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# Hydrothermal synthesis and characterization of nanocrystalline pyrochlore oxides $M_2Sn_2O_7$ (M = La, Bi, Gd or Y)

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A family of pyrochlore stannates, $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) has been prepared from hydrothermal systems at 240 °C and structurally characterized by powder X-ray diffraction, transmission electron microscopy and differential thermal analysis. The La and Bi stannates showed nanocrystalline characteristics with average particle sizes of *ca.* 20 nm. Hydrothermally synthesized pyrochlore stannates were thermally stable and showed ionically conducting properties at high temperatures.

## Introduction

Pyrochlore oxides are of importance for their catalytic activities and high-temperature stabilities in various reaction processes.[1] Recent interests in stannate pyrochlores have stemmed from their highly efficient oxidative coupling of methane and their potential uses as high-temperature gas sensors and fast ion conductors.[2] Additionally, stannate pyrochlores are used as model paramagnetic compounds in MAS NMR studies.[3]

$M_2Sn_2O_7$ stannates (M = La, Bi, Gd or Y) are conventionally prepared from solid state reactions at high temperatures (*ca.* 1000 °C).[4–7] Besides their high energy consumption, these solid-state reactions involve a series of laborious heating cycles at high temperatures and repeated grinding of starting oxide components. The resulting powders show extensive agglomeration and compositional inhomogeneity. However, particular morphology and compositional homogeneity of the powders are important in terms of electrical and optical applications. There is thus a real need to develop an alternative synthesis route for pyrochlore stannates. The hydrothermal synthesis technique has been shown to be promising in the preparation of complex oxides[8–11] in terms of the relatively low reaction temperatures employed, high quality of the crystals obtained and, in some cases, reduction in sizes of the particles of the product solids.

Here, we present the hydrothermal synthesis, structural characterization and electric properties of nanocrystalline pyrochlore stannates $M_2Sn_2O_7$ (M = La, Bi, Gd or Y).

## Experimental

### Synthesis

In the syntheses of $M_2Sn_2O_7$ (M = La, Bi, Gd or Y), $La(NO_3)_3$, $Bi(NO_3)_3$, $Gd_2O_3$, $Y_2O_3$, $Na_2SnO_3$ and NaOH were used as starting reactants. A typical synthesis procedure for $La_2Sn_2O_7$ is described as follows: 0.65 g $La(NO_3)_3$ and 0.33 g $Na_2SnO_3$ were added to 10 ml 0.1 M NaOH solution. This mixture was sealed in a Teflon-lined stainless steel autoclave and allowed to crystallize at 240 °C for 3 days under autogenous pressure. The crystalline product was filtered off, washed with distilled water and dried at room temperature. The syntheses of $Bi_2Sn_2O_7$, $Gd_2Sn_2O_7$ and $Y_2Sn_2O_7$ were by the same procedure as that for $La_2Sn_2O_7$, but using $Bi(NO_3)_3$, $Gd_2O_3$ or $Y_2O_3$, respectively.

### Characterization

All products were identified by powder X-ray diffraction (XRD) on a Riguku D/max-A, 12 kW XRD diffractometer with a rotating target and Ni-filtered Cu-Kα radiation. A $2\theta$ scan was employed to collect the diffraction data with a step size of 0.02°. Silicon powder (99.99% purity) was used as an internal standard for calibration of peak positions. The lattice parameters of the samples were determined by least-squares methods.

Scanning electron micrographs (SEM) were taken with a Hitachi X-650B electron microscope. The morphologies of the products were observed by electron microscopy (H-81001V transition electron microscope (TEM)) under an acceleration voltage of 200 kV. Particles of the samples to be measured were directly deposited onto Formvarcoated copper grids and air-dried before examination. IR spectra were recorded using a Nicolet 5DX FTIR instrument with the KBr pellet technique. Inductive coupled plasma analysis (ICP) was carried out for chemical analysis of products on a POEMS ICP instrument. Differential thermal analysis (DTA) and thermal gravimetric analysis (TG) were performed on a Perkin-Elmer 7000 differential thermal analyser and TG-7 thermogravimetric analyser with a heating rate of 10 °C $min^{-1}$.

In electrical measurements, powder samples were pressed into a compact pellet (6 mm in diameter and 2 mm in thickness) under a pressure of 12 MPa. Ionic conductivity measurements were performed using the ac complex impedance method at frequencies ranging from 0.1 Hz to 1 MHz on Solarton 1260 impedance/gain-phase analyzer.

## Results and discussion

### Crystallization

Selected hydrothermal conditions for the synthesis of $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) are listed in Table 1. Suitable conditions for the synthesis of single phase crystalline $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) powders were investigated by varying such factors

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**Table 1** Hydrothermal synthesis conditions for $M_2Sn_2O_7$ (M = La, Bi, Y or Gd)

| Starting materials and composition | Concentration of NaOH/mol dm$^{-3}$ | Temperature/°C | Time/days | Phase(s) in product |
|---|---|---|---|---|
| $La(NO_3)_3 : NaSnO_3 = 1:1$ | 0.1 | 240 | 3 | $La_2Sn_2O_7$ |
| $La(NO_3)_3 : NaSnO_3 = 2:1$ | 0.1 | 240 | 3 | $La_2Sn_2O_7 + La(OH)_3$ |
| $La(NO_3)_3 : NaSnO_3 = 1:2$ | 0.1 | 240 | 3 | $La_2Sn_2O_7 + SnO_2$ |
| $La(NO_3)_3 : NaSnO_3 = 1:1$ | 0.05 | 240 | 3 | $La(OH)_3$ + multiphase |
| $La(NO_3)_3 : NaSnO_3 = 1:1$ | 0.2 | 240 | 3 | $SnO_2$ + multiphase |
| $La(NO_3)_3 : NaSnO_3 = 1:1$ | 0.1 | 200 | 3 | $La(OH)_3$ + multiphase |
| $La(NO_3)_3 : NaSnO_3 = 1:1$ | 0.1 | 200 | 6 | $La(OH)_3$ + multiphase |
| $La(NO_3)_3 : NaSnO_3 = 1:1$ | 0.1 | 240 | 1 | $La(OH)_3$ + multiphase |
| $Bi(NO_3)_3 : NaSnO_3 = 1:1$ | 1 | 240 | 3 | $Bi_2Sn_2O_7$ |
| $Bi(NO_3)_3 : NaSnO_3 = 2:1$ | 1 | 240 | 3 | $Bi_2Sn_2O_7 + Bi_2O_3$ |
| $Bi(NO_3)_3 : NaSnO_3 = 1:2$ | 1 | 240 | 3 | $Bi_2Sn_2O_7 + SnO_2$ |
| $Bi(NO_3)_3 : NaSnO_3 = 1:1$ | 0.5 | 240 | 3 | $Bi_2O_3$ + multiphase |
| $Bi(NO_3)_3 : NaSnO_3 = 1:1$ | 2 | 240 | 3 | $SnO_2$ + multiphase |
| $Bi(NO_3)_3 : NaSnO_3 = 1:1$ | 1 | 200 | 3 | $Bi_2O_3$ + multiphase |
| $Bi(NO_3)_3 : NaSnO_3 = 1:1$ | 1 | 200 | 6 | $Bi_2O_3$ + multiphase |
| $Bi(NO_3)_3 : NaSnO_3 = 1:1$ | 1 | 240 | 1 | $Bi_2O_3$ + multiphase |
| $Y_2O_3 : NaSnO_3 = 1:1$ | 3 | 240 | 3 | $Y_2Sn_2O_7$ |
| $Y_2O_3 : NaSnO_3 = 2:1$ | 3 | 240 | 3 | $Y_2Sn_2O_7 + Y_2O_3$ |
| $Y_2O_3 : NaSnO_3 = 1:2$ | 3 | 240 | 3 | $Y_2Sn_2O_7 + SnO_2$ |
| $Y_2O_3 : NaSnO_3 = 1:1$ | 1 | 240 | 3 | $Y_2O_3$ + multiphase |
| $Y_2O_3 : NaSnO_3 = 1:1$ | 6 | 240 | 3 | $SnO_2$ + multiphase |
| $Y_2O_3 : NaSnO_3 = 1:1$ | 3 | 200 | 3 | $Y_2O_3$ + multiphase |
| $Y_2O_3 : NaSnO_3 = 1:1$ | 3 | 200 | 6 | $Y_2O_3$ + multiphase |
| $Y_2O_3 : NaSnO_3 = 1:1$ | 3 | 240 | 1 | $Y_2O_3$ + multiphase |
| $Gd_2O_3 : NaSnO_3 = 1:1$ | 6 | 240 | 3 | $Gd_2Sn_2O_7$ |
| $Gd_2O_3 : NaSnO_3 = 2:1$ | 6 | 240 | 3 | $Gd_2Sn_2O_7 + Gd(OH)_3$ |
| $Gd_2O_3 : NaSnO_3 = 1:2$ | 6 | 240 | 3 | $Gd_2Sn_2O_7 + SnO_2$ |
| $Gd_2O_3 : NaSnO_3 = 1:1$ | 3 | 240 | 3 | $Gd(OH)_3$ + multiphase |
| $Gd_2O_3 : NaSnO_3 = 1:1$ | 9 | 240 | 3 | $SnO_2$ + multiphase |
| $Gd_2O_3 : NaSnO_3 = 1:1$ | 6 | 200 | 3 | $Gd(OH)_3$ + multiphase |
| $Gd_2O_3 : NaSnO_3 = 1:1$ | 6 | 200 | 6 | $Gd(OH)_3$ + multiphase |
| $Gd_2O_3 : NaSnO_3 = 1:1$ | 6 | 240 | 1 | $Gd(OH)_3$ + multiphase |

as reactant composition, NaOH concentration, reaction temperature and time. NaOH acted as a mineralizer and played an important role in the syntheses of $M_2Sn_2O_7$ (M = La, Bi, Gd or Y). It is interesting that for some reactant mixtures, the reactant composition and temperature are the same for the crystallization of $M_2Sn_2O_7$ (M = La, Bi, Gd or Y), the only variable being the base concentration used for each reaction system. For example, for M/Sn = 1, the most favourable NaOH concentrations for $La_2Sn_2O_7$, $Bi_2Sn_2O_7$, $Gd_2Sn_2O_7$ and $Y_2Sn_2O_7$ were 0.1, 1, 6 and 3 M, respectively. At a NaOH concentration of $<0.05$ M in the La system, $La(OH)_3$ was formed as impurity, whereas 0.2 M NaOH led to the formation of $SnO_2$ as an impurity; the suitable NaOH concentration for the La system was *ca.* 0.1 M. The molar ratio M/Sn also influenced the formation of products. A ratio of M/Sn of 1 was necessary for pure and well crystallized product in all cases. Any deviation from this ratio led to the formation of impurities. In order to obtain well crystallized products, a crystallization temperature of 240 °C and a crystallization time of three days were optimal, although the use of higher temperature decreased the crystallization time.

A comparison of reaction temperatures for hydrothermal and solid state reactions is listed in Table 2. The lower temperature (*e.g.*, 240 °C) used for hydrothermal syntheses of nanocrystalline $M_2Sn_2O_7$ (M = La, Gd or Y) was a consequence of the high reactivity of the reactants in our hydrothermal systems. Compared to the traditional solid state method the reaction temperatures for hydrothermal syntheses of $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) were substantially lowered.

**Table 2** Comparison of temperatures for hydrothermal and solid state reactions for syntheses of $M_2Sn_2O_7$ (M = La, Bi, Y or Gd)

| Product | Reaction temperature/°C | Ref. |
|---|---|---|
| $La_2Sn_2O_7$ | 1550 | 4, 5, 6 |
| | 240 | This work |
| $Bi_2Sn_2O_7$ | 1000 | 7 |
| | 240 | This work |
| $Y_2Sn_2O_7$ | 1400 | 7 |
| | 240 | This work |
| $Gd_2Sn_2O_7$ | 1400 | 7 |
| | 240 | This work |

## Characterization

Powders of the products $M_2Sn_2O_7$ (M = La, Gd or Y) were white while $Bi_2Sn_2O_7$ was yellow. The compositions of products were measured by ICP.

Morphologies of the samples were examined by SEM and TEM at room temperature. TEM photographs of $La_2Sn_2O_7$ and $Bi_2Sn_2O_7$ are shown in Fig. 1. Nanocrystalline $La_2Sn_2O_7$ and $Bi_2Sn_2O_7$ were synthesized hydrothermally and the average particle size for each was *ca.* 20 nm. The avreage grain sizes of

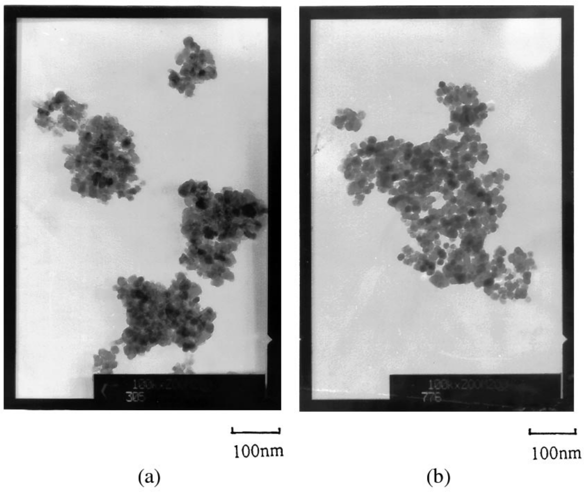

**Fig. 1** TEM of (a) $La_2Sn_2O_7$ and (b) $Bi_2Sn_2O_7$.

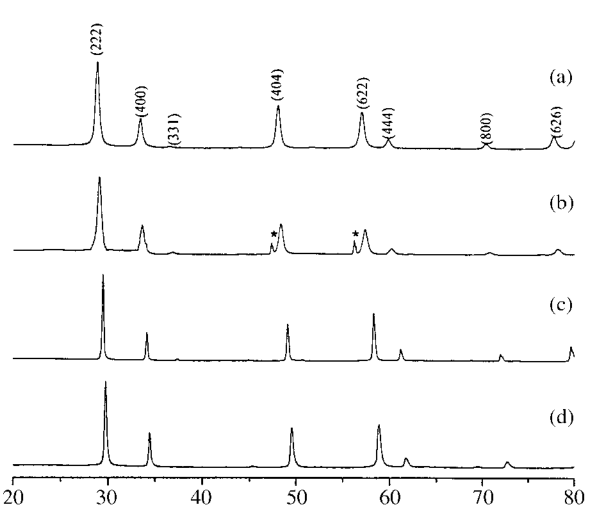

**Fig. 2** Powder XRD patterns of (a) $La_2Sn_2O_7$, (b) $Bi_2Sn_2O_7$ (* shows XRD peaks of internal standard Si), (c) $Gd_2Sn_2O_7$ and (d) $Y_2Sn_2O_7$.

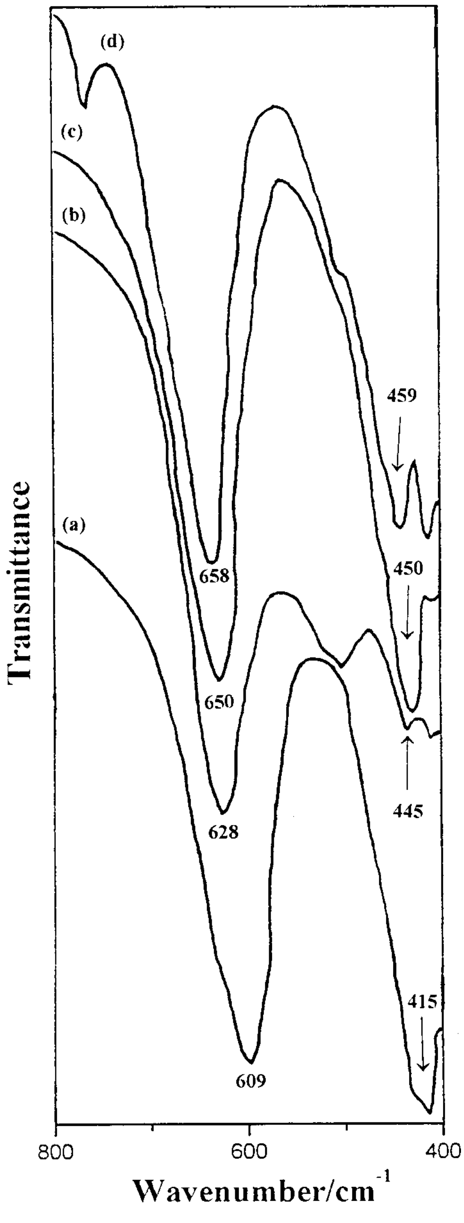

**Fig. 3** IR spectra of (a) $La_2Sn_2O_7$, (b) $Bi_2Sn_2O_7$, (c) $Gd_2Sn_2O_7$ and (d) $Y_2Sn_2O_7$.

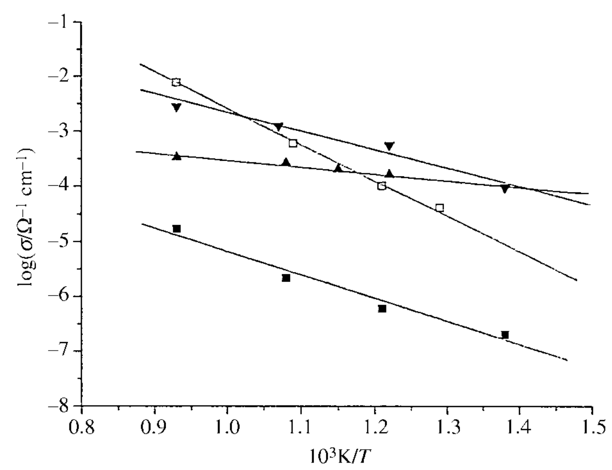

**Fig. 4** Arrhenius plots of ionic conductivities of (a) $La_2Sn_2O_7$ (■), (b) $Bi_2SnO_7$ (□), (c) $Gd_2Sn_2O_7$ (▼) and (d) $Y_2Sn_2O_7$ (▲).

$Gd_2Sn_2O_7$ and $Y_2Sn_2O_7$ range from 100 to 600 nm. The particle sizes of $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) correspond to the width of peaks of their XRD patterns, as shown in Fig. 2. Because of their extremely small dimensions, a large volume fraction of the atoms is located at the grain boundaries, which confers special attributes to these materals. The electrical and optical properties of nanocrystalline materials are very often superior to these of conventional polycrystalline coarse-grained materals.[12]

Powder XRD patterns of $M_2Sn_2O_7$ are shown in Fig. 2 and the lattice parameters were optimized by least-squares refinement. $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) crystallize in the cubic system with lattice parameters of 1.0714, 1.061, 1.0514 and 1.0407 nm, respectively, in accord with decreasing cation sizes; the values are comparable with those for the corresponding phases synthesized by solid-state reactions. The effect of the cation was also evident in the IR spectra of $M_2Sn_2O_7$ (Fig. 3). All spectra show two bands due to M–O–Sn vibrations which shift progressively to higher wavenumbers, as a consequence of differences in ionic size from La (1.06 Å), Bi (0.96 Å), Gd (0.94 Å) to Y (0.93 Å). DTA–TG of the products were conducted and demonstrated that these rare earth stannates, similarly to their corresponding phases prepared from solid state reactions, were stable up to 800 °C.

### Conductivity

Conductivity data showed that the products $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) were insulators at room temperature and oxygen ion conductors at high temperatures. Fig. 4 shows the temperature dependence of conductivity for $M_2Sn_2O_7$ (M = La, Bi, Gd or Y). The conductivities $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) at 800 °C are $1.7 \times 10^{-5}$, $7.85 \times 10^{-3}$, $2.55 \times 10^{-4}$ and $3.37 \times 10^{-4}$ $\Omega^{-1}$ $cm^{-1}$, and the activation energies are 0.34, 0.19, 0.32 and 0.11 eV, respectively.

## Conclusions

A number of pyrochlore stannates $M_2Sn_2O_7$ (M = La, Bi, Gd or Y) have been prepared by low temperature hydrothermal reactions, and characterized by means of XRD, SEM, TEM, IR, ICP, DTA, TG and ac impedance studies. The pH, M/Sn ratio of reaction mixture, reaction temperature and time influence the crystallization of the products. $La_2Sn_2O_7$ and $Bi_2Sn_2O_7$ are nanocrystalline with average particle sizes of *ca.* 20 nm.

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