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Dielectric and conductivity behavior of modified Li-based perovskite compounds

M.Girija^{1*}, S.B.Gama², R.L.Raibagkar³

¹Government First Grade College, Bidar - 585 401, Karnataka, (INDIA)

²B.V.Bhoomaraddi College Bidar - 585 403, Karnataka, (INDIA)

³Department of Post Graduate Studies and Research in Materials Science, Gulbarga University, Gulbarga - 585 106, Karnataka, (INDIA)

E-mail : mangalgatti77@gmail.com

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ABSTRACT

The dielectric and conductivity properties of complex perovskite with general formula $\text{Li}(\text{Nd}_{1/4}\text{B}_{1/2}\text{Nb}_{1/4})\text{O}_3$ where $\text{B}=\text{Ti}^{+4}$, Zr^{+4} and Mn^{+4} ceramics have been investigated. These ceramics were prepared by solid state reaction technique. Preliminary structural studies revealed that the material consists of hexagonal perovskite structure. The dielectric constant (k) and loss tangent of the samples were determined at different temperatures (32-500°C) and in the frequency range 100 Hz - 1 MHz. The conductivity behavior of the samples was also studied.

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KEYWORDS

Low-K materials;
 $\text{Li}(\text{Nd}_{1/4}\text{Ti}_{1/2}\text{Nb}_{1/4})\text{O}_3$;
 $\text{Li}(\text{Nd}_{1/4}\text{Zr}_{1/2}\text{Nb}_{1/4})\text{O}_3$;
 $\text{Li}(\text{Nd}_{1/4}\text{Mn}_{1/2}\text{Nb}_{1/4})\text{O}_3$;
Structure;
Solid state reaction technique;
Dielectric characterization;
AC conductivity.

INTRODUCTION

Developments of new dielectric material with low and/or high dielectric constant and loss tangent have been the basic aim of every electronic engineer and scientist. Lithium niobate (LiNbO_3) possesses a useful combination of piezoelectric and electro optical properties that enable the development of devices using visible or near infrared radiation for the logical processing of information and the routing of channels in telecommunication^[1]. LiNbO_3 is a member of ABO_3 perovskite family. It is interesting to note that, substitution at B-site cation by divalent and/or pentavalent impurities in ABO_3 -type perovskite compound, yields a number of modified compounds with different Curie temperature, dif-

fuseness and high dielectric constant^[2]. The dielectric constant and loss tangent of lithium niobate single crystal have been studied as a function of frequency and temperature^[3]. Dielectric constant, loss tangent and electrical conductivity of lithium niobate ceramics have been studied at room temperature in the frequency range 22 kHz to 70 MHz by Subhashchandra Bhatt et al.^[4]. The improvement in materials can be brought by typical ion substitution. Therefore, it is interesting to carry out substitution studies in dielectric materials and study their structural and dielectric properties.

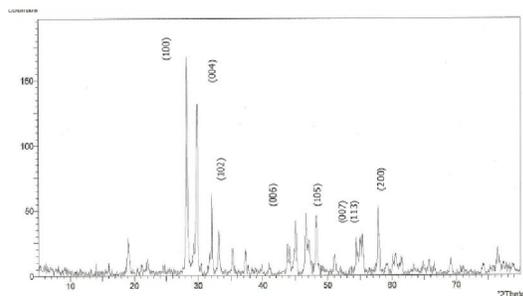
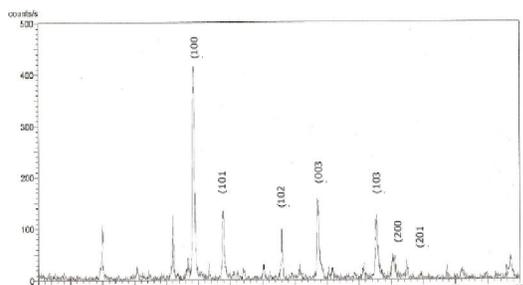
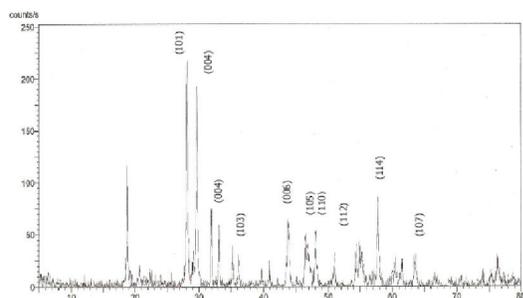
In the present paper, we made an attempt to study the effect of substitution of aliovalent ions at Nb-site of LiNbO_3 . The dielectric constant (k) and loss tangent ($\tan\delta$) of a sample have been measured at room

TABLE 1 : Crystallographic data of modified Li based perovskite compounds

Sample	a(A°)	c(A°)	Crystal Structure	Volume, V (A°) ³	X-ray density (gm/(cm) ³)	Particle size (nm)
LNN-T	3.773	12.081	Hexagonal	148.94	15.26	8.18
LNN-Z	3.550	5.632	Hexagonal	61.48	42.25	10.96
LNN-M	3.662	11.836	Hexagonal	134.45	17.31	16.38

TABLE 2 : The values of exponent 'n' from linear fit of conductivity for modified Li-based perovskite compounds

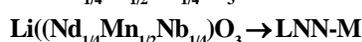
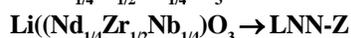
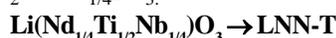
Temperature (°C)	LNN-T	LNN-Z	LNN-M
32	0.66	0.77	0.43
100	0.89	1.35	0.74
200	1.52	0.69	0.61
300	0.61	0.29	0.33
400	0.34	0.08	0.13
500	0.14	0.03	0.05

**Figure 1 : X-Ray diffraction pattern of LNN-T, LNN-Z and LNN-M**

temperature in the X-band frequency range i.e. 9 to 12

GHZ. Measurements have also been carried out for the frequencies 100 Hz to 1 MHz at different temperatures.

The purpose of this paper is to analyze the dielectric properties of ceramics prepared from the virgin LiNbO₃ system, with regard to their application in the microwave frequency region; we have synthesized the following compositions, each representing an excess electron charge carrier, having a member of more complex compound of the general formula-A[(B^I)_{1/4}(B^{II})_{1/2}(B^{III})_{1/4}]₃O₃.



EXPERIMENTAL

The samples were prepared by solid state reaction technique with high purity constituents of oxides and carbonates. The powder was calcined at 950°C for 6 hrs. The finally recalcined powder was then used to make circular pellets under a uniform pressure of 4T/m². The pellets were sintered at 600°C for 4 hrs.

Powder X-ray diffraction (Philips PRO PAN analytical, UK) data were collected using Cu-Kα radiation in the 2θ range of 20° to 70° with a scanning rate of 2 degree/minute at room temperature. Lattice parameters were obtained by least square fitting method. To measure the dielectric constant of the sample, air drying silver paint was pasted on both the faces of the sintered pellets to serve as electrodes. The capacitance, phase and dielectric loss were monitored as a function of both frequency (100 Hz to 1 MHz) and temperature (32°-500°C) using LCR meter (HIOKI 3532-50, Japan).

RESULTS AND DISCUSSION

The room temperature XRD peaks of the samples were shown in figure 1. The XRD peaks were found to be sharp and unsplit, indicating good homogeneity and formation of single phase compounds. The peaks were indexed with observed d-values and cell parameters were determined by standard computer program and the best possible selected parameters were refined by least square fitting method. TABLE 1 shows the crystallographic data for synthesized samples. From the x-

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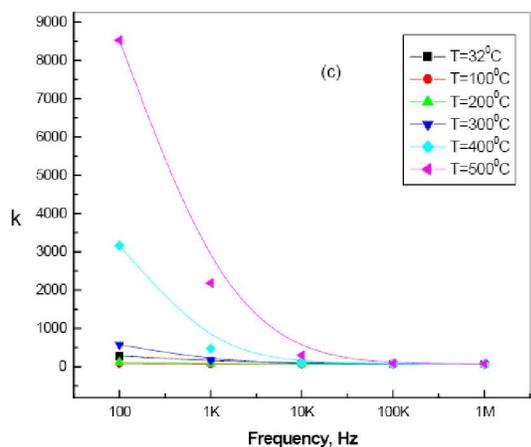
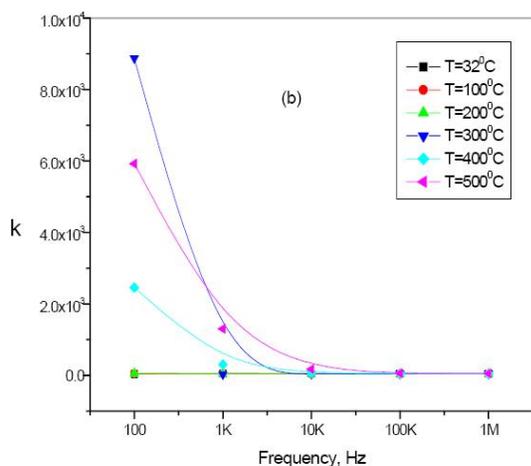
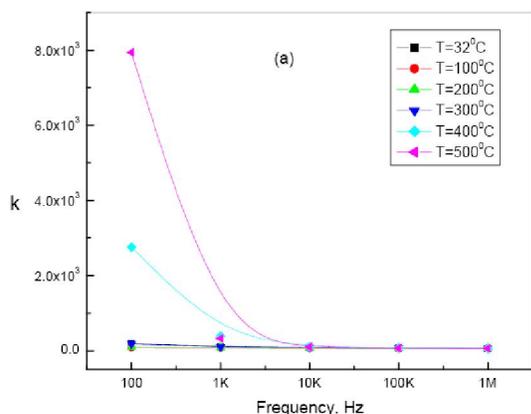


Figure 2 : Frequency dependence of k at various temperatures for (a) LNN-T, (b) LNN-Z and (c) LNN-M

ray analysis, the structures of the synthesized compounds are found to have hexagonal crystal symmetry.

Figure 2 (a), (b), (c) and figure 3(a), (b), (c) gives the variation of dielectric constant (k) and the dielectric loss ($\tan\delta$) as a function of frequency at different temperatures for ceramics LNN-T, LNN-Z and LNN-M respectively. It is found from the figures that both k and

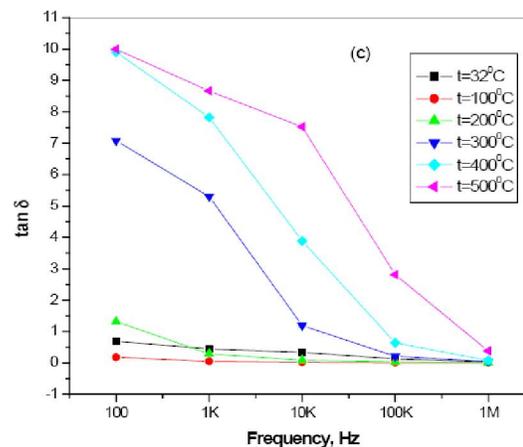
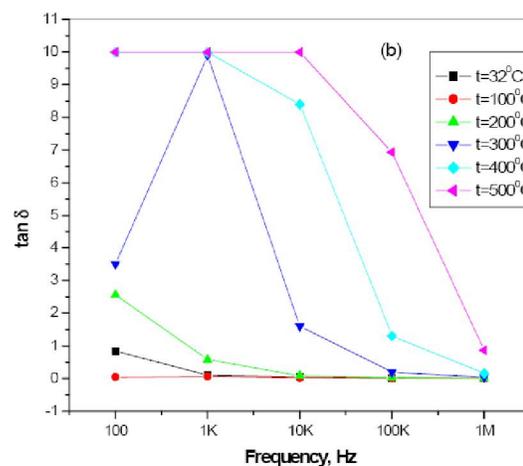
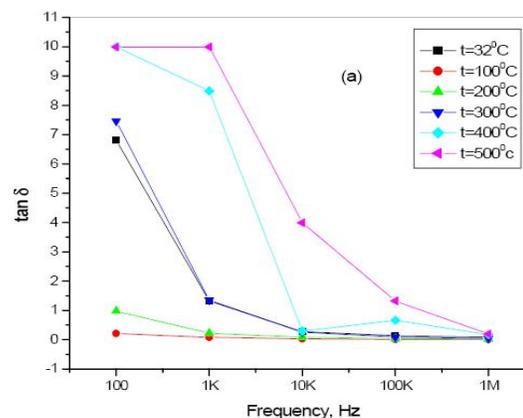


Figure 3 : Frequency dependence of $\tan\delta$, at various temperatures for (a) LNN-T, (b) LNN-Z and (c) LNN-M

$\tan\delta$ is maximum at 100Hz which decreases sharply up to 1 kHz and then remains constant almost up to 1MHz. This is a normal behaviour of any ferroelectric dielectric material.

The temperature variations of k are shown in figure 4 (a), (b) and (c). As the temperature increases, the k increases. For all the samples, k increases expon-

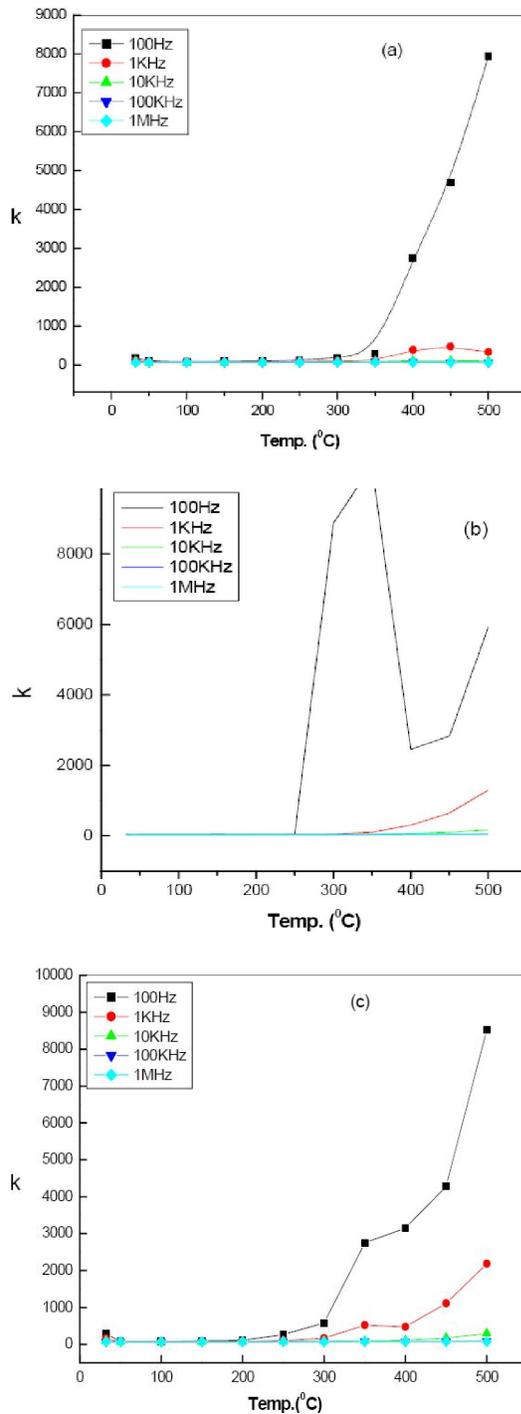


Figure 4 : Temperature dependence of k at various frequencies for (a) LNN-T (b) LNN-Z and (c) LNN-M

tially with increasing temperature at low frequencies (up to 1 kHz). At high frequencies, there is steady increase in k as a function of temperature. Dispersion in k shows presence of interfacial polarization. Since the material has been prepared by the solid state ceramic method, there is a possibility of micro heterogeneities which give

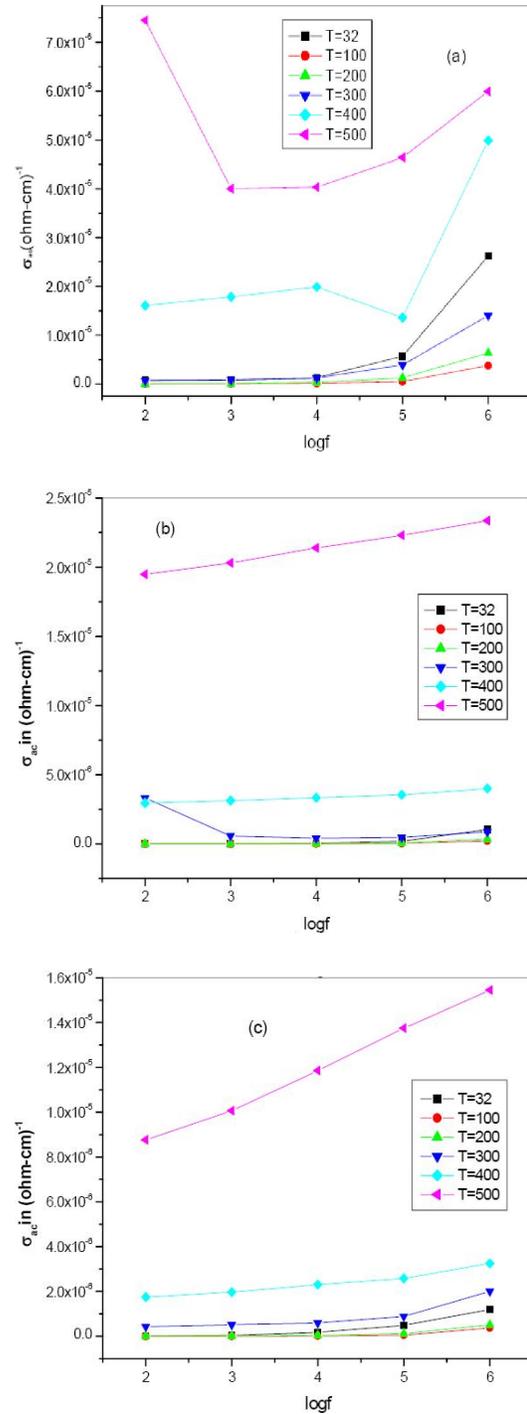


Figure 5 : Frequency dependence of conductivity at various temperatures for (a) LNN-T (b) LNN-Z and (c) LNN-M

rise to piling up of mobile charge carriers at the grain boundary, producing interfacial polarization giving rise to very high k . At higher frequencies, due to faster periodic reversal of the field, the perturbation of thermal motion of ionic or molecular dipoles takes place, which produces a net dipolar orientation in the direction of

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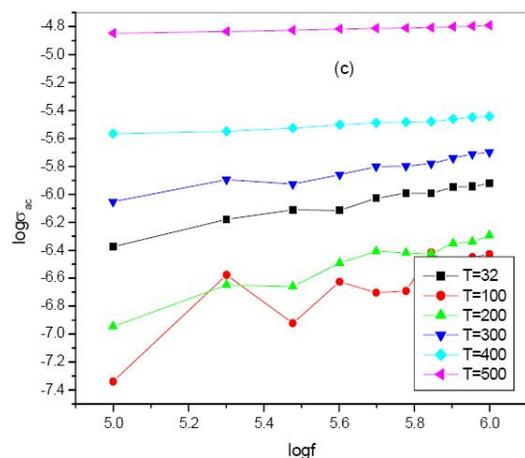
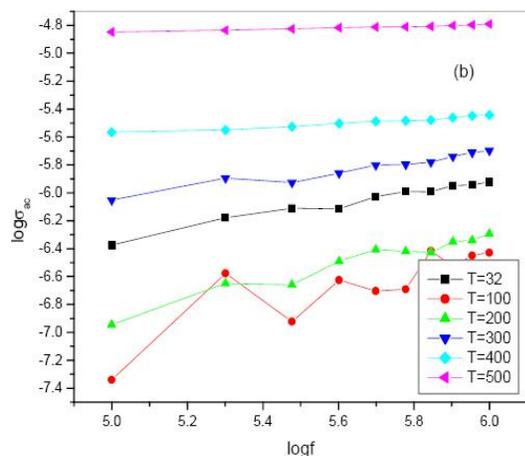
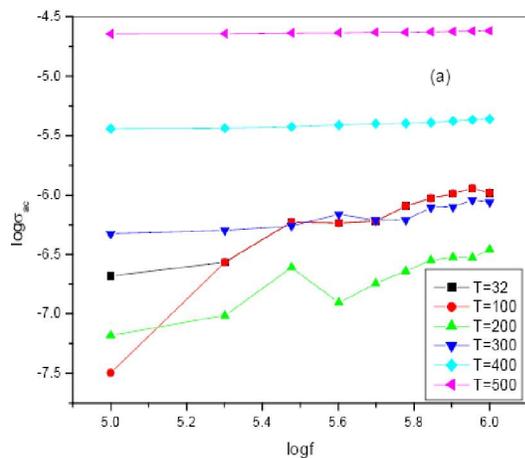


Figure 6 : Log – Log plots of conductivity for (a) LNN-T (b) LNN-z and (c) LNN-M

applied field and hence dipolar polarization becomes more prominent at these frequencies. This is the reason for the initial decrease and later steadiness in the value of k and $\tan\delta$ of these ceramics^[5].

For all the ceramics, we observed that the curves of σ_{ac} versus frequency (Figure 5 & 6), the curves con-

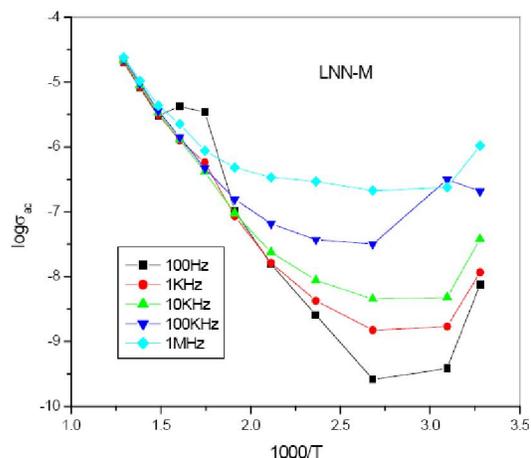
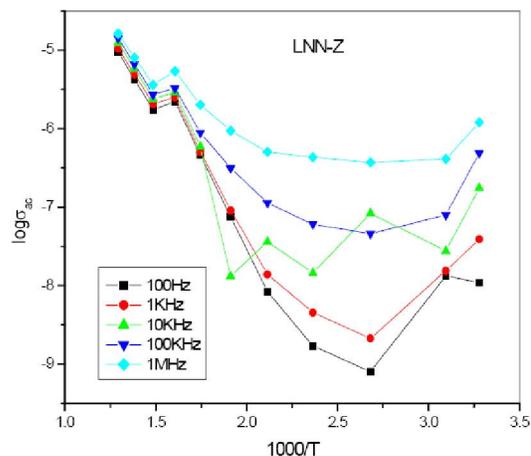
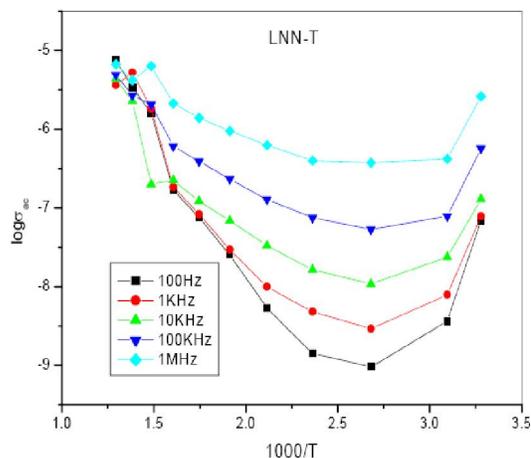


Figure 7 : Arrhenius plot of a) LNN-T (b) LNNz and (c) LNN-M

verge with one another at lower temperatures. This is because at higher temperatures the energy distribution of the traps become more uniform and the variation of the ac conductivity with frequency becomes less. The values of ac conductivity are found to be easily understood from the power law^[6].

$$\sigma(\omega) = A(T)\omega^n + \sigma_0(T) \quad (1)$$

where T is the absolute temperature, ω is the angular frequency, $\sigma(\omega)$ and $\sigma_0(T)$ corresponds to the a.c and d.c conductivities respectively and $0 < n < 1$.

The value of n computed for all the samples (Figure 7) at different temperatures and are listed in TABLE 2. Maximum n was found for LNN-T at 200°C whereas for LNN-Z and LNN-M; it is maximum at 100°C. As the temperature is high enough for the band- to- band transition to dominate the conduction process, n becomes almost zero, since electronic conduction is frequency independent. This makes the ac conductivity versus frequency curves for different temperature to converge with one another, at higher frequency indicating that the ac conduction becomes almost independent of temperature^[7].

The Arrhenius plots for ac conductivity at different frequencies are shown in figure 8. From these plots E_a , the activation energy was calculated and it is found to be in the range 0.05 to 0.283eV. As the frequency increases, the activation energy decreases for all the samples. Low value of E_a along with the dependence of conductivity shows that the ac conductivity mechanism is due to electron hopping. S. Bhat et.al reported that^[4] σ increases with increasing frequency for lithium niobate single crystal, which is true in our case also.

CONCLUSIONS

In conclusion, the effect of substituting trivalent (Nd) and tetravalent (Ti, Zr and Mn) ions at B-site in LiNbO_3 was investigated. It was found that all perovskites LNN-T, LNN-Z and LNN-M have hexagonal crystal symmetry. The reported value of k for LiNbO_3 single crystal at 25C for 1 MHz is 54.5, $\tan\delta$ is 0.026 and σ value is $21.96 \times 10^{-7} \text{ ohmm}^{-1}$. It was found that by substituting trivalent and tetravalent ions at B-site of LiNbO_3 increases k, σ and $\tan\delta$ values. σ_{ac} is found to obey the power law. The prepared ceramics show low E_a . i.e. samples show higher conduction.

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