Structural Analysis of Enhanced Ferroelectricity in Nano-Composite Films of Sodium Nitrite in poly-Vinyl Alcohol Matrix Fabricated at Moderate Elevated Temperature

Lakhbir Singh^{1,2,6}, Baljinder Kaur^{1,2,6}, Neeraj Kumar³, Dae-Yong Jeong⁴, Navneet Dabra^{5, *}, Jasbir S.Hundal⁶

¹ Department of YCoE Punjabi University Guru Kashi Campus Talwandi Sabo-151302, Punjab, India ²Research Scholar, IK Gujral Punjab Technical University Kapurthala-144001, Punjab, India

³Department of Physics, Amity University, Jaipur -302006, Rajasthan, India

⁴Department of Materials Science and Engineering, Inha University, Incheon-402-751, Republic of Korea

⁵Mata Sahib Kaur Girls College (affiliated to Punjabi University Patiala), Talwandi Sabo-151302, Punjab, India

⁶Materials Science Laboratory, Department of Applied Physics, Giani Zail Singh Campus College of Engineering and Technology, MRS State Technical University Bathinda-151001, Punjab, India ^{*}E-mail: <u>navneetdabra@gmail.com</u>

Received: 10 January 2016 / Accepted: 8 March 2016 / Published: 1 April 2016

In the present study, various composite films of NaNO₂-PVA differing in their weight percentage composition have been prepared on brass substrates by solvent drop cast method at optimized elevated temperature of 70 °C. Improved ferroelectric response was observed in the films with equal weight percentage composition giving remanant polarization, $P_r \sim 45.45 \ \mu C/cm^2$. The peak polarization current density J_{max} was also maximum for this composition with measured value of $J_{max} = +6.13 \times 10^{2}$ A/cm² at 3.09 kV/cm and $J_{max} = -6.13 \times 10^{-2}$ A/cm² at -2.68 kV/cm. The average crystallite size calculated using Scherrer relation was found to be lying in the nano-scale range. This calculated value from XRD studies was in good agreement with the particle size observed with transmission electron microscopy (TEM). The minimum strain ~ 0.62% and increased b/a ratio ~ 1.6269 in the NaNO₂ - PVA nano-composite film containing equal weight percentage might have improved the ferroelectric phase of the nano-scale system exhibiting improved remanant polarization.

Keywords: Ferroelectricity, NaNO₂-PVA composite-films, XRD, strain, crystallite size, TEM

1. INTRODUCTION

The study of ferroelectric nano-composites has become an important and interesting area of research these days. The reason for this interest is the reported improvement of characteristic

properties of composites over their constituent materials. With an aim to improve a chosen property of a selected material usually 'a dielectric', it is dispersed into a matrix provided by another 'suitably selected material'; the mixture is appropriately treated to make a sustainable composite for the desired response. The coercivity of ferroelectric materials is quite high, so, in order to make their operation viable at low operating voltage thin ferroelectric films have remained a preference for fabrication. Reaney *et al* used sol-gel spin coating method to deposit ferroelectric PZT thin films successfully with high piezo-, pyro- and ferroelectric response [1]. In ultrathin PbTiO₃ films, Lichtensteiger *et al* studied ferroelectric, structural and ferroelectric properties of the material to a great extent. In ferroelectric thin films, the annealing conditions employed to fabricate them modify grain size, porosity and influences the value of resistance. In ferroelectric PZT thin films grown by sol–gel method, Cho and Jeon studied the influence of annealing conditions on the leakage current characteristics [3]. Annealing conditions can also affect crystallite size and dielectric properties of specimen. This type of study has been reported in ultrafine Ba_{1-x}Sr_xTiO₃ (0<x<1) powders [4].

Sodium nitrite (NaNO₂) is a well known order–disorder type ferroelectric material at room temperature. The structural, thermal, and electrical properties of bulk NaNO₂ in the ferro- and paraelectric phases are well known [5-11]. In 1958, S. Sawada *et al* reported ferroelectricity in NaNO₂ [5]. Further experimental and theoretical studies on ferroelectricity in NaNO₂ and that related to its domain structure were made by S. Nomura and his co-workers [6-7]. Alfredsson *et al* made ab-Initio calculations of spontaneous polarization in ferroelectric NaNO₂ [8]. The measurements on spontaneous polarization in NaNO₂ were made by Hamano in 1973 [9]. The experimental studies related with dielectric relaxation in NaNO₂ were carried by Hatta [10]. Zeigler (1931) worked upon the crystal structure of Sodium Nitrite [11].

The study of ferroelectricity and related phenomenon in nano-composite films in different ceramic-polymer systems has remained a thrust area of research. The effect of change in doping concentration on structural and other properties has also been widely studied. Dabra *et al* have made investigation on structural and ferroelectric properties in spray deposited composite films of KNO₃ and $Cs_{1-x}K_xNO_3$ with PVA, and also studied polarization switching behavior of ferroelectric (NH₄)_{0.39}K_{0.61}NO₃ Films [12-16]. K. C. Sekhar and R. Nath have reported optimum ferroelectric behaviour in NaNO₂ –Poly(vinyl alcohol) nano-composites prepared by solvent cast method on steel substrate at room temperature as well as by spray deposition technique at high elevated temperature of 200 ⁰C [17, 18]. It would be interesting to study these composites at moderate elevated temperature also.

NaNO₂ exhibits ferroelectricity at room temperature. The wetting ability of NaNO₂ facilitates production of its nano-composites with various topology and dimensionality on the basis of different porous matrix. Major thrust in material research always remains on to synthesize new materials with properties tailored to a specific application. It is natural to make further research to understand the mechanism to determine as well as inherently understand these properties. NaNO₂ can be considered as a model object for studying the physical properties of materials embedding in an artificial matrix. Polymer provides a matrix to the filler ceramic and generally, the behaviour of ceramic-polymer composites improves over their constituent materials.

Poly (vinyl alcohol) (PVA) is a water-soluble, bio-friendly and non-expensive polymer. Its nontoxic nature provides additional advantage in terms of its safe storage, safe handling during sample fabrication process and investigation. It acts as a matrix of viscous medium which facilitates in controlling the crystallization process of salts. It is capable of forming stable systems through its -OH groups from its macromolecular chain and three dimensional networks with different organic/inorganic substances [19]. As PVA and NaNO₂ both are soluble in water i.e. water being their common solvent, so PVA is quite suitable to form nano-composite films with NaNO₂.

In literature not much research work has been reported on the structural analysis of ferroelectric studies of nano-composites belonging to the family of metal nitrate/nitrite -polymer composite systems in the thin film form at moderate elevated temperature. In the present study, NaNO₂-PVA composites with different weight percentages of NaNO₂ were fabricated on brass substrate at an optimized moderate elevated temperature of 70 °C to study any enhancement of ferroelectric response in such films. The choice of brass over steel is made due to its being non-magnetic, and as an excellent electrical and thermal conductor. The choice of film fabrication at moderate elevated temperature over that at room as well as at high elevated temperature is made to ensure that the film-substrate interface may become more smooth without appearance of any cracks in the texture of the film and to study as to whether it would (i) modify the ferroelectric response and/or (ii) have some lattice plane of NaNO₂ dispersed in PVA matrix which would explain the ferroelectricity (if any).

The strain analysis is very useful to explain the observed ferroelectric response of the composites under optimized conditions. Strains are imparted into thin films due to differences in lattice parameters between the film and the underlying substrate as well as due to the difference in their thermal expansion behavior. Freund *et al* reported that strains can also result from defects encompassed during film fabrication [20]. As the polarization state of a ferroelectric is directly related to the non-centric positions of atoms in the unit cell, so phase transitions contribute towards ferroelastic strains in significant proportions. So, ferroelectricity can be probed through those methods capable of providing direct information on structure. It has been found in literature that laboratory-source experiments can determine the strain in ferroelectric films with thicknesses down to a few unit Cells [3]. Thus X-ray diffraction can be used to understand the manifestation of ferroelectricity by a specimen in terms of strain analysis under given conditions. The ferroelectric behaviour in composites has been analyzed with structural change and strain response.

2. EXPERIMENTAL DETAIL

The composite films of NaNO₂-PVA (Sodium Nitrite-Polyvinyl Alcohol) differing in their weight percentage composition have been prepared on brass substrates by 'solvent drop cast' method at optimized elevated temperature 70 ^oC. For the said purpose, fine crystals of NaNO₂ (purity 98%) were taken from Qualikems Fine Chemicals Pvt. Ltd., New Delhi (India)and re-crystallised as NaNO₂ can be easily purified by re-crystallization from aqueous solution [21].

The Polyvinyl alcohol (molecular weight 85,000-1,24,000) procured from 'sd fine-chem limited', Mumbai (India) has been used in the present studies. The precursor solution in each case has

been prepared by dissolving NaNO₂ by weight varying from 10-90% and remaining of PVA in double distilled water to cast the corresponding film. Pure NaNO₂ film was also prepared and analyzed. At the time of pouring the solution on to the substrate, the solution as well as the substrate was kept at the same temperature 70 °C i.e. at film deposition temperature. Thereafter the solution was allowed to dry out for 3-4 hours at the same temperature. Subsequently the samples were annealed at 175 °C for 24 hours in a hot air oven. To form metallic contacts, indium metal electrodes of cross-sectional areas 0.022 cm^2 were deposited in vacuum ~2x10⁻⁵ Torr. The vacuum deposition of electrodes was carried out with 'NIRVAT High Vacuum System' (R&D) manufactured by Vacuum Equipment Company (VEQCO) New Delhi, India. The ferroelectric response of the films prepared by drop cast method was studied with modified Sawyer-Tower circuit. 1MHz Function Generator, Scientech 4060 model of Scientech Technologies Pvt. Ltd. Indore, India was used for ac-signal with peak to peak voltage, V_{pp} =30 V at 50 Hz. The output of modified Sawyer-Tower circuit is recorded with Digital Storage Oscilloscope, Model NB115C1 manufactured by Nvis Technologies Pvt. Ltd. Indore (India). The XRD studies of the nano-composite films was carried out with PANalytical x-ray deffractometer, with Cu source, $K_{a1} = 1.5406$ Å. XRD is used to study the crystal structure and for strain analysis. To corroborate the crystallite size determined from XRD study, transmission electron microscopy (TEM) study was done with Hitachi Transmission Electron Microscope, Model H-7500.

3. RESULTS AND DISCUSSION

3.1 Ferroelectric Studies



Figure 1. Ferroelectric (P-E) loops of NaNO₂-PVA composites with (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 (f) 60 and (g) 80 wt% of NaNO₂ (Inset shows variation of Remanant polarization P_r with change in NaNO₂ wt% in NaNO₂-PVA composites)

The present ferroelectric studies on NaNO₂-PVA nano-composite films were carried at room temperature with the help of modified Sawyer-Tower circuit. The remanant polarization P_r is found to increase in the range 3.63 - 45.45 μ C/cm² when the weight of NaNO₂ in the composite film is increased from 10 to 50%. Further increase in the weight percentage of NaNO₂ in NaNO₂-PVA composites led to decrease in P_r and lowers to 11.36 μ C/cm² in the composite with 90% of NaNO₂ by weight.

Typical ferroelectric hysteresis (P-E) loops of NaNO₂-PVA nano-composite films having 10, 20, 30, 40, 50, 60 and 80 wt% of NaNO₂ are shown in Figure 1. The optimum value of $P_r \sim 45.45 \mu$ C/cm² is observed in case of equal weight percentage NaNO₂ – PVA nano- composite film. The inset to the Figure 1 shows the variation of remanant polarization P_r with change in wt% of NaNO₂ in the composite films.

The dependence of remanant polarization on the frequency of input field in equal weight percentage $NaNO_2$ - PVA nano-composite film is shown in Figure 2. At lower frequency ~10 Hz, it is space charge polarization which contributes to the remanant polarization and further increase in frequency ensue the dipolar polarization to come into play. The remanant polarization almost remains stabilized in frequency range 200 Hz to 1 kHz.



Figure 2. Variation in Remanant polarization P_r of NaNO₂-PVA (50:50 wt%) composite with frequency of ac field

In a NaNO₂ molecule, the dipole is composed of a NO₂⁻ ion and nearest neighboring Na⁺ ion. The ordered alignment of NO₂⁻ groups along b-axis give rise to spontaneous polarization. On the basis of point charge model with optimized geometry, the theoretical ab-initio calculations predict spontaneous polarization for pure NaNO₂ ~20.3 μ C/cm² [7]. However, the highest experimental value of polarization in pure NaNO₂ at room temperature is reported to be ~11.9 μ C/cm² [8]. In the PVA matrix, NaNO₂ nano particles forms a more stable nano-composite system at optimized conditions since the presence of the polar –OH groups in PVA three dimensional network allows the physical interactions through H-bonding or by van der Waals dipole-ion or dipole-dipole interactions [19]. The

improved ferroelectric response in equal weight percentage NaNO₂-PVA nano-composite films under optimized conditions might be due to formation of more stable nano-composite system which is found to be consistent with the strain analysis.

The butterfly nature of polarization current density-electric field (J-E) loops is indicative of the presence of ferroelectricity. J-E loops of the four different weight percentage NaNO₂-PVA composite films differing with wt% of NaNO₂ (10, 30, 50 and 80) recorded at optimized conditions are shown in Figure 3.



Figure 3. Polarization current density-Electric field (J-E) loops of NaNO₂-PVA composites for (a) 10 (b) 30 (c) 50 and (d) 80 wt% of NaNO₂ (Inset: Inset shows variation of polarization current density with change in NaNO₂ wt% in NaNO₂-PVA composites)

As the ac electric field changes from the -ve maxima to +ve maxima, the peak value of the current density appears on the positive side of the field and vice versa. The domains are switched from the -ve to +ve direction and contribute to the polarization current and vice versa. Similar kind of behaviour has been reported in NaNO₂–PVF and CsNO₃-PVA composite films [22, 23].

All the composite films exhibit the butterfly and non-linear behavior. In equal weight percentage NaNO₂–PVA nano-composite film, the value of peak current density J_{max} is maximum at field corresponding to the coercive field with measured value $J_{max} = +6.13 \times 10^{-2} \text{A/cm}^2$ at 3.09kV/cm and $J_{max} = -6.13 \times 10^{-2} \text{A/cm}^2$ at -2.68 kV/cm. The appearance of current density peaks at field corresponding to the coercive field value has been reported in other polymer based ferroelectric composite films also [24]. The values are not exactly symmetrical corresponding to +ve and -ve ac signals which may be due to different kinds of electrodes on the two sides of the film viz: brass substrate itself as an electrode on one side and indium metal electrode contact established on its other side. The coercive voltage in each composite films estimated from the J-E studies shown in Figure 3 was found to be in agreement with the values exhibited by P-E characteristics as shown in Figure 1.

3.2 XRD Study

The XRD patterns of single crystal NaNO₂, PVA and the equal weight percentage composite films of NaNO₂-PVA have been analyzed. In XRD pattern of single crystal NaNO₂ peaks were observed at $2\theta = 13.25^{\circ}$, 15.24° , 19.55° , 20.59° , 26.59° , 27.96° , and 29.99° . The miller indices (h k l) of the corresponding planes are identified with the standard pattern of sodium nitrite JCPDS card 03-0628 and are indexed in Figure 4.



Figure 4. XRD patterns of (a) pure NaNO₂ (b) PVA and (c) NaNO₂-PVA (50:50 wt%) composites



Figure 5. XRD patterns of (a) pure NaNO₂ film; of NaNO₂-PVA composite films with (b) 90 (c) 70 (d) 50 (e) 30 (f) 10 wt% of NaNO₂ and of (g) pure PVA film. 'δ' indicates peak responsible for ferroelectric phase. '*' indicates substrate peaks.

The (h k l) values suggest that NaNO₂ has orthorhombic structure at room temperature. The lattice parameters with values a = 3.6274 Å, b = 5.8756 Å and c = 6.7954 Å have been determined using lattice planes (1 0 1), (2 2 0) and (0 4 0). These values of lattice parameters match with the reported values of lattice parameters available in literature [25]. The XRD patterns of different weight percentage NaNO₂-PVA composite films differing with wt% of NaNO₂ fabricated under optimized conditions were further analyzed and are shown in Figure 5.

It has been found from XRD study of the composite films of NaNO₂-PVA that all the XRD peaks present in pure NaNO₂ film get revived at $2\theta = (13.20\pm0.38)^0$, $(15.33\pm0.39)^0$, $(19.43\pm0.61)^0$, $(20.55\pm0.19)^0$, $(26.56\pm0.11)^0$, $(27.85\pm0.39)^0$ and $(30.02\pm0.10)^0$ with same 'relative intensity pattern' in that NaNO₂-PVA composite film which contain their equal proportions by weight indicating its orthorhombic nature. The lattice parameters a, b and c have been found to be 3.6263 Å, 5.8996 Å and 5.8815 Å respectively. The volume of the unit cell in this nano-composite film over single crystal NaNO₂ has been found to have increased from 0.124 (nm)³ to 0.126 (nm)³ by 1.8%. The 'b/a ratio' in non-cetrosymmetric (ferro) structure of NaNO₂ is reported to be 1.5624 [26]. In the present study, the increase in 'b/a ratio' from 1.6196 in single crystal NaNO₂ film to 1.6269 in nano-composite film might led to enhanced polarization in NaNO₂-PVA nano-composite film.

From the XRD patterns of pure NaNO₂, PVA films and of equal weight percentage NaNO₂-PVA nano-composite film in Figure 4, it could be observed that all the major peaks of pure NaNO₂ film are revived in the equal weight percentage NaNO₂-PVA nano-composite film and the peak intensities follow the same order as found in the pure NaNO₂ film except for the (0 0 4) peak at 2θ = 30.02^{0} . This (0 0 4) peak becomes more prominent in equal weight percentage NaNO₂- PVA nano-composite film in comparison to its intensity in pure NaNO₂ film. It can be observed from Figure 5 that the intensity of all characteristic peaks of NaNO₂ except that of (0 0 4) is a function of weight percentage of NaNO₂ in the composites. However, unlike other NaNO₂ characteristic peaks of NaNO₂-PVA nano-composite films, the intensity of (0 0 4) has no correlation with the weight percentage of NaNO₂ in the composite. So, in equal weight percentage NaNO₂-PVA nano-composite film, the orientation corresponding to (0 0 4) might have improved the ferroelectric phase. Therefore, this peak may also be responsible for the improved ferroelectric response, giving improved remanant polarization ~45.45 μ C/cm² in equal weight percentage NaNO₂-PVA nano-composite films fabricated under optimized conditions. The XRD studies further corroborates the optimized ferroelectric response in equal weight percentage nano-composite film.

3.3 Strain and Crystallite Size Analysis

The x-ray diffraction patterns can provide useful information to determine strain and particle size. The strain present in the composite films can be estimated from the x-ray diffraction peak broadening using modified Scherrer's equation [12, 27];

$$\beta(\theta)\cos\theta = \frac{0.9x}{t} + \eta\sin\theta \tag{1}$$

Here $\beta(\theta)$ is the full width at half maximum (FWHM) of the diffraction peak, t is the effective particle size, and η is the crystallite strain.

By plotting the $\beta(\theta)\cos\theta$ versus $\sin\theta$ graph, we can find a very useful information regarding internal strain and particle size. A typical plot of this kind for equal weight percentage NaNO₂-PVA nano-composite films is shown in Figure 6.



Figure 6. $\beta(\theta) \cos\theta$ vs sin θ graph for equal wt% NaNO₂-PVA composite (Inset shows variation of Strain (%) with wt% of NaNO₂ in the composite)

The effective particle size and crystallite strain of NaNO₂ in different compositions of the composite films were estimated from the intercept and slope of straight line respectively. The variation of crystallite strain with change in composition of NaNO₂ in the composite films is depicted in the inset of Figure 6. The measured crystallite strain ~ 0.62% in equal weight percentage NaNO₂ –PVA nano-composite film is found to be smaller in comparison to other weight percentage composite films. It is also smaller as compared to pure NaNO₂ film.

NaNO₂ belongs to a class of order-disorder type of ferroelectric materials in which the polarization arises due to transition from disordered to an ordered arrangement of oxygen atoms. The degree of polarization depends upon the degree of this order which further depends upon the symmetrical projection of oxygen atoms along one direction in structural confinement of NO₂⁻ ions. The PVA matrix appears to have facilitated the enhancement of such order in the NaNO₂-PVA nano composite film due to the presence of the polar -OH groups in PVA three dimensional network. This allows the physical interactions through H-bonding or by van der Waals dipole-ion or dipole-dipole interactions [19]. The rise in strain above equal weight percentage composition is quite prominent and may be due to increase in porosity with increased brittleness due to higher weight percentage of NaNO₂, which might have led to decrease in the remanant polarization. The decrease in remanant polarization below equal weight percentage composition may be due to lack of cumulative alignment of the individual domains of NaNO₂ in the PVA matrix.

The intercept of $\beta(\theta)\cos\theta$ versus sin θ graph of Fig 6 is used to find the particle size of NaNO₂ in the composite films. The particle size of NaNO₂ is observed to vary from 36 to 88 nm as its weight percentage in the composite is increased from 10 to 100. The particle size calculated in the film with equal weight percentage observed to be ~ 38.59 nm. The dependence of particle size on the weight percentage composition of NaNO₂ in the fabricated nano-composite films is shown in Figure 7. Thus, with the observed particle size, crystallite strain in case of equal weight percentage NaNO₂-PVA nano-composite forms a stable system and accordingly shows improved ferroelectric response under the conditions optimized for nano-composite film fabrication.



Figure 7. Particle size vs wt% of NaNO₂ in NaNO₂-PVA composite

The strain and crystallite size in different weight percentage composite nano-composite films of NaNO₂-PVA have been calculated and are placed in the following Table 1.

Table 1. Strain and particle size as a function of wt% of NaNO₂ in its composite

NaNO ₂ wt% in the nano-composite	Strain (%)	Crystallite size (nm)
10	0.96	36.70
30	0.92	39.03
40	0.82	40.32
50	0.62	38.59
60	0.91	44.74
70	0.97	50.77
80	1.16	55.93
90	1.42	70.49
100	1.55	88.12

3.4 TEM Study

TEM study of NaNO₂-PVA composite film with equal weight percentage composition was carried. Typical TEM image as shown in Figure 8 shows the particle clusters of sizes varying from 20 to 45 nm. The TEM study confirms that such NaNO₂-PVA composite films fabricated under optimized conditions form a nano-composite system. The observed particle size ~38.59 nm has been found to be of the same order as that obtained from XRD studies on these films.



Figure 8. TEM image of NaNO₂-PVA composite film with equal wt% at optimized conditions

4. CONCLUSIONS

The ferroelectric studies carried over the NaNO₂-PVA nano-composites with different weight percentage composition fabricated at optimized elevated temperature reveal that the remanant polarization is maximum ~45.45 μ C/cm² for the equal weight percentage composite film. The butterfly nature of J-E loops confirms the ferroelectric phase in the NaNO₂-PVA composites. The maximum peak polarization current density J_{max} in equal weight percentage composite further confirm the improved ferroelectric response manifestation by this particular nano-composite film. The strain analysis in the present study of NaNO₂-PVA nano-composite films reveals that the strain in all the composites is less than that of single crystal NaNO₂ film [Table 1]. Further, the nano-composite film with equal weight percentage is characterized with lowest value of crystallite strain. The ferroelectric response in this composite film in comparison to others is observed to have improved. It might be due to the enhanced degree of order in equal weight percentage NaNO₂-PVA nano-composite film leading

to reduced crystallite strain as observed from calculated values of strain in the composites with different weight percentage compositions.

As determined with the help of XRD scan studies, the particle size in the composite film showing optimum ferroelectric response is found to be ~ 38.59 nm. In different weight percentage composite films and that in case of single crystal film of NaNO₂, the particle size varies from 36 to 88 nm as the weight percentage of NaNO₂ in the composite is increased from 10 to 100. TEM study also reveals that the particle size lie in the nano-scale range. As the polarization is the induced dipole moment per unit volume, so the equal weight percentage NaNO₂-PVA nano-composite film with this particle size might have formed a composite with optimum number of dipoles per unit volume aligned in an ordered way forming comparatively stable ceramic-polymer nano-composite system with reduced strain giving improved ferroelectric response. The (0 0 4) peak seems to be a characteristic of equal weight percentage composition only and unlike other NaNO₂ characteristic peaks in other NaNO₂-PVA nano-composite films, it has no correlation with the weight percentage of NaNO₂ in the composite. So, in equal weight percentage NaNO2-PVA nano-composite film, increased b/a ratio, increased unit cell volume, reduced strain and the orientation corresponding to (0 0 4) plane might have improved the ferroelectric phase in the nano-composite system giving improved remanant polarization. Thus a new lattice plane (0 0 4) appears to have emerged giving enhanced ferroelectric response to the equal weight percentage NaNO₂-PVA nano-composite film fabricated at moderate elevated temperature of 70 °C on brass substrate which is non-magnetic, and an excellent electrical and thermal conductor. NaNO₂ being order-disorder type of ferroelectric materials; the polarization arises due to transition from disordered to an ordered arrangement of oxygen atoms in NO₂⁻ ions; in the present study, the choice of nano-composite film fabrication at moderate elevated temperature might have given conducible time and environment to the NO_2^- ions to embed them into PVA matrix with enhanced dipolar order and therefore acquired enhanced degree of polarization.

ACKNOWLEDGEMENTS

The authors acknowledge IK Gujral Punjab Technical University Kapurthala for providing research facilities. The authors are also grateful to Sophisticated Analytical Instrumentation Facility, Panjab University Chandigarh for providing X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) facility. The cooperation and help rendered in the research work by the staff of Department of Applied Physics, Giani Zail Singh Campus College of Engineering and Technology Bathinda is also acknowledged. In addition, the first two authors acknowledge their parent organization Punjabi University Patiala, Punjab (India) for granting permission to pursue research work.

References

- 1. I. M. Reaney, D. V. Taylor and K. G. Brooks, J. of Sol-Gel Sci. and Techn., 13 (1998) 813.
- 2. C. Lichtensteiger, J. Junquera, P. Ghosez and Triscone, *Phys. Rev. Lett.*, 94 (2005) 047603.
- 3. S. M. Cho and D. Y. Jeon, Thin Solid Films, 338 (1999) 149.
- 4. G. Caruntu, R. Rarig Jr, I. Dumitru and C. J. O'Connor, J. Mater. Chem., 16 (2006) 752.
- 5. S. Sawada, S. Nomura, S. Fujii and I. Yoshida, *Phys. Rev. Lett.*, 1 (1958) 320.
- 6. S. Nomura, Y. Asao and S. Sawada, J. Phys. Soc. Japan, 16 (1961) 917.

- 7. S. Nomura, J. Phys. Soc. Japan, 16 (1961) 2440.
- 8. M. Alfredsson, K. Hermansson and R. Dovesi, *Phys. Chem. Chem. Phys.*, 4 (2002) 4204.
- 9. K. Hamano, J. Phys. Soc. Japan, 35 (1973) 157.
- 10. I. Hatta, J. Phys. Soc. Japan, 24 (1968) 1043.
- 11. G. E. Zeigler, Phys. Rev., 38 (1931) 1040.
- 12. N. Dabra, J.S. Hundal, K.C. Sekhar, A. Nautiyal and R Nath, J. Am. Ceram. Soc., 92 (2009) 834.
- 13. N. Dabra, J.S. Hundal, K.C. Sekhar, A. Nautiyal and R Nath, *IEEE Ultra., Ferro., and Freq. Cont.*, 56 (2009) 1627.
- 14. A. Nautiyal, N. Dabra, J.S. Hundal, N. P. Pathak and R. Nath, *IEEE Dielectric and Electrical Insulation*, 22 (2015) 251.
- 15. N. Dabra and J.S. Hundal, J. Adv. Mater. Res., 93 & 94 (2010) 49.
- 16. N. Dabra, J.S. Hundal, K.C. Sekhar, A. Nautiyal and R. Nath, *J. Appl. Phys.*, 108 (2010) 024108.
- 17. K. C. Sekhar and R. Nath, J. Appl. Phys., 102 (2007) 0441141.
- 18. K. C. Sekhar, A. Nautiyal and R. Nath, J. Appl. Phys., 105 (2009) 0241091.
- 19. C. Vasile and A.K. Kulshreshtha, *Handbook of Polymer Blends and Composites* (Vol. 4A), Rapra Technology Ltd., England (2003).
- 20. L. B. Freund and S. Suresh, *Thin Film Materials: Stress, Defect Formation and Surface Evolution,* Cambridge University Press Cambridge, England (2010) 770.
- 21. M. H. Brooker and D. E. Irish, Candian Journal of Chemistry, 46 (1968) 229.
- 22. K. C. Sekhar, A. Nautiyal and R. Nath, Adv. Mater. Res., 67 (2009) 83.
- 23. A. Nautiyal, K. C. Sekhar, N. P. Pathak and R. Nath, *Appl. Phys. A: Mater. Sci. Process.*, 97 (2009) 205.
- 24. N. Kumar and R. Nath, J. Phys. D. Appl. Phys., 36 (2003) 1308.
- 25. JCPDS International Centre for Diffraction Data, 1998; *JCPDS card 03-0628 in Reference to Zeigler Phys. Rev.*, 38 (1931) 1040.
- 26. F. Jona and G. Shirane, Ferroelectric crystals, Dover Publications, New York (1993).
- 27. B. D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley publishing company, Inc, Massachusetts (1956).

© 2016 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).