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Influence of synthesis methodology on the ionic transport properties of $BaSnF_4$

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ABSTRACT

The high performance fluoride ion conductor $BaSnF_4$ has been prepared by a simple precipitation in addition to both solid state reaction and mechanochemical synthesis techniques. XRD results indicate that the material $BaSnF_4$ obtained by all the methods crystallizes with the same tetragonal structure (P_4/nmm). The crystallite size and morphology of the $BaSnF_4$ particles determined by XRD and FE-SEM show a variation with respect to different methods of preparation. The transport properties of $BaSnF_4$ have been investigated by impedance spectroscopy and the results show that the conductivity values are closely related to the crystallite size and micro-strain. The transport number measurement and NMR studies further confirm that the increase in conductivity is due to fluoride ions. The scaling result of complex impedance plots shows that the dynamical process occurring at various frequencies are independent of temperature.

1. Introduction

Investigations of fluoride ion conducting materials are of much importance due to their promising applications in solid state ionic devices especially in chemical sensors for monitoring fluorine in gaseous ambient [1,2]. The motivation behind the present work on $BaSnF_4$ compound is due to its similarity in structure to the well known $PbSnF_4$, which has remained to date as the best conducting fluoride ion conductor [3]. Recent studies on these compounds show the presence of giant dielectric constant properties ($\varepsilon' \sim 10^5$), which expands further the application of these ionic materials in electronic devices [4,5]. $BaSnF_4$ exhibits the maximum conductivity among SnF_2–BaF_2 binary systems. It crystallizes in a layered tetragonal structure with a $\cdots$BaBaSnSn$\cdots$ order parallel to *c*-axis of the unit cell. The combination of interstitial sites and the fluoride ions in the distorted fluorite type sites are held responsible for the high value of ionic conductivity [6,7]. Earlier work on these systems describes the preparation of $BaSnF_4$ through direct solid state reaction between BaF_2 and SnF_2 at higher temperatures (773 K), taken in a specially designed evacuated copper tube [8]. In the case of fluorides, the use of copper tubes provide an inexpensive and convenient alternative to gold and platinum for solid state reactions at high temperatures under non-oxidizing atmospheres [9]. However in the present work, the above preparation method with copper tube has been simplified with a copper foil kept inside an evacuated quartz ampoule. The present work also highlights the preparation of $BaSnF_4$ compound in another new, simple and economic route using the respective chlorides as the starting materials and NH_4F as the fluorine source by aqueous route. The characteristics of the compound prepared by the above method have been compared with the same prepared by conventional solid state reaction and mechanochemical synthesis techniques. In the case of ionic conductors, the conductivity results are known to vary with both crystallite size and micro-strain. In the present case, it can be expected that the development of various methods of preparation may lead to the formation of the same compound $BaSnF_4$ of various size and micro-strain. Hence, a comparative investigation of conduction characteristics of $BaSnF_4$ both as a function of size and strain, prepared by different methods has been attempted. Although, the same material is prepared by different means, each method has its own advantages. Mechanochemical route is known to produce ultra-fine powders, good for achieving high ionic conductivity with enhanced electrode–electrolyte contacts in solid-state ionic devices [10]. However the solution based methods provide a simple, low temperature and cost effective approach in comparison to other techniques. It also overcomes the use of inert gas condition and expensive metal containers. The formations of the material with their microstructure are examined by XRD, HR-TEM and FE-SEM. The crystallite size and strain values are calculated using Debye–Scherrer formula. The transport properties of these materials both as a function of temperature and frequency are investigated by impedance spectroscopy. The impedance data corresponding to the sample showing high value of ionic conductivity have been analyzed further to highlight the dynamics of the fluorine ion transport with respect to various temperatures. The electronic contribution to the total conductivity was evaluated using dc polarization technique. Solid state ^{19}F magic angle spinning (MAS)

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NMR technique has been used in the case of fast ion conductors to probe the local order and motion of fluoride ions that are held responsible for ionic conduction. The variations of ^{19}F NMR line width with temperatures are also investigated in the present work to highlight the nature of the mobile ions.

2. Experimental details

2.1. Chemical reagents

As procured powder samples of SnF_2 (99%, Aldrich) and BaF_2 (99%, Alfa Aesar) were used in the present study. For the preparation through wet methods, $SnCl_2$ or SnO and $BaCl_2{\cdot}2H_2O$ or $BaCO_3$ were taken as the starting materials for Sn and Ba sources, respectively. NH_4F or HF was used to serve as the source for fluorine.

2.2. Preparation of $BaSnF_4$ by dry process

2.2.1. Solid state reaction

The preparation of $BaSnF_4$ through solid state reaction was a two step process. Initially, stoichiometry ratio of the reagents SnF_2 and BaF_2 were mixed together in an agate mortar and thus palletized using conventional hydraulic press. Further, the pellet was taken in a quartz ampoule with inner surface, covered with copper foil as shown in Fig. 1 and then evacuated to a pressure of 10^{-5} Torr. At the end, the sealed tube was heated at 473 K for 4 h and at 773 K for a further period of 1 h.

2.2.2. Mechanochemical synthesis

$BaSnF_4$ was synthesized through an alternative approach, which employs ball milling and subsequent firing. For this, stoichiometry amount of respective fluorides, BaF_2 and SnF_2 have been used as the starting materials. Mechanical activation was carried out in the acetone medium with the use of a planetary ball mill (Insmart Systems) keeping weight ratio of the balls to materials as 10:1 at a rotation speed of 300 rpm for 10 h. Followed by milling, the active material was annealed at 573 K for 2 h in the nitrogen atmosphere.

2.3. Preparation of $BaSnF_4$ by wet process

2.3.1. Wet method-I

The reaction was carried out by the addition of appropriate amount of NH_4F to the aqueous solution of 1 M $BaCl_2{\cdot}2H_2O$ and 1 M $SnCl_2$, on stirring. A white precipitate was formed immediately. Further, the precipitate was centrifuged and washed several times with distilled water. Finally, the solid was dried in vacuum.

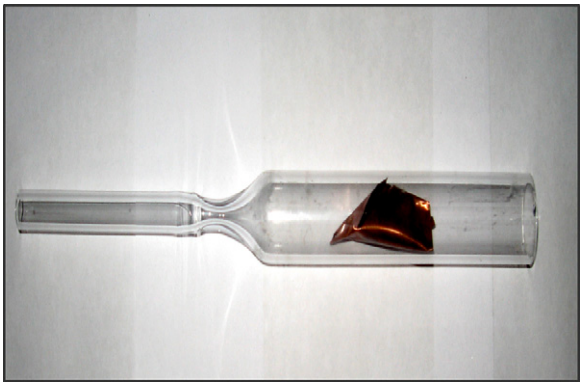

Fig. 1. Photograph of the ampoule used for the synthesis of $BaSnF_4$ through solid state reaction.

The above reaction can be represented as follows:

$$BaCl_2 \cdot 2H_2O + SnCl_2 + 4NH_4F \rightarrow BaSnF_4(s) + 4NH_4Cl + 2H_2O \quad (1)$$

2.3.2. Wet method-II

Stoichiometric weights of SnO and $BaCO_3$ were dissolved in HF, on stirring. A white solid resulted when the water in the above solution was distilled off after heating at 373 K. The reaction was carried out in a Teflon beaker. The above reaction is given by

$$BaCO_3 + SnO + 4HF \rightarrow BaSnF_4(s) + 2H_2O + CO_2 \quad (2)$$

2.4. Characterization

XRD measurements were carried out using X-ray diffractometer (PANalytical X'pert PRO) with Cu K_α radiation (λ = 1.5418 Å). The samples were scanned in the 2θ range of 10–90°, at a step size of 0.016. Scanning electron micrographs were obtained by using a high resolution scanning electron microscope (FEI QUANTA 400 F). High resolution TEM (HRTEM) characterization was performed with a JEOL JEM-3010 transmission electron microscope operated at 200 kV. Conductivity measurements were carried out using a HP4192A impedance analyzer over the temperature range of 300–473 K. For the above measurement, a pellet form of the sample with a diameter of 12 mm had been employed. Both the faces of the pellet serving as the electrodes were smeared with silver powder. ^{19}F MAS NMR experiments in the temperature range of 253–333 K were carried out in AV500S-500 MHz High Resolution Multinuclear FT-NMR Spectrometer instrument, operating frequency at 470 MHz.

3. Results and discussions

3.1. XRD and morphology analysis

The XRD patterns of $BaSnF_4$ synthesized by different routes are shown in Fig. 2. The data is in agreement with the standard JCPDS values confirming the formation of the materials by all four different methods. Fig. 3 shows both the observed and calculated XRD pattern of the mechanochemically prepared sample after the Rietveld refinement carried out using GSAS programme. The value of weighted refined parameter and χ^2 (goodness of the fit) are found to be 0.08 and 1.7, respectively. The material is found to crystallize in tetragonal structure (P_4/nmm) with lattice param-

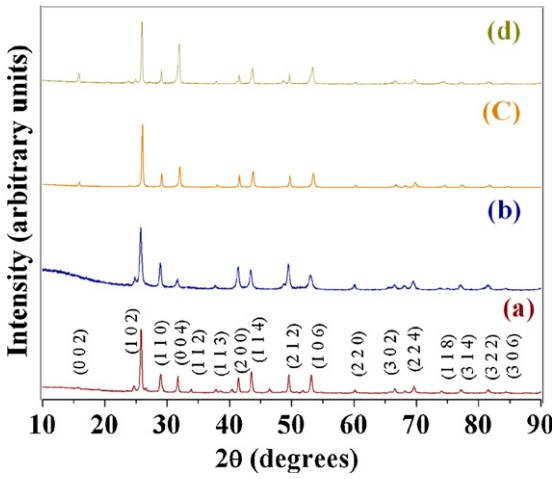

Fig. 2. XRD patterns of $BaSnF_4$ synthesized by (a) solid state reaction, (b) mechanochemical milling, (c) wet method-I and (d) wet method-II.