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# Electrical characterization of $Pr^{3+}$ containing lithium borate glasses by impedance spectroscopy

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## ABSTRACT

The role $Pr^{3+}$ ions in the lithium borate glasses have been investigated by electrochemical impedance spectroscopy technique. The glasses were prepared by conventional melt quench technique with formula 27.5 $Li_2O$-(72.5-X) $B_2O_3$-X $Pr_6O_{11}$ (where, X= 0.5, 1, 1.5 and 2). It is observed that the conductivity of the glasses decreases with the addition of $Pr^{3+}$ ions which was correlated with increase in the activation energy of the glasses. The observed conductivity behavior in the present study is mostly govern by the $Pr^{3+}$ as it has higher molecular weight as compared to other component in the glass system. Insight of conduction mechanism was revel by the scaling of modulus and conductivity data of the prepared samples. Scaling confirms that the conduction mechanism is compositional dependent. Based on the present study it is possible to use and modified these glasses as an insulating and dielectric material. Copyright © 2016 VBRI Press.

**Keywords:** $Li^+$ conduction; glasses; impedance spectroscopy; rare earths.

## Introduction

There is a phenomenological interaction between good solid electrolytes and characterization technique for these electrolytes. The impedance spectroscopy is one of the best known tools to study and characterize the electronic properties of the materials (e.g. amorphous, crystalline and liquid) [**1**]. This technique based on the frequency response of the material to a change in impedance. This technique widely used to explore conductivity, relaxation processes and dielectric response of the materials [**1-6**].

The lithium based glasses are the best known ion conducting material and have a potential application as solid state batteries [**7-20**]. Although these glasses offer less ionic conductivity as compared to $Ag^+$ ion based glasses but high electropositive nature of $Li^+$ ions have advantageous for solid state batteries [**7**]. Glass former e.g. $SiO_2$, $P_2O_5$, $V_2O_5$, $B_2O_3$, $SeO_2$ and $TeO_2$ with lithium as modifier shows the ionic conductivity [**9**]. Among these glass systems, lithium borate glasses are widely studied by the researcher as it offers wide composition range, easy formability and good rare earth solubility [**10-11**]. The complexity and functionality of these glasses mostly govern by the $Li^+$ content and the boron anomaly [**10-20**]. The conductivity of these glasses increases with the increase in $Li^+$ content. Addition of another glass former in lithium borate glasses also increases the conductivity which term as mixed former effect. There are various reports available on the electrical properties of lithium borate glasses [**11-20**]. Thakur *et al.* [**21**] recently reported the effect of $BaTiO_3$ on $Dy_2O_3$ containing glasses on the electrical properties of Lithium borate glasses. These glasses follow the correlated barrier hopping model (CBH). Scaling shows perfect overall of data on single master curve indicates relaxation dynamics in these glasses. Yusub *et al.* [**22**] investigated the effect of MnO on the $Li_2O$-PbO-$B_2O_3$-$P_2O_5$ glasses where semiconducting nature of the glasses increases with the addition of MnO.

Rare earth oxides are the technically important class in the periodic table as they offer the ample range of functional materials like high-temperature superconductors, ferroelectric and optical materials [**23**]. Rare earth oxides are chemically active and thermally stable. Their chemical activity is interesting to study because of partially filled 4f shell and totally filled $5s^25p^6$ electron shells [**24**]. Despite of their unique chemical behavior, the effect of rare earth addition on electrical properties of glasses is not well studied by the researcher. There are some reports available on electrical properties of rare earth oxide containing glasses [**25-27**].

Earlier we report spectroscopic properties of $Pr^{3+}$ ions containing lithium borate glasses that show their usefulness in solid state light application [**28**] and this manuscript is a continuation of previous work. There are no reports available on the electrical properties of $Pr^{3+}$ ions containing lithium borate glasses. The purpose of this paper to understand the conduction phenomenon and effect of $Pr^{3+}$ ions the lithium borate glasses as it is necessary to understand the fundamentals before any practical applications. We reported the data about conductivity, relaxation properties and scaling behavior of $Pr^{3+}$ ions containing lithium borate glasses.

 

## Experimental

### *Materials*

The glasses were prepared by convention glass quenching technique with general formula 27.5 $Li_2O$-(72.5-X) $B_2O_3$-X $Pr_6O_{11}$. High purity chemicals lithium carbonate ($Li_2CO_3$), boron trioxide ($B_2O_3$) and dysprosium oxide ($Pr_6O_{11}$) Merck Germany make of purity 99.99 % were used as starting materials in the present study.

### *Method*

Appropriate quantity of these chemicals weighs and mixed in acetone to ensure homogeneity. Mixture was then transferred to programmable furnace for melting. The mixture was melted at 1253 K and then quench quickly in metallic mold. The bulk sample further transferred to annealing furnace to remove the thermal stresses. Bulk glass samples were cut and polished for Impedance study.

### *Characterizations*

Electrode contact were made by applying silver paint on the parallel faces of the glasses and then placed in between two silver electrodes after checking contact and continuity. Impedance measurements were performing on the using high resolution dielectric analyzer (Novocontrol Make) in the frequency range 2 mHz to 20 MHz. All the measurements were done by computer controlled WinDETA software. To determine the conductivity physical dimension of the sample and bulk resistance from impedance plot was taken in to account. DTA for all glass samples were recorded using Perkin-Elmer Diamond Thermal Analyzer with heating rate of 10 °C/min for determining glass transition temperature ($T_g$).

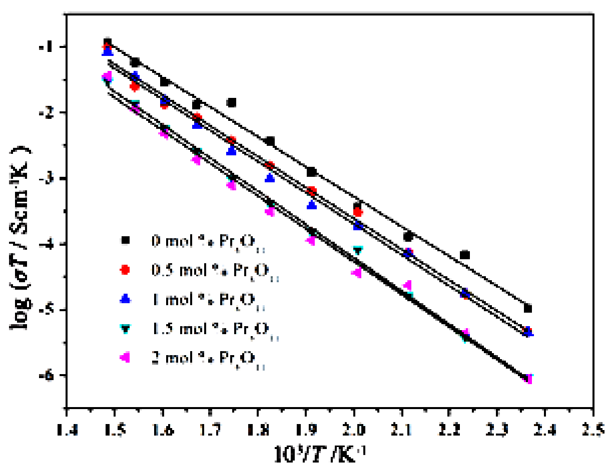


**Fig. 1.** Variation of conductivity with temperature for glasses.

## Results and discussion

The impedance spectra were measured over the temperature range of 673 K to 423 K. DC resistances was determined from the impedance plot and by using the physical dimension of the samples conductivities were determined [**10**]. The bulk ionic conductivities from measured impedance follow the Arrhenius equation as expected (**Fig. 1**).

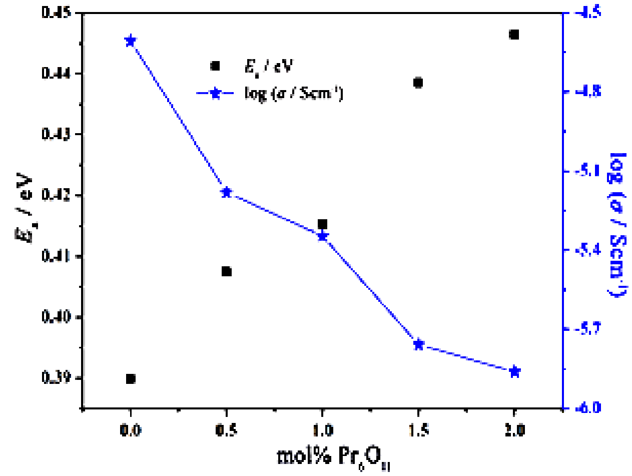


**Fig. 2.** Variation of conductivity and activation energy with $Pr_6O_{11}$

From the slope of Arrhenius plot activation energy was calculated and plotted as function of $Pr_6O_{11}$ along with the conductivity of the glass sample at 573 K (**Fig. 2**). From **Fig. 2** it is observed that the conductivity of glasses decreases and activation energy increases with the addition of $Pr_6O_{11}$. The decrease in conductivity can be understood on the basis of the increase in activation energy. As lithium concentration is constant, decrease in conductivity is correlated with a decrease in available vacant sites for mobile $Li^+$ ions.

This decrease in vacant sites may be due to the conversion of $BO_3$ units to units. The increase in units increases the cross-linking ability of glass network, therefore, the rigidity of glass structure increases. An increase in the rigidity of the glass structure results in a decrease in the pathways for mobile lithium ions. The increase in rigidity of glass structure is evident from the increase in glass transition temperature (Tg) as shown in **Table 1**. In addition to that large size of $Pr^{3+}$ ions may also affect the mobility of $Li^+$ ions therefore the conductivity of glasses decreases and activation energy increases with the addition of $Pr_6O_{11}$ [**10, 25-27**].

**Table 1.** Glass transition temperature ($T_g$ ), $E_{a(dc)}$ and $E_{a(\tau)}$ values for glass samples.

| *mol % $Pr_6O_{11}$* | *Glass transition temperature (Tg)* | *$E_{a(\tau)}$ (eV)* | *$E_{a(DC)}$ (eV)* |
|---|---|---|---|
| *0 (PR0)* | 755 K | 0.3791 | 0.3899 |
| *0.5 (PR1)* | 759 K | 0.3828 | 0.4075 |
| *1 (PR2)* | 763 K | 0.3896 | 0.4153 |
| *1.5 (PR3)* | 767 K | 0.4221 | 0.4385 |
| *2 (PR4)* | 770 K | 0.4442 | 0.4464 |

To study the relaxation behavior, electric modulus formalism was introduced and discussed [**29, 30**]. Electric modulus is defined as [**31-32**]:

$$M^*(\omega) = \frac{1}{\varepsilon^*} \quad \text{Eq. 1}$$

$$M^*(\omega) = \frac{\varepsilon'(\omega)}{|\varepsilon^*(\omega)|^2} - i\frac{\varepsilon''(\omega)}{|\varepsilon^*(\omega)|^2} \quad \text{Eq. 2}$$

$$M^*(\omega) = M'(\omega) + iM''(\omega) \quad \text{Eq. 3}$$

where, $M'$ and $M''$ are real and imaginary part of modulus.

**Fig. 3** shows the variation of real part of an electric modulus ($M'$) with frequency for PR 3 glass sample as a representative. From the figure, it is observed that at low-frequency $M'$ is zero due to lack of restoring forces for mobile lithium ions and there is an increase in $M'$ with increase in frequency. $M'$ reaches a maximum value corresponding to $M_\infty = (\varepsilon_\infty)^{-1}$ due to the relaxation process [**29**]. Similar qualitative behavior is observed for other glass samples of this series.

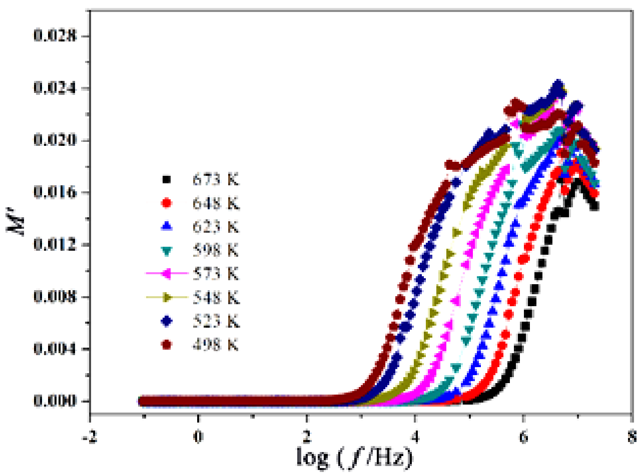


**Fig. 3.** Variation of real part of electric modulus (M').

**Fig. 4** shows the variation of imaginary part of the electric modulus ($M''$) with frequency. Form this figures it is observed that $M''_{Max}$ shift towards higher frequencies with the increase of temperature. The center of the relaxation peak is characterized by $f_P$ and further used to calculate relaxation time 'τ' ($\tau = 1/2\pi f_P$) by using condition $\omega_c\tau = 1$.

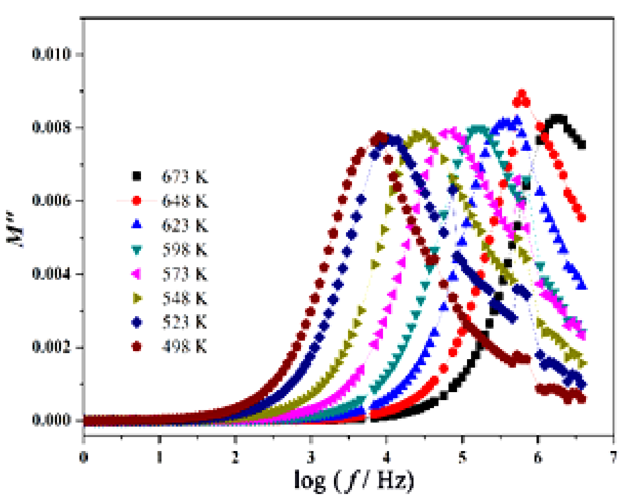


**Fig. 4.** Variation of imaginary part of electric modulus ($M''$) with frequency and temperature for PR 3 glass sample.

The calculated value of relaxation time $\tau$ is plotted against $10^3$/T as shown in **Fig. 5** [**25**] and it is observed that it follows the relation given by the equation $\tau = \tau_0 \exp(E_{a(\tau)}/k_B T)$. From the slope of fitting lines of **Fig. 5** $E_{a(\tau)}$ was calculated and depicted in **Table 1**. The similarity in the values of $E_{a(dc)}$ (**Fig. 1**) and $E_{a(\tau)}$ confirms the involvement of $Li^+$ ions as a charge carrier in both the relaxation and conduction processes (**Table 1**).

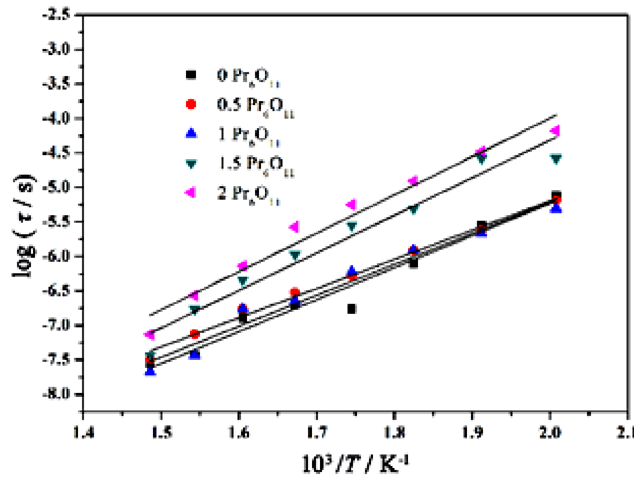


**Fig. 5.** Variation of relaxation time with temperature.

To examine the effect of composition and temperature on conduction mechanism scaling is introduced. Normalized plots of conductivity and imaginary part of modulus have been studied using the master plots. **Fig. 6** shows the result of normalized plot where *log* $(\sigma'/\sigma_{dc})$ used as the *Y*-axis parameter and *log* $(f/\sigma_{dc}T)$ as an *X*-axis parameter for PR 3 glass samples as a representative [**20, 24, 25**]. Data is found to be scaled very well on the single master curve for different temperature.

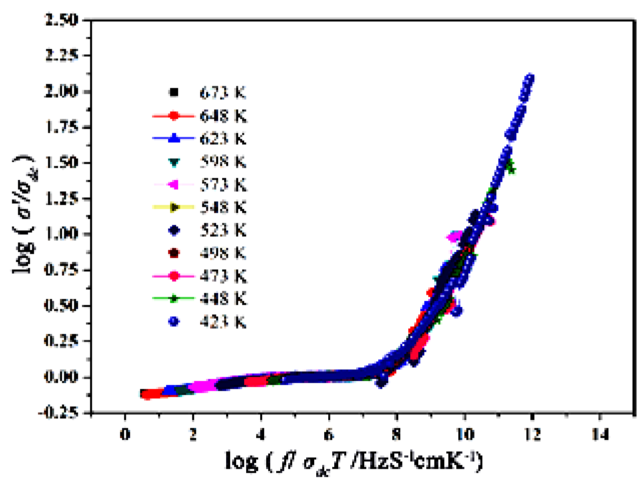


**Fig. 6.** Conductivity scaling data of PR 3 glass sample.

The reduced imaginary part of a modulus ($M''/M''_{Max}$) has been plotted as a function of log ($f/f_P$) for PR 3 glass sample as a representative is shown in **Fig. 7**. It is observed from this figure that the data also collapses excellently $M''/M''_{Max}$ versus log ($f/f_P$)) for all temperatures [**25, 29**]. This study suggests that the dynamical processes and conduction mechanism is temperature independent [**25, 29**].

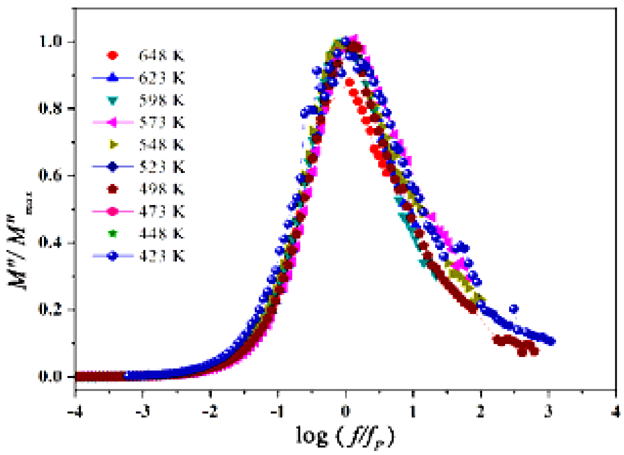


**Fig. 7.** Imaginary part of the electric modulus M"/M"Max as a function of log f/fP.

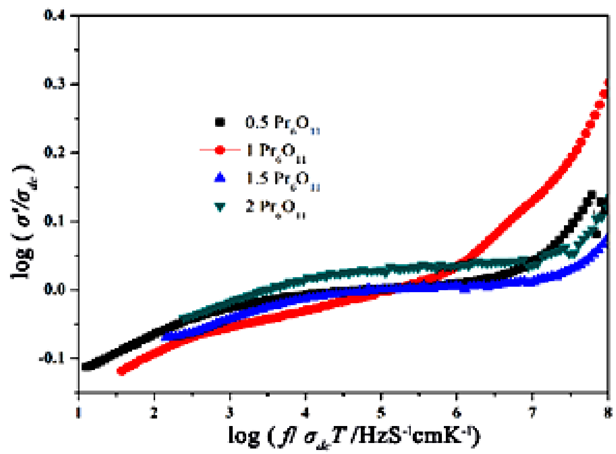


**Fig. 8.** Scaling data for different mol % $Pr_6O_{11}$ containing glasses.

To study the effect of composition on conduction mechanism additional mol % factor was introduced like previous series. *Y*-axis is scaled with log $(\sigma'/\sigma_{dc})$ and log $(fx/\ \sigma_{dc}T)$ as a *X*-axis for PR 3 glass sample as shown in **Fig. 8**. Data fails to form a single master curve. Non-overlapping of data is in good agreement with the previous argument that the addition of $Pr_6O_{11}$ decreases the conductivity of glasses. Further these results are also supported by non-overlapping of the imaginary part of an electric modulus (at 573 K) **Fig. 9** [**29**].

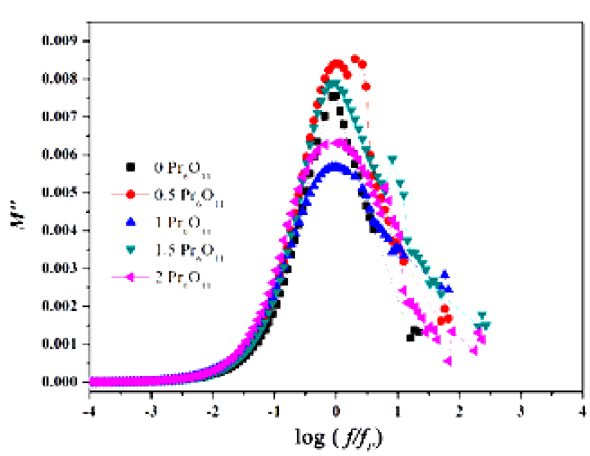


**Fig. 9.** Imaginary part of electric modulus of glasses at 573K.

## Conclusion

The frequency and temperature dependent study were performed on the 27.5 $Li_2O$-(72.5-X) $B_2O_3$-X $Pr_6O_{11}$ glass series in the wide range of frequency and temperature. From this study it is confirm that $Li^+$ ions are the main charge carriers responsible for conduction process. With the addition of $Pr^{3+}$ ions in the glass matrix conductivity of glasses decrease. The decrease in conductivity is mainly due to the increase in the rigidity of glass structure. Higher ionic radius and molecular weight of $Pr^{3+}$ ions also hinder the movement of $Li^+$ ions in the glass matrix.

These results are in accordance with Tg results. Performed scaling suggests that during the conduction process and relaxation process, Li+ ions have to overcome the same potential barrier. The calculated activation energy associated with the dc conductivity and that associated with the relaxation process are very close to each other which proves the involvement of Li+ ions in conduction as well during relaxation process. Further, the present study proves that the conduction processes in the prepared glasses are compositional dependent and not the temperature dependent. Based on the present study we propose that these glasses can be useful as insulating material after certain modifications in the compositions.

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### Reference

1. Macdonald J. R.; Barsoukov, E. Impedance spectroscopy: theory, experiment, and applications. Second Ed., John Wiley & Sons, United States of America **2005**.
**DOI**: 10.1002/0471716243
2. Irvine, J. T.; Sinclair, D. C.; West, A. R., Advanced Materials, **1990** 2(3), 132-138.
**DOI**: 10.1002/adma.19900020304
3. Bragatto C.B., Cassar D.R., Peitl O., Souquet J.-L., Rodrigues A.C.M., J. Non-Cryst. Solids, **2016** 437, 43-47.
**DOI**: 10.1016/j.jnoncrysol.2016.01.010
4. Gellert M., Gries K. I, Sann J., Pfeifer E., Volz K, Roling B., Solid Sate Ionics, **2016** 287, 8-12.
**DOI**: 10.1016/j.ssi.2016.01.031
5. Niinomi H., Motoyama M., Iriyama Y., Solid Sate Ionics, **2016** 285, 13-18
**DOI**: 10.1016/j.ssi.2015.10.010
6. Orazem, M.E.; Tribollet, B., Electrochemical impedance spectroscopy (Vol. 48). John Wiley & Sons **2011**.
**DOI**: 10.1002/9780470381588
7. Knauth, P., Solid State Ionics, **2009** 180(14), 911-916.
**DOI**: 10.1016/j.ssi.2009.03.022
8. Levasseur, A.; Menetrier, M., Mater. Chem. Phys., **1989** 23(1), 1-12.
**DOI**: 10.1016/0254-0584(89)90013-8
9. Tatsumisago, M.; Minami, T., Materials chemistry and physics, 1987, 18(1), 1-17.
**DOI**: 10.1016/0254-0584(87)90107-6
10. Ramteke, D.D.; Gedam, R.S., Ionics **2015**, 21(7), 1931-1935.
**DOI**: 10.1007/s11581-015-1381-7
11. Rodrigues, A.M.; Duclot, M.J., Solid State Ionics, **1988**, 28, 729-731.
**DOI**:10.1016/S0167-2738(88)80134-6
12. Fusco, F.A; Tuller, H. L.; Button, D. P., Materials Science and Engineering: B, **1992**, 13(2), 157-164.
**DOI**:doi:10.1016/S0167-2738(88)80134-6
13. Kamitsos, E.I.; Karakassides, M.A.; Chryssikos, G.D., The Journal of Physical Chemistry, **1986**, 90(19), 4528-4533.
**DOI**: 10.1021/j100410a010

 

14. Tho, T.D., Ion conduction mechanisms in fast ion conducting oxide glasses for rechargeable batteries (Doctoral dissertation) **2010**.
**DOI**: http://scholarbank.nus.edu.sg/handle/10635/25836
15. Balkanski, M.; Wallis, R.F.; Deppe, J.; Massot, M., Dynamical Properties of Fast Ion Conducting Borate Glasses. In Solid State Materials (pp. 53-67). Springer Berlin Heidelberg, **1991**.
**DOI**: 10.1007/978-3-662-09935-3_4
16. Gowda, V.V.; Anavekar, R.V., Ionics, **2004**, 10(1-2): 103-108.
**DOI**: 10.1007/BF02410315
17. Lee, C.H.; Joo, K.H.; Kim, J.H.; Woo, S.G.; Sohn, H.J.; Kang, T.; Oh, J.Y., Solid State Ionics, **2002**, 149(1), 59-65.
**DOI**: 10.1016/S0167-2738(02)00137-6
18. Shembel, E.M.; Nosenko, A.V.; Kvasha, A.M., Ionics, **2005**, 11(1-2): 132-139.
**DOI**: 10.1007/BF02430412
19. Horopanitis, E.E.; Perentzis, G.; Pavlidou, E.; Papadimitriou, L., Ionics, **2003**, 9(1-2): 88-94.
**DOI**: 10.1007/BF02376543
20. Takahashi, T.; Yamamoto, O., Chemistry Letters, **1979**, (2): 135-136.
**DOI**: 10.1016/0022-3093(82)90267-8
21. Thakur V., Singh A., Awasthi A. M., Singh L., AIP Advances **2016,** 5, 0871101- 08711010
**DOI**: 10.1063/1.4928339
22. Yusub S., Rao P. S., Rao D. K., J. Alloys Compd., **2016,** 663, 708–717
**DOI**: 10.1016/j.jallcom.2015.12.147
23. Yamane, M.; Asahara, Y., Glasses for photonics. Cambridge University Press, Cambridge **2000**.
**DOI**: 10.1017/cbo9780511541308
24. Ogasawara, K.; Watanabe, S.; Toyoshima, H.; Brik, M.G., Handbook on the Physics and Chemistry of Rare Earths **2007**, 37, 1-59.
**DOI**: 10.1016/S0168-1273(07)37031-1
25. Ali, A.A.; Shaaban, M.H., Solid State Sci., **2010**, 12(12): 2148-2154.
**DOI**: 10.1016/j.solidstatesciences.2010.09.016
26. Shaaban, M.H.; Ali, A.A.; El-Nimr, M.K., Materials chemistry and physics, **2006**, 96(2), 433-438.
**DOI**: 10.1016/j.matchemphys.2005.07.035
27. Ali, A.A.; Shaaban, M., Bulletin of Materials Science, **2011**, 34(3), 491-498.
**DOI**: 10.1007/s12034-011-0103-7
28. Ramteke, D. D.; Swart, H. C.; Gedam, R. S., Physica B., **2015**, 40, 111-115
**DOI**: 10.1016/j.physb.2015.08.003
29. Patel, H.K.; Martin, S.W., Physical Review B, **1992**, 45(18): 10292.
**DOI**: 10.1103/PhysRevB.45.10292
30. Maia, L.F.; Rodrigues, A., Solid State Ionics, **2004**, 168(1), 87.
**DOI**: 10.1016/j.ssi.2004.02.016
31. Ramteke, D.D.; Gedam, R.S., Solid Sate Ionics, **2014,** 258, 82-87.
**DOI**: 10.1016/j.saa.2014.05.005
32. Ramteke, D.D.; Gedam, R.S., Spectrochim. Acta, Part A, **2014**, 113, 19-23.
**DOI**: 10.1016/j.ssi.2014.02.006