Synthesis of a Bismuth Oxide-Based Powder Via an Ion Complexing Method for Solid Oxide Electrolytes

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ABSTRACT

A powder of the stoichiometry (Bi$_2$O$_3$)$_{0.8}$(SrO)$_{0.2}$ was synthesized through an ion complexation technique using n-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA). The synthesis was performed in an aqueous solution, then dehydrated, and the resin charred and calcined. The resulting powder was found to have a rhombohedral crystal structure associated with the ionically conductive phase of this system. The powder had a flaky to granular morphology, with an average particle size of 0.5 - 1.5μm.

1. INTRODUCTION

It has been found that a bismuth-based oxide ceramic of the stoichiometry (Bi$_2$O$_3$)$_{0.8}$(SrO)$_{0.2}$ is an excellent ionic conductor of O$^{2-}$ ions(1). Its ionic conductivity is up to an order of magnitude higher than that of Yttria stabilized Zirconia (YSZ). Contrary to other conductive bismuth oxide species which exhibit a fluorite structure that is only metastable at room temperature(2), the above composition (designated BSO) has a rhombohedral phase stable from room temperature to its melting point(2).

In order to exploit the above advantages in devices such as oxygen separators and solid oxide fuel cells, good quality initial powders are required. A novel chemical synthetic method has been devised for this purpose (Figure 1). The synthetic method is based upon an ion complexation of the associated metal ions in order to form a viscous resin that can be subsequently charred and calcined to yield a final powder with desirable properties(3).
2. EXPERIMENTAL

Stoichiometric amounts of bismuth nitrate and strontium nitrate were weighed out using an analytical balance. The bismuth nitrate was dissolved in 3M nitric acid to yield a 1M clear and colourless solution. A stoichiometric amount of n-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) was then dissolved in the solution. The pH of the resultant solution was raised to 8-8.2 using ammonium hydroxide (NH₄OH) in order to stabilize the organometallic complex between the Bi³⁺ ion and the HEDTA molecule, yielding a complexed solution that was clear and mildly straw yellow in appearance. The strontium nitrate, being readily soluble in neutral solutions, was dissolved in deionized water, forming a 1M clear, colourless solution. A stoichiometric amount of HEDTA was added and the solution was also stabilized at pH=8.8-2 with NH₄OH to yield a clear, colourless solution. The two solutions were thoroughly mixed to produce a homogeneous, clear, slightly yellow solution. Upon heating via a hot plate, the solution was dehydrated to form a white-to-yellow resin. Upon cooling and aging for 24 hours, the resin formed a translucent, crystalline solid.

In order to determine the best charring and calcination temperature cycles differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on the solid resin. DTA experiments were conducted over the temperature range of 25°C to 800°C at a heating rate of 10°C/min under an air atmosphere. A typical DTA plot is given in Figure 2. The strong exothermic peak at 225°C corresponded to the combustion of the organic resin. It was therefore decided to char the resin at 225°C for 30 minutes under a lowered oxygen partial pressure in order to allow for the slow removal of the organic resin. Since no transformation peaks could be seen in the DTA plot above 500°C a calcination temperature of 600°C for 12 hours was considered reasonable.

The resin was charred at 225°C for 30 min. to yield a grey-black foamed char. The oxygen partial pressure was kept at approximately P_0₂=0.05-0.15 in order to prevent combustion that would otherwise lead to a decomposed phase. The char was then milled on a ball mill for 30 minutes using a zirconia grinding medium. Finally, the powder was sieved through a 150 mesh screen and collected.

Calcination was performed in air at a temperature of 600°C for up to 12 hours. A low P_0₂ was maintained to an hour before completion of calcination in order to assure the complete removal of all organics and to prevent the rapid preferential oxidation of the bismuth in the powder. The resulting powder was then collected and analyzed.

The powder was analyzed for its homogeneity, crystal phases, particle size and morphology. Powder x-ray diffractometry (XRD) using Cu-Kα radiation was used to determine the crystallographic phases and the relative amounts of the products present. Powder morphology was studied using scanning electron microscopy (SEM). Chemical homogeneity in the bulk powder was analyzed by energy dispersive x-ray analysis (EDX) and particle size and distribution were quantified using sedimentation particle size analysis (PSA).
3. RESULTS

Upon study of the powder via XRD, it was found that a material of a single crystallographic phase could be achieved (Table 1). The XRD pattern of BSO corresponded to the rhombohedral phase of the ionically conductive species. The primary contaminant phase was that of monoclinic Bi$_2$O$_3$, which represented a decomposed phase, although it was present only in minute quantities that could often not be detected by the XRD used.

SEM studies showed that the powder exhibited a flaky to granular morphology with the majority of the visible particles being less than 1µm in size (Figure 3). Both the spot EDX and mapping EDX scans showed no visible chemical concentration gradients or compositional differences.

Quantitative particle size analysis showed that the powder exhibited a mean particle size of 1.38µm and a standard deviation of 1.74µm (Figure 4). While this suggested a small particle size and narrow particle size distribution, it should be noted that the detection limit of the analyzer was set at 0.5µm and may have influenced the collected results.

4. DISCUSSION

The above synthetic method was developed in response to the need to overcome many of the problems with the processing of bismuth based materials. The primary difficulties in the synthesis of powders containing bismuth are that bismuth is easily oxidized and that it has a low melting temperature (271°C for the Bi metal and 825°C for Bi$_2$O$_3$). Bismuth as an ion (e.g. Bi$^{3+}$) is also soluble only in strongly acidic aqueous media. Since strontium has poor solubility in acidic media, a complexing agent would be required in order to produce an aqueous solution capable of supporting both ionic species.

The use of HEDTA for the synthesis of bismuth-containing superconductive oxides has proven to be successful and practical. HEDTA forms strong complexes with metal ions in aqueous systems through coordination bonding(3). It is a pentadentate molecule where the three acid groups and the two nitrogens' valence electron pairs coordinate with metal ions forming a "cage" structure. The remaining hydroxyethyl group may either aid in coordination or hydrogen bond to other HEDTA molecules. It is also possible that the resin formation was in fact caused by excess HEDTA promoting a reaction between the hydroxyl and acid groups on adjacent molecules via a condensation reaction to form a polyester similar to that formed by the citrate gel method(4)(Figure 5).

In the aqueous solution, all ions of bismuth and strontium have chelated with HEDTA and have been stabilized at a common pH. The nature of this solution assures complete homogeneity of both ionic species throughout the solution. During dehydration and formation of the solid resin, the viscosity of the solution rises dramatically. As in the case of other syntheses involving organic resins, the high viscosity prevents
segregation of the ionic species and therefore maintains chemical homogeneity in the resin (4,5).

In its chelated state, bismuth is highly susceptible to oxidation under heating. This was of great concern when charring in the presence of a large amount of oxygen. The resin would combust, causing premature oxidation of bismuth yielding a powder containing very large amounts of Bi$_2$O$_3$. This reaction could not be reversed by the calcination stage. It was therefore essential to assure a controlled burnout of the organic resin via the maintenance of a lowered P$_{O_2}$ during charring and early calcination. Subsequently, a long calcination time was used in order to assure the formation of the desired phase.

It was not difficult to produce a powder with a very fine particle size. The calculated value however does not take into account the fact that significant amounts of the powder could have been below 0.5μm in size. It was seen in the SEM micrograph that the powder was below 1μm in particle size and therefore some caution should be taken in considering the given value. Some necking was also occasionally observed in the micrographs. The difficulty with powders based on bismuth oxide is that sintering can often be present at temperatures as low as 600°C (≈0.8T$_m$ for our material). The practicality of a slightly lower calcination temperature (i.e. 550°C) is therefore being investigated.

5. CONCLUSIONS

It was possible to synthesize a solid oxide electrolyte powder of the composition (Bi$_2$O$_3$)$_{0.8}$SrO$_{0.2}$ using a novel complexation method based on HEDTA. The resulting powder was of a rhombohedral crystallographic phase, with a flaky to granular morphology, and a particle size of 0.5-1.5μm.

6. REFERENCES

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TABLE 1
XRD Data for Characteristic Peaks of BSO

| 2θ(BSO) (1) | BSO obs. |
|-------------|----------|
| 25.8        | 25.8     |
| 26.7        | 26.7     |
| 28.4        | 28.4     |
| 30.5        | 30.5     |
| 34.1        | 34.1     |
| 45.8        | 45.8     |
| 49.2        | 49.2     |
| 51.8        | 52.5     |
| 54.3        | 54.3     |

\[ 1.6 \text{m Bi(NO}_3\text{)}_3\cdot 5\text{H}_2\text{O} \quad \text{Dissolve in } 3\text{M HNO}_3 \quad \text{Add } 1.6\text{m HEDTA} \quad \text{Add NH}_4\text{OH to pH = 8-8.2} \quad \text{Mix} \quad \text{Dehydrate} \quad \text{Char} \quad 225°C \text{for 30 Min.} \quad \text{Calcine} \quad 600°C \text{for 12 Hrs.} \quad 0.2\text{m Sr(N}_2\text{O}_3\text{)}_{1.2} \quad \text{Dissolve in } H_2O \quad \text{Add 0.2m HEDTA} \quad \text{Add NH}_4\text{OH to pH = 8-8.2} \]

Figure 1 Flow Chart for the Synthetic Method for BSO.
Figure 2  DTA Plot for BSO Precursor Resin.

Figure 3  Scanning Electron Micrograph of Calcined Powder.
Figure 4 Probability Number Distribution for BSO.

Figure 5 Chemistry of Complexed Organometallic Polymerized Resin.

Median : 0.87μm
Mean(nl): 1.38μm
S.D. (nl): 1.74μm
Conf (nl) : 99.94%