

Oxidative control of surface plasmon resonance of bismuth nanometal in bismuth glass nanocomposites

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ABSTRACT

We demonstrate here a novel oxidative process to control the metallic bismuth (Bi^0) nanoparticles (NPs) formation in bismuth glass nanocomposites by using KClO_4 and KNO_3 as oxidant instead of usual reducing technique. The formation of Bi^0 NPs has been monitored by its distinctive surface plasmon resonance (SPR) band at 460 nm in the UV-visible absorption spectra. It is further confirmed by the TEM images of Bi^0 NPs using KNO_3 and KClO_4 which show the formation of spherical Bi^0 NPs of 2-15 nm sizes and the SAED pattern reveals their crystalline rhombohedral phase. Using this technique it is possible to control the SPR band of nanobismuth (Bi^0) in bismuth glasses.

Keywords: Glasses, Bismuth nanoparticles, Transmission electron microscopy, Optical properties

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1. Introduction

The successful progress of nanoscience and technology has been accelerated by discoveries of the various unique properties associated with the size and shape of the nanomaterials. Nanoparticles exhibit novel properties that notably different from those of corresponding bulk state due to the small size effect such as nanometals show a very intense color which is absent in the bulk material [1, 2]. During the past years, metal nanoparticles have mainly studied because of their unique physical and chemical properties and potential application in diverse areas, such as catalyst, electronic devices, optical applications, conductive materials, etc. A lot of interests have been given on the study of surface plasmon resonance [3-5] of metal NPs and their potential applications in plasmonics. When various applications in plasmonics are concerned, the greatest challenge is the development of the controlled synthetic methodologies. Numerous chemical approaches have been explored, and some have been proven to be successful in the control of size and morphology of the nanoparticle.

In recent times, glass researchers have been expressed their extensive interest in the bismuth glasses as it is one of the most important amongst the heavy metal oxide (HMO) glasses due to their several properties such as high refractive index, wide transmission window, broad band near infrared (NIR) luminescence, [6-10] etc. Bismuth oxide glasses are usually obtained in dark-brown or black color, which deepens with increasing Bi_2O_3 content and when melted at higher temperature [7, 8]. Hence, it is very difficult to control the nanobismuth particle formation as well as its SPR in bismuth glasses. Therefore, synthesis of controlled Bi^0 NPs [11] in bismuth glasses is very important both academically as well as technological point of views. Sanz *et al.* [7] and

Zhang *et al.* [8] have studied the transparency of bismuth glass by addition of color oxidizing additives as dopant such as As_2O_3 , Sb_2O_3 , CeO_2 etc. However, they have not paid their attention to above issues. To the best of our knowledge there is no previous report on the control synthesis of Bi^0 NPs and its plasmon in bismuth glasses by applying the oxidation technique using KNO_3 and KClO_4 as oxidant.

In view of above, in this communication we report the controlled formation of Bi^0 NPs during melting process in the B_2O_3 - ZnO - Bi_2O_3 - SiO_2 - K_2O glass system using KNO_3 and KClO_4 as oxidizing agent. The efficiency of oxidant on the formation of Bi^0 NPs and its SPR in bismuth glasses is characterized by UV-Vis spectroscopy, transmission electron microscopy (TEM), and selected area electron diffraction (SAED) analysis.

2. Experimental details

High purity chemicals of bismuth trioxide, Bi_2O_3 (99%, Loba Chemie), boric acid, H_3BO_3 (99.5%, Loba Chemie), zinc oxide, ZnO (99%, Loba Chemie), potassium carbonate, K_2CO_3 (99.9%, Loba Chemie), silicon dioxide, SiO_2 (99.8%, Bremthaler/Quarzitwerk), potassium nitrate, KNO_3 (99%, Loba Chemie) and potassium perchlorate, KClO_4 (99%, Sigma, Aldrich) were used as raw materials. The composition (wt %) of glasses are: $19\text{B}_2\text{O}_3$ - 23ZnO - $45\text{Bi}_2\text{O}_3$ - 9SiO_2 -(4-x) K_2O -x K_2O , where x is the equivalent amount of K_2O (wt. %) has taken from KNO_3 (x = 0, 0.2, 0.5, 0.9 and 1.4) and KClO_4 (x = 0, 0.2, 0.3, 0.7 and 1) sources. 25 g glass was melted in a 50 ml high purity silica crucible at 1100°C in air for 30 min in a raising hearth electrical furnace with intermittent stirring for 0.5 min. The molten glass was cast into a carbon plate and annealed at 420°C for 2h to release the internal stresses. Samples of 2 ± 0.01 mm thickness were prepared by cutting, grinding and polishing for optical measurements.

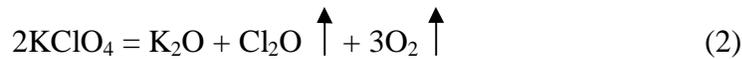
The UV-Vis absorption spectra in the range of 300-800 nm were recorded using a double beam UV-visible spectrophotometer (Lambda 20, Perkin-Elmer) at an error of ± 0.1 nm. The TEM and SAED images were taken using a FEI instrument (Tehnai-30, ST G^2) operating at an accelerating voltage of 300 kV.

3. Results and discussion

The bismuth glasses are one of the most important among the heavy metal oxide glasses for its high refractive index. But the browning or blackening of bismuth glasses when melted at higher temperature are serious problem for controlling of Bi⁰ NPs and its SPR band. The intensity of browning or blackening increases with increase in melting temperature as well as Bi₂O₃ concentration due to auto-thermo reduction of Bi³⁺ ions to bismuth metal (Bi⁰) during the melting process. The reduction of Bi₂O₃ occurs through the following thermal dissociation reaction [7, 8]



The above equilibrium reaction shifted towards right side with the release of oxygen as melting temperature increases and the metallic Bi⁰ is formed. When the oxidizing agent, such as KNO₃ or KClO₄, is added in the glass composition, it increases the oxygen partial pressure as a result of its thermal dissociation during melting at high temperature as follow.



Consequently, the reaction of the Eq. (1) proceeds in the reverse direction due to reactions of the Eqs. (2) and (3). By comparing the standard reduction potentials [12] as listed in Table 1, it is clear that the standard potential of ClO₄⁻/Cl⁻ (1.34V) and NO₃⁻/NO (0.96V) are higher than that of Bi³⁺/Bi⁰ (0.50 V), Bi³⁺/Bi⁰ (0.31 V), Bi³⁺/Bi⁺ (0.20 V) and Bi³⁺/Bi²⁺ (<0.20 V) species, so it easily favors the backward reactions of the Eq. (1). It

suppresses the uncontrolled auto-reduction of Bi₂O₃. Hence, controlled formation of Bi⁰ NPs in the glasses gradually increases with increasing KClO₄ or KNO₃ content. The KClO₄ is more effective than the KNO₃ due to its higher reduction potential that is, it favors the oxidation reaction and reduces the uncontrolled formation of Bi⁰ nanometal more effectively than KNO₃. This fact could be visualized clearly by the remarkable changes in the transparency as shown in the bottom photograph of Figs. 1 and 2.

The UV-Vis absorption spectra of bismuth glasses are shown in Figs. 1 and 2. The broad SPR absorption band at 460 nm is due to the Bi⁰ NPs. The spherical particle gives an SPR absorbance band centered at a wavelength, λ , which can be calculated by the relation [13]

$$\lambda^2 = (2\pi c)^2 m_o N e^2 (\epsilon_\infty + 2n_o^2) / \epsilon_o \quad (4)$$

where c is the velocity of light, m_o is the mass of particle, N is the concentration of the particle, e is the charge of the electron, ϵ_∞ is the optical dielectric function of the metal, n_o is the refractive index (RI) of the host material and ϵ_o is the free-space permeability. From the Eq. 4, it is clear that the absorbance band position proportionate directly to the RI of the host material. The absorbance band of Bi⁰ NPs was observed in the host water (RI = 1.33) at around 400 nm [3] whereas our glass having higher RI (1.76) shows a red shift of the band to 460 nm. Khonthon *et al.* [8] has also reported the broad band due to SPR of Bi⁰ NPs at 460 nm, which is similar to our result. The absorption band of the base glass has shown in the inset of the Figs. 1 and 2. The base glass is black and shows a very weak SPR band. When 0.2 wt% of K₂O from equivalent amount of oxidizing agent KNO₃ or KClO₄ has added to the base glass, the plasmon band has visualize very distinctly. The intensity of SPR band decreases with addition of further amount of KClO₄ or KNO₃ (up

to 1 or 1.4 equivalent wt % of K₂O respectively). However, the SPR band position remains unchanged at 460 nm for all the cases of KNO₃ and KClO₄ containing glasses. The significant effects of KNO₃ and KClO₄ are the controlled production of Bi⁰ NPs and removal of deep browning or blackening of bismuth glasses.

The TEM images of glass containing 0.2 wt % of K₂O from KNO₃ and KClO₄ sources (Figs. 3 and 4) clearly reveals homogeneously dispersed and densely embedded Bi⁰ NPs of spherical shape with size range 2-5 nm and 10-15 nm respectively. The particle size of the Bi⁰ NPs in KClO₄ treated glass shows smaller size (2-5 nm) than that of KNO₃ containing glasses (10-15 nm) because it restricted the further formation of NPs more effectively due to its higher reduction potential ($E^{\circ} = 1.34\text{V}$) than that of KNO₃ ($E^{\circ} = 0.96\text{V}$). Therefore, KClO₄ treated glass have not shown any distinct SAED spots and lattice fringes in high resolution transmission electron microscopy (HRTEM) due to its very small particle size. The SAED image of KNO₃ containing glass depicts the clear patterns of $\langle 024 \rangle$ and $\langle 119 \rangle$ *hkl* planes of rhombohedral Bi nanometallic particles. It also shows lattice fringes of $\langle 012 \rangle$ *hkl* planes in HRTEM image, which have been identified from the d-spacing as provided in the JCPDS File Card No.: 85-1329.

4. Conclusions

The formation of Bi⁰ NPs in bismuth glass nanocomposites have been controlled by a novel oxidation process using KClO₄ and KNO₃ as oxidant. The UV-visible absorption spectra show the characteristic invariable SPR band of Bi⁰ NPs at 460 nm. TEM images confirm the formation of spherical shaped rhombohedral Bi⁰ of 2-5 nm and 10-15 nm nanoparticles of KNO₃ and KClO₄ treated glasses respectively. The KNO₃

treated glass shows the SAED pattern and HRTEM images of $\langle 119 \rangle$, $\langle 024 \rangle$ and $\langle 012 \rangle$ planes of rhombohedral bismuth. The KClO_4 is more efficient oxidant for the oxidation process of $\text{Bi}^0/\text{Bi}^{+3}$ than that of KNO_3 .

Acknowledgements

The authors gratefully acknowledge the financial support of the NMITLI Scheme of CSIR, New Delhi. They thank Dr. H. S. Maiti, Director of the institute for his keen interest and kind permission to publish this paper. They also acknowledge the Electron Microscope Division of this institute for recording the TEM and SAED images.

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Table 1

Reduction potentials of perchlorate, nitrate and bismuth ions.

| Redox reaction | Reduction potential (E° , V) |
|---------------------------------|--|
| $\text{ClO}_4^-/\text{Cl}^-$ | 1.34 |
| NO_3^-/NO | 0.96 |
| Bi^+/Bi^0 | 0.50 |
| $\text{Bi}^{3+}/\text{Bi}^0$ | 0.31 |
| $\text{Bi}^{3+}/\text{Bi}^+$ | 0.20 |
| $\text{Bi}^{3+}/\text{Bi}^{2+}$ | $< 0.20^a$ |

^aExact value is not available

Figure caption

Fig. 1. (Color online) Absorbance spectra of glasses containing (a) 0 (inset), (b) 0.2, (c) 0.5, (d) 0.9, and (e) 1.4 wt. % of K_2O from KNO_3 . Displayed photograph is of the polished glasses (thickness = 2 mm and identifiable by their bottom letters) laid on black lines to show their transparency to the naked eye.

Fig. 2. (Color online) Absorbance spectra of glasses containing (a) 0 (inset), (k) 0.2, (l) 0.3, (m) 0.7, and (n) 1.0 wt. % K_2O from $KClO_4$. Displayed photograph is of the polished glasses (thickness = 2 mm and identifiable by their bottom letters) laid on black lines to show their transparency to the naked eye.

Fig. 3. TEM, HRTEM images and SAED pattern of the glass containing 0.2 wt % of K_2O (from KNO_3).

Fig. 4. TEM images and SAED pattern of the glass containing 0.2 wt % of K_2O (from $KClO_4$).

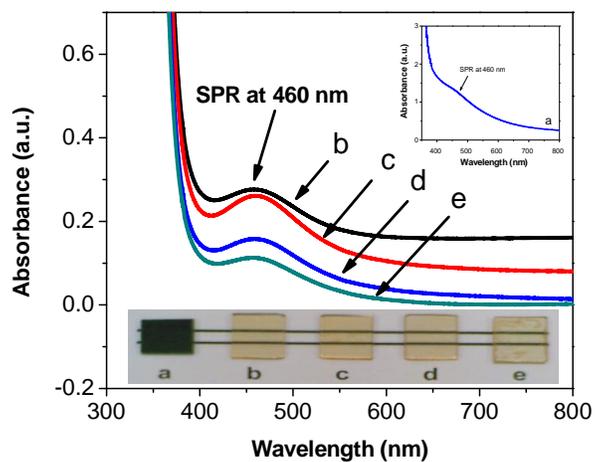


Fig. 1. (Color online) Absorbance spectra of glasses containing (a) 0 (inset), (b) 0.2, (c) 0.5, (d) 0.9, and (e) 1.4 wt. % of K₂O from KNO₃. Displayed photograph is of the polished glasses (thickness = 2 mm and identifiable by their bottom letters) laid on black lines to show their transparency to the naked eye.

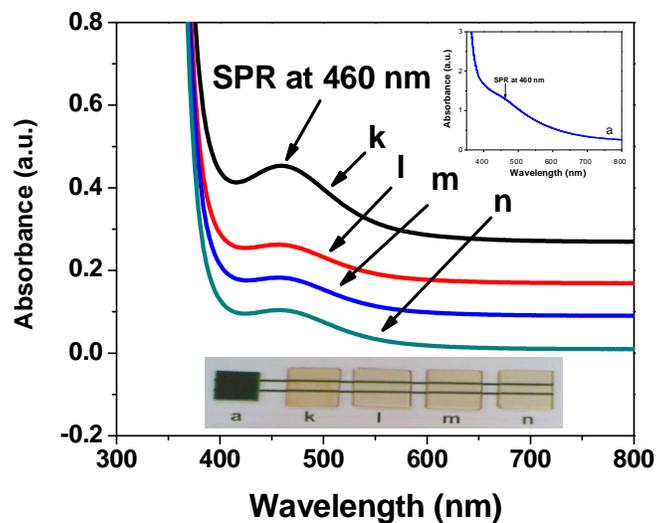


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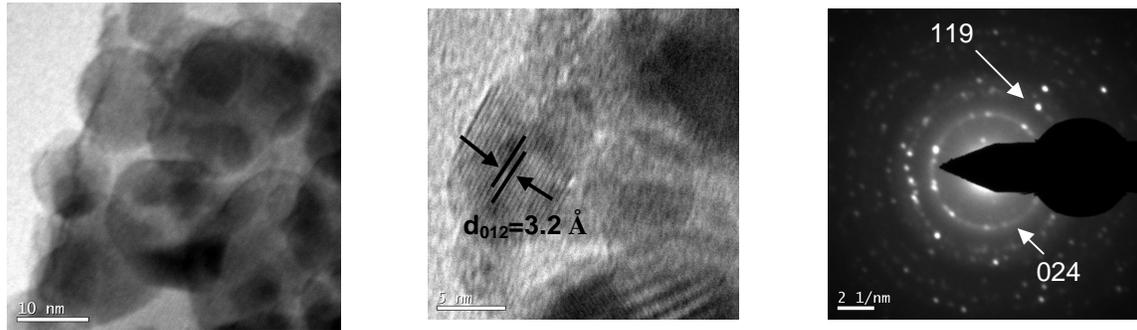


Fig. 3. TEM, HRTEM images and SAED pattern of the glass containing 0.2 wt % of K_2O (from KNO_3).

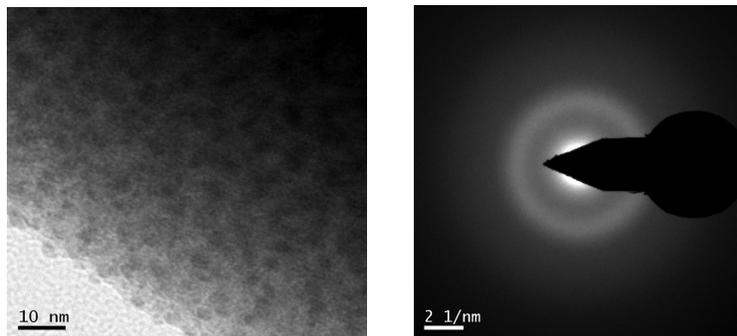


Fig. 4. TEM images and SAED pattern of the glass containing 0.2 wt % of K_2O (from KClO_4).