

# SPECTROSCOPIC STUDIES OF PMMA BLEND PEO WITH NaClO<sub>4</sub> HYBRID SOLID POLYMER ELECTROLYTE

M. Jaipal Reddy<sup>1</sup>, M. Ravindar Reddy<sup>2</sup>, A.R. Subrahmanyam<sup>2</sup>

<sup>1</sup>Dept. of Physics, Palamuru University, Mahaboobnagar, Telangana., India,

<sup>2</sup>Dept. of S&H, MVSR Engineering. College, Hyderabad, Telangana, India

**Abstract**— PMMA, PEO polymer thin films and PMMA: PEO complexed with NaClO<sub>4</sub> hybrid solid polymer electrolyte films of different wt.% were prepared by means of solution casting procedure. These films were characterized with different spectroscopic studies such as IR and UV. The IR results revealed that the interaction between two polymers PMMA, PEO and with Na<sup>+</sup> ion. From the plots of UV spectroscopy, it was observed that considerable decrease in the values of direct and indirect band gap energy with increasing of NaClO<sub>4</sub> salt content to PEO: PMMA blend polymer.

**Keywords**— PMMA, PEO, NaClO<sub>4</sub> salt, FTIR, UV

## 1. INTRODUCTION

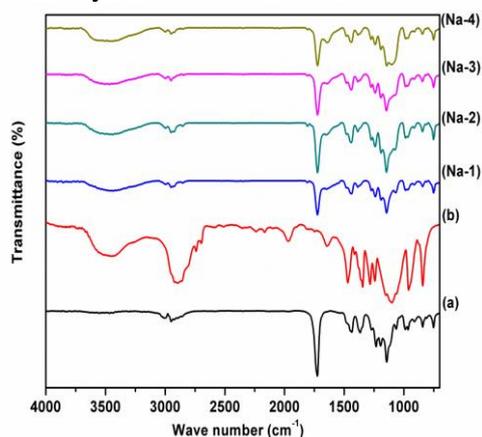
Polymer or polymeric material consists of huge number of atoms or molecules which are created by adding two or more kinds of monomers and they form almost continuous branch of chain or network [1]. The property of polymers depends on their long-chain structure. And physical properties are depends on molecular weight and structure [2]. The polymer electrolyte materials are having special attention in the subject of electrochemistry [3, 4]. The solid polymer electrolytes are one of the most sought components to develop next generation batteries [5, 6]. PMMA and PEO polymers are used in

the present study to carry out different properties in presence of NaClO<sub>4</sub> as hybrid solid polymer electrolyte. PMMA polymer is an amorphous, transparent polymer and it is special polymer due to its high mechanical strength, best processing ability, large surface area to volume [7, 8, 9]. PEO polymer is water soluble and crystalline or semi-crystalline in nature and it is a copolymer for the preparation of PMMA: PEO blend films because of its good conducting nature with the addition of ionic salt [10]. Blending of PMMA with PEO polymer is the suitable approach to achieve the variety of required properties for the electrochemical cell applications [11, 12]. Adding salts like Ag<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, Mg<sup>+</sup>, etc., to polymer blend facilitate high ionic transport [13].

## 2. EXPERIMENTAL

Poly (methyl methacrylate) (PMMA) (M.W ~15000) and poly (ethylene oxide) PEO (M.W ~ 2×10<sup>5</sup>) were obtained from Sigma-Aldrich. Dried NaClO<sub>4</sub> salt also obtained from Sigma-Aldrich. The THF (Tetrahydrofuran) solvent were used to dissolve the polymers and salt. Solution-cast procedure [14] was used to obtain PMMA, PEO thin films and PMMA: PEO complexed with NaClO<sub>4</sub> hybrid electrolyte thin films. FT-IR spectrometer–BrukerALPHA instrument has been used to record the IR data. The IR data is generally studied to identify the presence of functional groups and

complexation of salt in polymer blends [15-17]. UV-Visible double-beam spectroscopy photometer 2202 has been used to record the UV data. Using UV data the direct and indirect band gap energy values ( $E_g$ ) were calculated for the PMMA, PEO films and PMMA: PEO complexed with  $\text{NaClO}_4$  hybrid electrolyte films.



### 3. RESULT AND DISCUSSION

#### 3.1. FTIR

FTIR spectra of PMMA, PEO and PMMA: PEO complexed  $\text{NaClO}_4$  hybrid polymer blend films are shown in Fig. 1. Among all polymers, PEO polymer has a higher tendency to make intermolecular hydrogen bonding with other polymers [18]. Characteristic bands in PMMA spectra appeared at  $2920\text{ cm}^{-1}$  (C - H stretching mode),  $1336\text{ cm}^{-1}$  ( $\text{CH}_2$  deformation),  $1255\text{ cm}^{-1}$  (CH rocking),  $956\text{ cm}^{-1}$  (trans - CH wagging mode),  $835\text{ cm}^{-1}$  (C - Cl stretching mode) and  $615\text{ cm}^{-1}$  (C-CHwagging) respectively. In PEO spectra, characteristic bands found at  $2891\text{ cm}^{-1}$  (C - H stretching) and  $1096\text{ cm}^{-1}$  (C - O stretching) respectively. When PEO and  $\text{NaClO}_4$  salt components increase to PMMA, it was observed that found vibrational bands intensities decreased, which suggests miscibility of two polymers PMMA, PEO with  $\text{NaClO}_4$  salt.

It is found that some bands positions shifted towards lower wave number and also some new vibrational peaks present and some known peaks disappeared in

the studied IR region. The appearing of new peaks along with changes in the existing vibrational bands in the FT-IR spectra establishes the interaction of two polymers PMMA and PEO blend formation along with interaction of  $\text{Na}^+$  ion i.e., the formation of polymer-salt complexation. Similar results have been reported by other researchers on PEO-PMMA polymers when complexed with  $\text{LiClO}_4$  salt [19].

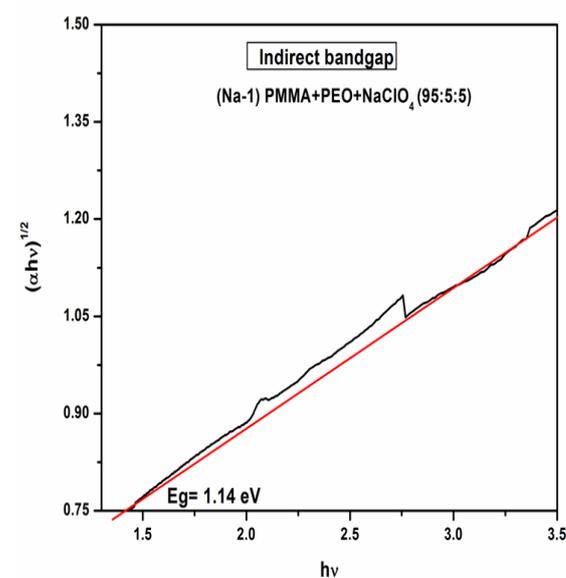
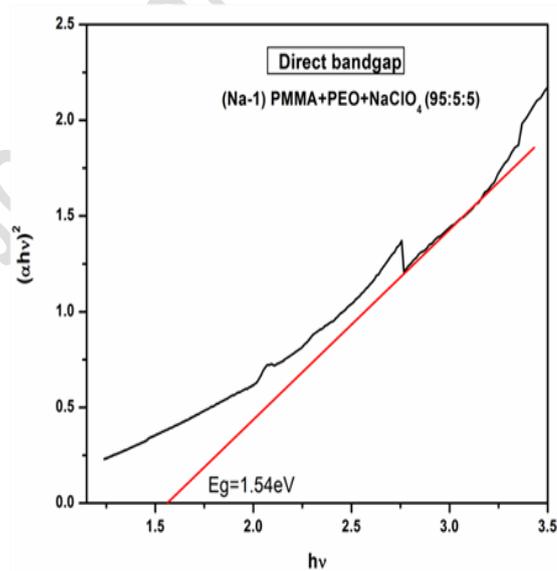
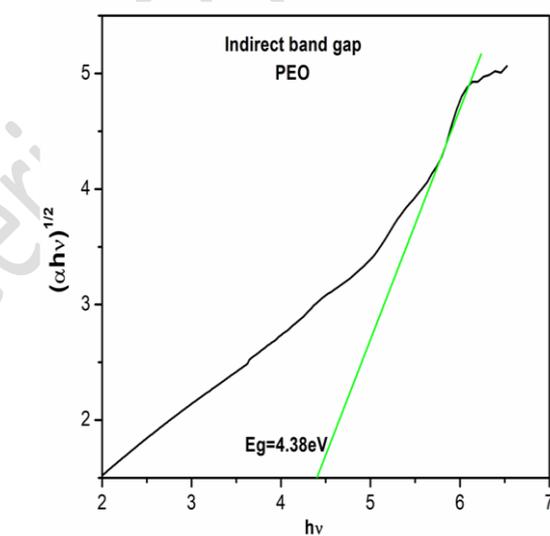
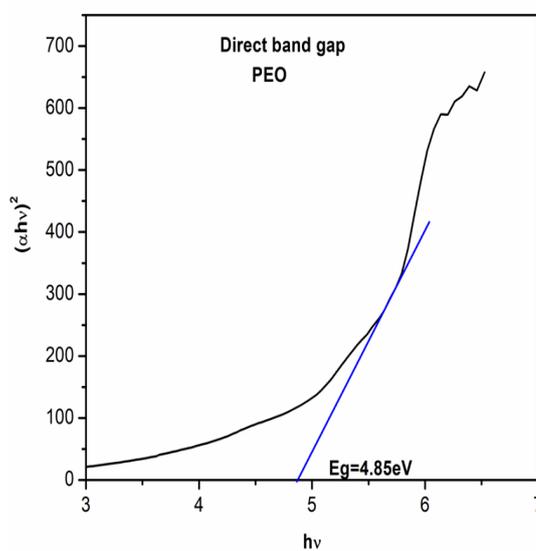
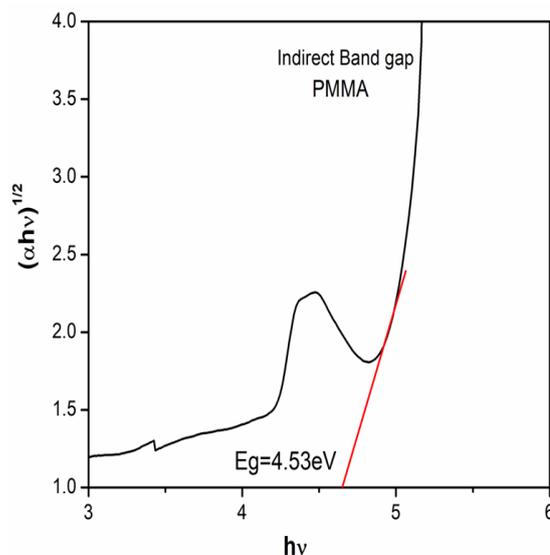
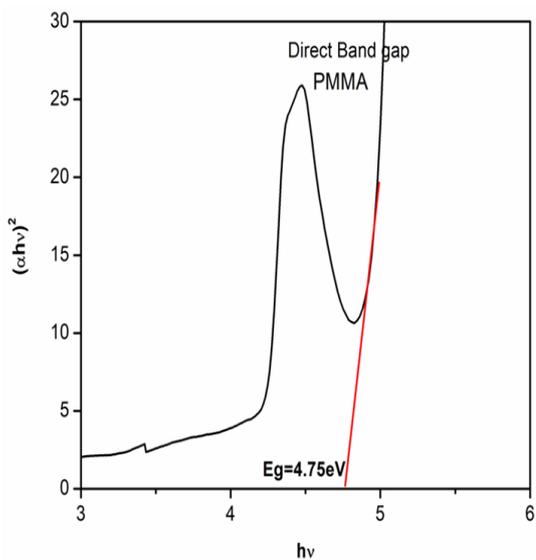
Fig. 1: FTIR Spectra of (a) PMMA, (b) PEO, different wt.% of PMMA: PEO:  $\text{NaClO}_4$  hybrid electrolyte thin films (Na-1)(95: 5: 5), (Na-2)(90: 10: 10), (Na-3)(85: 15: 15) and (Na-4) (80: 20: 20)

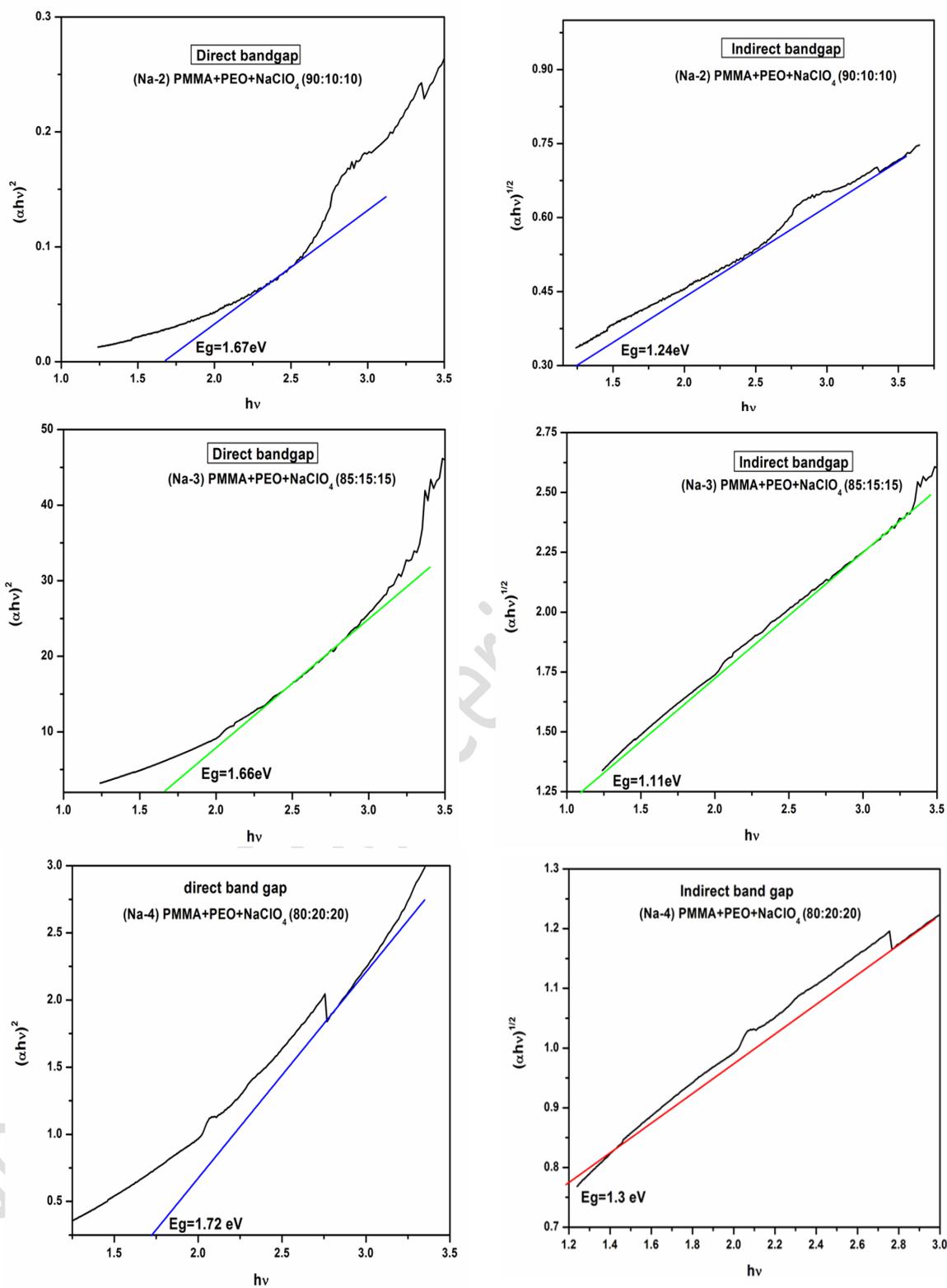
#### 3.2. UV-VIS

The UV plots of PMMA, PEO and PMMA: PEO complexed with  $\text{NaClO}_4$  polymer blend hybrid electrolytes presented in Fig. 2. The calculated direct and indirect band gap energy values are tabulated in Table-1. Existence of direct band gap, the following equation is evident for the dependence of  $\alpha$  (absorption coefficient) on to the energy of the incident radiation [20-22].

$$\alpha h\nu = C (h\nu - E_g)^{1/2}$$

Where  $C (=4\pi\sigma_0/nc\Delta E)$  is a constant which depends on structure of the material. Similarly, to calculate indirect band gap the following equation is evident for the dependence of  $\alpha$  (absorption coefficient) on to the energy of the incident radiation [20-22].





**Fig. 2:** UV plots of PMMA, PEO polymers and different wt.% of PMMA: PEO: NaClO<sub>4</sub> hybrid electrolyte polymer blend thin films.

$$\alpha h\nu = A (h\nu - E_g - E_p)^2 + B (h\nu - E_g - E_p)^2$$

Where ‘A’ and ‘B’ are constants, depend on the band structure of the material. To obtain band gap energy values of these films, graphs were plotted  $(\alpha h\nu)^2$  Vs.  $h\nu$  for direct band gap energy and  $(\alpha h\nu)^{1/2}$  Vs.  $h\nu$  for indirect band gap energy values. From the Table-1, it is found that there was a dramatic change in the direct and indirect band gap values. It is that band gap energy values of PMMA: PEO complexed with NaClO<sub>4</sub> hybrid electrolyte thin films are decreased when compared to PMMA and PEO films. This significant decrease in band gap energy values may be because of presence of NaClO<sub>4</sub> salt in PMMA: PEO polymer electrolyte. And may modify the structure of PMMA: PEO blend i.e., disorder to PMMA: PEO blend in presence of NaClO<sub>4</sub> salt. These observations are very much corroborates with the FTIR spectroscopic result.

Table I. Band gap energy values of prepared films.

Sample code	Wt. %	(E <sub>g</sub> ) eV	
		Direct band gap	Indirect band gap
PEO	100	4.75	4.53
PMMA	100	4.85	4.38
PMMA: PEO: NaClO <sub>4</sub>	95: 5: 5	1.55	1.14
PMMA: PEO: NaClO <sub>4</sub>	90: 10: 10	1.67	1.24
PMMA: PEO: NaClO <sub>4</sub>	85: 15: 15	1.66	1.12
PMMA: PEO: NaClO <sub>4</sub>	80: 20: 20	1.72	1.3

## CONCLUSION

Solution-cast procedure was used to prepare PMMA, PEO films and PMMA: PEO: NaClO<sub>4</sub> hybrid electrolyte films. IR spectra results revealed that functional groups in PMMA and PEO

films with NaClO<sub>4</sub> salt were some shifted and some known bands disappeared in the IR region elucidated the complexation NaClO<sub>4</sub> salt with PMMA: PEO blend and formation of hybrid polymer electrolyte. From UV-VIS plots it is noticed that the energy gap values of both direct and indirect decreased when NaClO<sub>4</sub> salt added to PMMA and PEO blend polymers.

## REFERENCES

- [1] Jackson, N & Dhlr, R.K, "Civil Engineering Materials" Macmillan Education .LTD, 4th Ed (1988).
- [2] Ulrich, H., "Introduction to Industrial Polymers" New York (1982).
- [3] S.B. Aziz, Lip ion conduction mechanism in poly (ε-caprolactone)-based polymer electrolyte, Iran. Polym. J. 22 (2013) 877-883.
- [4] Shujahadeen B. Aziz, Thompson J. Woo, M.F.Z. Kadir , Hameed M. Ahmed, A conceptual review on polymer electrolytes and ion transport models, Journal of Science: Advanced Materials and Devices 3 (2018) 1-17.
- [5] T. Takamura, Trends in advanced batteries and key materials in the new century, Solid State Ionics 152–153 (2002) 19–340.
- [6] Vijay Shankar Rangasamy, Savitha Thayumanasundaram, Jean-Pierre Locquet, Solid polymer electrolytes with poly(vinyl alcohol) and piperidinium based ionic liquid for Li-ion batteries, State Ionics 333 (2019) 76-82.
- [7] H. Dong, K.E. Strawhecker, J.F. Snyder, J.A. Orlicki, R.S. Reiner, A.W. Rudie, Cellulose nanocrystals as a reinforcing material for electrospun poly(methylmethacrylate) fibers: Formation, properties and nanomechanical characterization, Carbohydr. Polym. 87 (2012) 2488–2495.
- [8] T. P. Lodge, E. R. Wood, J. C. Haley, Two calorimetric glass transitions do not necessarily indicate immiscibility: the case of PEO/PMMA. J. Polym. Sci., Part A: Polym. Phys. 44 (2006) 756-763.
- [9] Princy Philip, E. Tomlal Jose, Jacob K. Chacko, K.C. Philip, P.C. Thomas, Preparation and characterisation of surface roughened PMMA electrospun nanofibers from PEO - PMMA polymer blend nanofibers, Polymer Testing (2019).

- [10] X. Y. Sun, L. R. Nobles, H. G. Børner, R. J. Spontak, Field-Driven Surface Segregation of Biofunctional Species on Electrospun PMMA/ PEO Microfibers, *Macromol. Rapid Commun.* 29 (2008) 1455-1460.
- [11] Utracki, L. A. *Polymer Alloys and Blends* Carl Hanser Verlag Munich FRG, 1990.
- [12] Anji Reddy Polu, Ranveer Kumar and K Vijaya Kumar, *Adv. Mat. Lett.* 2012, 3(5), 406.
- [13] M. Ravindar Reddy, *PEO blend solid polymer electrolytes and its applications*, 2019
- [14] M.JaipalReddy,T.Sreekanth, M.Chandrasekhar,U.V.Subbarao *J.Mater.Sci* 35 (2000) 2841-2845
- [15] H.M.Randall, R.G.Fowler, N.Fuson and J.R.Dangl, *Infrared Determination of Organic Structures*; New York 1949; D.VanNorstand.
- [16] R.P. Bauman, *absorption Spectroscopy*, New York:1962; John Wiley and Sons, Inc.
- [17] W.Brugel, *An introduction to Infrared spectroscopy*, London: Methuen and Co Ltd; 1962.
- [18] ElMetwally M. Abdelrazek, Amr M. Abdelghany , Shalabya . Badr , Mohamed . Morsi, *Structural, optical, morphological and thermal properties of PEO/PVP blend containing different concentrations of biosynthesized Au nanoparticles*, *JMRTEC-293* (2017) 1-13.
- [19] Shazia Farheen, R. D. Mathad, *Effect of Nano TiO<sub>2</sub> on structural, Thermal and Ionic Transport properties of PEO-PMMA polymer blend Electrolyte for Li-ion batteries*, *Materials Today: Proceedings* 3 (2016) 3632-3636.
- [20] Mott, NF. Davis, EA. In "Electronic Process in Non-Crystalline Materials, Clarndon Press, Oxford (1971) p238.
- [21] Davis, P.D., Shalliday, T.S., *Bull. Am. Phys. Soc. Ser.*, 114 (1959) 133.
- [22] Thutupalli, GKM. Tomlin, SG. *J.Phys. D9* (1976) 1639.