Voigt Fitting is of Special Interest for Impedance and Raman Spectroscopic Analysis for Two-Layered Aurivillius Compound

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Abstract—Bi_3TiNbO_9 compound is a good ferroelectric with high Curie temperature among other bismuth layered structure ferroelectric (BLSF) of Aurivillius family. To explore the plausible fundamental information about dielectric relaxation, observed in the radio frequency region, a criterion, based on the spectroscopic peak value along with its full width at half maximum, is necessary. In view of this, Voigt profile is fitted to the unsymmetrical bell shaped impedance spectroscopic data of our earlier work made on samarium modified Bi_3TiNbO_9 *ceramics. In the present investigation,* systematic studies like Lorentzian and Gaussian fitting were also made. Voigt profile *(V_f and V'_f)* and its parameters are found to be useful to understand the dielectric relaxation mechanism. The results were corroborated to the Raman spectroscopic plots. Such systematic studies are hitherto not reported.

Keywords— BLSF, Impedance, Raman spectroscopy, relaxation, Gaussian, Lorentzian, Voigt fitting.

I. INTRODUCTION

The Voigt function is considered to be a special and important in depiction of the symmetric feature of any respond peak profile because of its theoretical importance and practically well-fit in to experimental data [1]. It is a known fact that the impedance spectroscopic plots show relaxation peaks in the radio frequency region, correspond to the different relaxing species that are present in the composition. Generally, the dielectric relaxation peaks give information about the competitive interaction of both long-range and short-range ordering that are present in the sample. The same information can be extracted from the specified peak shape and its width [1]. Spectroscopic peaks are generally described either by Gaussian or Lorentzian fitting [2-3]. The former explains about the single relaxation and the later describes multiple relaxation phenomena. In addition, it provides information about the instrument- limitation. The Voigt function (V(x)) is defined as the convolution between Lorentzian (L(x)) and Gaussian function (G(x)), expressed as:

$$V(x) = G(x) \oplus L(x) \qquad (1)$$

The Voigt function can interpret the data in twofold: (i) graphical point of view, (ii) numerical point of view. Ida et al [4] pointed out that the Gaussian width and the parameter (a) give an asymptotic explanation for dielectric relaxation data. Here, the parameter (a) defined as the ratio of Lorentzian and Gaussian full width at half maxima (FWHM). Many researchers adopted Voigt fitting to resolve the overlapping line shapes of different modes of Raman spectra [5-7]. Based on this, one can say that the true line-intensity and shape of any spectroscopic data along the instrument distortion can be studied by means of Lorentzian and Gaussian functions. This type of combined analysis in the literature, especially on BLSF is very limited.

In our earlier results, the modulus spectroscopic plots, (complimentary to the dielectric data) have shown broad peaks [8, 9]. To interpret the relaxation results, alone temperature-dependent dielectric study cannot give information about thermally activated process and therefore a systematic study is necessary. In view of aforementioned, importance, G(x), L(x) and Voigt equation are used to fit the modulus spectroscopy data.

Modulus data can be extracted from the dielectric data. The real and imaginary part of modulus (M' and M") is calculated based on the following equations [10]:

$$M' = \frac{\varepsilon'}{\left(\varepsilon'^2 + \varepsilon''^2\right)} \quad (2)$$

$$M'' = \frac{\varepsilon''}{\left(\varepsilon'^2 + \varepsilon''^2\right)} \quad (3)$$

Where ε' and ε" are the real and imaginary parts of dielectric constant. Here it should be noted that the complex modulus respond function is described as the combination of real and imaginary part of modulus *($M^*(\omega)$ = M'+ i M")*.

Gaussian, Lorentz and Voigt equations are given in the following expressions:

$$Y = Y_0 + \left(\frac{A}{w \times \sqrt{\frac{\pi}{2}}} \right)$$

$$\times \exp \left(\frac{-2((x - x_c)}{W} \right)^2 \quad \text{(Gaussian) (4)}$$

$$Y = Y_0 + \left(2 \times \frac{A}{\pi} \right) \times \left(\frac{w}{(4 \times (x - x_c)^2 + W^2)} \right) \quad \text{(Lorentz) (5)} Y =$$

$$Y_0 + \left(\frac{A \times 2 \times \ln(2) \times w_L}{\pi^{1.5} \times w_G{}^2} \right) \times \int \left(\frac{\exp(-t^2)}{\left(\sqrt{\ln(2)} \times \frac{w_L}{w_G} \right)^2} \right) + \left(\sqrt{4 \times \ln(2)} \times \right.$$

$$\left. \frac{(x - x_c)}{w_G - t} \right)^2 \text{(Voigt)} \quad (6)$$

Here Y_0 is the offset value; A is area under the curve and W is width of the curve and X_c center of peak position. The Gaussian and Lorentzian parameters, w_G and w_L are related to FWHM of Gaussian and Lorentzian [5, 11].The peak area, width and peak position were also obtained by fitting the Voigt function, using the equation (6).

The main purpose of the present study is to extract the following inheriting properties:

i). Explanation about change over mechanism (long-range to short-range order vice versa).
ii) The plausible relaxation mechanism can be understood by means of parameters, obtained by fitting the data with L(x), G(x) and Voigt equations, in the lower frequency domain of imaginary part of modulus spectroscopic data.
iii) Finally, the results are corroborated to Raman spectroscopic fitting data.

II . METHODOLOGY

$Bi_{3-x}Sm_xTiNbO_9$ (BSTN-x, x=0.2 0.4 0.6 0.8&1.0), single phase ceramics were prepared by solid state route. The reactant oxide powders were AR grade with 99.99% purity. The powders of Bi_2O_3, Sm_2O_3, TiO_2 and Nb_2O_5 were taken in a stoichiometric ratio. The powders were mixed thoroughly using agate mortar and pestle. The dried

mixture was pre-sintered at 900°C for 2 hour. Requisite amount of polyvinyl alcohol was added as a binder before making it into pellets. The pressed pellets were once again sintered at 1050–1100∘C for 5 h. A detailed synthesis process was described elsewhere [9]. The impedance measurements were made by Hewlett-Packard (HP4192A) impedance analyser. Raman spectroscopic data is obtained by using Nd-YAG-532 nm LASER alpha 300 of Witec-Germany made.

IV. RESULTS AND DISCUSSION

To understand the defect role, the imaginary part of modulus with frequency at 450°C is shown in Figure *1*, for all the samples. The data is fitted up to specified peak in lower frequency range only. Dotted, dash and scattered lines represents a Lorentzian, Gaussian and Voigt fitting. As seen in the parameters obtained (not shown) from the

fitting is incomplete and may not give any conclusions and therefore an alternative profile is necessary.

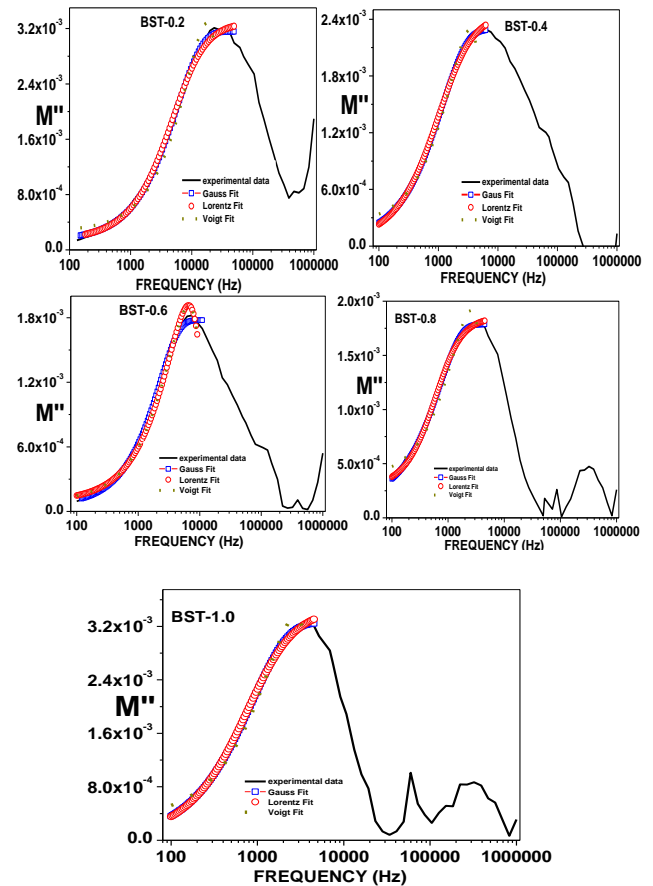Figure *1. Gaussian, Lorentzian and Voigt fitting for BSTN-x*

(x=0.2 0.4 0.6 0.8 1.0)

Raman spectroscopy is well known technique to identify the chemical species and its vibrational modes. Figure 2 shows the Raman spectra for all the samples of BSTN-x.
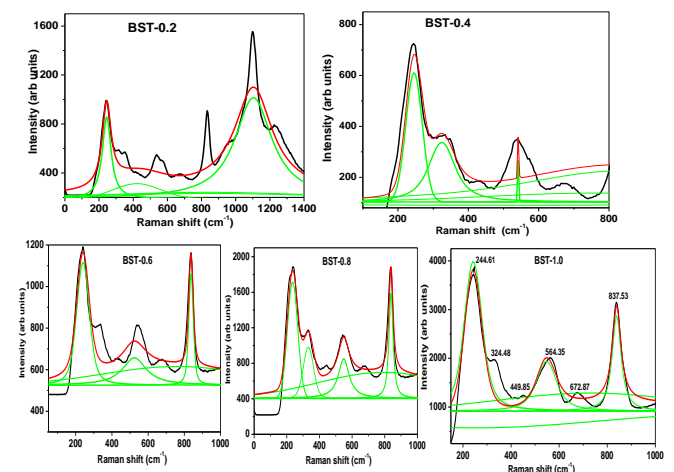

Figure *2. Raman shift Vs. Intensity (arb. units) with respect to*

BSTN-x Samples.

It is important to resolve the broad Raman peaks and its vibrational modes by means of convolution of Lorentzian (L_w) and Gaussian (G_w) functions. Therefore one can accurately understand the line width and peak position of Raman spectra by fitting the spectra using Voigt function. However in literature many researchers were quoted [11-13], that Pseudo-Voiget profile V_w (x) gives the explanation for specific modes which are inherently hidden the function $V_w(x)$, expressed as:

$$V_w = \eta L_w + (1-\eta)G_w \quad (7)$$

Where Lorentzian (L_w) and Gaussian (G_w) profiles are described as

$$L_w = \frac{\gamma \pi^{-1}}{(w-c)^2 + \gamma^2}$$

$$G_w = \frac{1}{\sqrt{2\pi}\gamma} exp \frac{-(w-c)^2}{2\gamma^2}$$

$$L_w = \frac{\gamma \pi^{-1}}{(w-c)^2 + \gamma^2}$$

Voigt profile is calculated by adopting the following two methods.

(1) The complete Voigt profile is calculated by using the equation :

$$\boldsymbol{f_v} = \rho \times W_G + \rho \times W_L \quad (8)$$

Where ρ is arbitrary value (in the present case by assuming as: $\rho = 0.3$,0.7 and 1.0)

W_G , W_L are related (proportional) to FWHM of Gaussian ($\acute{\Gamma}_G$) and Lorentzian($\acute{\Gamma}_L$) respectively.

(2) Voigt profile can also be constructed by considering height time width or height divided by width of the peaks.

From the equation (8), the Voigt function profile can be approximated from the experimental value, therefore the following equation is more evident and suitable in the present study. Based on the arbitrary values of ρ and FWHM of Gaussian ($\acute{\Gamma}_G$) and Lorentzian($\acute{\Gamma}_L$) Voigt profile function (f_v) is approximated and finally given in the following equation [12, 13].

$$f_V(x; \acute{\Gamma}_G, \acute{\Gamma}_L) = \left[\frac{1}{\acute{\Gamma}_G + \acute{\Gamma}_L}\right] \times \rho \times \left[\frac{x}{\acute{\Gamma}_G + \acute{\Gamma}_L}\right] \quad \textbf{(9)}$$

Figure 3 shows the variation of Voigt profile as a function of arbitrary values of x for chosen different arbitrary ρ values (say ρ=0.3, 0.7& 1.0.)**.** The variation of Voigt function with different arbitrary values of x gives the complete picture of Voigt profile. By using the above equation, all f_v values were calculated for all samples. From the Figure.3, it is observed that f_v is found to increase with increasing the arbitrary parameter ρ and x. The f $'_v$ (*slope values obtained from the **Figure.3**)* were also found to increase with the arbitrary (x) values. The kind of theoretical Voigt profile can be visualized by giving different ρ and f_v values. It should be noted here that ideal condition, $W_G+W_L=1$ is maintained while evaluating the f_v.

Figure.4 (a) shows the variation of f $'_v$ with the composition. Many researchers are pointed out that Gaussian width is more important when compared to Lorentzian; however the ratio between Gaussian and Lorentzian is always less than 1.Several asymptotic expressions are necessary to analysis the data. In this connection, Voigt profile is seems to be more valid. In the Voigt profile 'a' and 'b' defined as:

$$a = \frac{W_L}{W_G} \ \& \ b = \frac{x}{W_G} \quad (10)$$

Where w_L and w_G are related to $\acute{\Gamma}_L$ and $\acute{\Gamma}_G$.

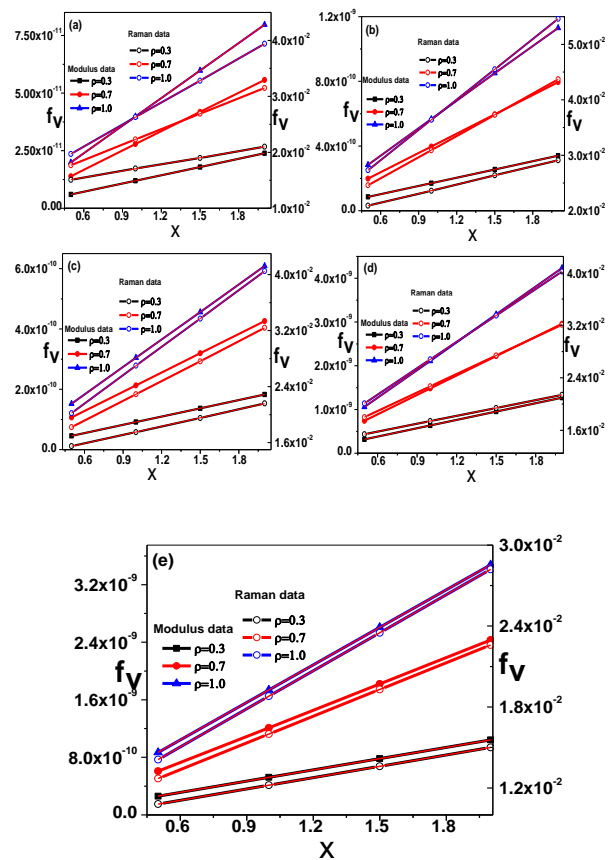Based on the above equation a, value is calculated for all the samples and shown in inset Figure.*4* (a)

Figure 3. *Voigt Profile of Modulus and Raman data as a function of augment at different* ρ *values*
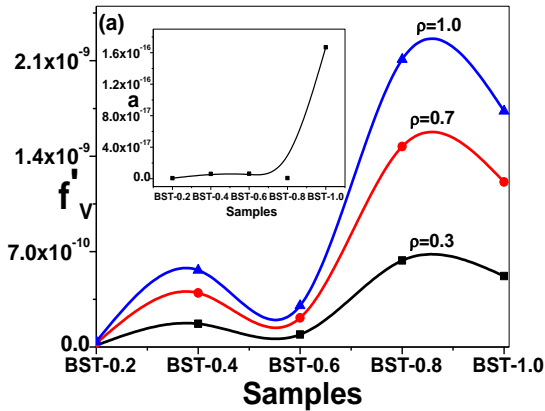
Figure *4 (a)* .*f* ′*$_v$* Vs. BSTN-x (obtained from modulus data)
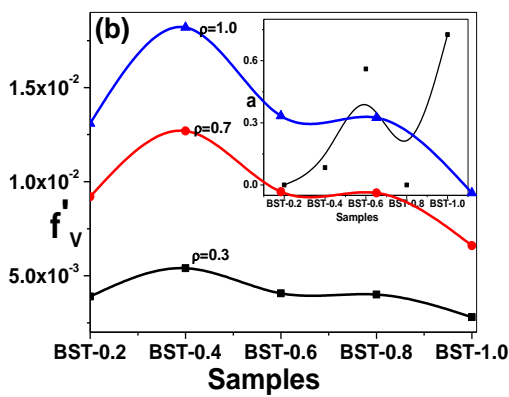Inset Figure .*Parameter (a) Vs. sample composition (SBTN-x)*
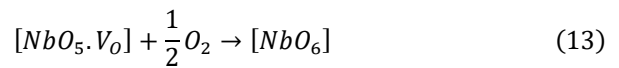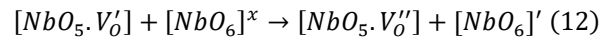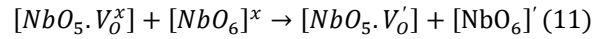

Figure *4(b)* .*f* ′*$_v$* Vs. BSTN-x samples (obtained from Raman data)
Inset Figure. *Parameter (a) Vs sample (BSTN-x)*

In order to analyse the Raman spectrum (*shown in Figure.*2) one has to resolve the overlapping line shapes. The line width and peak positions were taken from fitting the Raman spectroscopic plot (*Figure.2*).Figure.*3* also shows, the Voigt profile obtained for different composition of Raman spectra of BSTN spectroscopic data (shown as marked open circles in Figure.*3*). From the figure *3* the variation of $_f$ '$_v$ with the sample composition is shown in Figure.*4 (b)*.The parameter, calculated by the adopting similar approach made in earlier impedance results. The variation of 'a' with respect to all the samples is shown as inset figure.*4 (b).*

It has been reported in literature that the oxygen vacancies, which are created due to the fact of bismuth loss at higher temperature. These vacancies get accumulated at the grain boundaries and acts as opposite polarizing process and hence they may result into broad peaks near 450°C in all the samples [9]. Moreover the multiple rare-earth ionic incorporation at bismuth site creates more vacancies or complex defect dipoles owing to fact of electron hopping process in a single ionized on doubly ionized vacancies (Kroger-Vink reaction). This kind of hopping mechanism is also established in single crystals, grown by gel technique. Recent report on mixed Cobalt Levo-Tartrate

crystals grown by gel technology have shown limited hopping mechanism and the results are reflected in their dielectric data [14].

The following Kroger–Vink model suggests that increase in the temperature reduces the disorder and creates electron-captured oxygen vacancies, according to equations:

$$[NbO_5.V_O^x] + [NbO_6]^x \rightarrow [NbO_5.V_O'] + [NbO_6]' \quad (11)$$

$$[NbO_5.V_O'] + [NbO_6]^x \rightarrow [NbO_5.V_O''] + [NbO_6]' \quad (12)$$

$$[NbO_5.V_O] + \frac{1}{2}O_2 \rightarrow [NbO_6] \quad (13)$$

Where $[NbO_6]'$ is donor, $[NbO_5.V_O']$ is donor–acceptor and $[NbO_5.V_O'']$ is acceptor vacancies. Here, the oxygen vacancies from complexes defect dipoles in the intermediate structure. In this structure, $[NbO_5.V_O^x]$ complex cluster is a donor candidate and $[NbO_6]^x$ is an acceptor candidate.

The results are consistant with the degree of preferred orientation (P_c) and A-site ionic radii with composition [9] shown in figure 5**.** The same can be seen in'a' parameter value, as shown in inset figure 4 (a-b) . The relative error estimated in the present Voiget profile is found to be very less (below 1%).The relative error profile fitting (E), calculated by using the following formula:

$$E = \frac{\sum_i \left| \left(\frac{y_i}{y_{max}}\right) - b - I(x, Ǵ_G, Ǵ_L)\right|}{\sum y_{i_{max}}} \quad (14)$$

Y is the ratio of intensity to maximum intensity value y_i/y_{max} , the term b represents background value .The value of b=1 for maximum background and b=0 for having no back ground, and x is the arbitrary closer value and $Ǵ_G$ and $Ǵ_L$ are its used significances.
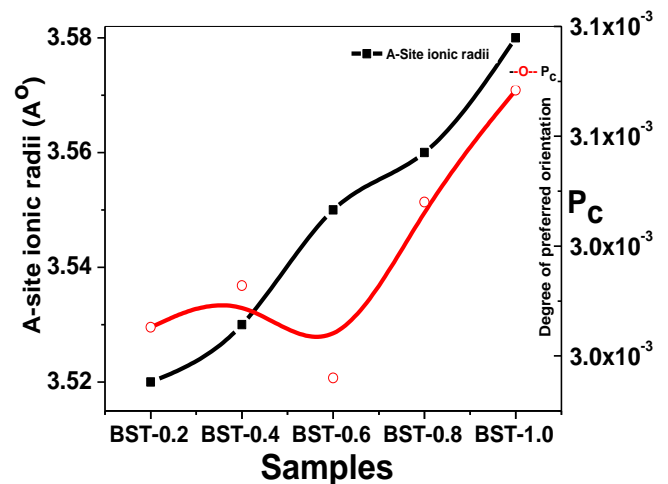

Figure *5* .*A-site Ionic radii and degree of preferred orientation*

Vs. all the samples (BSTN-x)

V. CONCLUSION AND FUTURE SCOPE

The convolution function of both Gaussian and Lorentian gives the most important description of symmetric feature of the peak. The theoretical interpretation gives the complete picture of the experimental data keeping the instrumental limitations. Since the single impedance spectroscopic approach may not be sufficient to explain the asymmetric or non-Debye behavior, therefore, the complete picture of relaxation requires an advanced mathematical approach is necessary. It has also reported that pseudo-Voigt approximation is best fitting among all other fittings. All the spectroscopic Raman curves of experimental data were well fitted by Voigt profile. The true vibrational modes can be approximated by convolution of Gaussian $G(x)$ and Lorentzian $L(x)$ functions. The standard deviation observed in these functions is found to be within the experimental error. The proposed Voiget function and its profile are clearly comparable to impedance and Raman spectroscopic results. The error found in profile is typically less than 1% even considering large background value (b=1). A conclusion is arrived that discrimination of the continuous (broad) peak and the function represents augment, which depends on Voigt profile. However, further studies are needed to speculate the complete Voigt profile.

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