Indian Journal of Pure & Applied Physics
Vol. 51, November 2013, pp. 758-764

Overall expanded uncertainty estimation in polaron concentration of *p*-toluene sulfonic acid doped polyaniline by EPR spectroscopy

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Received 12 June 2013; revised 5 August 2013; accepted 17 September 2013

Conjugated polymers like polyaniline (PANI) are peculiar in terms that a minor change in doping level leads to only a slight change in polaron concentration but orders of magnitude change in electrical conductivity. Therefore, precise and accurate determination of polaronic concentration is essential to predict the exact doping status which is not a straight forward task. Herein, we report use of Electron Paramagnetic Resonance (EPR) spectroscopy technique for the quantitative estimation of polaron concentration in *p*-toluene sulfonic acid (PTSA) doped PANI (PANI-PTSA) samples with evaluation of overall uncertainty in the results calculated as per GUM guidelines. EPR spectra of the samples and reference were recorded under identical temperature and relative humidity conditions and all kind of uncertainty sources i.e. Type A and Type B were identified and quantified. In particular, the random effects viz. sample preparation, instrument stability, reference material, calibration of balance, operator etc. are categorized under above uncertainty sources. DPPH standard used in these measurements has spin concentration $1.52718\times10^{18} \pm 0.075421624\times10^{18}$ spins/g at 95% confidence level.

Keywords: EPR spectroscopy, Polaron, Polyaniline, Uncertainty estimation, Spin concentration

1 Introduction

Organic conducting polymers also known as synthetic metals are drawing enormous scientific attention over last two decades due to their novel optical and electrical attributes and a wealth of proven applications[1-18]. Like conventional inorganic semiconductors, these π-conjugated polymers can also be doped with different organic and inorganic moieties. However, here the doping level tends to be high (up to 50 mole %) that affects the inter- and intra-chain interactions and governs the electrical, structural and processing attributes. Among other conducting polymers, polyaniline (PANI) has received special attention due to distinguished advantages like cheap monomer, facile and economic synthesis, good environmental/thermal stability and tunable electrical properties[4-10,15-18]. Depending on the nature and concentration of dopant, optical and electronic properties can be precisely tuned to cater the need of a specific sector e.g. organic photovoltaic, organic light emitting diodes, sensors, electrochromic devices, electromagnetic interference (EMI) shielding and electrostatic charge dissipation[1-5] (ESD). It is important to point out that in case of PANI, a minor change in doping level leads to only a slight change in polaron concentration but orders of magnitude change in electrical conductivity. Therefore, precise and accurate determination of polaronic concentration is essential to predict the exact doping status.

There are several techniques[3-5,10,15,19] that can furnish qualitative (e.g. normalized intensity of exciton band in UV-Visible spectra, relative intensity of polaronic and benzenoid/quinoid bands in FTIR spectra, elemental ratio of specific element present in counter-anion to N-atoms of PANI in energy dispersive X-ray (EDX) or complete C, H, N elemental analysis, polaronic-N/total-N ratio in XPS, intensity ratio of 25 deg and 20 deg XRD peaks etc.) or quantitative (normalized area of EPR spectrum, temperature dependent resistivity/magnetic susceptibility, magneto resistance measurements). However, EPR spectroscopy with extremely high sensitivity towards paramagnetic species having unpaired electrons (e.g. free radicals or radical cations) has emerged as most popular and accurate tool for accurate and precise quantitative analysis of polaron concentration[20-25]. This can be attributed to the fact that doping of polyaniline produces localized defects within the band leading to generation of charge carriers. In case of polyaniline, polaron (q=+e, s=1/2) and bipolaron (q=+2e, s=0) are charge carriers, where symbols 'q' and 's' denote carrier's charge and spin, respectively. The spin-less nature of bipolarons (dications) made them EPR inactive. However,

polarons (radical cations) with associated unpaired electron act as paramagnetic centers and gives a distinct signal in the EPR spectrum. Therefore, spin concentration (spins/g) obtained by EPR system reflects exclusively the polaron concentration. In this process, the integrated intensity of the obtained derivative resonance signal has been used to measure the concentration of unpaired electrons (spins) present in the specimen. We have used standard 1,1-diphenyl 2-picryl hydrazyl (DPPH) as reference sample for polaron concentration estimation.

As per ISO/IEC 17025 standard, the quantitative value of any parameter must be assigned with uncertainty value in its measurement. This establishes the measuring capability of laboratory, quality of measurement and global acceptance of the measured value[26-32]. As per ISO, NIST and EAL guidelines[28-32], the overall uncertainty estimation is categorized into two sources: Type A (random sources) and Type B (systematic sources). Uncertainty evaluated from experimental data statistically through repeated number of times under similar conditions comes under Type A sources of uncertainty. This comprised of small independent random variables like measuring process, environmental conditions, inherent instability of the instrument, the operator etc. The random component of uncertainty, for the finite number of measurements were carried out to evaluate a particular parameter as defined in standard procedure. Type B uncertainty was evaluated from the contribution of three major sources (i) measuring instrument, (ii) operating procedure and (iii) characteristics of the sample under calibration. Uncertainty values of these components were taken from the calibration certificate provided by the manufacturer/literature available. The variations in uncertainty component from systematic errors generally follow normal, rectangular or triangular probability distribution. After estimating Type A and Type B components of uncertainty, they were combined for the estimation of combined uncertainty. The final result is reported as overall uncertainty at 95% confidence level. This procedure has been used to evaluate the overall uncertainty in polaron concentration of PANI:PTSA analogues by EPR spectroscopy.

2 Experimental Details

Aniline (Loba Chemie, India) was freshly double distilled before use. Analytical grade hydrochloric acid (35.5% HCl, Merck), ammonia (25% aqueous solution), para toluene sulfonic acid (PTSA, MERCK) and ammonium peorxydisulfate (APS, MERCK) were used on as received basis. Aqueous solutions were prepared from the Millipore water of resistivity value 18 M Ω-cm.

The polyaniline was prepared by chemical oxidative polymerization[15]. In a typical synthesis, 0.1 mol of aniline and 1.0 mol of HCl were mixed in 1.0 L of distilled water. The polymerization was initiated by the drop wise addition of pre-cooled aqueous solution of APS [0.1 mol, $(NH)_4S_2O_8$ in 100 ml H_2O]. The polymerization was carried out at a temperature of −2.0°C under continuous stirring so as to maintain reaction homogeneity throughout the bulk and to control the reaction exothermicity. After completion of polymerization, the polymer has been formed directly in the doped state as a dark green precipitate dispersed in the reaction mixture. The polymer was isolated from the reaction mixture as a dense cake by filtration and washed repeatedly with distilled water till the filtrate became colourless and neutral. The repeated washings help in removing oxidant and oligomeric impurities as well as any free dopant (HCl) moiety from the polymer. The washed polymer cake was then dried under vacuum at 50°C and crushed to obtain the powder of the doped polymer designated as PANI-HCl. The above-synthesized powder (PANI-HCl) was then treated with 0.1 M aqueous ammonia and stirred for 2 h to remove the dopant by neutralization and obtain the undoped i.e. emeraldine base (EB) form of the polymer. The EB powder was then obtained by the processes of filtration, rinsing, drying and crushing successively. The redoping was performed by taking 1.0 g of the EB and treating it with 0.1 M, 0.5 M and 1.0 M PTSA.

The as synthesized samples were characterized by XRD, FTIR, UV-VIS techniques to confirm their formation. EPR spectra were recorded on X–band EPR spectrometer (E-line Century Series E-112, Varian, USA) at operating frequency: 9.36 GHz ± 5.5 MHz, modulation frequency: 100 kHz, microwave power: 10 mW, centre magnetic field: 3250 G± 15 mG, scan range: ±50 G and modulation amplitude: 0.05 G. Before recording the spectrum, EPR spectrometer was stabilized for one hour. The known mass of samples were taken in cleaned transition metal ion free quartz capillary tubes (ID: 1 mm, OD: 2 mm, length: 25 mm) and then inserted in a quartz tube of (ID: 2 mm, OD: 3 mm OD, length: 250 mm). The sample tubes were placed at the centre of the rectangular EPR cavity having TE_{102} mode. DPPH

was used as a standard reference sample for determination of polaron concentrations in different samples by comparing the integrated area of absorption curves of EPR signal with known amount of DPPH. The same spectrometer settings, except different receiver gain factors, were used for recording the spectra of all samples for subsequent determination of polaron concentration.

3 Results and Discussion

An interesting feature of PANI arises from the fact that the insulating/semiconducting emeraldine base (EB) form of PANI can be doped to a conducting emeraldine salt (ES) by non-redox doping without changing the total number of electrons. Such doping is achieved by protonation of the –NH group of EB by mineral or organic acids having free protons and known as protonic acid doping. This leads to formation of positively charged defects (Fig. 1) as charge carriers (polarons/bipolarons) resulting in several orders magnitude increase in the conductivity. The constituent parts of both polaron and bipolaron are very tightly bound owing to valence restrictions of the N-atoms. Consequently, the radical and cation of the polaron are confined to a single aniline unit whereas bipolaron with doubly protonated quinone-diimine unit is confined to aniline diamer. The doping level is related to polaron concentration and the present work deals with uncertainty involved in the measurement of polaron concentration. In actual practice, undoped polyaniline (EB) can be represented by general structure consisting of four repeat units. These units are organized to form quinoid and benzenoid units separated by two imine and two amine nitrogen atoms. Out of these four nitrogen atoms, only two can be protonated to form electrically conducting emeraldine salt form. The doping level refers to mol % of charged nitrogen atoms per repeat unit. Therefore, maximum achievable doping level for doped polyaniline is 50%. EPR spectroscopy is a very sensitive and precise technique for detection and quantitative estimation of paramagnetic centers which are polarons (radical cations) in this case formed upon PTSA doping of PANI.

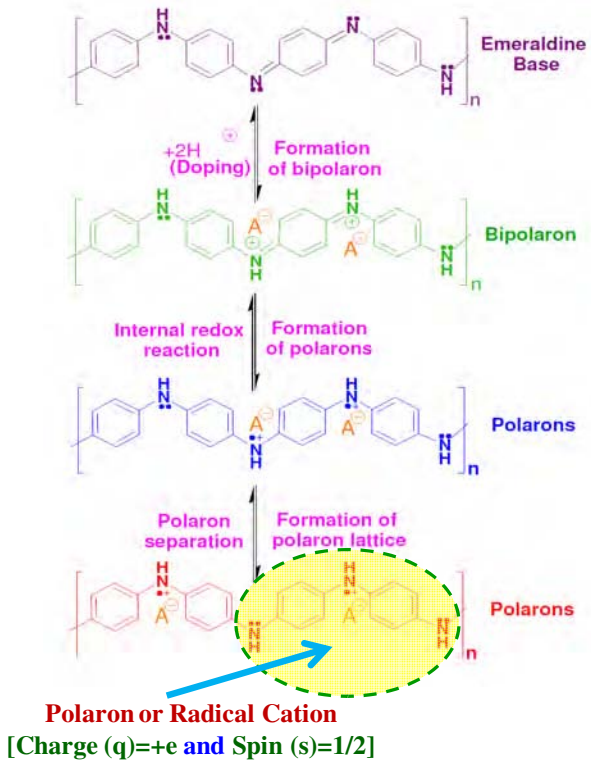


Fig. 1 — Protonic acid doping of emeraldine base form of polyaniline to form emeraldine salt form bearing polaron charge carries along the chain

The quantitative estimation of spin concentration of paramagnetic centers/defects in any material by EPR spectroscopy can be evaluated by two ways viz. Absolute method and Comparison method. In absolute method, the spin concentration was calculated by using the instrument parameters with inbuilt instrument error/uncertainty sources some of them are not easy to quantify. Some of the primary and secondary error sources considered to be induced by the sample and EPR spectrometer associated problems, data acquisition, standards used for calibration and human factor for recording EPR spectrum, are shown in Fig. 2.

In order to minimize the influence of such error sources, one has to define and quantify each error source and accordingly correction is made by adding/subtracting error value from the measured value of that parameter. The most effective way would be to use the same standardized procedures for all EPR measurements and post-recording spectra manipulations. Hence, the value of uncertainty component in spin concentration of paramagnetic centers/defects in material obtained by absolute method has higher value than that obtained by comparison method.

In comparison method, the measurement of spins-concentration of unknown sample is carried out relative to standard sample with known concentration of spins. This method minimizes errors which are arising due to instrument and environmental factors because the EPR spectra were recorded for both the

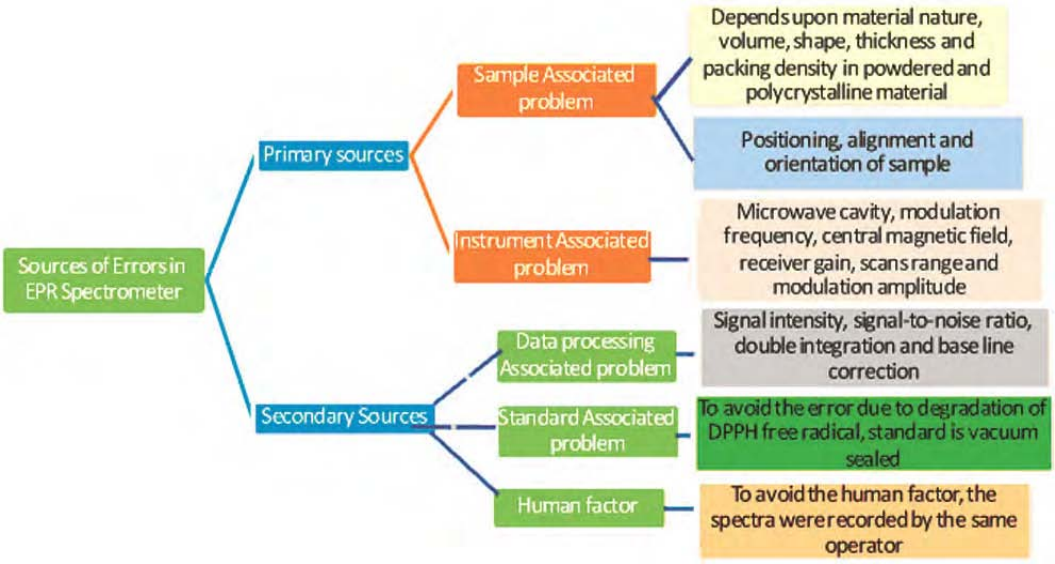


Fig. 2 — Schematic of various sources of error during the measurement of polaronic concentration by EPR measurements on a fixed sample weight

sample and standard reference sample under same operating conditions (like same center magnetic field, scan range, microwave frequency, modulation amplitude and receiver gain for EPR resonance signal, sample position in cavity) and environment. The spin concentration of the paramagnetic centers is evaluated by the following equation:

$$N_x = \left[\frac{A_x \ (Scan_x)^2 G_s M_s (g_s)^2 [S(S+1)_s]}{A_s \ (Scan_s)^2 G_x M_x (g_x)^2 [S(S+1)_x]} \right] N_s \quad \ldots (1)$$

where subscripts s and x represent the standard and unknown sample, respectively, A is area measured under absorption curve, M is modulation amplitude, G is the relative gain of signal amplifier, Scan is horizontal scale in gauss per unit length, S is the spin number, and g is the g-factor of EPR signal. The above expression shows that the estimation of area under the curve is very important parameter for precise calculation. Other important factor is the mass of the standard and unknown samples to specify spin concentration in terms of spins/g. For weighing digital balance was used and each measurement was repeated ten times to reduce instrumental errors. EPR spectra of PANI:PTSA analogues were recorded at (23±2)°C, (45±5)% relative humidity and shown in Fig. 3. The relevant uncertainty sources for estimation of overall uncertainty in polaron concentration for different acids doped polyaniline are shown in the cause and effect diagram in Fig. 4.

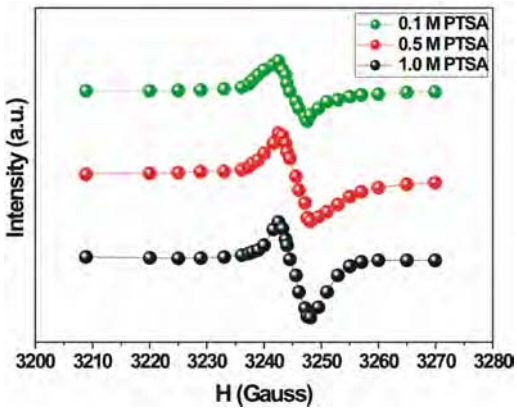


Fig. 3 — EPR resonance spectra of PANI:PTSA analogues

The purity of chemicals used for synthesis is taken as quoted by the supplier's certificate. This is important because the concentration of polarons in PANI:PTSA samples is influenced and this can be corrected by the repeated preparation experiment and this contribution can be neglected.

For EPR measurements, the preparation involves the weighing of samples. The relevant mass of PANI:PTSA analogues is determined by a tared weighing, giving m = 0.001 g. In the tared weighing, three sources of uncertainty are identified which are repeatability, readability (digital resolution) of balance scale and calibration function of the scale. There are two sub-sources of uncertainty in the calibration function which are sensitivity of balance and its linearity. The sensitivity contribution is

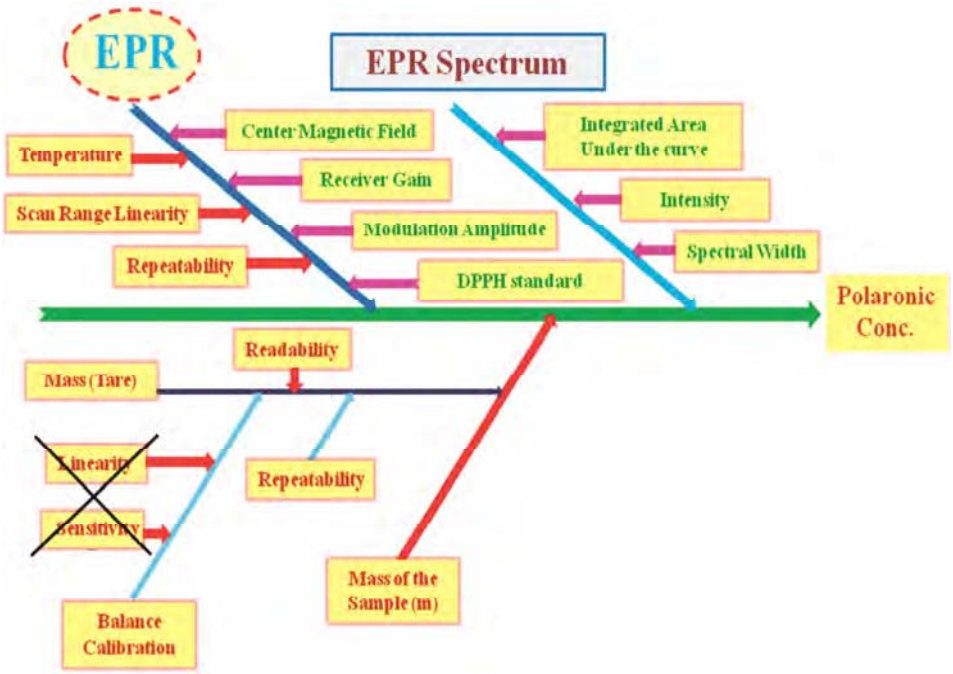


Fig. 4 — Cause and effect (Fish bone) diagram presenting sources of uncertainty

neglected as the mass by difference is done on the same balance over a very narrow range. The buoyancy correction is not considered as all the weighing is done under same atmosphere.

3.1 Type A uncertainty

3.1.1 Area under the curve (A)

The derivative spectrum of each known weight sample is repeated ten times under same environmental and operating conditions. The standard uncertainty is calculated by the statistical standard deviation. For the PANI: 0.1M PTSA, the area is 102 ± 0.5 square units and its uncertainty contribution is 0.1699672.

3.2 Type B uncertainty

3.2.1 Uncertainty in operating frequency

Operating frequency calibration value provided by the supplier is ± 0.00055 GHz. By assuming rectangular distribution, standard uncertainty in the value of operating frequency i.e. $u_1(\delta\nu_1)$ was $0.00055/\sqrt{3} = 3.1754\times10^{-4}$.

where degree of freedom $(\nu_1) = \infty$

3.2.2 Uncertainty in scan range linearity

Scan range linearity required during scanning the magnetic field from minus to plus range around the central magnetic field is 0.1% scan range i.e. in the case of DPPH for 2*100 G scan range the variation in its value is ± 0.2 G. Assuming rectangular distribution, the standard uncertainty for scan range linearity used in selection of scan range i.e. u_3 (δV_3) was 0.1154

where degree of freedom $(\nu_3) = \infty$

3.2.3 Magnetic field homogeneity

The centre magnetic field homogeneity is ± 0.015 G at 3400 G as provided by the supplier. We have used the same amount in our measurements also. Assuming rectangular distribution, Standard uncertainty for magnetic field homogeneity used in selection of: $u_4(\delta\nu_4) = 0.0086$

where degree of freedom $(\nu_4) = \infty$

3.2.4 Uncertainty mentioned in Digital Balance certificate

This is 0.00005 g supplied by the manufacturer at 95% confidence level

Standard uncertainty = U(Ms) = 0.000025 g

3.2.5 Uncertainty of standard DPPH sample used

The uncertainty in spin concentration of standard DPPH sample used ± 0.075421624×10^{18} spin/g at 95% confidence level. Uncertainty budget for these measurements is listed in Table 1. For the calculation of combined uncertainty, the following two

Table 1 — Uncertainty budget for the evaluation of uncertainty in polaron concentration by EPR spectroscopy technique

Quantity	Estimated Value, x_i	Limits Δx_i	Probability Distribution/ Type A & B	Sensitivity Coefficient	Degree of Freedom	Uncertainty Contribution	$[u_i^2(y)]$
A	102	0.5	Normal, Type A, √10	1	9	0.1699672	0.0288
δv_1	9.36 GHz	0.00055 GHz	Rectangular, Type B, √3	1	∞	3.1754×10^{-4}	0.0101×10^{-5}
δv_2	2*100G	0.2G	Rectangular, Type B, √3	1	∞	0.1154	0.0133
δv_3	3400G	0.015G	Rectangular, Type B, √3	1	∞	0.0086	0.0739×10^{-3}
m	0.001 g	0.0001	Normal, Type B, 2	1	∞	0.000025	0.0625×10^{-7}
DPPH	1.52718E18	0.00013E18	Normal, Type B, 2	1	∞	0.03771E18	0.001422×10^{36}

Table 2 — Estimated Polaron concentration with overall uncertainty at 95% confidence level, for $k = 2$

Sample	Polaron concentration (spins/g)	Overall uncertainty (spins/g)
PANI: 0.1M PTSA	1.3×10^{19}	0.0183×10^{19}
PANI: 0.5M PTSA	3.5×10^{19}	0.0214×10^{19}
PANI: 1.0M PTSA	4.2×10^{19}	0.0328×10^{19}

parameters are considered because the values of δv_1, δv_2 and δv_3 parameters are negligible.

	Value (x)	U(x)	U(x)/x
Mass (g)	0.001	0.0000250	0.00250000
Area (sq. units) (A)	102.0	0.1699672	0.0016663
DPPH	1.52718×10^{18}	0.001422×10^{36}	0.00093112×10^{18}

Spins in PANI: 0.1M PTSA = 1.3×10^{19} spins/gm

$$\text{Combined Uncertainty} = \left[\frac{\text{Uc PANI:0.1M PTSA}}{\text{Spins in PANI:0.1M PTSA}}\right]$$

$$= \left[(U(M)/M)^2 + (U(A)/A)^2 + (U_{DPPH})^2\right]^{1/2}$$

Overall expanded uncertainty = 2xUc PANI: 0.1M PTSA = 0.00915×10^{19} spins/g.

At 95% confidence level i.e. K = 2 = 0.0183×10^{19} spins/g.

Similarly by using the same procedure, the overall uncertainty in polaron concentration in other PTSA doped analogues were also calculated and listed in the Table 2. The uncertainty values of these studies can be further improved by taking the weigh-the samples at high precision weighing balance having very low value of uncertainty.

4 Conclusions

The overall uncertainty in the spin concentration value of doped polyanilines has been calculated by EPR spectroscopy as per international guidelines. In these cases, the spin concentration of paramagnetic centers was calculated by using comparison method in which DPPH was used as a standard reference sample. Area under the derivative curve and mass of the sample are two important parameters which affect the overall uncertainty. For more precise studies, the use of very high accuracy and low least count weighing balance is suggested. Once the polaron concentration is known accurately, the electrical and electromagnetic properties of the polyaniline can be fine tuned so that efficient microwave absorbers can be designed. Similarly, the precise determination of polaronic concentration can be useful in the chemical sensors application.

Acknowledgement

The authors are grateful to Director, CSIR-NPL, New Delhi for according permission to publish the work. Encouragement and support for the work by Prof. Vikram Kumar, Ex Director, CSIR-NPL is also gratefully acknowledged. Authors also acknowledge late Dr. Harish Bahadur of CSIR-NPL for extending the EPR facility and for useful discussions.

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