Morphology Control of SrBi$_2$Nb$_2$O$_9$ Prepared by a Modified Chemical Method

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Abstract:
SrBi$_2$NbO$_9$ compounds were prepared through three methods: oxalate co-precipitation, molten salt synthesis and polymerizable complex. The effect of the molecular precursor route has also been investigated. For oxalate co-precipitation method, a solution obtained from acid oxalate, niobium oxide, bismuth nitrate and strontium nitrate are precipitated by ammoniac solution. Then, the precipitated sample is calcined at 1100 °C. A methanol-citric acid solution of solution of NbCl$_5$, ethylene glycol, bismuth and strontium nitrates were used as precursors. A black powder ash was crystallized by heat-treating at 1100 °C. Molten salt technique using oxides and carbonate as starting materials and NaCl and KCl to form a reaction medium. The formation temperature was at 1110 °C. Multiple characterizations mainly X-ray diffraction, Fourier transformed infrared spectroscopy and scanning electron microscopy (SEM) measurements have provided to validate the structural feature. Careful, X-ray diffraction analysis showed the presence of two-layered Aurivillius structure. The crystallite size is discussed by Scherrer and Williamson–Hall approaches. SEM images of SrBi$_2$NbO$_9$ ceramics showed plate-like, polygonal and structureless morphologies obtained at different synthesis conditions. Whatever the synthesis process, there is no change on the band of infrared spectra.

Keywords: SrBi$_2$NbO$_9$; Co-precipitation; polymerizable; Molten salt; Microstructure.

1. Introduction

The Aurivillius phases were written by Aurivillius and published in 1949 [1], with a general formula of (Bi$_2$O$_2$)$^{2+}$(A$_{m-1}$B$_m$O$_{3m+1}$)$^{2-}$, consisting of m-perovskite units sandwiched between bismuth oxide layers, where A and B are the two types of cations that enter the perovskite unit [2]. Four their excellent fatigue endurance, these materials are candidates for a new generation of non-volatile ferroelectric random access memory devices [3]. The effect of the synthesis and processing of SrBi$_2$Nb$_2$O$_9$ materials on physical properties has been attracting a lot of attention, in order to involve eco-friendly rapid and cost-effective of green protocols for the synthesis of nanoparticles, or in order to enhance types of properties. Thus, through polymerizable complex processing, the methanol or ethanol was used as a solvent to dissolve NbCl$_5$. However, a large excess of citric acid should be added to the NbCl$_5$-
methanol, to produce a solution of niobium-citric acid complexes, which is stable with respect to hydrolysis for several months [4]. For solid-state method, at elevated temperature greater than 1100°C, it is very difficult to maintain cation to anion ratio. Thus, the bismuths gradually volatilize. We have been synthesized SrBi$_2$NbO$_9$ samples through different methods. The outcome is found to be depended especially on precursors and how to choose the calcination temperature and time duration. The crystalline phase in the SrBi$_2$Nb$_2$O$_9$ samples takes place at 1180, 800 and 500 °C when used solid state route, hydrothermal method and hybrid process (co-precipitation-hydrothermal) [5-8]. A small change was observed in the lattice parameter value, which indicates that the expansion is slightly greater in the unit cell for solid-state route than in the co-precipitation method. This finding may be attributed to the crystallite size and the effect of temperature on the lattice strain. A promising way for obtaining SrBi$_2$Nb$_2$O$_9$-based ceramics is their preparation via low temperature processing. In order to avoid oxygen vacancies arising from volatilization of bismuth at the higher temperature sintering process. The dielectric constant performed on ceramics elaborated by the solid-state method is found to be four times bigger than co-precipitation ones. In this part of the work, we focus on the measurement and control of SrBi$_2$NbO$_9$ powder processes. The key issues are control of the formation of the desired crystalline phase.

2. Materials and Experimental Procedures

For oxalate co-precipitation method, through a stoichiometric amount of Sr(NO$_3$)$_2$.6H$_2$O (Normatom) and Bi(NO)$_3$.5H$_2$O (Fluka Chemika, 99 %) are dissolved in distilled water and in HNO$_3$ (Panreac, 65 %) respectively. Nb$_2$O$_5$ (Acros Organics, 99.5 %), is ultrasonicated with oxalic acid (Sigma-Aldrich, 89 %) to break the soft agglomerates. Nitrate solution is added drop wise into the suspension of oxalic acid and Nb$_2$O$_5$. Precipitation occurs at a pH of 9, by feeding ammoniacal solution. After filtration, washing by distilled water and drying, the obtained samples are calcined at 1050 °C during 24 h. Utilization of a methanol-citric acid solution of NbCl$_5$ (Fluka) as a niobium precursor has been studied by Toru Okubo et al.[4]. The Sr(NO$_3$)$_2$.6H$_2$O and Bi(NO)$_3$.5H$_2$O precursors were dissolved together and simultaneously in diluted nitric acid according to the appropriate metal proportions. NbCl$_5$ is dissolved in ethanol. A large excess of citric acid was added with continuous stirring to the NbCl$_5$-ethanol solution. The mixture of three solutions was magnetically stirred. Subsequently ethylene glycol was added to this solution. After drying at 190 °C, a black powder was heat-treated in a furnace at 1000 °C during 12 h. For modified chemical method, Bi$_2$O$_3$, Nb$_2$O$_5$, and SrCO$_3$, were mixed thoroughly in a stoichiometric amount and further combined in an agate mortar with NaCl/KCl (50:50 wt.). The mixture was subsequently calcined at 1100 °C for 4 h. The samples was examined through X-ray diffraction of Rigaku monochromatized CuK$_\alpha$ radiation (λ=1.54Å), Fourier transform infrared spectroscopy recorded on KBr pellets, Bruker Vertex 70 and scanning electron microscopy (EDAX AMETEK).

3. Results and Discussion

Fig. 1 shows XRD of SrBi$_2$Nb$_2$O$_9$ powders. Narrowed peaks with the annealing temperature at 1050 °C during 24 h, 1000 °C during 12 h and 1100 °C during 4 h, indicating that these samples can be indexed using JCPDS-ICDD pattern number 01-081-1190 referring to SrBi$_2$Nb$_2$O$_9$ single-crystal. It is expected that no distinct precursor-related intermediate phase may form and consequently onset of SrBi$_2$Nb$_2$O$_9$ crystallization around 1000-1100 °C. In addition, the average size of the crystallites was estimated from the broadening of the
highest diffraction peak, using the Scherrer equation [9]. The crystallite size using the Debby–Scherrer (D_{D-S}) formula:

\[ D_{D-S} = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

where \( \beta \) is a half width of the peak and \( \lambda = 1.5406 \) Å is the wavelength of CuK\( \alpha \) radiation.

Fig. 1. XRD patterns of SrBi\(_2\)Nb\(_2\)O\(_9\) ceramic powders.

Fig. 2 shows the crystallite size calculated from each peak’s data. The crystallite size (D_{D-S}) at highest peak corresponding to (1 1 5) reflection varies from 119 to 123 nm and 200 nm for oxalate co-precipitation, molten salt synthesis and polymerizable complex. Except for the main peak (1 1 5), the simple prepared through polymerizable complex method has as crystallite sizes, varying between 24 and 64 nm. The average crystallite size is found to be
around 75 and 21 nm for molt salt method. However, oxalate co-precipitation method, shows the important tendency towards larger distribution of crystallite size (38-182 nm) than both methods.

The Williamson-Hall method used to understand the contributions of lattice strain and crystalline size to the XRD peak [10]. The different variants of the method such as an isotropic strain model, anisotropic strain model and uniform deformation energy density model are used may be useful. Estimation of lattice isotropic strain ($\varepsilon$) and crystallite size ($D_{W-H}$) by Williamson-Hall method is given by:

$$\beta \cos \theta = \frac{0.9\lambda}{D_{W-H}} + 4\varepsilon \sin \theta \quad (2)$$

![Williamson-Hall plot of SrBi2Nb2O9 ceramic powders.](image)

The strain ($\varepsilon$) present in the materials and the crystallite size ($D_{W-H}$) are, respectively, determined from the slope and from the $\beta \cos \theta$ -intercept of $\sin \theta$ versus $\beta \cos \theta$ as shown in Fig. 3. All samples undergo the same strain value ($1 \times 10^{-3}$). The crystallite size ($D_{W-H}$) is 279 nm, 178 nm and 83 nm for polymerizable complex, oxalate co-precipitation and molten salt synthesis, respectively. However, in many cases, material cannot be having identical values of a property in all directions. Stress and strain relations for elastic behavior are described by Hooke’s law (stress is directly proportional to strain) which is valid only up to the proportionality limit of a material. Beyond this limit, Hooke’s law no longer applies. We can write Williamson-Hall equation (2) another way:

$$\beta \cos \theta = \frac{0.9\lambda}{D_{W-H-ASM}} + \frac{4\varepsilon \sin \theta}{E} \quad (3)$$

where, $\sigma$ is uniform stress and $E$ is the constant of proportionality and is known as the Modulus of Elasticity or Young’s Modulus ($E$) in the direction perpendicular to the set of crystal lattice planes (hkl). In an orthorhombic material, the elastic moduli can be determined along any orientation, from the elastic constants ($s_{ij}$) [11], by the application of the following equations:

$$\frac{1}{E} = \frac{s_{11}h^2 + s_{22}k^2 + s_{33}l^2 + (2s_{12} + s_{66})hlk + (2s_{13} + s_{55})h^2l^2 + (2s_{23} + s_{44})k^2l^2}{(h^2 + k^2 + l^2)^2} \quad (4)$$
Due to the lack of experimental data in this system, Young's Modulus was estimated at around 0.287 TPa [11-12]. A scatter plot with a regression line of \(\frac{\sin(\theta)}{E}\) versus \(\beta \cos(\theta)\) is plotted in Fig. 4, where \(0.9I/D_{W-H-ASM}\) is the slope of the line, and \((4\sigma)\) is the \(\beta \cos\theta\)-intercept. The magnitude of the deformed stress \((\sigma)\) is found at around 250 MPa for all samples. Here, the introduction of the anisotropic Young's modulus does not bring significant change on the crystallite size.

\[ u = \frac{E \varepsilon^2}{2} \] (5)

The relationship of Equation 4-5 can be expanded and equated to Equation 3 to give:

\[ \beta \cos(\theta) = \frac{0.9\lambda}{D_{W-H-EDM}} + 4\sin(\theta)\sqrt{\frac{(2\sigma)}{E}} \] (6)

The graph drawn between \(\beta \cos\theta\) and \(\sin(\theta)/(2/E)^{1/2}\) is shown in Fig. 5. Using the regression equation to calculate slope and intercept, the crystallite size \(D_{W-H-EDM}\) remains almost unchanged as compared to \(D_{D-S}\) and \(D_{W-H-ASM}\). The deformation energy density \((u)\) is estimated to be 250 kJ/m\(^3\) for all samples. In our case, all the three models give the similar order of strain and crystallite size, implying that the inclusion of strain in various forms has a very small effect on the average crystallite size.

\[ \text{Fig. 4. Williamson-Hall plot with Young's modulus of SrBi}_2\text{Nb}_2\text{O}_9\text{ ceramic powders.} \]

\[ \text{Fig. 5. Williamson-Hall plot with deformation energy density of SrBi}_2\text{Nb}_2\text{O}_9\text{ powders.} \]
Fig. 6 shows the FTIR spectra of SrBi$_2$Nb$_2$O$_9$ powders. The bands at 3448 and 1630 cm$^{-1}$ correspond to the bending mode of the H-O-H group of water. The well-pronounced bands at 1361 cm$^{-1}$ and 1319 cm$^{-1}$ correspond to stretches of CO$_2$, which might be due to the absorption of atmospheric carbon dioxide during the experiments. Both spectra of the powders heat-treated at 1000 and 1050°C exhibited a characteristic Nb—O bond vibrations of crystalline SrBi$_2$Nb$_2$O$_9$ at 740 and 630 cm$^{-1}$[13-14]. When comparing FTIR spectra, it is indicated that all bands do not shifting.

The effect of calcination temperatures was examined tacking on consideration. The results obtained in this study suggest that the temperature 1050 °C promotes the reaction between Sr(NO$_3$)$_2$, Bi(NO)$_3$ and Nb$_2$O$_5$—oxalate forming the phase SrBi$_2$Nb$_2$O$_9$. Thus, at 500 °C the oxalate group persist in powder, which is confirmed by examining by infrared transmission (FTIR) [15]. The total absence of the oxalate was attained at higher temperatures greater than 800 °C. Meanwhile, the powder calcined between 700-800 °C consists of the pyrochlore phase along with some unknown crystalline phase [16]. Further, a modified polymerizable complex method, the formation of SrBi$_2$Nb$_2$O$_9$ occurred when the precursor was heat-treated at 1000 °C. Refereeing to the thermal decomposition behavior of the Y$_3$NbO$_7$ powder [4]. Between 500-700 °C, an intermediate phase is required and the powder precursors were amorphous in structure, which is confirmed by TG- DTA analysis and X-ray diffraction. Among molten salt method was carried out at high temperatures (typically > 1000 °C), and it is difficult to remove the salt of KCl in the molten salt method, when heated to temperatures ranging from 500 to 700 °C [17]. So, the molten salt synthesis process of SrBi$_2$Nb$_2$O$_9$ with high purity were successfully obtained at 1100 °C.

![Fig. 6. FTIR spectra of SrBi$_2$Nb$_2$O$_9$ powders.](image)

The SEM analysis was performed to complete this investigation of the structural characteristics of these compounds. The SEM images are shown in Fig. 7. The calcined powders were remilled, ground, and pressed into pellets. The pressed pellets were then sintered at 1100 °C for 2 h. The sample synthesized through molten salt route evidenced the presence of plate-like grains, the thickness of which varied between 0.5 and 0.4 μm. The formation of plates in molten salt could be attributed to dissolution-precipitation mechanism [18]. However, oxalate co-precipitation route allows the formation of a predominantly polygonal shaped, with grain size heterogeneity. In contrast, when the SrBi$_2$Nb$_2$O$_9$ was prepared by polymerizable complex route, crystals lose its sharp edges, and the morphology
has been modified to the structureless appearance. The dimension of all samples varied between 1 and 6 μm.

![SEM micrographs of SrBi₂Nb₂O₉ ceramics obtained after sintering at 1100 °C for (a) Molten salt method, (b) oxalate co-precipitation method and (c) polymerizable complex route.](image)

Fig. 7. SEM micrographs of SrBi₂Nb₂O₉ ceramics obtained after sintering at 1100 °C for (a) Molten salt method, (b) oxalate co-precipitation method and (c) polymerizable complex route.

The dependence of the crystallite/grain size of SrBi₂Nb₂O₉ has not achieved to an appropriate reasonable approach. Thus, the average crystallite size estimated from XRD data is found at around nanoscale particle. However, SEM micrographs witness that the obtained samples are micrograined.

4. Conclusion

The mentioned methods were used for oxide powder preparation. Raw materials, including intermediates and processing aids are the foundation of chemical properties and structure. After thermal treatment in the temperature range from 1000 to 1100 °C, SrBi₂Nb₂O₉ structure was required. These processes seem affording a promising way for obtaining bulk ceramics with various microstructure and high density. Meanwhile, every material has its own unique grain scale heterogeneity. The Debye-Scherrer’s method used to understand the contributions the crystalline size of the XRD peak, may be useful if different variants of the method such as Williamson-Hall, Isotropic Strain Model, anisotropic strain model and
Uniform Deformation Energy Density Model are used. In case all the models give the similar order of strain and crystalline size that may be some evidence of single phase.

**Summary statement**

- SrBi$_2$NbO$_9$ compounds were prepared through oxalate co-precipitation, molten salt synthesis and polymerizable complex.
- X-ray diffraction, Fourier transformed infrared spectroscopy and scanning electron microscopy measurements have provided to validate the structural feature.
- The crystallite size is discussed by Scherrer and Williamson–Hall approaches.

5. References

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је преципитиран амонијачним раствором. Преципитирани узорак је калцинисан на 1100 °C. Metanol цитратни кисели раствор састављен из раствора NbCl₅, етилен гликола, биџамана и стронцијум нитрата је коришћен као прекурсор. Црни пепељаст прах је искристалисао загревањем на 1100 °C. Техника отопљених соли кориси оксиде и карбонате као почетне материјале, а NaCl и KCl формирају рекациони медијум. Температура формирања је била 1110 °C. Потврду о структури добијених једињења су дале технике као што су XRD, FTIR и SEM. Рендгенска дифракција је указала на присуство двослојне Ауривилијус структуре, а величина кристалита је одређена Шереровим и Вилијамсон-Холовим приступом. SEM микрографије SrBi₂NbO₉ керамике показује равну, полигоналну и безструктурну мирфологију постигнуто различитим методама синтезе. Без разлике у процесу синтезе, нема промена у инфрацрвеним спектрима.

Кључне речи: SrBi₂NbO₉, копреципитација, полимеризабилност, отопљена со, микроструктура.

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