© Applied Science Innovations Pvt. Ltd., India Carbon – Sci. Tech. 11/2 (2019) 72-77

Carbon – Science and Technology

ISSN 0974 – 0546

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

RESEARCH ARTICLE Received: 21/02/2019; Accepted: 18/05/2019

Dielectric properties of Al and Ti co-doped $Bi_2VO_{5.5-\delta}$ system

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Abstract: The Polycrystalline ceramic samples with formula unit $Bi_2V_{1-x}Ti_{x/2}Al_{x/2}O_{5.5-\delta}$ (x = 0.1 and 0.175) were synthesized. The specimens were characterized by AC Impedance Spectroscopy for dielectric studies. The variation of dielectric parameters: dielectric constant (ε_r), dielectric loss (tan δ), complex electric modulus and AC conductivity, as a function of frequency and temperature, have been analyzed. The dielectric loss peaks and AC conductivity plots revealed different relaxation mechanisms i.e. electrode-electrolyte, conduction and dipolar occurring at low, intermediate and high-frequency regimes respectively. The shifting of the dielectric relaxation peaks and hopping frequency in AC conductivity plots towards higher frequency sides with an increase in temperature imply these materials are ionic conductor.

Keywords: Dielectric constant, dielectric loss, complex electric modulus, AC conductivity.

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1. Introduction: The ME (MEtal cation)-doped $Bi_2VO_{5.5-\delta}$ (BIVOX) materials, $Bi_2V_{1-x}ME_xO_{5.5-\delta}$ well known as BIMEVOX (ME-doped BIVOX) group, are the fast oxide ion conductors. In these solid oxide electrolytes, the structural and electrochemical properties are altered to a great extent by ME-doping [1 - 5]. The BIMEVOX compounds are promising candidates due to their wide range of applications in various fields [6 - 10]. In general, in solid oxide electrolytes, apposite information of dielectric properties facilitates to understand the types and nature of the relaxation mechanisms taking place in the material. Particularly, the real and complex permittivity, dielectric loss, electric modulus, and AC conductivity are the parameters to invoke the salient features pertaining to mechanism in these compounds. The oxide ionic conductivity of a solid oxide electrolyte depends upon different transport mechanisms associated with it. The electrical modulus analysis reveals the dynamical aspects like the nature of conduction mechanisms in the material. Given the background, this work deals with the dielectric properties of Al and Ti co-doped $Bi_2VO_{5.5-\delta}$ system. The current work presents the dielectric, electric modulus and AC conductivity studies of $Bi_2V_{1-x}Ti_{x/2}Al_{x/2}O_{5.5-\delta}$: x = 0.10 and 0.175, oxide ion conductors, to have a better understanding of the conduction phenomena and oxide ion transportation behaviour in these compounds.

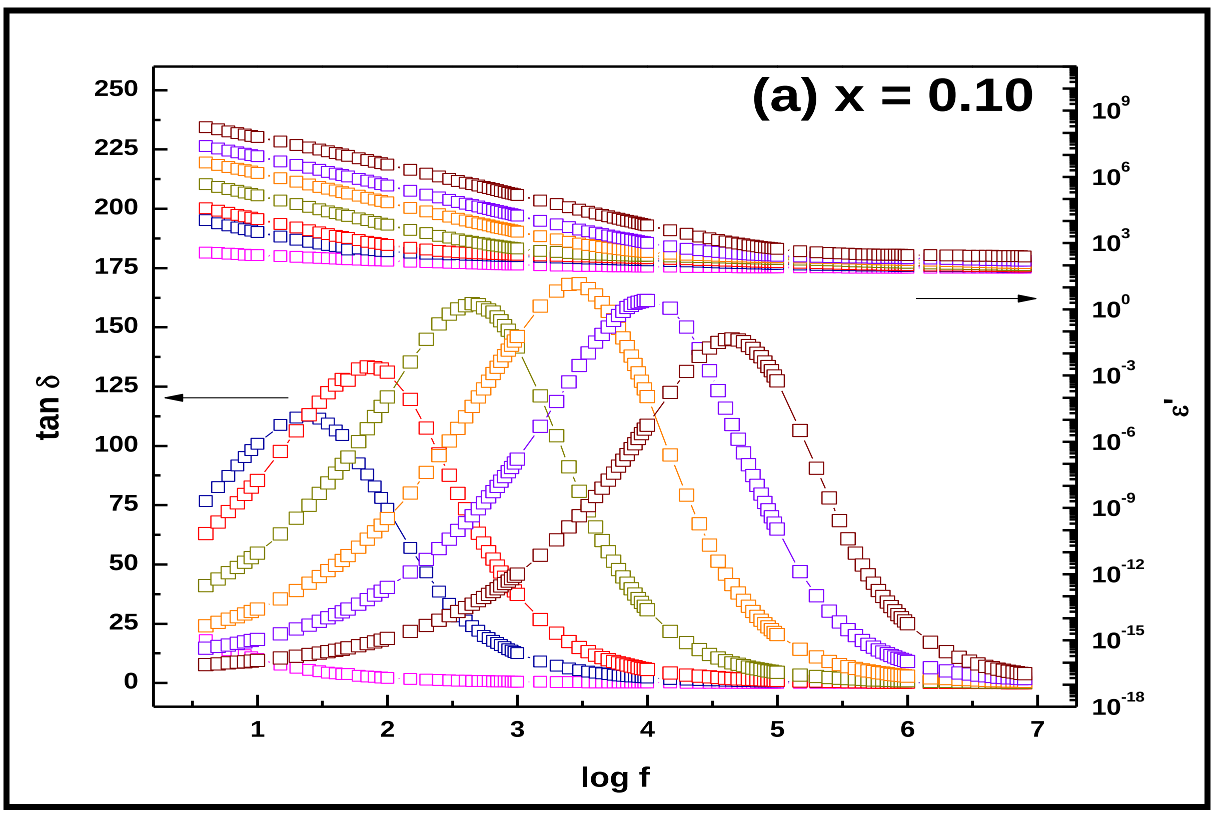
2. Experimental:

2.1. Sample preparation: $Bi_2V_{1-x}Ti_{x/2}Al_{x/2}O_{5.5-\delta}$ (x = 0.10 and 0.175) samples were synthesized from Bi_2O_3 (LOBA CHEMIE, Purity: 99 %), V_2O_5 (LOBA CHEMIE, Purity: 99 %), Al_2O_3 (SIGMA-ALDRICH, Purity: 99.5 %) and TiO_2 (SIGMA-ALDRICH, Purity: 99.7 %) by conventional solid state method. The weighed oxides (according to stoichiometric formula) were systematically mixed and ground for 10 hours in wet media (ethanol:acetone : 1:1) using pestle and mortar. The first calcination was done at 650 °C for 15 hours followed by the second one at 750 °C for 10 hours. In between an intermediate grinding was done for 10 hours. The powders obtained after calcinations were ground further for 10 hours and then mixed with 5 wt. % polyvinyl butyral (PVB) binder. Then, cylindrical pellets (Dimension: diameter -12 mm and the thickness -2 ~ 3 mm) were prepared by pressing the obtained powder uniaxially under a pressure of 5 Ton. Finally, the pellets were sintered at 800 °C for 8 hours and then allowed for furnace cooling down to room temperature **[11]**.

2.2. Characterization: The impedance measurements were carried out between RT (Room Temperature) to 650 °C in the air over the frequency range of 4 Hz to 8 MHz using HIOKI-LCR TESTER IM3536.

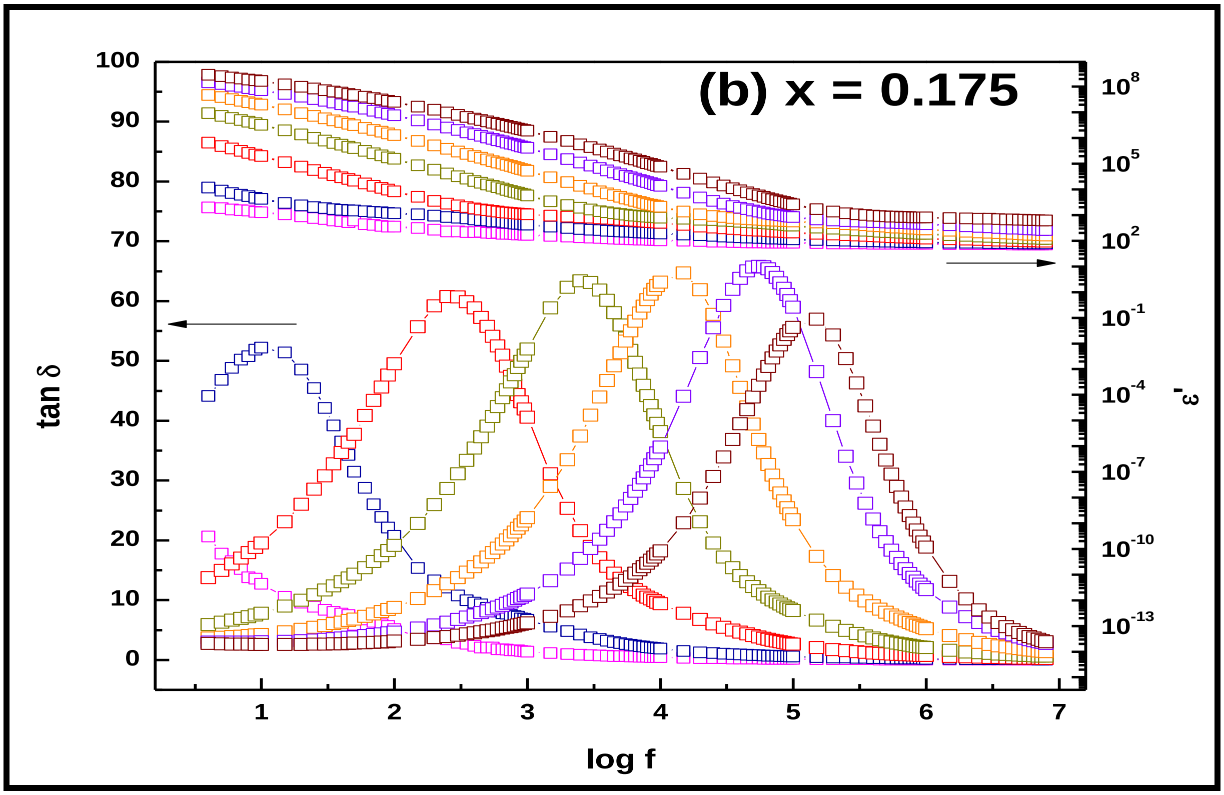
3. Results and Discussion:

Figure (1) depicts the variation of ε': the real part of the dielectric constant for both x = 0.10 and x = 0.175 of $Bi_2V_{1-x}Al_{x/2}Ti_{x/2}O_{5.5-\delta}$ with frequency at selected temperature (100 – 400 °C). From the Figure, it has been noticed that ε' decreases with increasing frequency (at all temperature) and a strong low frequency dielectric dispersion (LFDD) is observed which, is typical dielectric behavior of ferroelectric materials with good ionic conduction properties **[11, 12]**. The higher value of ε' at lower frequencies side is owing to contributions from the electronic, ionic, dipolar and interfacial polarization. Whereas, the contribution of the space charge polarization and orientational polarization reduces with the increase in frequency, so dielectric constant decreases **[13, 14]**. At higher frequencies side, the dielectric constant completely ceases. The peak frequency of the dielectric loss peaks (shown in Figure 1) coincide the cross over frequency in ε' plots, which imply that the losses are due to conduction **[15]**. The shifting of the peak maxima in the direction of high frequency region with the rise in temperature reflects that the conduction mechanism in these compounds is thermally activated **[11]**.



(a)

Figure (1a)



(b)

□: 100°C, □: 150°C, □: 200°C, □: 250°C, □: 300°C, □: 350°C, □:400°C.

Figure (1): Variation of tan δ (the loss tangent) and ε' (real part of the dielectric constant) with frequency of $Bi_2V_{1-x}Al_{x/2}Ti_{x/2}O_{5.5-\delta}$ (a) x = 0.10 & (b) x = 0.175 at selected temperature.

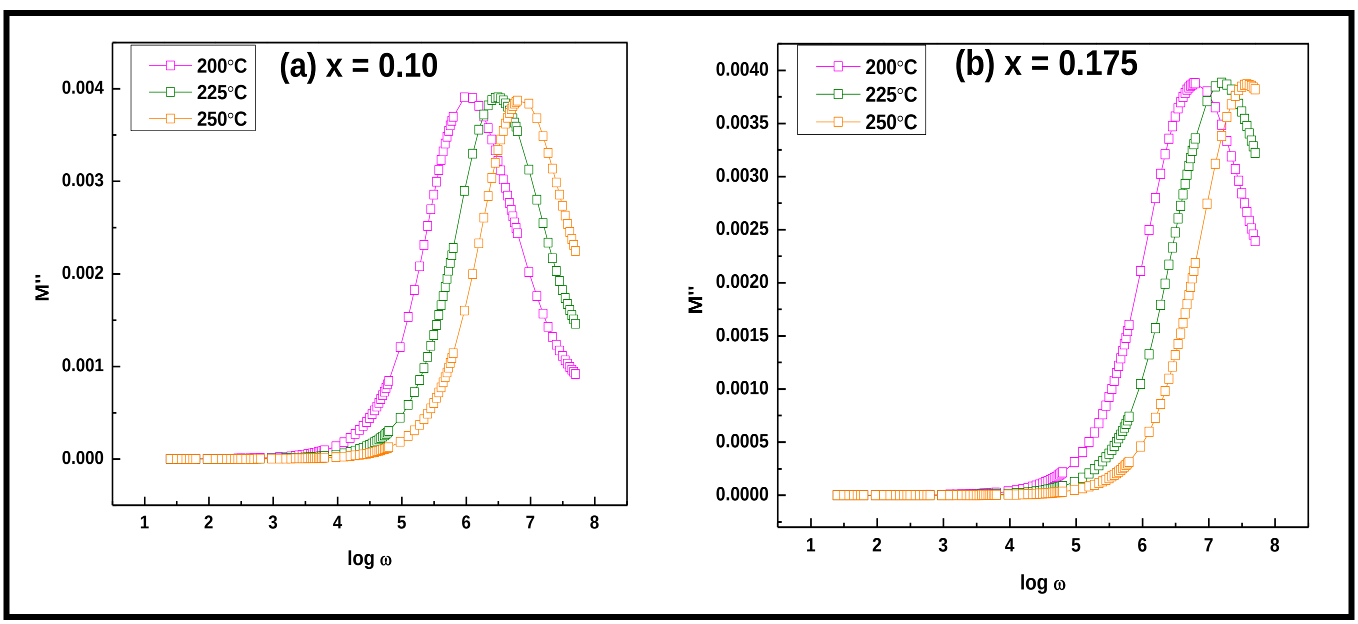


Figure (2): Variation of M'' with frequency of $Bi_2V_{1-x}Al_{x/2}Ti_{x/2}O_{5.5-\delta}$ (a) x = 0.10 & (b) x = 0.175.

Figure (2) depicts the variation of M'', the imaginary part of the complex electric modulus, with the frequency of both the specimens. In the measured frequency range, a single relaxation peak has been noticed. In the lower frequency region of the peaks, the mobile oxygen ions are in the long range movement and in the high frequency side; the oxygen ions are confined in their potential well and are in restricted motion **[16, 17]**. The shifting of the peak maxima in the direction of high frequency regime with the rise in temperature reflects the thermally activated conduction process in these materials **[11]**.

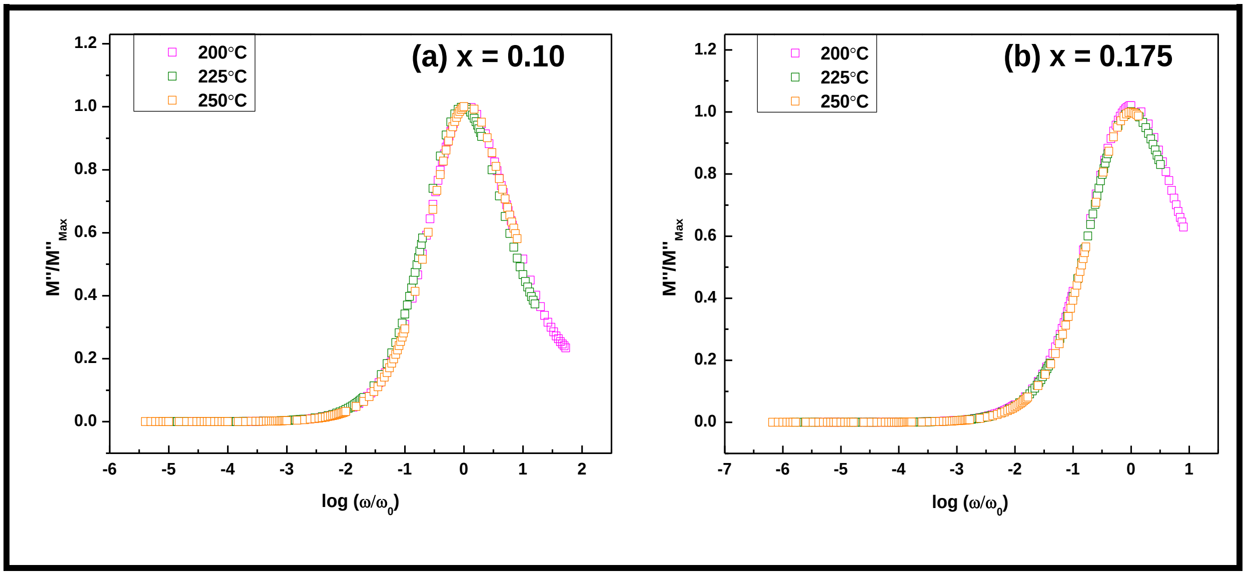
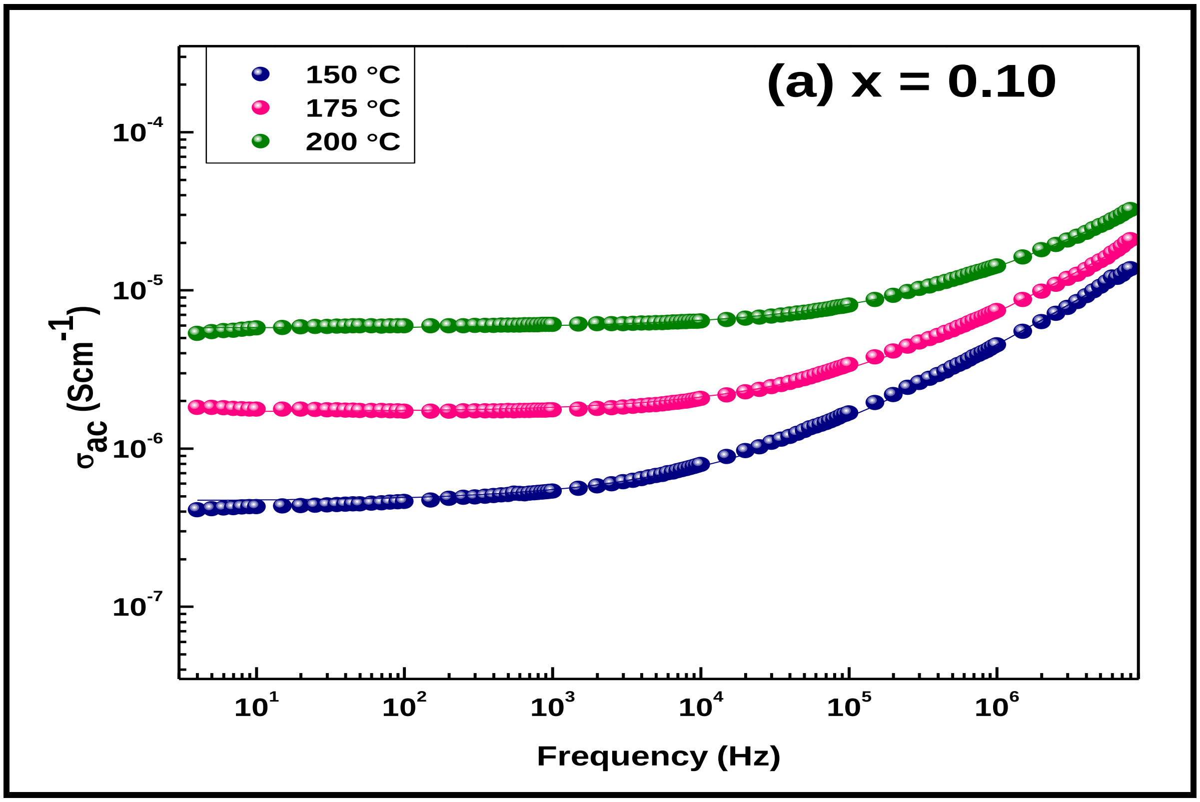


Figure (3): Normalized frequency versus $M''(\omega)/M''_{max}$ (a) x = 0.10 & (b) x = 0.175.

Figure (3) shows the normalized frequency versus $M''(\omega)/M''_{max}$ plots of both compositions in different selected temperature (200 – 250 °C). The merging of the spectra of all the three temperatures as a single curve reflects temperature independent ion relaxation mechanism and hence suggests a single dynamic process at every temperature in the present Al and Ti co-doped $Bi_2VO_{5.5-\delta}$ system **[16]**.

Table (1): Values of extracted parameters from Jonscher's power law fit.

x	Temperature	σ_0 (DC-Conductivity) Scm^{-1}	n	Goodness of fit (R^2)
0.10	150°C	4.67 X 10^{-7}	0.56276	0.9994
	175°C	1.71 X 10^{-6}	0.56922	0.9991
	200°C	5.80 X 10^{-6}	0.54679	0.9994
0.175	150°C	1.30 X 10^{-6}	0.51791	0.99979
	175°C	8.85 X 10^{-6}	0.54022	0.99885
	200°C	2.27 X 10^{-5}	0.49918	0.99866



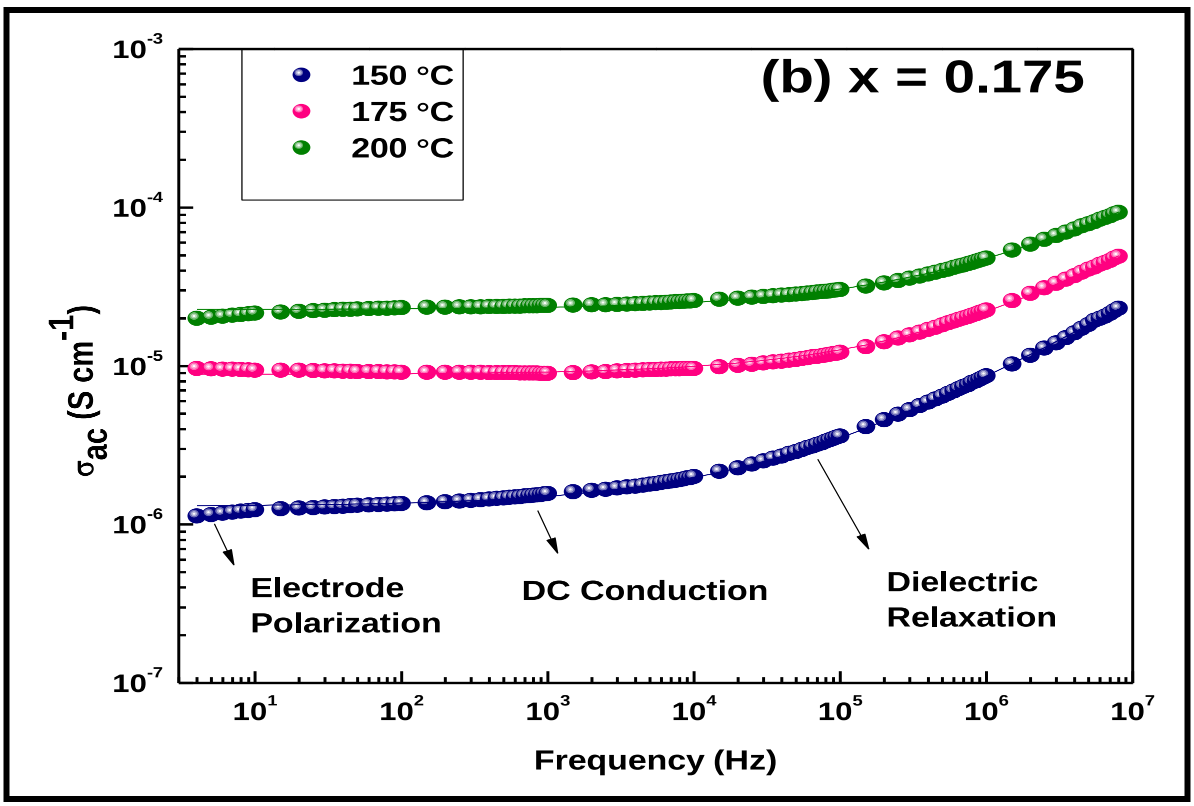


Figure (4): Frequency vs. AC conductivity of (a) x = 0.10 & (b) x = 0.175.

Figure (4) shows the frequency vs. AC conductivity plots of both compounds. The solid line shows the non-linear fitting of the conductivity spectra using Jonscher's Power law. Table (1) presents the fitting parameters obtained**.** The values of the 'n' are found between 0 and 1 ($0 < n < 1$), which confirms the ionic nature of the electrical conduction in these materials **[13, 18]**.

4. Conclusions: Al and Ti co-doped $Bi_2VO_{5.5-\delta}$: $Bi_2V_{1-x}Al_{x/2}Ti_{x/2}O_{5.5-\delta}$, x = 0.10 and 0.175 compounds have been synthesized. The value of n (the power law exponent), obtained from the fitting of AC conductivity spectra, are found between 0 and 1 ($0 < n < 1$). This reflects that the electrical conduction in these compounds is ionic i.e. because of the transportation of oxide ions. Shifting of loss peaks and relaxation peaks in the direction of the high-frequency regime with the rise in temperature reflects that the oxide ions (the charge carriers) are thermally activated in these compounds.

Acknowledgments: The authors gratefully acknowledge the FIST facility of the Physics Department provided by DST, New Delhi, vide sanction order No.SB/52/CMP-093/2013. One of the authors (AJS) gratefully acknowledges DST, New Delhi for INSPIRE fellowship.

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