**Abstract**

Solid oxide fuel cells (SOFCs) have attracted great attention in electrochemical devices because of their high energy conversion efficiency, little pollution and widely flexible fuel choices. Scheelite type based oxide ion conducting materials like PbWO$_4$, BaMoO$_4$, SrMoO$_4$ having more ion conductivity and these can be used as electrolyte for intermediate temperature solid oxide fuel cell (ITSOFC) applications. The present work aims to develop nanocrystalline Dy$^{3+}$ doped BaMoO$_4$ to increase the ionic conductivity for ITSOFC applications. Nanocrystalline dysprosium doped BaMoO$_4$ samples were prepared by using acrylamide assisted gel combustion process. All the samples were characterized by TG/DTA XRD, FTIR and SEM techniques. For the sintered dysprosium doped BaMoO$_4$ crystalline samples, electrical conductivity of grain interior and grain boundary effects are evaluated from the analysis of the impedance plots, obtained at different temperatures.

**Key words:** Acrylamide assisted gel combustion Process, Scheelite type nanocrystalline oxide, XRD, FTIR, SEM, Impedance and Electrical conductivity.

**1. Introduction**

Generally, Oxygen ion conductors are much imperative samples and can be used in various technological devices such as solid oxide fuel cells, oxygen sensors, electrochemical oxygen pumps, etc. [1-2]. Several families of oxygen ion conductors are being investigated for intermediate temperature solid oxide fuel cells (ITSOFCs) like fluorite type (stabilized ZrO$_2$, CeO$_2$ and δ-Bi$_2$O$_3$) oxides, pervoskite type (LaGaO$_3$, BaCeO$_3$ and SrCeO$_3$) oxides, brownmillerite type (Ba$_3$In$_2$O$_7$) oxides, aurivillius type (BIMEVOX) oxides, pyrochlore type (Gd$_2$Zr$_2$O$_7$) oxides and scheelite type (PbWO$_4$) oxides [3-5].

In these, scheelite type oxides exhibit high ion conductivity, which are comparable with the yttria stabilized zirconia.[6-8] Takao Esaka et al., systematically investigated the composition dependent of electrical conductivity for PbWO$_4$ scheelite type samples and reported the higher electrical conductivity, 4.2×10$^{-2}$ Scm$^{-1}$ at 800 °C for Pb$_{0.8}$La$_{0.2}$WO$_{4.1}$. [7] V.Thangadurai et al.

**2. Experimental**

**2.1. Acrylamide assisted gel combustion process**

Different compositions of nanocrystalline Dy$^{3+}$ doped BaMoO$_4$ samples were synthesized by using acrylamide assisted gel combustion process using acrylamide and citric acid as fuels. The precursor chemicals (barium nitrate, dysprosium nitrate and ammonium molybdate) were taken according to their respective molecular weight percentage. Barium nitrate is dissolved in distilled water and mixed with citric acid and acrylamide as a solution. Dysprosium nitrate solution is prepared by dissolving the required amount of dysprosium nitrate in the distilled water. Ammonium molybdate is added with distilled water and stirred the solution till the transparent solution is formed. Dysprosium nitrate solution is mixed with the previous barium nitrate solution under constant stirring. Half an hour later, ammonium molybdate...
solution is also added to the previous mixture solution and stirred continuously at 80 °C, till the formation of the gel. The prepared gels were dried and heated at various temperatures to form the nanocrystalline dysprosium doped BaMoO₄ samples and are structurally characterized by FTIR technique.

2.2. TG-DTA, XRD and FTIR measurements

The TG-DTA curves of the BDM samples were recorded using TA instruments SDT Q600 V20.5 DTA-TGA thermal analyzer. The fine powdered dried gel sample of ~6 mg was placed in the alumina crucible heated at the rate of 10 °C per minute from 40 °C to 900 °C under nitrogen atmosphere. XRD patterns were recorded, for the fine powdered dried gels, using panalytical X’pert pro diffractometer with Cu Kα as the source radiation of wavelength λ=1.5418 Å. The fine powdered mixture of calcined gel sample and KBr powder in 1:20 ratio are palletized using KBr press to form the thin transparent pellet samples, prepared at different calcined temperatures. FTIR spectra were recorded using Schimadzu FTIR/8300/8700 spectrophotometer in the frequency range of 4000 – 400 cm⁻¹ with 2 cm⁻¹ resolution for 20 scans.

The synthesized nanocrystalline dysprosium doped BaMoO₄ powder samples were pressed into 10mm diameter and 2-3 mm thickness pellets at 5000 kg/cm² using KBr press. The prepared pellets were sintered at various temperatures to perform the electrical characterization of the nanocrystalline dysprosium doped BaMoO₄ samples.

3. Result and discussion

3.1. TG-DTA

Fig. 1. shows the TG-DTA curves of nanocrystalline dysprosium doped BaMoO₄ gel samples. The observed two wide endothermic peaks between 40 °C and ~150 °C and the observed weight losses for the dried gel samples are due to the evaporation of water molecules existing in the sample. From fig 1, in all TG/DTA curves, the observed exothermic curve at 178 °C is also due to the decomposition of citric acid and decomposition of nitrates from barium nitrate as well as from dysprosium nitrate. The observed exothermic DTA curve is intensified with the increase of dysprosium content in the BaMoO₄ sample. This may be due to the different binding energies of barium nitrate and dysprosium nitrate. Doping of dysprosium in the BaMoO₄ increases the total quantity of nitrates in the precursor, which increases the oxidant ratio and helpful for combustion reaction. In all TG/DTA curves, the observed exothermic curve at ~ 570 °C and the corresponding weight losses may be due to the decomposition of metal acrylate complex, which might have formed from acrylamide and metal nitrates. However, after 600 °C, there is no weight loss is observed in the TG curve, which indicates that there is complete decomposition of organic derivatives from the sample and the same is also confirmed from FTIR and XRD results.

3.2. FTIR

Fig. 2. shows the FTIR spectra recorded for various compositions of dysprosium doped BaMoO₄ dried gel samples calcined at 900 °C.

Fig. 2. FTIR spectra for various compositions of dysprosium doped BaMoO₄ samples obtained at 900 °C.

In fig. 2, for all the compositions of dysprosium doped barium molybdate samples, the appearance of the IR peak
at ~820 cm$^{-1}$ is attributed to the Mo-O stretching vibration and also the showed IR band at 702 cm$^{-1}$ is assigned to the Dy-O network formation. When the dopant quantity increases, the defects concentrations increase and hence, at the higher composition BDM 0.2 ($\text{Ba}_{0.8}\text{Dy}_{0.2}\text{MoO}_4$), the newly observed IR bonds 660 and 795 cm$^{-1}$ are attributed to the formation of Dy-O-Ba and Dy-O-Mo bonds. Further, the formation of phase and microstructure are conformed from XRD and SEM results.

### 3.3. XRD

Fig. 3. shows the XRD patterns of the dysprosium doped BaMoO$_4$ samples, obtained at 900 °C. The observed crystalline peak in the XRD patterns are confirmed the formation of the scheelite type BaMoO$_4$ crystalline phase, by comparing the obtained XRD peaks with the standard ICDD 00-029-0193 data. The crystalline size of all the composition of dysprosium doped BaMoO$_4$ sample were calculated using scherrer’s formula: $D = \frac{0.9\lambda}{\beta \cos \theta}$, where $\lambda$ is the X-ray wave length (0.15418 nm), $\beta$ is full width half maximum (FWHM) of the peak. The crystalline size of all the sample were found to be <100 nm. Furthermore, conductivity studies are made on the dysprosium doped BaMoO$_4$ sample pellets sintered at 900 °C.

![Fig. 3. XRD patterns for the various compositions of dysprosium doped BaMoO$_4$ samples obtained at 900 °C.](image)

### 3.4. SEM measurement

Fig. 4. shows SEM image of the particular composition of dysprosium doped BaMoO$_4$ ($\text{Ba}_{0.8}\text{Dy}_{0.2}\text{MoO}_4$) powder, obtained at 900 °C. SEM micrograph showed agglomerated spherical particles of $\text{Ba}_{0.8}\text{Dy}_{0.2}\text{MoO}_4$ powder sample. Their particle sizes are measured and it is found to be <100 nm.

![Fig. 4. SEM image of dysprosium doped BaMoO$_4$ ($\text{Ba}_{0.8}\text{Dy}_{0.2}\text{MoO}_4$) powder obtained at 900 °C.](image)

### 3.5. Electrical conductivity studies

At ambient temperature, electrical impedance data are measured for all the compositions of dysprosium doped BaMoO$_4$ pellet samples sintered at 900 °C. The total resistances obtained from the intercept of the depressed semicircles with the real axis and the total conductivity is calculated using the resistance and also the pellet dimensions. In the Dy doped barium molybdate samples, the composition BDM0.2 ($\text{Ba}_{0.8}\text{Dy}_{0.2}\text{MoO}_4$) is having higher conductivity than the other compositions.

Fig. 5. shows the impedance plots obtained at various temperatures for the nanocrystalline BDM0.2 sample. From fig. 5., the two depressed semicircles are observed in the impedance plots, where, large semicircle in the lower frequency region indicates the grain boundary response and the lower semicircle in the higher frequency region indicates the grain interior response of the nanocrystalline BDM0.2 sample.

![Fig. 5. Impedance plots ($Z'$ vs $-Z''$ ) for BDM 0.2, obtained at various temperatures.](image)
The grain interior conductivity ($\sigma_{gi}$) and grain boundary conductivity ($\sigma_{gb}$) for nanocrystalline Ba$_{0.8}$Dy$_{0.2}$MoO$_{4.1}$ sample were calculated using the formula:

$$\sigma = \frac{t}{A} \times \frac{1}{R}$$

Where R is the resistance, t is the thickness of the sintered pellet and A is the area of the sintered pellet. Fig. 6., show the log $\sigma$ vs 1000/T plots for the grain interior and grain boundary conductivities for Ba$_{0.8}$Dy$_{0.2}$MoO$_{4.1}$ sample pellet sintered at 900 °C.

Fig. 6. Log $\sigma$T vs 1000/T plots for bulk and grain boundary conductivities of Ba$_{0.8}$Dy$_{0.2}$MoO$_{4.1}$ sintered at 900 °C.

The activation energy is calculated from the Log $\sigma$T vs 1000/T plots of nanocrystalline Ba$_{0.8}$Dy$_{0.2}$MoO$_{4.1}$ sample and it is found to be 0.97±0.03 eV for grain interior conductivity and 0.94±0.02 eV for grain boundary conductivity. In the grain interior region, the observed higher conductivity and activation energy may be due to the formation and also the migration of oxygen ion charge carriers in the nanocrystalline dysprosium doped BaMoO$_{4}$ sample (Ba$_{0.8}$Dy$_{0.2}$MoO$_{4.1}$).

4. Conclusion

Different compositions of the nanocrystalline dysprosium doped BaMoO$_{4}$ samples were synthesized by using acrylamide assisted gel combustion process. TG/DTA curves of the dysprosium doped BaMoO$_{4}$ samples showed the complete crystallization at ~577 °C. XRD patterns confirmed the phase of the scheelite type BaMoO$_{4}$ crystalline samples and the crystalline size calculated by using the Scherer’s formula, is found to be <100nm. Formation of MoO$_{3}$ is identified by FTIR spectra. SEM micrograph showed an agglomerated spherical particles and their particle sizes are found to be <100 nm. The Ba$_{0.8}$Dy$_{0.2}$MoO$_{4.1}$ (BDM0.2) sample showed the highest conductivity at ambient temperature compared to all other compositions of Dy doped BaMoO$_{4}$ samples.

Acknowledgement

Dr N.S is gratefully acknowledged CSIR, DRDO, AICTE and DST, Govt. of India, for receiving the financial support in the form of major research projects. NN acknowledge CSIR-SRF [CSIR : 9/559/(0054)/2008/EMR-I], for receiving fellowship for doing Ph.D. Authors also acknowledge CIF, Pondicherry university for using TG/DTA and SEM facilities.

References


* Corresponding author : N. Satyanarayana
Phone: +94143 2654404
E-mail: nallanis2010@yahoo.com