© Applied Science Innovations Pvt. Ltd., India Carbon – Sci. Tech. 11/2 (2019) 78-84

Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

RESEARCH ARTICLE *Received: 21/02/2019; Accepted: 17/05/2019*

Dielectric study of $La_{2-x}Tb_xMo_2O_9$ (x=0.1, 0.2, 0.5) oxygen ion conductor

Gyati Tachang Tado, Diptimayee Tripathy, Amarjyoti Saikia, Arvind Pandey

Department of Physics, North Eastern Regional Institute of Science and Technology, Nirjuli, 791109, Arunachal Pradesh, India.

Abstract: $La_2Mo_2O_9$ based Tb-doped compound, $La_{2-x}Tb_xMo_2O_9$ (x=0.1, 0.2, 0.5), was synthesized and characterised by EIS studies. The frequency and temperature dependent dielectric, electric modulus and ac conductivity studies have been done. Different formalisms have been used to understand relaxation mechanism in our compound. The conductivity in these specimens appears to be due to mobility of oxygen ions.

Keywords: Solid electrolyte, ionic conductor, dielectric loss, electric modulus, relaxation mechanism.

1. Introduction: Numerous research works are underway in the area of oxygen ion conduction based solid electrolytes because of their suitable applications in SOFCs, oxygen sensors and oxygen pumping devices **[1-3]**. Among other electrolytes, LAMOX and its derivatives are one of the most promising candidates to be used as an ionic conductor. The parent compound with the formula unit, $La_2Mo_2O_9$, has higher ionic conductivity (~10^{-2}) at relatively lower temperature (at 800 ^oC) and is comparable with YSZ (at 1000 ^oC). The major drawback of parent compound is that it undergoes an order-disorder phase transition around 580 ^oC, known as α-β phase transition **[4]**. Another demerit is, it has high conductivity only at high temperatures which is undesirable in many applications. To suppress phase transition, doping by various elements at La/Mo or both the sites have been performed by various researchers and to some extent have achieved desired results **[5-11]**. We have attempted Tb doping at La-site in search of phase transition suppression and higher conductivity as compared to parent material at moderate temperature range. Since the dielectric studies of ionic conductors could provide vital information regarding the conduction mechanism in these materials, hence, in the present work we have tried to explore this aspect via dielectric, ac conductivity and modulus formulation.

2. Experimental: Appropriate quantities of La_2O_3, MoO_3 and Tb_2O_3, were weighed according to formula unit, $La_{2-x}Tb_xMo_2O_9$ (x=0.1, 0.2, 0.5), mixed and grinded under the wet condition by employing acetone/ethanol followed by calcination of resulting powders at 500 ^oC for 12 hrs. Repeated grindings and calcinations were carried out at 700 ^oC and 800 ^oC for above mentioned period. Finally, powder was pressed and sintered at 1000 ^oC for 12 hrs **[12]**.

For dielectric measurements, both side of sintered pellet were coated with gold paste and was heated at 900 ^oC for 15 minutes to obtain a good electrical contact. HIOKI-LCR TESTER IM3536 (frequency range 4 Hz – 8 MHz) was used for this study in temperature range RT -750 ^oC.

3. Results and discussion

Dielectric study: In Figure 1(a), (b) and (c) frequency dependence of ε′ for all specimens i.e. $La_{2-x}Tb_xMo_2O_9$ (x=0.1, 0.2, 0.5), as a function of temperature are plotted. It is observed that ε′ sharply decreases with increase in frequency for all specimens. This observation is due to the oscillation of free dipoles with respect to alternating field. At low frequency, we have $\varepsilon' \approx \varepsilon_s$ (ε_s is low frequency dielectric constant), the dipoles oscillates in accordance with the field variation, thus, space charge region is formed at electrode-electrolyte interface due to charge accumulation leading to net polarization and hence, ε′ increases. At high frequency, $\varepsilon' \approx \varepsilon_\alpha$ (ε_α is high frequency dielectric constant), the dipoles no longer able to follow the field, thus, no charge accumulation takes place (here, space charge contribution is dominated by ionic and electronic charge contribution) as a result ε′ remains constant. It is also observed that ε′ increases with increase in temperature. This may be due to temperature dependent charge carrier's polarization mechanism **[13 - 15].**

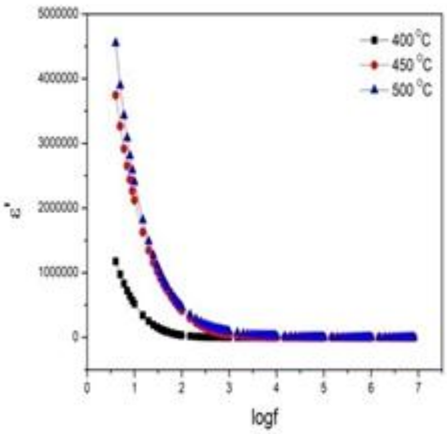
In Figure 1(d), (e) and (f) frequency dependence of dielectric loss for all specimens as a function of temperature are plotted. It is observed from Fig.1 that shifting of dielectric loss peak towards high frequency with increase in temperature takes place. This observation further confirms the essence of dielectric relaxation phenomena in the specimen **[16]**.

Electric modulus study: Modulus studies were carried out using complex electric modulus formulation **[17]**. The variation of M′ and M″ with frequency for all specimens at different temperatures is shown in Figure 2(a-f). In Fig. 2(a-c), for frequencies below 10^3 Hz, the value of M′ is very small for all the specimens at all temperatures. This observation suggests suppression of electrode polarization. The increasing M′ with frequency suggests short range conduction mechanism. Also, it is observed that M′ decreases with increase in temperature further suggesting temperature dependent relaxation process in the specimen **[13, 18]**.

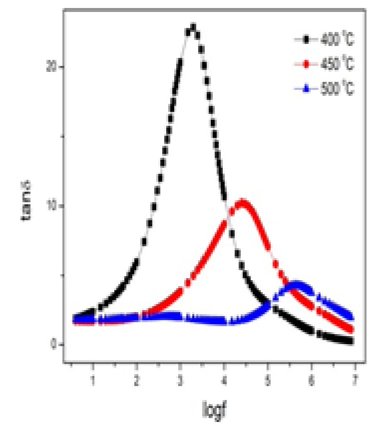
In Figure 2(d-f), the single relaxation peak M''_{max} at a particular frequency for all specimen at different temperature shift towards higher frequency. This is predominant behavior of thermally activated charge carriers hopping type conduction mechanism. The charge carriers exhibit long range type conduction mechanism below the peak frequency whereas above the peak frequency the mobility is confined to potential wells, hence, exhibiting short range type of conduction mechanism **[18, 20]**.

The variation of normalized parameter M''/M''_{max} as a function of normalized frequency log (ω/ω_{max}) is shown in Figure 3(a-c). For all the specimens, curves plotted at different temperature almost overlap to a single master plot, thus, indicating occurrence of temperature independent single relaxation mechanism and dynamic process at every temperature **[13, 17, 19]**.

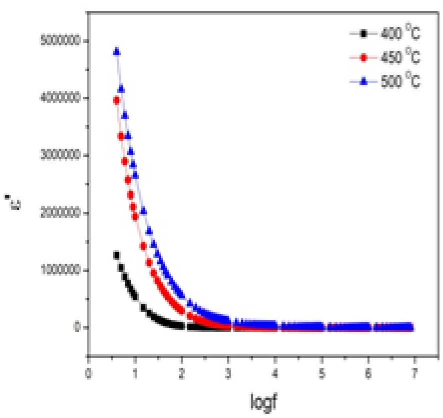
(a) x=0.1



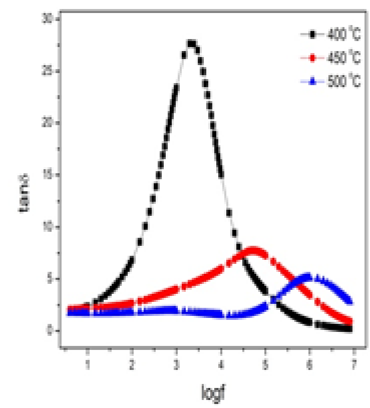
(d) x=0.1



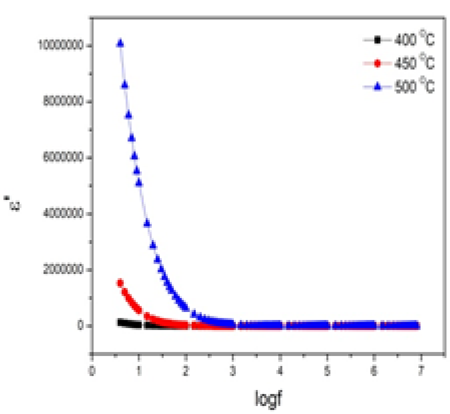
(b) x=0.2



(e) x=0.2



(c) x=0.5



(f) x=0.5

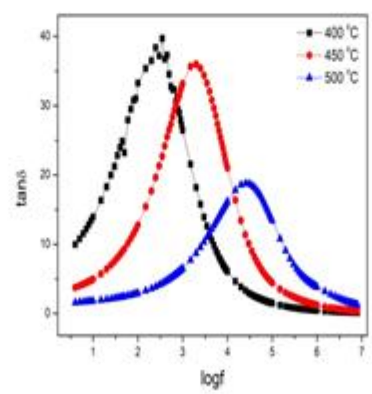


Figure (1): variation of dielectric constant as a function of frequency for (a) x=0.1 (b) x=0.2 (c) x=0.5 and variation of dielectric loss as a function of frequency for (d) x=0.1 (e) 0.2 (f) x=0.5.

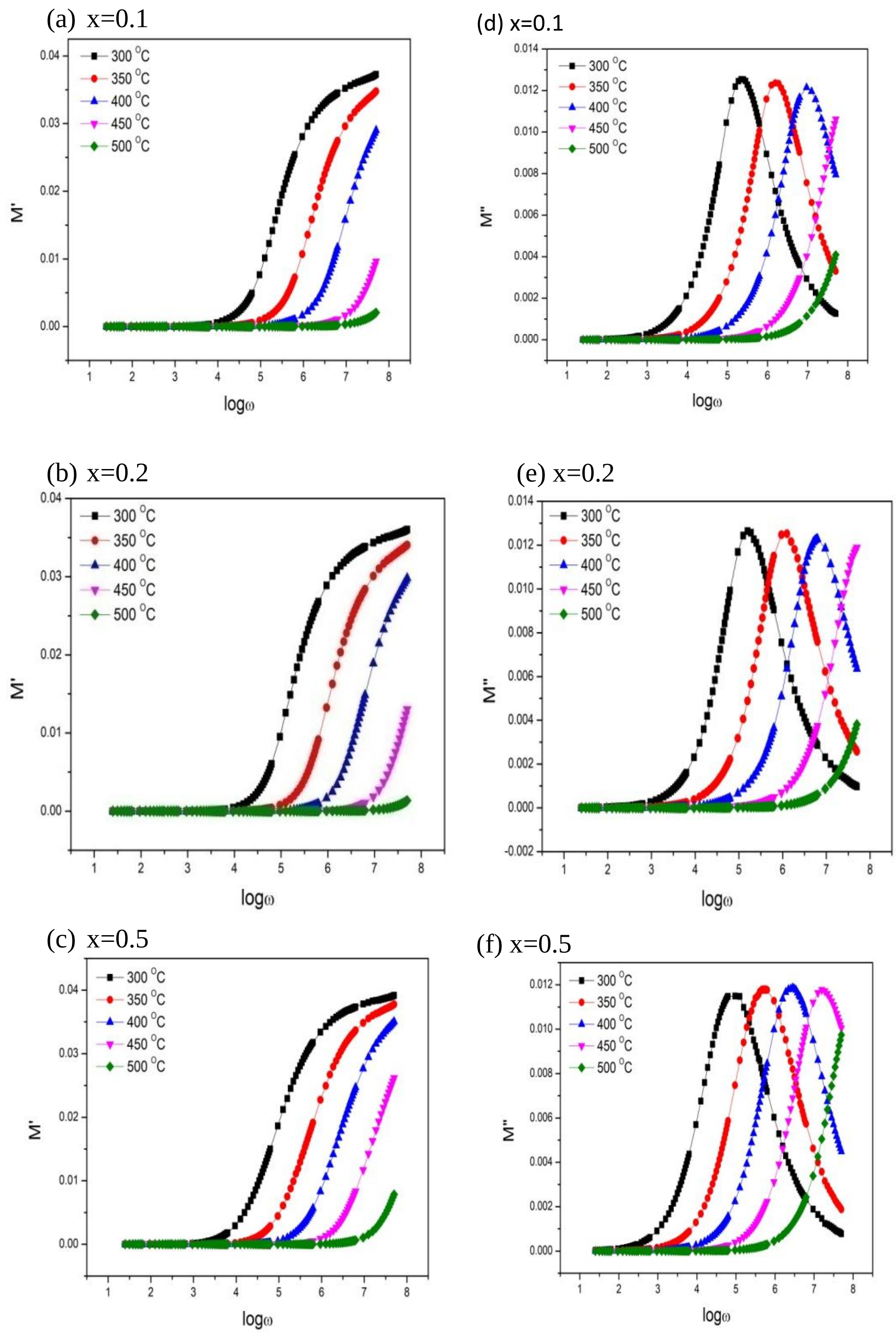


Figure (2): variation of M′ and M″ as a function of frequency where, (a) x=0.1 (b) x=0.2 (c) x=0.5 are plots of real part and (d) x=0.1 (e) x=0.2 (f) x=0.5 are plots of imaginary part.

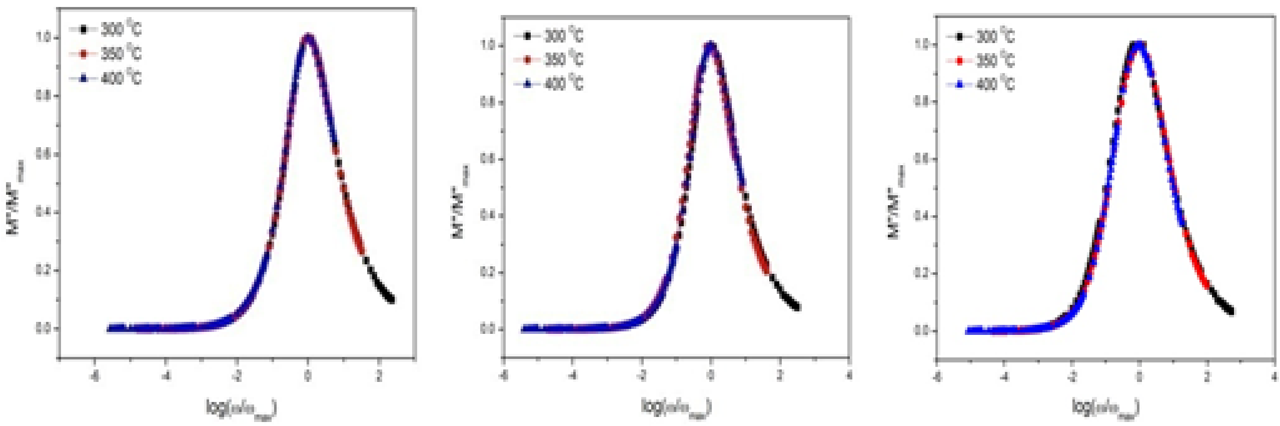
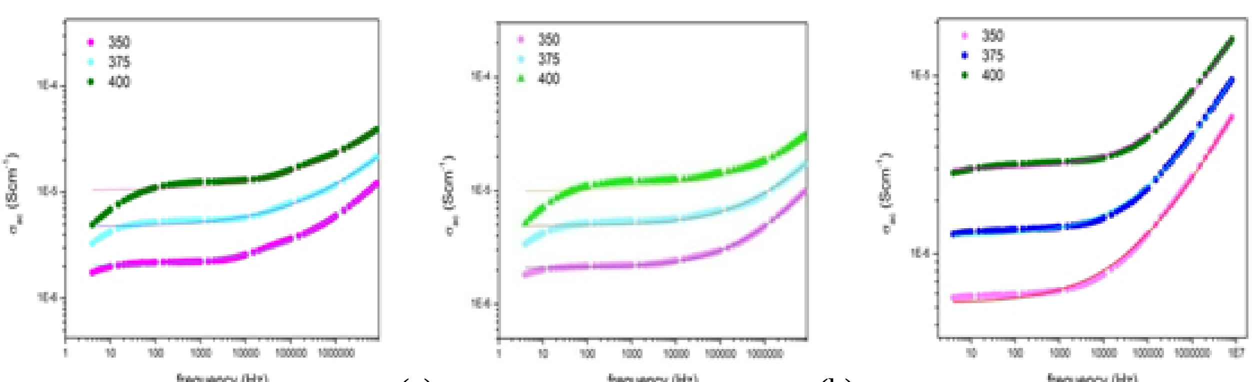


Figure (3): variation of normalized modulus as a function of normalized frequency for (a) x=0.1 (b) x=0.2 (c) x=0.5.

AC conductivity: The ac conductivity studies have been tried to understand in the light of Jonscher’s law **[17]**. In Figure 4(a-c), ac conductivity with frequency at different temperatures is plotted. At low frequencies, more charge accumulation occurs at electrode-electrolyte interface causing decrease in mobile ions resulting polarization effect and decrease in ac conductivity. This behavior can be well observed for x=0.1 and x=0.2 at different temperatures. For x=0.5, the low frequency falls outside the frequency range (4 Hz – 8 MHz) of the present measurement. At intermediate frequencies below hopping frequency known as plateau region, the region is almost frequency independent due to dc conductivity contribution. Ions moves fast at low frequency and successfully hop from one available site to another. Long relaxation time is responsible for this hopping, thus, contributes to the dc conductivity **[20]**. The intermediate plateau region can be observed for all specimens. The dc conductivity values associated is given in Table (1). At higher frequencies above hopping frequency, conduction phenomenon is dispersive due to increase in random hopping and long range diffusion of mobile ions. The ac conductivity is frequency dependent and rises rapidly with increase in frequency. This behavior is observed for all specimens. Also, at measured temperatures shifting of hopping frequency towards higher frequency occurs, further confirming hopping type conduction phenomena **[16, 17]**. Using Jonscher’s power law, the ac conductivity curves were analyzed and fitted. The values thus obtained are given in Table (1). The values of dc conductivity are at par with the conductivity plot. The value of the exponent ‘n’ lies between 0 and 1 which further indicates conduction mechanism is due to oxygen ions **[21]**.



(a) (b) (c)

Figure (4): Variation of ac conductivity with frequency for $La_{2-x}Tb_xMo_2O_9$ (x=0.1, 0.2, 0.5) at selected temperatures (a) x=0.1; (b) x=0.2 and (c) x=0.5.

Table (1): Values obtained after fitting using Jonscher's power law.

X	Temperature (ºC)	σ_o	N	Goodness of fit (R^2)
0.1	350	2.03666×10^{-6}	0.43039	0.99890
	375	4.74733×10^{-6}	0.39184	0.99440
	400	1.04231×10^{-5}	0.38834	0.96647
0.2	350	2.09353×10^{-6}	0.49727	0.99922
	375	4.90560×10^{-6}	0.46150	0.98921
	400	9.80417×10^{-6}	0.33609	0.94210
0.5	350	5.28039×10^{-7}	0.44142	0.99955
	375	1.25379×10^{-6}	0.44806	0.99899
	400	2.99095×10^{-6}	0.46698	0.99871

Conclusions: The compound $La_{2-x}Tb_xMo_2O_9$ (x=0.1, 0.2, 0.5) was synthesized and investigated. The dielectric study shows sharp decrease of dielectric constant and shifting of dielectric loss peak suggesting polarization mechanism and dielectric relaxation process. In electric modulus study, shifting of M′ and M″ suggests temperature dependent relaxation process and thermally activated conduction process. The normalized plot further confirms temperature independent single relaxation and dynamic process. From ac conductivity study, hopping type conduction mechanism is further confirmed.

Acknowledgements: The authors acknowledge FIST facility under Department of Physics, NERIST, funded by DST, New Delhi sanction order no. SB/52/CMP-093/2013 for EIS analysis. The author also acknowledges UGC, New Delhi for granting fellowship under UGC faculty development programme.

References:

[1] J. W. Fergus, J. Power Sources 162 (2006) 30.
[2] S. J. Skinner, J. A. Kilner, Mater Today 6 (3) (2003) 30.
[3] B. C. H. Steel, 'Oxygen ion conductors', in High Conductivity Solid Ionic Conductors, Recent Trends and Applications, T. T. Takahashi, ed., World Scientific Publishing, Singapore, p. 402, (1989).
[4] P. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux, Y. Laligant, Nature 404 (2000) 856.
[5] C. Tealdi, G. Chiodelli, L. Malavasi and G. Flor, J. Mater. Chem. 14 (2004) 3553 – 3557.
[6] X. P. Wang, Q. F. Fang, Solid State Ion. 146 (2002) 185–193.
[7] G. Corbel, Y. Laligant, F. Goutenoire, E. Suard, P. Lacorre, Chem. Mater. 17 (2005) 4678-4684.
[8] C. Li, Q. F. Fang, X. P. Wang, J. X. Wang, D. Li, and Z. Zhuang, J. App. Phys. 101 (2007) 083508.
[9] C. Li, X.P. Wang, J. X. Wang, D. Li, Z. Zhuang, Q. F. Fang, Mater. Res. Bull. 42 (2007) 1077–1084.
[10] D. M. Zhang, Z. Zhuang, Y. X. Gao, X. P. Wang, Q. F. Fang, Solid State Ion. 181 (2010) 1510 - 1515.
[11] D. Li, X. P. Wang, Z. Zhuang, J. X. Wang, C. Li, Q. F. Fang, Mater. Res. Bull. 44 (2009) 446 – 450.
[12] L. Borah, B. Paik, A. Pandey, Solid State Sciences 14 (2012) 387-393.
[13] A. Dutta, T. P. Sinha, J. Phys. Chem. Solids 67 (2006) 1484.

[14] M. Roy, S. Sahu, S. K. Barbar, S. Jangid, J. Therm. Anal. Calorim. 113 (2013) 873 – 879.
[15] T. Badapanda, R. K. Harichandan, S. S. Nayak, A. Mishra, S. Anwar, Processing and Application of Ceramics 8/3 (2014) 145 – 153.
[16] T. V. kumar, A. S. Chary, S. Bhardwaj, A. M. Awasthi, S. N. Reddy, International Journal of Materials Science and Applications 2/6 (2013) 173 - 178.
[17] D. Tripathy, A. Saikia, G. T. Tado and A. Pandey, Indian J. Phys. (2018).
[18] R. B. Belgacem, M. Chaari, A. F Brana, B. J. Garcia, A. Matoussi, J. Am. Ceram. Soc. 100 (2017) 2045.
[19] L. Borah and A. Pandey, Acta Metall. Sin. (Engl. Lett.) 26/4 (2013) 425 – 434.
[20] N. Shukla, A. K. Thakur, A. Shukla, D. T. Marx, Int. J. Electrochem. Sci. 9 (2014) 7644 – 7659
[21] N. K. Mohanty, R. N. Pradhan, S. K. Satpathy, A. K. Behera, B. Behera, P. Nayak, J. Mater. Sci.: Mater. Electron 25 (2014) 117–123.

*****