional glasses that contain conventional network-formers is over 100 K. The ΔT for the BTO glass microspheres obtained by containerless flame-spraying technique is as low as 40 K, which is too low to form glasses using a conventional melting process.

2.2 Preparation and characterization of LNO

Nb_2O_5-based glass microspheres can also be prepared by the containerless flame-spraying technique. The XRD pattern of the

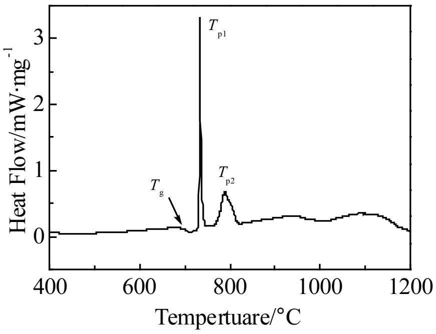

Fig.5 DSC curve of the BTO microspheres

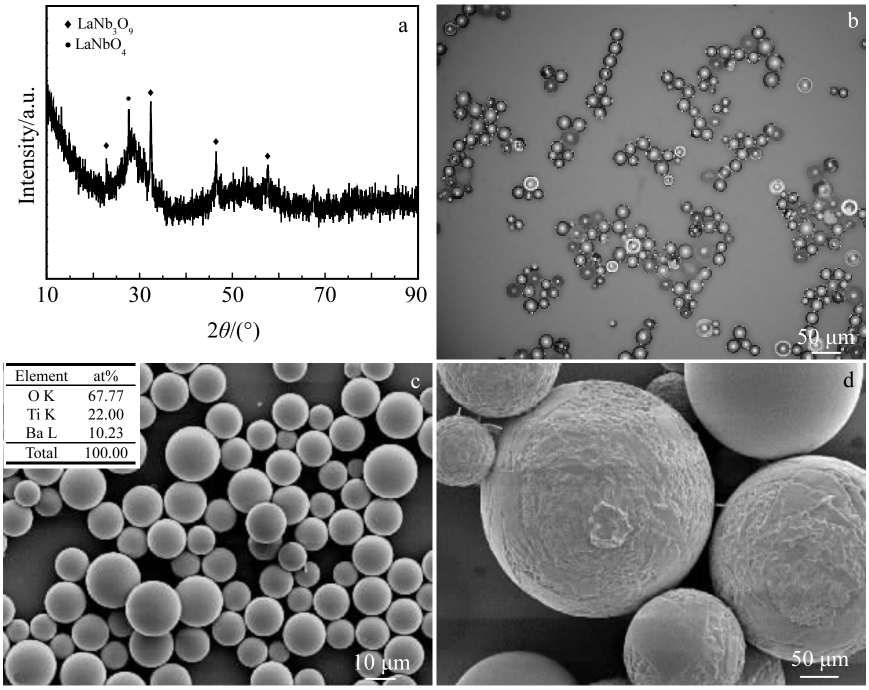

Fig.6 XRD pattern (a), optical microscopy photograph (b), SEM image and embedded EDS result (c) of LNO microspheres, and SEM image of the crystalline LNO microspheres (d)

prepared LNO microspheres are illustrated in Fig.6a. The LNO microspheres exhibit mainly amorphous peak, and weak crystallization peaks of $LaNbO_4$ and $LaNb_3O_9$ crystalline phases. Fig.6b shows that the LNO microspheres are transparent in visible light region. Fig. 6c shows that most of the LNO glass microspheres have the particle size distribution of 10~40 μm, which have the perfectly spherical shape and smooth surfaces, indicating that these microspheres are amorphous. Nevertheless, Fig.6d shows that some microspheres with larger diameters have rough surfaces composed of several micron-sized crystal grains, which are accordance with the $LaNbO_4$ and $LaNb_3O_9$ crystalline phases of the XRD result. The presence of crystalline microspheres may be attributed to the existence of large temperature gradient during the containerless flame- spraying process. The EDS result of the LNO microspheres is shown in the inset of Fig.6c, indicating that all the compositional elements La, Nb, and O exist and the semi-quantitative results are in agreement with the stoichiometric ratio of $35La_2O_3$-$65Nb_2O_5$.

2.3 Average refractive index of BTO and LNO glass microspheres

Refractive index (n) is an important parameter for designing optics. Oxide glass materials with a refractive index greater than 2.0 can be used to prepare optical instruments and window materials. The average refractive index n of the prepared BTO and LNO glass microspheres can be simply calculated using the empirical Gladstone-Dale equation[20]:

$$\frac{n-1}{\rho} = \sum_i k_i p_i \tag{1}$$

where ρ is the density, k_i is the specific refractive energy, and p_i is the mass fraction of the component. The values of k_i can be obtained from the Ref.[21]: k_{BaO}=0.128, k_{TiO_2}=0.393, $k_{La_2O_3}$= 0.148 and $k_{Nb_2O_5}$=0.268. The values of density are taken from the literature [2,6]: ρ_{BTO}= 4.56 g/cm^3 and ρ_{LNO}=5.6 g/cm^3. The calculated refractive index of BTO and LTO glass microspheres is 2.20 and 2.23, respectively.

3 Conclusions

1) The transparent BTO glass microspheres without conventional network-forming oxides can be fabricated by the containerless flame-spraying technique. And they have the particle size distribution of 8~40 μm, and smooth surfaces without crystal traces, which indicate they are amorphous glass microspheres. And the amorphous forming ability of BTO glass microspheres is low. Their calculated average refractive index is 2.20.

2) The transparent LNO glass microspheres without conventional network-forming oxides can be also obtained by the containerless flame-spraying technique. Most LNO glass microspheres have the particle size distribution of 10~40 μm. Their surface is smooth and has no crystal traces, indicating that they are amorphous. Some LNO microspheres with large particle sizes have rough surfaces which are caused by micronsized crystals of $LaNbO_4$ and $LaNb_3O_9$. The calculated

average refractive index of LNO glass microspheres is 2.23.

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火焰喷淬制备 $BaO\text{-}TiO_2$ 和 $La_2O_3\text{-}Nb_2O_5$ 玻璃微球及性能研究

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摘　要：分别以 BaO、TiO_2 和 La_2O_3、Nb_2O_5 为原料采用火焰喷淬法制备了不含网络形成体的 $BaTi_2O_5$（BTO）和 $35La_2O_3\text{-}65Nb_2O_5$（LNO）玻璃微球。结果表明，所有 BTO 为透明的、表面光滑、无结晶痕迹的玻璃微球，粒径分布集中在 8~40 μm，且具有较低的非晶形成能力；而大部分的 LNO 为透明的、具有光滑表面的玻璃微球，粒径分布集中在 10~40 μm，少量粒径较大的 LNO 微球表面粗糙，存在微米级 $LaNbO_4$ 和 $LaNb_3O_9$ 晶粒。计算结果显示，BTO 和 LNO 玻璃微球均具有高折射率，分别为 2.20 和 2.23，是非常有应用前景的窗口、镜头以及反光标志膜材料。

关键词：火焰喷淬；玻璃微球；TiO_2 基玻璃；Nb_2O_5 基玻璃

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