Impedance Studies of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ Oxide Ion Conductors

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A series of compounds $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ ($x=0-0.3$) have been synthesized by solid-state reaction technique. Materials have been characterized by XRD, SEM, DSC and impedance study. In the temperature regime 520 °C–590 °C, the specimens with $x \leq 0.05$ have the conductivity higher than $\text{La}_2\text{Mo}_2\text{O}_9$. Conductivity of Sn-doped compound decreases consistently with increasing Sn-doping, compared to the undoped compound both below and above phase transition, barring the specimens with $x \leq 0.05$, where conductivity values remains almost same as that of undoped specimen in high temperature region. In the intermediate temperature regime (520 °C–590 °C), the conductivity of doped compounds increases for $x \leq 0.05$ as compared to parent compound. Also, there is no indication of phase stabilization with Sn-doping in this compound even with the highest doping level, $x=0.3$. Electric modulus analysis suggests that thermally activated oxygen ion hopping mechanism is responsible for the conduction in Sn-doped compound.

KEY WORDS: Ionic conduction; $\text{La}_2\text{Mo}_2\text{O}_9$; Oxide ion conductor; Impedance spectroscopy; Electric modulus

1. Introduction

Plethora of research activities are on in the field of oxygen ion conductors considering their tremendous application potential in various solid state ionic devices such as the electrolytes in solid oxide fuel cells (SOFCs), oxygen sensors, oxygen pumping devices, oxygen separation membranes oxygen-permeable catalyst *etc.*^[1–4]. Of late, LAMOX family of oxygen ion conductors has been attracting attention due to their comparable ionic conductivity with YSZ at comparatively low temperature^[5]. The parent compound of the LAMOX family of oxygen ion conductors is $\text{La}_2\text{Mo}_2\text{O}_9$ which undergoes a reversible $\alpha \leftrightarrow \beta$ phase transition at and around 580 °C, where its ionic conductivity drastically increases. From the application point of view, in various solid state ionic devices, improvement in its ionic conductivity and phase stabilization at lower temperature is very essential. In order to increase ionic conductivity

and suppress phase transition in parent LAMOX, dopants at both La and Mo-sites have been used. In addition simultaneous doping at La as well as Mo-sites has also been reported. There has been some success as far as suppression of phase transition is concerned by dopants like, W at Mo-site or rare-earths, like Nd in higher concentrations (≥ 0.5) at La-site^[6–9]. Increase in conductivity has been reported in Dy and W doped LAMOX^[10].

Partial substitution of aliovalent ion may introduce extra oxygen ion vacancies in the crystal lattice and so increase in conductivity could be expected. From the crystal structure study it has also been an indication that the greater affinity of variable coordination number of Mo ion has also its effect on the conductivity of this compound. Keeping this in mind, Sn was doped at Mo-site in $\text{La}_2\text{Mo}_2\text{O}_9$. Sn is found in Sn^{2+} and Sn^{4+} states and, therefore, may create extra oxygen vacancies which may lead to increase in the conductivity. Earlier in a brief communication^[11], we have reported that the overall conductivity increases in $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compound for $x=0.03$ at temperature above 700 °C as compared to the parent compound. Though, we believed the reason for this increase in conduction due to the creation of

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Fig. 1 XRD patterns of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ (a), and lattice parameter, a (b) and crystalline size, L (c) as a function of Sn content in $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$

extra oxygen ion vacancies, it turns out however, that the diffusion of silver electrodes in the grain boundaries at high temperature might be responsible for the enhancement of conductivity for $x=0.03$. This paper explores the detailed systematic study on Sn doped LAMOX compound with conducting gold paste as electrode material. The structural, thermal analysis and electrical studies in the framework of complex impedance and modulus formalism of the Sn doped compounds are presented here.

2. Experimental

High temperature solid-state reaction method has been employed to synthesize material. As per formula unit $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ ($x=0-0.3$), appropriate proportions of La_2O_3 (99.5%), MoO_3 (99.5%) and SnO_2 (99.9%) were used followed by thorough grinding and calcination at 500 °C for 12 hours. Powders were re-ground and claimed two more times at 650 °C and 700 °C, before the powder was pelletized and sintered at 1000 °C for 12 hours^[11]. The parent $\text{La}_2\text{Mo}_2\text{O}_9$ compound has 95% of the theoretical density. It is 90% in case of $x \leq 0.05$ whereas it is about 88% for the compound $x \geq 0.1$. Thus, as Sn concentration increases, there is decrease in the density of these compounds. X-ray diffraction (XRD) studies on these compounds were carried out at room temperature in the 2θ range of 10° to 70°. Differential scanning calorimetric (DSC) analysis was performed on a DSC-60 thermal analyzer (Shimadzu, Japan) to determine the phase transition in the temperature range of room temperature to 570 °C with a heating rate of 10 °C/min. Surface morphology of the sintered pellets was studied by scanning electron microscopy (SEM). Electrical characterization was performed by using HIOKI-LCR Tester 3532-50. The details of electrical measurement are given in Ref. [12].

3. Results and Discussion

3.1 XRD analysis

XRD reflection peak for the specimens $x=0, 0.05,$

0.1, 0.2 and 0.3 are shown in Fig. 1. The analysis of XRD shows that these materials have pseudo-monoclinic crystal structure, and reflection peaks can be indexed as P213 space group. The splitting on the reflection peak of the high temperature cubic phase of $\text{La}_2\text{Mo}_2\text{O}_9$ is present for the compound which indicates the monoclinic distortion^[12]. This distortion is present in Sn doped compounds as well. Three unidentified peaks (*) at 26.7°, 33.6° and 51.9° were found for the doped compounds with the increase in intensity with increasing Sn content. Impurity peaks (o) associated with the reflection of $\text{La}_2\text{Mo}_2\text{O}_7$ and La_2O_3 have been found in the XRD reflection patterns of doped compounds.

Analysis of XRD data was carried out as described in the earlier works^[12,13]. The cell parameter was found to be $a=7.1618$ Å for $\text{La}_2\text{Mo}_2\text{O}_9$ and is comparable with those reported in the literature for the pure phase of $\text{La}_2\text{Mo}_2\text{O}_9$ ^[12]. The cell parameter increases a little bit for the specimen with $x=0.05$ ($a=7.1648$ Å). The value of cell parameter decreases with increase in the amount of Sn doping for $x>0.05$ and is depicted in Fig. 1(b). An estimation of the crystallite size calculated with Scherer formula from the FWHM of the X-ray diffraction peak with highest intensity ((210) peak at $2\theta=27.89^\circ$) gives the value in the range of ~40 nm to ~43 nm as shown in Fig. 1(c). The crystallite size is larger than the parent compound for all Sn doped compound and it is maximum for $x=0.05$.

3.2 SEM studies

Scanning electron micrographs taken on Sn-series of specimens with $x=0, 0.05, 0.1$ and 0.2 have been shown in Fig. 2. Surface morphology of these specimens indicates that for the pure and Sn substituted specimens, with $x=0.05$ are having good grains size with well grain-grain connectivity and no segregation at the grain boundaries is present in these specimens. The average grain size for parent compound is ~6 μm. The grain size increases to ~8 μm in case of $x=0.05$. On the other hand, samples with higher amount of

Fig. 2 SEM micrographs of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ samples : (a) $x=0$; (b) $x=0.05$; (c) $x=0.1$; (d) $x=0.2$

Sn substitution ($x \geq 0.1$), have segregated grains with small grain size and high porosity. This may be due to the solubility limit, since the difference in ionic radius and oxidation state of Sn^{4+} and Mo^{6+} , may hinder the solubility of Sn in $\text{La}_2\text{Mo}_2\text{O}_9$. Also, it could be due to the lower sintering temperature as the melting temperature of SnO_2 is high (1630°C). Thus, for obtaining good microstructure the sintering temperature of Sn-doped compounds appears to be higher than 1000°C .

3.3 DSC study

DSC thermograms for undoped and doped compounds are presented in Fig. 3. The endothermic peak appeared in DSC curves indicate a clear phase transition on heating for each undoped and Sn doped $\text{La}_2\text{Mo}_2\text{O}_9$ ^[14]. From the DSC analysis for $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compounds the values of transition temperature, transition width ($T_{\text{off}} - T_{\text{on}}$) and enthalpy are tabulated in Table 1. The enthalpy has been calculated from the area under the peak with the help of DSC 60 TAW program. It can be concluded from Table 1, when Sn doping increase up to $x=0.2$, the monoclinic distortions increases, which indicating that the disordering in the lattice increase (for $x=0.2$, enthalpy is -6.13 J/g). Above this doping level there is slight a decrease in enthalpy value which could be due to more ordered state. It is evident from the Table 1 that there is no suppression of phase transi-

Fig. 3 DSC plots for $\text{La}_{2-x}\text{Sn}_x\text{Mo}_2\text{O}_{9-\delta}$ compounds

tion with Sn doping upon heating. The small peak at around 520°C – 540°C for $x=0.1$ and $x=0.3$ could not be assigned to any phase transition since enthalpy values are very low. Also, in this temperature region no other transition was obtained in the conductivity plot.

3.4 AC impedance studies

The electrochemical impedance spectroscopy (EIS) is an easy tool to analyze ionically conducting materials^[15]. The impedance spectra of Sn doped and undoped $\text{La}_2\text{Mo}_2\text{O}_9$ compounds were collected at different temperatures over a wide range of the frequency range and fitting of these spectra was carried out

Table 1 DSC peak analysis of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compound

x	$T_r(^{\circ}\text{C})$	$T_{\text{on}}(^{\circ}\text{C})$	$T_{\text{off}}(^{\circ}\text{C})$	$T_{\text{off}} - T_{\text{on}}(^{\circ}\text{C})$	Enthalpy (J/gm)
0	567.13	561.48	570.4	8.92	−4.64
0.05	561.03	550.40	567.07	16.67	−4.89
0.1	565.11	554.36	567.28	12.92	−6.11
0.3	560.58	550.90	564.98	14.08	−5.16

Table 2 Capacitance values obtained for $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compounds by fitting impedance spectra with equivalent circuit at 400 $^{\circ}\text{C}$

x	Bulk (pF/cm)	Grain boundary (nF/cm)	Electrode polarization ($\mu\text{F/cm}$)
$x=0$	10.8	0.25	2.6
$x=0.05$	21.48	19.5	3.7
$x=0.1$	14.02	14.3	0.74
$x=0.3$	8.34	0.81	0.43

Fig. 4 Complex impedance spectra of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ at 400 $^{\circ}\text{C}$ (a) and 500 $^{\circ}\text{C}$ (b), the solid lines are the fitted plots with equivalent circuit shown in Fig. 4(a) and Fig. 4(b)

with the help of EIS spectrum analyser (β version) software^[16]. The relative deviations of the fitted spectrum from the measured data were less than 2%. These spectra were fitted with an equivalent circuit consisting of three parallel $R - Q$ elements (Q is constant phase element) connected in series with each other as well with as an inductor as described elsewhere^[12,13].

Fig. 4 shows the impedance spectra of the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ specimens at the temperatures 400 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$. The capacitance obtained for pure and doped compounds in the different regions of impedance plots at 400 $^{\circ}\text{C}$ evaluated by fitting the impedance spectra with equivalent circuit discussed above are shown in Table 2. The first semicircular arc in the impedance plot is associated with the capacitance value in the range of pF/cm and is the contribution of bulk of the material. The bulk resistivity increases with the increase in Sn content in $\text{La}_2\text{Mo}_2\text{O}_9$ at 400 $^{\circ}\text{C}$. The intermediate semicircular arcs present in the impedance plots associated with the capacitance value in the range of nF/cm represent the effect of grain boundary in the compound. With increasing temperature the grain boundary contribution decreases but for the higher doping compound ($x \geq 0.1$)

it is present even up to 550 $^{\circ}\text{C}$.

Fig. 5 shows the impedance spectra of the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compounds at different temperatures. It is evident from impedance plots that above 550 $^{\circ}\text{C}$ there is a drastic decrease in the value of resistance. At low frequency region of the impedance plot associated with the capacitance value in the range of $\mu\text{F/cm}$ assigned to electrode polarization effect, indicates a typical signature of ionically conducting polycrystalline material^[17–19]. At high temperature, the electrode polarization dominates the bulk behavior so the point of intercept of the arc on the real axis is considered as the resistance due to bulk of the samples^[13].

Fig. 6 shows the variation of reactive part (Z'') of the impedance with frequency at different temperatures (loss spectrum) for the representative samples $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ with $x=0-0.3$. From the spectra, it is clearly seen that Z'' decreases with the increase in temperature and shows peak at a unique frequencies with the peak shifting towards the higher frequency region as the temperature increases. In the loss spectrum at low frequency another relaxation peak associated with the short migration is observed. The low frequency relaxation peak diminishes as temperature increases. The dielectric loss $\tan \delta$ has been calcu-

Fig. 5 Complex impedance spectrum at different temperature for the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compounds

lated following equation $\tan \delta = -Z'/Z''$. Fig. 7(a) shows the variation of $\tan \delta$ with temperature for compound with $x=0$ and 0.05 at 100 kHz. The curve is characterized by the peak corresponding to the relaxation process associated with the short range diffusion of oxygen ions *via* vacancies at low temperature, whereas the high temperature dielectric loss peak corresponds to the $\alpha \leftrightarrow \beta$ phase transition. Similar dielectric relaxation peak (P_d) observed in the plot of dielectric loss versus frequency is shown in Fig. 7(b). Using a non linear fitting method (NLS fitW1, Lorentz fit), the experimental data were fitted and the area under the peak (P_d) was calculated. The area under the relaxation time peak is 195.8 for $\text{La}_2\text{Mo}_2\text{O}_9$ and is 177.9 for $\text{La}_2\text{Mo}_{1.95}\text{Sn}_{0.05}\text{O}_{9-\delta}$, which is proportional to the content of movable oxygen vacancies^[20]. This is less for the doped specimen than the $\text{La}_2\text{Mo}_2\text{O}_9$. It suggests that charge carrier concentration for the doped compound decreases.

3.5 Electrical conductivity analysis

At different temperatures and over a wide range of frequencies, the electrical conductivity of the compounds has been investigated. The dc conductivity is calculated from the analysis of complex impedance spectrum data at different temperatures. Dependence of dc conductivity with temperature for the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compounds is shown in Fig. 8.

There is an increase in conductivity with rise in temperature with a typical Arrhenius type behavior. It is clear from the plots that the specimens undergo $\alpha - \beta$ phase transition between 550–570°C. The transition region shifts to the lower temperature for the higher concentration of doping compared to undoped compound. We have found the increase in conductivity of Sn-doped compounds in the temperature regime 520–590 °C for $x \leq 0.05$, although, at high temperatures (>590 °C) conductivity of this compound systematically decreases as the Sn concentration increases except for the specimens having Sn concentration ≤ 0.5 for which conductivity values are almost same as that of the parent compound conductivity. The value of dc conductivities at 700 °C are 0.036 S/cm for undoped, 0.03 S/cm for $x=0.05$ and 0.022 S/cm for $x=0.1$ compound. In the earlier report^[11], it was reported that conductivity of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ ($x=0.03$) was slightly higher than the $\text{La}_2\text{Mo}_2\text{O}_9$ at temperatures above 700 °C, whereas below that temperature conductivity was low. In the present study up to 700 °C, the conductivity of the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ with $x \leq 0.05$ compounds is almost same with undoped one.

The ionic radius of Sn^{4+} is 0.69 Å and that of Mo^{6+} is 0.62 Å. Slightly greater ion Sn^{4+} also occupies some free space of O ion vacancy which leads to decrease in free volume in the lattice and cause difficulty for O ion migration since the cell volume does

Fig. 6 Variation of imaginary part of impedance (Z'') as a function of $\lg\omega$ for the representative samples $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ with $x=0-0.3$

Fig. 7 Variation of $\tan \delta$ with temperature at $\omega=100$ kHz (a) and variation of $\tan \delta$ with frequencies at 400°C (b) for the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ ($x=0$ and 0.05) compounds, solid lines is the fitting curves

Fig. 8 $\lg\sigma_{dc}\cdot T$ vs. $1000/T$ plot for Sn doped series of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ specimens

not increase with the substitution of Sn in $\text{La}_2\text{Mo}_2\text{O}_9$ ($x \leq 0.05$). For the higher amount of Sn doping, the difference in ionic radius and in oxidation state of Sn^{4+} and that of Mo^{6+} hinders the solubility of Sn^{4+} in $\text{La}_2\text{Mo}_2\text{O}_9$. The appearance of impurity peaks in XRD diffractogram and segregated grains in SEM indicate that the maximal doping amount of Sn in $\text{La}_2\text{Mo}_2\text{O}_9$ is $x=0.05$. There is a systematic decrease in cell parameters with increasing Sn content in doped compounds for $x > 0.05$. Since the free volume in unit cell determines the volume available for mobile charge carriers, therefore, in our present study the free space in lattice crystal V_f have been estimated

Table 3 Conductivity (σ_{dc}) and activation energy (E_g) for the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compounds

x	σ_{dc} (S/cm)			E_g (eV)	
	550 °C	600 °C	700 °C	α phase	β phase
0	6.8×10^{-4}	0.014	0.036	1.14	1.10
0.05	1.1×10^{-3}	0.014	0.030	1.16	1.01
0.1	6.1×10^{-4}	8.9×10^{-3}	0.021	1.19	1.03
0.3	3.51×10^{-4}	4.5×10^{-3}	0.012	1.23	1.08

by the following equation^[12]:

$$V_f = a^3 - \frac{16\pi}{3} \left(r_{\text{La}}^3 + \frac{2-x}{2} r_{\text{Mo}}^3 + \frac{x}{2} r_{\text{Sn}}^3 + \frac{9-\delta}{2} r_{\text{o}}^3 + \frac{\delta}{2} r_{\text{vo}}^3 \right) \quad (1)$$

where a is the lattice constant, r_{o} is the oxygen radius (1.38 Å) and r_{vo} is oxygen vacancy radius (1.164 Å)^[12,20]. V_f is 136.31 Å³ for $x=0.05$, which is slightly greater than 135.74 Å³ of $\text{La}_2\text{Mo}_2\text{O}_9$. Since, charge carrier concentration for $x=0.05$ decreases, so even though, there is slight increase in free cell volume, but conductivity remains the same, as compared to parent compound at high temperatures. At higher doping concentrations ($x>0.05$), due to the decrease in total unit cell volume there is a decrease in free volume in unit cell (135.2 Å³ for $x=0.3$). In addition to the decrease in cell volume, small traces of secondary phases present, as discussed earlier, at higher concentration ($x>0.05$) may also be responsible for decrease in conductivity of doped compounds. The activation energy has been obtained from dc conductivity plots using Arrhenius equation:

$$\sigma = \frac{A}{T} \exp \left(- \frac{E_g}{KT} \right) \quad (2)$$

where, A is a constant, K is Boltzmann constant and E_g the activation energy. The values of activation energy are in the range of 1.14 eV to about 1.23 eV for the low ionic conducting phase (α phase), and 1.01 eV to 1.10 eV for β phase, as shown in Table 3. The activation energies are appreciably high for the higher amount of Sn doping ($x>0.1$). Thus, conductivity reduced appreciably at high temperatures.

The frequency dependent conductivity at various temperatures is shown in Fig. 9 for the pure and doped compound with $x=0.05$, 0.1 and 0.3. The plots are characterized by a low frequency plateau which corresponds to the DC conductivity of the bulk and a high frequency dispersive region, which corresponds to the ac conductivity. This behavior can be explained in terms of Jonscher's power law^[21]:

$$\sigma_{ac} = \sigma_o + A\omega^n \quad (3)$$

The conductivity increases with the increase in temperature in low frequency region. The hopping frequency tends to shift towards the higher frequency region with increase in temperature. The values for the exponent of the power law n (upon fitting Eq. (3)) is found to be 0.46 for the $x=0$ and it is 0.4 for the $x=0.1$

at 400 °C. Frequency dependent conductivity at different temperatures for doped and undoped specimens are normalized and plotted against normalized frequency and is shown in Fig. 10. The scaling behavior of the $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ compound indicates temperature independent conductivity mechanism and it is same for the both pure and doped compound which further confirms the predominantly ionic transport in doped compounds.

3.6 Electric modulus analysis

Electrical modulus analysis is convenient method to study dynamics of relaxing species^[15]. In Fig. 11, variation of imaginary part of modulus with frequencies are shown at different temperatures for specimens with $x=0$, 0.05, and 0.2. The variations of imaginary component of modulus (M'') as a function of frequency at different temperatures for the samples are characterized by clearly resolved peaks at unique frequency. At different temperature levels, it shows a tendency to shift towards the high frequency region with corresponding increase in temperature. The behavior of the modulus spectra indicates the thermally activated hopping type of mechanism for electrical conduction in the system. It also indicates the change in short-range mobility to long-range mobility of thermally activated ions^[22].

The conduction relaxation time (τ_σ) can be estimated from the peak frequency of the pattern. The variation of τ_σ as a function of inverse temperature appeared to be linear, as shown in Fig. 12. An estimate of activation energy using the following relation:

$$\tau_\sigma = \tau_o \exp(-E_g/k_B T) \quad (4)$$

gives $E_g=1.06$ eV, 1.11 eV and 1.14 eV for $x=0$, 0.05 and 0.1, respectively before phase transition. The values of relaxation time for these specimens above phase transition could not be evaluated as peak in the imaginary modulus spectra shifts towards higher frequencies, which are beyond our measuring instrument limit. The values of the activation energies obtained for these specimens from relaxation time data are almost the same before phase transition as obtained from dc conductivity plots. This indicates a similar type of relaxation, which is responsible for both doped and undoped compound.

The modulus spectra of the specimens with $x=0$ and 0.1 has been normalized and plotted against nor-

Fig. 9 $\lg \sigma_{ac}$ vs. $\lg \omega$ plots for $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ with $x=0, 0.05, 0.1$ and 0.3 at different temperatures

Fig. 10 $\lg(\sigma_{ac}/\sigma_o)$ vs. $\lg(\omega/\omega_o)$ plots for $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ with $x=0, 0.05, 0.1$ and 0.3

Fig. 11 Variation of imaginary part of modulus (M'') as a function of frequency for $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ with $x=0$, 0.05 and 0.2

Fig. 12 Variation of relaxation time as a function of inverse of temperature for $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$

Fig. 13 Normalized modulus spectra *vs.* normalized frequency for $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ specimens with $x=0$ and 0.1

malized frequency and are shown in Fig. 13. The scaling behavior of the electric modulus of the samples

characterized by the nearly perfect overlapping of different temperature data, in a single master curve indicates the single relaxation process occurring within the sample at different temperatures^[23] which is in conformity with the scaling behavior of ac conductivity.

4. Conclusions

A series of compounds have been synthesized with a composition $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ ($x=0-0.3$) by standard solid-state reaction technique. Material formation has been confirmed by X-ray diffraction studies. In the temperature regime 520–590 °C, the specimens with $x \leq 0.05$ have the conductivity higher than $\text{La}_2\text{Mo}_2\text{O}_9$. Conductivity of Sn-doped compound decreases consistently with increasing Sn-doping, compared to the undoped compound both below and above phase transition, barring the specimens with $x \leq 0.05$, where conductivity values remains almost the same as that of undoped specimen in high temperature region. The activation energy increased with the higher amount of Sn doping and makes oxygen ion migration more difficult. Solubility limit of Sn substitution in $\text{La}_2\text{Mo}_2\text{O}_9$ and/or low sintering temperature affects the sample microstructure as well as the conductivity of $\text{La}_2\text{Mo}_{2-x}\text{Sn}_x\text{O}_{9-\delta}$ ($x \geq 0.05$). Also, there is no indication of phase stabilization with Sn-doping in this compound even at the highest doping level ($x=0.3$). Electric modulus analysis suggests that thermally activated hopping mechanism is responsible for the conduction in Sn-doped compound which is predominantly ionic in nature.

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