Importance of Impedance Spectroscopy Technique in Materials Characterization: A Brief Review

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Importance of Impedance Spectroscopy Technique in Materials Characterization: A Brief Review

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ABSTRACT. Impedance spectroscopy is a popular analytical tool in materials research and gives plenty of information after careful analysis. Experimentally obtained data can be analyzed by using a mathematical model based on possible physical theory that predicts theoretical impedance or a relatively empirical equivalent circuit. In the present review the complex impedance plots, i.e. Nyquist plots are analyzed by Z-view software and the values of grain and grain boundary resistances and capacitances are evaluated and the equivalent circuits are proposed for different materials. The results of pure and doped lead tartrate crystals, pure and amino acid doped ADP crystals and pure Hydroxyapatite nano-particles are reviewed. It has found that grain and grain boundary effects are very sensitive to doping and it is reflected in Nyquist plots. From the results it is found that the impedance spectroscopy technique is a sensitive technique to detect impure or doped system.

Introduction. Impedance spectroscopy is an analytical tool in materials science and can be used to study mass transport, rates of chemical reaction, corrosion, dielectric properties, defects, microstructures and conductance in solids. Impedance spectroscopy also finds application in assessing the performance of chemical sensors and fuel cells, electrochemical processes and study of membrane behavior of living cells [1-3].

Several workers have reported the impedance study on different materials, for example, potassium selective silicone rubber membranes [4], effect of Cr concentration on the electrical properties of SnO2 based ceramics [5], CdS nanoparticles [6], lead free $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) ferroelectric ceramics [7], manganese mercury thiocyanate (MMTC) [8], polycrystalline $Pr_{0.8}Ca_{0.2}MnO_3$ [9], Co-implanted ZnO single crystals [10] and granular type barrier magnetic tunnel junctions based on $Co/Co_x(Al_2O_3)_{1-x}/$ Co tri-layer structures very recently [11]. In bio-medical applications, the monitoring of the tissue responses to inserted neural implants [12] and for body fluid volume measurements [13] the impedance spectroscopy used.

In the present brief review the attempt is made to give the over view of the results obtained in the author's laboratory in last couple of years on different systems, viz., pure and doped lead tartrate dendrite crystals grown by the gel method, pure and amino acid L-serine doped ammonium dihydrogen phosphate (ADP) crystals and Hydroxyapatite (HAP) nano-particles. In terms of applying complex impedance study, particularly, the Nyquist plots, in order to evaluate the grain and grain boundary contributions. It is worth noting that these three different types of crystalline and nano-crystalline samples are very important from the application point of view [14-16] and considered in this review.

Experimental Technique. Three different systems of samples have been used for the complex impedance study.

(1)For the growth of pure and doped lead levo tartrate crystals, the single diffusion gel growth technique was used with glass test tubes as a crystallization apparatus. To grow pure and mixed lead levo tartrate crystals, 1M levo tartaric acid solution was mixed with sodium meta-silicate solution of specific gravity 1.05 in such a manner that 4.5 pH of the mixture could be obtained. The mixture was transferred into different test tubes to set in to the gel form. After setting the gel the supernatant solutions consisting of lead nitrate ($Pb(NO3)2$) for the growth of pure lead levo tartrate was poured, while the solution of appropriate metal nitrate was poured in different volume along with lead nitrate solution for the growth of doped crystals. After 20 days the crystals were grown in the gel medium. Three different ions, viz., iron, cobalt and cadmium, were selected to dope in lead levo tartrate crystals, and the details are discussed elsewhere in detail [17-19].

The EDAX analysis was performed to estimate the exact concentration of dopant in crystals. Figure 1 shows the growth of lead levo tartrate dendrite crystals in the test tube.

Fig. 1. Crystal of Lead levo tartrate.

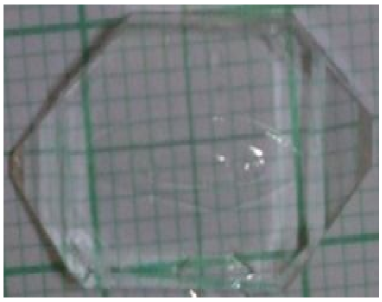


Fig. 2. Crystal of 0.8wt% L-Serine doped ADP.

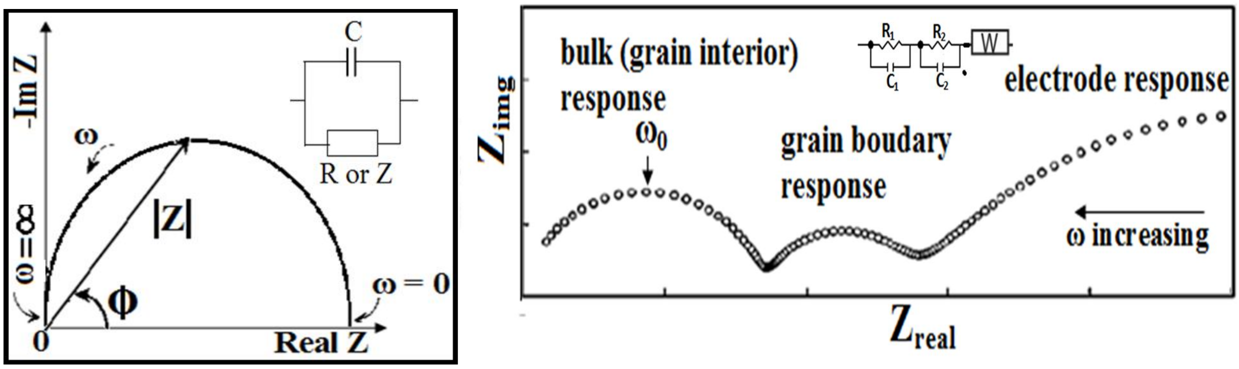
(2) For the growth of non- linear optical (NLO) material ADP crystals and doping with different amount of amino acid L-Serine, the slow solvent evaporation method was used. For the growth of L-serine doped ADP crystals the different amount of L-serine, i.e., 0.4 wt %, 0.6 wt % and 0.8 wt %, was added in ADP solution. The confirmation of successful doping was obtained from FTIR spectroscopy studies. The details are given by Joshi et al [20]. Figure 2 shows the type of crystal grown.

(3) HAP nano-particles were synthesized by the surfactant mediated approach, using calcium nitrate hexahydrate and potassium dihydrogen phosphate, Triton X-100 (a surfactant), while ammonia solution was used to set the pH 9. The molarities of the reacting chemicals were chosen to obtain the Ca/P ratio as 1.67. The resultant precipitates were filtered, washed and dried in a natural atmosphere [21]. The samples were characterized by employing TEM and powder XRD analysis to confirm the nano-size of the particles.

The impedance spectroscopy study was carried out on pelletized samples using HIOKI 3532 LCR HITERSTER Meter set up in the range from 100Hz to 10MHz. The complex impedance data were fitted with software Z- view.

Complex Plane Analysis

The complex plane analysis is a mathematical technique involving real and imaginary parts of the complex electrical quantities like complex impedance, complex admittance, complex permittivity and complex modulus. The expression for impedance $Z(\omega)$ is composed of a real and an imaginary part. If the real part is plotted on the X-axis and the imaginary part on the Y-axis of a chart, a "Nyquist plot" is obtained, which is shown Figure 3a schematically.



a) *b)*

Fig. 3. (a) Typical Nyquist plot (Inset parallel R-C circuit), (b) Grain and Grain boundary response (Inset parallel R-C circuit).

In Fig. 3, a the low frequency data are on the right side of the plot and the higher frequencies are on the left. On the Nyquist plot the impedance can be represented as a vector of length |Z|. The angle between this vector and the X-axis is φ. The typical Nyquist plot of Fig. 3, a results from the inset electrical circuit. The semicircle is a characteristic of a single "time constant". Many times the impedance plots contain several time constants and as a result, only a portion of one or more of their semicircles is seen.

Grain and Grain Boundary Effects

Generally, the ac response of the system considers only the relation between the applied voltage and the current through the test sample. However, the physical nature of the test sample, e.g., single crystal, polycrystalline, blocking or non-blocking electrodes, etc. and its electrical properties, i.e., ionic, electronic or mixed conductor, ferroelectric, etc., are important for consideration. The plausible equivalent circuits, that is, some networking containing ideal resistive and reactive components can be proposed representing these properties of the system and provide model for the collected data. Figure 3b shows the typical Nyquist plot for grain, grain boundary and electrode response and the equivalent circuit shown in inset is widely used to represent the bulk and grain boundary phenomenon and Warburg impedance for electrode response in polycrystalline material [22]. One useful model has been proposed to describe the electrical response of polycrystalline ionic conductors is the brick layer model [23]. The contribution of grain and grain boundaries in the Nyquist plots was discussed in thin yttria stabilized stabilized zirconia layers [24] and in Ba5 HoTi3V7 O30 ceramic [25].

Result and Discussion

The Nyquist plots of pure lead levo tartrate crystal exhibits two semi-circular arcs. The arc at high frequency region near the origin gives a notch that was fitted into semi-circular arc by using software Z-view.

Figure 4 shows the typical schematic representation of grain and grain boundary contributions along with the equivalent circuit suggested. The values of grain resistance (R_g), grain boundary resistance (R_{gb}), grain capacitance (C_g), grain boundary capacitance (C_{gb}) and relaxation frequency for grain (f_g) and grain boundary (f_{gb}) were obtained as 0.145 MΩ, 2.38 MΩ , 103 pF, 66.5 pF, 10.6 kHz and 1 kHz, respectively, for the pure lead levo-tartrate crystals. On doping cobalt, cadmium and iron ions the values of grain resistance increased and the grain capacitance decreased, but no contribution from grain boundary was detected and displayed only one semi-circular arcs in the Nyquist plots indicating the grain contribution only and that was fitted with one R-C parallel circuit as shown in Figure 3a schematically. From the EDAX analysis, it was found that even minimum value of dopant around 0.22 wt % gave the single circular arc in the Nyquist plot [17-19].

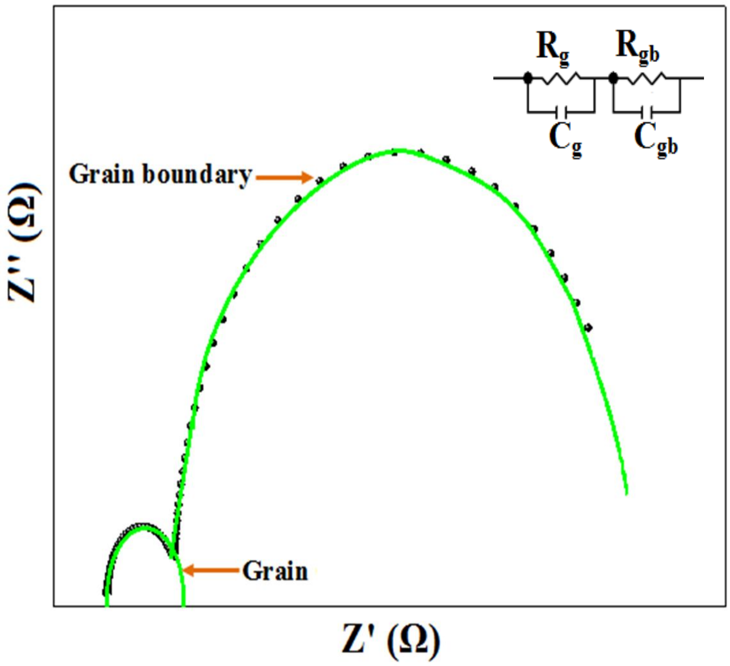


Fig. 4. Nyquist plot (inset parallel R-C circuit).

The Nyquist plot of pure ADP crystal indicated two semi-circular arcs with grain and grain boundary contributions. The values of R_g, R_{gb}, C_g, f_g and f_{gb} were found to be 27.8 MΩ, 51.1 MΩ, 65.8 pF, 34.9 pF, 546Hz and 561 Hz, respectively. Again it was found that on doping amino acid L-serine in ADP crystals the grain boundary contribution disappeared and only one semi-circular arc was observed. The grain boundary resistance value increased on doping, whereas the grain capacitance value decreased on doping [20].

Altogether, the same behavior was obtained for pure HAP nano-particles. Two semi-circular arcs were obtained in the Nyquist plots indicating grain and grain boundary contributions. The values of R_g, R_{gb}, C_g, f_g and f_{gb} were found to be 14.12 MΩ, 369 MΩ, 9.93 pF,40.41 pF, 3.447kHz and 278 Hz, respectively [21].

From the results of the study conducted on various samples it was found that the dopant entered the grain and modified it properties by changing the grain resistance and grain capacitance values. The dopant also modified the grain boundary behavior and within the range of the frequency studied the grain boundary behavior was not detectable. This behavior was sensitive to the minimum dopant level of 0.22 wt % obtained from EDAX analysis.

Summary. The Nyquist plots were found to be sensitive to pristine and impure or doped samples. The pure or pristine samples exhibited both grain and grain boundary contributions with two semi-circular arcs, whereas the doped samples exhibited only one semi-circular arc with grain contribution only within the frequency range studied. This was observed for the smallest amount of doping used around 0.22 wt %. It could be concluded that the complex impedance study, particularly, Nyquist plot representation, is sensitive to the purity of the sample and small amount of impurity or doping is reflected in the nature of the plot. However, further study is needed for standardization and validation of this technique.

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