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► **To cite this version:**

P A Kochuparampil, J H Joshi, H O Jethva, M J Joshi. Impedance Spectroscopy of Sodium Sulphide Added ADP Crystals . Mechanics, Materials Science & Engineering Journal, 2017, 9, 10.2412/mmse.4.87.814 . hal-01502455

**HAL Id: hal-01502455**

**<https://hal.science/hal-01502455>**

Submitted on 5 Apr 2017

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## Impedance Spectroscopy of Sodium Sulphide Added ADP Crystals

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DOI 10.2412/mmse.4.87.814 provided by [Seo4U.link](http://Seo4U.link)

**Keywords:** slow solvent evaporation, ADP, Chalcogenide, dielectric, complex impedance, complex modulus.

**ABSTRACT.** Ammonium dihydrogen phosphate (ADP) is popular nonlinear optical material with wide applications. Chalcogenide compounds are very poorly soluble in water and hence difficult to add during growth of ADP from aqueous solution to engineer and modify properties of ADP. Hence the solubility of chalcogenide compound  $\text{Na}_2\text{S}$  was increased by synthesizing its nano-particles with capping agents. The growth of pure and  $\text{Na}_2\text{S}$  added crystal was achieved by the slow solvent evaporation method. Complex impedance plots were recorded in the frequency range of 100 Hz to 1MHz at room temperature. Dielectric constant and loss exhibited normal behaviour with respect to frequency. The complex modulus spectra indicated effect of grain and grain boundary in pure ADP sample. From Jonscher's plot various parameters were calculated and found to decrease for doped samples compared to pure ADP. The non Debye type relaxation was found from plots of  $Z''$  and  $M''$  versus frequency.

**Introduction.** Complex Impedance Spectroscopy is an effective experimental technique used to characterize a.c. electrical properties of crystalline materials. It enables to resolve the relaxation contributions, like, bulk effects, grain boundaries and electrode interface effects in the frequency domain of materials [1]. Ammonium Dihydrogen Phosphate (ADP) is widely used in the area of nonlinear optics, electric-optics, harmonic generation and optical mixing [2].  $\text{Na}_2\text{S}$  can be used as thermo-chemical storage system [3]. In present paper authors studied dielectric, complex impedance and modulus spectroscopic aspects of pure and  $\text{Na}_2\text{S}$  doped ADP crystals. The authors aim is to add  $\text{Na}_2\text{S}$  in ADP crystal to engineer and modify its properties.

**Experimental:** Sodium sulphide ( $\text{Na}_2\text{S}$ ) was synthesised by co-precipitation method and then sample was irradiated through microwave to increase the solubility of precipitate nanoparticles. 0.5M sodium acetate ( $\text{CH}_3\text{COONa}$ ) and 1.5M thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ) were taken as starting materials. The solution of sodium acetate was filled in burette. 10ml capping agent ethylene diammine was added in the thiourea solution at 70°C. The solution of sodium acetate was added in drop-wise manner into the thiourea solution, resulting towards light yellowish precipitate. After continuous stirring of 7 hours the colloidal solution was subjected to the microwave irradiation in domestic microwave oven of Kenstar having input power of 1450W and by adjusting microwave irradiation 10% of input power, 145W for 15 minutes till that the solution completely evaporated and only solid remained which was further washed by distilled water and acetone. The dried irradiated sample was crushed using mortar pestle. As the chalcogenide compound  $\text{Na}_2\text{S}$  nanoparticles were very less soluble in water to increase its solubility capping agent ethylene diammine was used. Its solubility was increased and found to be 0.18g in 100ml. Pure ADP and  $\text{Na}_2\text{S}$  added ADP crystals were grown by using the slow solvent evaporation method at room temperature. Required amount of ADP was added to 400ml distilled water under constant stirring to achieve saturation. After rigorous stirring for 4 hours the solution was filtered using Watmann filter paper no.1. Then the solution was subdivided into four beakers; one beaker contains 100ml pure ADP solution and in the other three for 2ml, 5ml and 10ml  $\text{Na}_2\text{S}$  solution was added in ADP solution and stirred for 3 hours. After 15 days the highly transparent and good

quality crystals have been grown, due to the doping of  $\text{Na}_2\text{S}$  in ADP crystal there was no colour change, but the change in morphology indicates the presence of dopants in ADP crystals as shown in Fig. 1.

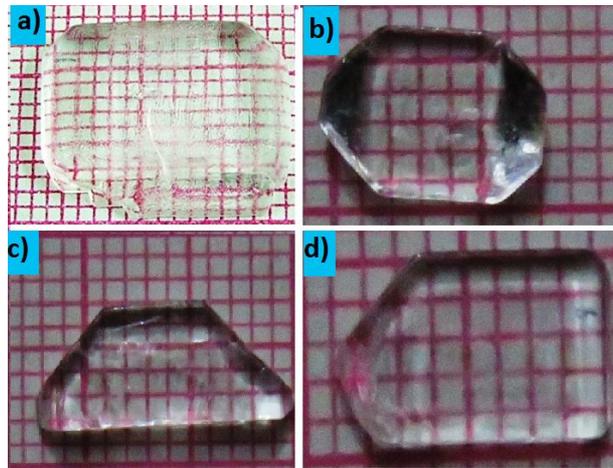


Fig. 1. a) pure ADP, b) 2NADP, c) 5NADP and d) 10NADP.

The AAS was carried on Shimadzu AA-6200 with sodium source was used to detect sodium in doped crystals and the results were listed in table 1. The complex impedance spectra were recorded for pelletized samples in a frequency range of 10Hz to 10MHz at room temperature using HIOKI 3532 LCR HITERSTER meter.

### Result and discussion

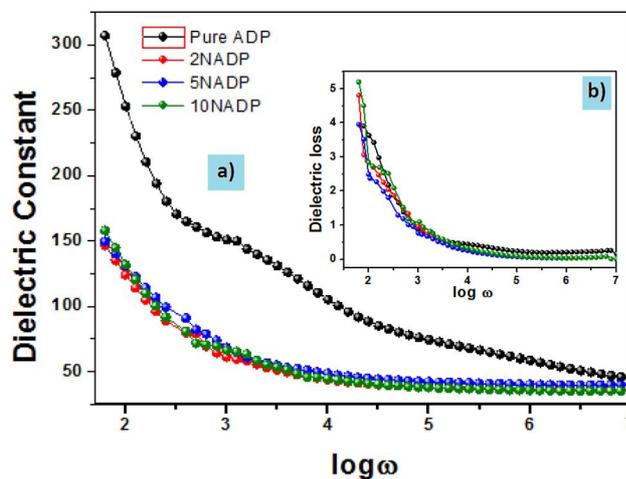


Fig. 2. a) Dielectric constant versus  $\log \omega$  and b) Dielectric loss versus  $\log \omega$ .

Fig. 2 a) shows variations of dielectric constant with respect to applied angular frequency for pure and different mole percentage  $\text{Na}_2\text{S}$  added ADP crystals. High dielectric constant at lower frequency for all samples which may due to the contribution of all kinds of polarization, Viz., electronic, ionic, orientation and space charge polarizations. As frequency increases the dielectric constant decreases because the dipoles can not comply with the variation of the external field and hence the polarization decreases. The doped samples possessed low dielectric constant compared to pure. Fig.2 b) shows variation in dielectric loss with respect to the angular frequency. From the Fig. it can be seen that the

doped sample exhibits less dielectric loss compared to pure ADP, which indicates that the doped samples possessed minimum defect and good optical properties [4].

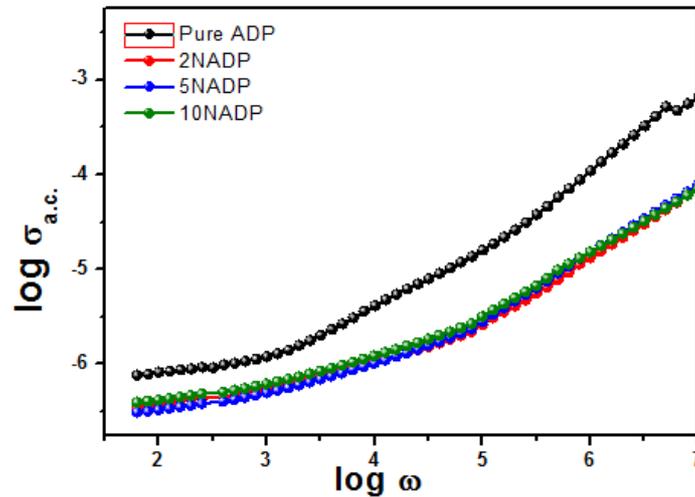


Fig. 3. Jonscher's Plot.

Fig.3 shows Jonscher's plot of both pure and Na<sub>2</sub>S added ADP crystals. Jonscher's power law is:

$$\sigma_{tot} = \sigma_{dc} + A\omega^n$$

where  $A$  is dependent on temperature and indicates the strength of polarizability and exponent  $n$  – is the degree of interaction of mobile ions with lattice.

The a.c. conductivity value is lower for all Na<sub>2</sub>S added ADP crystals as compared to pure ADP. The a.c. conductivity decreases slightly with increases the doping concentration. The main reason for conduction is due to L-defect in intra-bond jump of proton generates the vacancy and D-defect at inter-bond jump to a double occupied bond [5]. The electric conduction in ADP is ionic and the migrating charge carrier is proton, which moves in the three-dimensional hydrogen bond network, affecting the motion of neighbouring protons. To occupy the Na<sub>2</sub>S molecule in site it creates a defect. As the conduction in ADP is protonic and mainly due to the anion [(H<sub>2</sub>PO<sub>4</sub>)<sup>-</sup> ion] and not due to the cation [(NH<sub>4</sub>)<sup>+</sup> ion], the additional hydrogen bonds created may reduce the L-defect and as a result obstruct the movement of protons. This may be the reason for the decrease in a.c. conductivity value in all Na<sub>2</sub>S added ADP crystals. Here the higher value of 'n' for pure ADP indicates large energy stored in such collective motion [6]. The values of 'A' and 'n' are listed in table 1.

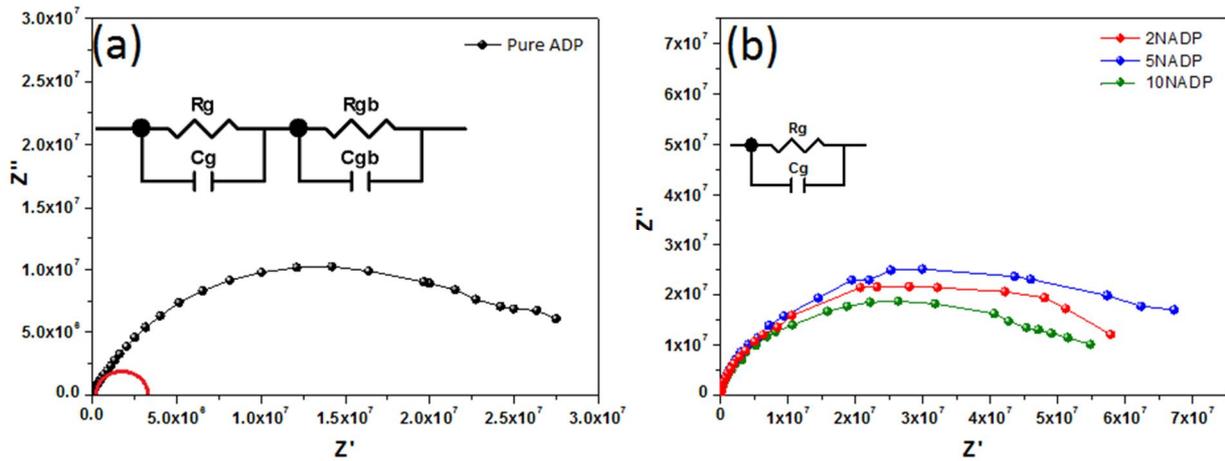


Fig. 4. Nyquist plot a) Pure ADP and b) Na<sub>2</sub>S added ADP.

Fig.4. shows Nyquist plots of pure ADP and Na<sub>2</sub>S added ADP crystal. The small semi-circle near the origin for pure ADP at higher frequency region indicates the grain effect and the large semi-circle at lower frequency indicates the grain boundary effect, while same plots for the Na<sub>2</sub>S added ADP samples shows single semi-circle indicates grain effect only. The equivalent R-C parallel circuits are presented at inset of fig. 4.

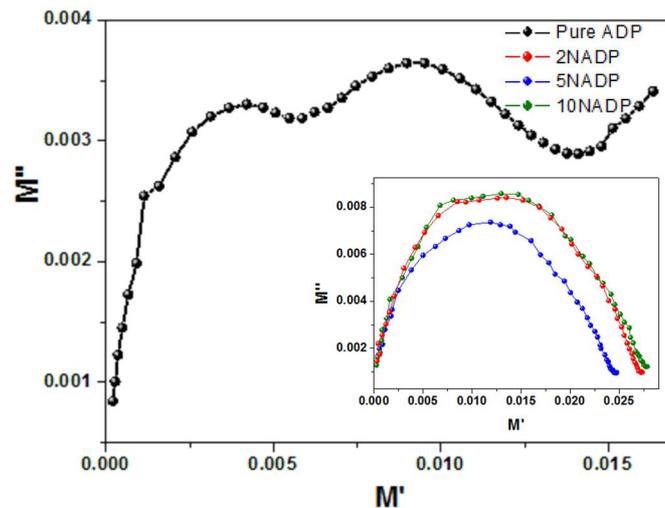


Fig. 5. Complex modulus.

To discriminate the electrode polarization and grain boundary effect complex electric modulus is used. Fig. 5 shows complex modulus plots for pure and Na<sub>2</sub>S added ADP. In pure ADP spectrum two clear semi circles appear due to grain at higher frequency and grain boundary effect at lower frequency, while for doped ADP crystals, single semicircles are observed confirming the presence of grain effect only.

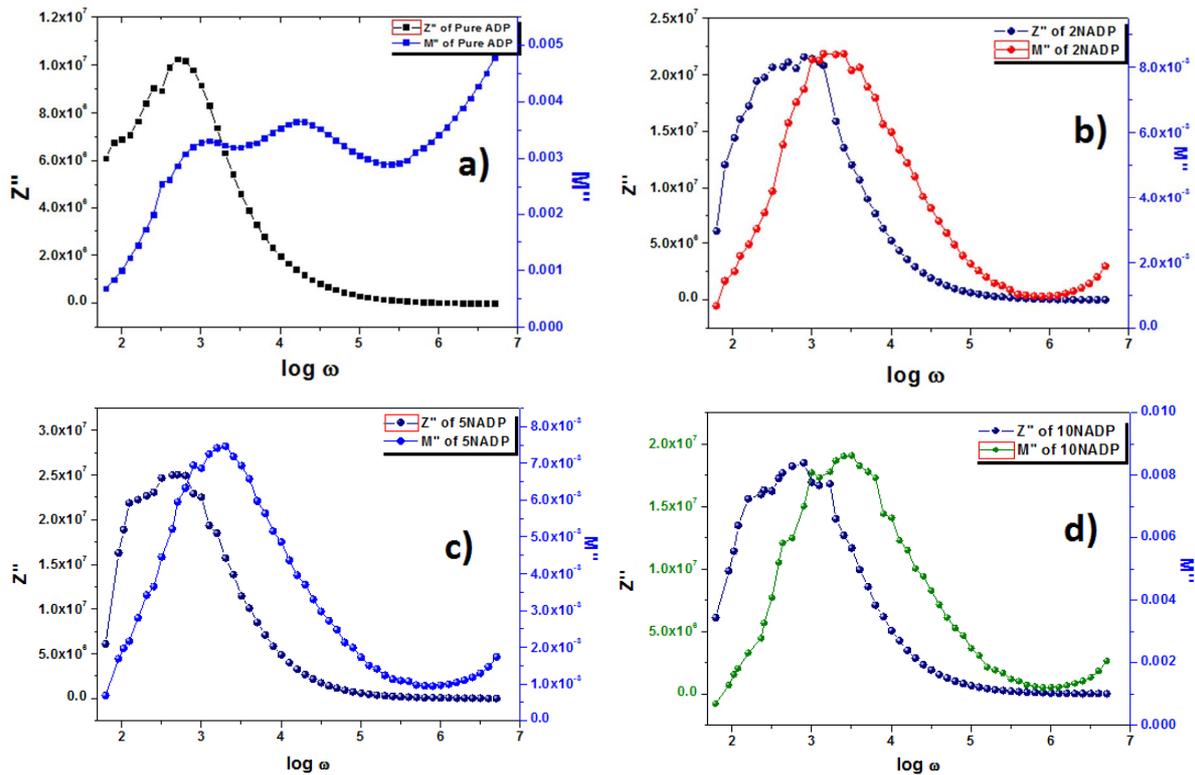


Fig. 6.  $M''$  and  $Z''$  versus  $\log \omega$  a) Pure ADP, b) 2NADP, c) 5NADP and d) 10NADP.

Fig.6 shows the plots of  $M''$  and  $Z''$  versus applied angular frequency. The modulus spectra of pure and  $\text{Na}_2\text{S}$  added ADP crystals, exhibit broad and asymmetric nature indicating non-Debye type relaxation process with distributed relaxation times about mean relaxation time. The non-Debye type relaxation immediately indicates the stretched exponent parameter  $\beta$ , given as  $\beta = 1.196/W - 0.047$ , where  $W$  is FWHM from  $M''$  Vs  $\log \omega$  plot. The smaller the value of  $\beta$  the greater is the deviation with respect to Debye type relaxation. The  $\beta$  value is always less than unity for a system in which the dipole-dipole interaction is significant [7]. From table no.1 it can be seen that the  $\beta$  parameter of doped samples approaches to higher value compare with pure ADP indicates more debye type relaxation behaviour in doped samples compare to pure.

Table 1. AAS data and parameters of complex impedance and complex modulus.

Sample	ppm counts of $\text{Na}^+$	$R_g$ (M $\Omega$ )	$C_g$ (pF)	$R_{gb}$ (M $\Omega$ )	$C_{gb}$ (pF)	$\tau_g$ (mS)	$\tau_{gb}$ (mS)	$n$	$A$ (S.m <sup>-1</sup> .rad <sup>-n</sup> )	$\beta$
Pure ADP	-	28.9	141.5	30.75	58.47	4.08	1.79	0.71	$8.26 \times 10^{-6}$	0.145
2NADP	0.89	66.97	43.07	-	-	2.88		0.51	$1.58 \times 10^{-8}$	0.517
5NADP	1.98	98.28	18.44	-	-	1.81		0.50	$1.62 \times 10^{-8}$	0.520
10NADP	3.66	48.83	38.32	-	-	1.87		0.47	$2.51 \times 10^{-8}$	0.4990

**Summary.** Pure and  $\text{Na}_2\text{S}$  added ADP crystals have been successfully grown using slow solvent evaporation method. The AAS data confirms the presence of sodium ion in  $\text{Na}_2\text{S}$  added ADP crystals.

Dielectric constant and dielectric loss found to be lower in Na<sub>2</sub>S added ADP compared to pure ADP. The Jonscher's Plot is applied to the a.c. conductivity. The complex modulus spectra showing two semi-circle for pure ADP due to presence of grain and grain boundary and single semi circle for Na<sub>2</sub>S added ADP due to effect of grain only. The stretched exponent reveals more Debye type relaxation in doped samples compared to pure one. The Impedance and Modulus spectroscopy found to be very sensitive for small concentration of dopant in ADP.

**Acknowledgement.** Authors are thankful to Prof. H.H. Joshi (HOD, Department of Physics, Saurashtra University, Rajkot, Gujarat, India), Prof. D.K. Kanchan (M.S. University, Baroda, Gujarat, India) for their keen interest and also the authors acknowledge the financial assistance under SAP DRS-II and DST FIST.

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Cite the paper

A.P. Kochuparampil, J.H. Joshi, H.O. Jethva and M.J. Joshi, (2017). [Impedance Spectroscopy of Sodium Sulphide Added ADP Crystals](#). *Mechanics, Materials Science & Engineering*, Vol 9. Doi [10.2412/mmse.4.87.814](https://doi.org/10.2412/mmse.4.87.814)