Tạp chí Khoa học và Công nghệ, Số 27, 2017

DIELECTRIC PHENOMENA AT PHASE TRANSITION TEMPERATURE OF NANOCOMPOSITES BASED ON FERROELECTRICS AND NANOCRYSTALLINE CELLULOSE ACETOBACTER XYLINUM

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Abstract. Dielectric phenomena at phase transition temperature for nanoparticles of triglycine sulfate (TGS) and Sodium Nitrite ($NaNO_2$) embedded into the pores of bacterial nanocrystalline cellulose Acetobacter Xylinum have been investigated. It was shown that the phase transition temperature of these ferroelectrics at nanoscale level strongly changes as compared to those of the massif ferroelectrics: for hydrogen-containing triglycine sulfate nanoparticles the phase transition temperature was shifted to higher temperatures and for non-hydrogen-containing Sodium Nitrite nanoparticles – lower temperatures. The obtained results are explained by knowledge of size effects and the interaction between the matrix and ferroelectric inclusions through hydrogen-bond system as well as dipole-dipole interaction between TGS nanoparticles using a mathematical expansion based on Landau-Ginzburg-Devonshire theory.

Keywords. nanocomposite, nanocrystalline cellulose, phase transition, triglycine sulfate, Sodium Nitrite.

CÁC TÍNH CHẤT ĐIỆN BẤT THƯỜNG TẠI NHIỆT ĐỘ CHUYỂN PHA TRONG VẬT LIỆU NANOCOMPOSITE ĐƯỢC TỔNG HỢP TỪ CHẤT SẮT ĐIỆN VÀ TINH THỂ XENLULO ACETOBACTER XYLINUM

Tóm tắt. Bài báo nghiên cứu các tính chất điện bất thường tại nhiệt độ chuyển pha đối với các hạt nano sắt điện được đưa vào trong tinh thể xenlulo AcetobacterXylinum. Kết quả nghiên cứu cho thấy, nhiệt độ chuyển pha của chất sắt điện ở kích thước nano thay đổi rất đáng kể so với chất sắt điện ở kích thước thông thường: tăng lên đối với các hạt nano triglycine sulfate có liên kết hidro và giảm xuống đối với với các hạt nano $NaNO_2$ không có liên kết hidro. Các kết quả nghiên cứu trên có thể được giải thích dựa trên những hiểu biết về các hiệu ứng kích thước của vật chất ở kích thước nano và sự tương tác giữa mạng tinh thể xenlulo với các hạt nano của chất sắt điện thông qua liên kết hidro cũng như sự tương tác lưỡng cực giữa các hạt nano với nhau thông qua sử dụng công thức toán học mở rộng dựa trên thuyết Landau-Ginzburg-Devonshire.

Từ khóa. nanocomposite, tinh thể xenlulo, sắt điện, tính chất điện vật liệu, sự chuyển pha, triglycine sulfate, Sodium Nitrite.

1 INTRODUCTION

The transition from micro- to nanoelectronics substantially is related to the improvement of processing technology for new materials. In the first place, for heterogeneous nanostructures, which allow us to strongly change their properties corresponding to the practice demands by using size effects at the nanoscale level. Among these materials, the composites with embedded ferroelectric components have a special place due to the softness of crystal lattice in ferroelectrics in the vicinity of their phase transition to ferroelectric state, leading to the wide spectrum of variation of the properties in these composites.

Experience shows that all dielectric properties and characteristics of ferroelectric nanocomposites, including dielectric susceptibility, spontaneous polarization, coercive field, domain structure, etc. undergo significant changes. Particularly, the temperature of the phase transitions to polar state in these nanostructures changes significantly as compared to homogeneous bulk ferroelectrics [1-7]. The shift of Curie point of the ferroelectric composites in dependence on the material type and the sizes of components can reach up to several tens of degrees. At some critical size of embedded ferroelectric particles, their ferroelectric properties might disappear entirely [8].

The anomalies indicated above are characterized by significant changes in structures of ferroelectrics at the nanoscale level, expressing in the changes of the distance between atoms and the symmetry of the arrangement of nanoparticles. Another important factor distinguishing the properties of nanocomposites from homogeneous single crystals is the interaction of a nanoscale inclusion with a matrix. When reducing the particle size, the part of surface atoms and their contribution to the properties of composite increases.

Until now, the porous matrices used to create matrix ferroelectric composites are mostly aluminum oxide Al_2O_3, silica, glasses and opal [1-3,5,6]. The use of nanocrystalline cellulose (NCC) as a matrix for creating electric composites can be considered as a rather new step. Unlike previously used matrices, its attractiveness is related to the fact that the properties of nanocrystalline cellulose as well as properties of hydrogen-containing ferroelectrics are substantially determined by hydrogen bonds. Therefore, the investigation of properties in nanocomposites based on NCC with hydrogen-containing ferroelectric TGS as a filler is a particular interest. In the present work, with the purpose of comparing phase transition properties of hydrogen-containing and non-hydrogen-containing ferroelectric inclusions we used triglycine sulfate (TGS) as a hydrogen-containing filler and Sodium Nitrite ($NaNO_2$) as a non-hydrogen-containing filler embedded into NCC matrix for analyzing the influence of hydrogen-bond system on electrophysical properties of these composites. It should be noted that in a previous study [9], a shift of phase transition point in the composite based on NCC and TGS to higher temperatures was found. However, the phase transition nature of the indicated composite was not explained by a persuasive method based on mathematical aspects, that will be added in the present work.

2 MATERIAL PREPARATION AND EXPERIMENTAL METHODS

The samples of composite nanocrystalline cellulose – triglycine sulfate (NCC+TGS) and nanocrystalline cellulose – Sodium Nitrite (NCC+$NaNO_2$) were prepared by using gel films from nanocrystalline cellulose synthesized by Acetobacter Xylinum bacteria [10] as a reinforcement matrix, TGS salt $(NH_2CH_2COOH)_3{\cdot}H_2SO_4$ and Sodidum Nitrite $NaNO_2$ – as ferroactive fillers.

The nanocrystalline cellulose synthesized by Acetobacter Xylinum bacteria belongs to the monoclinic system, its structure consists of microfibrillar ribbons playing role of not only a reinforcing grid, but also the hydrophilic layers, which are able to absorb on their surface water molecules as well as other water-soluble compounds. The sorption and desorption properties of NCC are explained by the presence of a large number of nanochannels with a width of 50-100 nm and a length exceeding the width of a thousand or more times, that is formed from the faces (–110) and (110) with high surface energy caused by the primary OH – groups on these faces [10-12].

Pure sodium nitrite $NaNO_2$ is a ferroelectric at room temperature with a structure belonging to the body-centered orthorhombic group. The unit cell dimensions of sodium nitrite according to X-ray studies [12] at temperature of 338 K are a= 3.5817 Å, b= 5.5873 Å, c = 5.3869 Å, V_c = 107.801 Å^3. The phase transition to ferroelectric state occurs at $T_C \approx +164$ ºC. Nanoparticles of sodium nitrite can be easily embedded into various matrices such as porous glass, aluminum oxide, SBA-15 or opal [1,6,13-17] with pores at nanoscale level due to their high wettability.

TGS crystal is monoclinic and belongs to the $P2_1$ space group. The transition from ferroelectric to paraelectric phase (Curie point) is equal +49 ºC [13]. In paraelectric phase, the space group becomes $P2_1/m$ with two mirror planes *m* at *y* = ¼ and ¾. The spontaneous polarization in the ferroelectric phase is related to the asymmetrical arrangement of three glycine groups. The hydrogen-bond system plays a leading role for all properties of TGS and in compounds with TGS inclusion.

For the study on dielectric properties of the composites we prepared samples from partially dried nanocrystalline cellulose with TGS or $NaNO_2$ inclusions. From the initial gel films of NCC water was removed by filter paper to reduce the sample thickness approximately by twice. The saturated TGS or $NaNO_2$ solutions heated up to +50 ºC was introduced into these NCC pieces, drop by drop in several stages, each time to complete absorption from both sides. The NCC nanochannels are perpendicular with respect to the sample surface. The crystal structure consists of SO_4^{2-}, $2(N^+H_3CH_2COOH)$ and $^+NH^3CH_2COO^-$ species held together by hydrogen bonds.

The prepared samples were heated to +100 ºC, kept for 3 hours at this temperature to completely remove residual water and then dried at room temperature. The obtained composite films with a thickness of ~ 0.3 ÷ 0.4 mm were cut into samples with a surface area of ~ 35 mm^2.

Dielectric measurements were carried out by using a digital LCR-821 meter in a weak electric field with an amplitude of 1 V·cm^{-1} in temperature ranges from room temperature to 120 ºC (for NCC+TGS composite) and 170 ºC (for NCC+$NaNO_2$). The measurement error did not exceed 1%. A digital thermometer with an error of 0.1 K measured the temperature. All data were automatically recorded on the computer.

3 EXPERIMENTAL RESULTS AND DISCUSSION

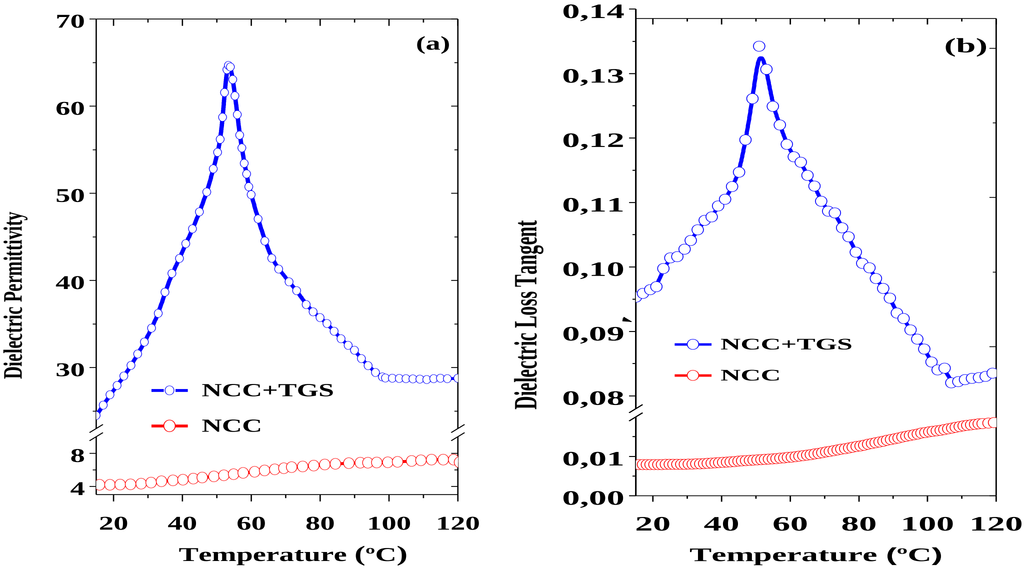

Figure 1. Temperature dependences of dielectric constant (a) and dielectric loss tangent (b) for the samples of NCC+TGS composite and NCC matrix.

Figure 1 shows the temperature dependences of dielectric constant *ε(T)* (Fig.1a) and dielectric loss tangent *tgδ(T)* (Fig.1b) for the composite based on TGS nanoparticles embedded into an initial dried NCC matrix (NCC+TGS) and for NCC matrix only. As seen in Fig. 1, in the case of NCC+TGS composite, a maximum is observed for all two of *ε(T)* and *tgδ(T)* at temperature ~ +54 ºC i.e. higher than the phase transition temperature in TGS single crystals (+49 ºC) by 5 ºC. In addition, the phase transition maximum is strongly smeared as compared to those for TGS single crystals [12]. For the initial NCC matrix, the indicated maximum doesn't appear and the values of *ε* and tg*δ* for NCC matrix are quite small in comparison with those of the NCC+TGS composite. It should be noticed that the experimental results for NCC matrix agree well with the published data [10].

Temperature dependences of dielectric constant *ε(T)* and dielectric loss tangent *tgδ(T)* for NCC+$NaNO_2$ composite and NCC matrix at 1 kHz from room temperature to the highest possible heating temperature for NCC matrix (+170 ºC) are represented in Fig. 2. As seen in Fig. 2a for NCC+$NaNO_2$ composite, there is only an increase of dielectric constant ε observed with increasing temperature without the presence of the peak typical for single crystal of $NaNO_2$ (+164 ºC). This behavior was also observed for the composite based on nanoporous Al_2O_3 with $NaNO_2$ inclusions [14,15]. The values of dielectric constant in the studied composite unlike those for the composite NCC+TGS are comparable to other composites created by different matrices such as aluminum oxide, glass with $NaNO_2$ inclusion [14-16]. The character of temperature dependences of dielectric loss tangent (Fig. 2b) is different from those for Al_2O_3+$NaNO_2$ composites [14,16], in which maxima of *tgδ(T)* were observed. In the case of NCC matrix, the values of *ε* and *tgδ* are quite small as compared to those for NCC+$NaNO_2$ composite.

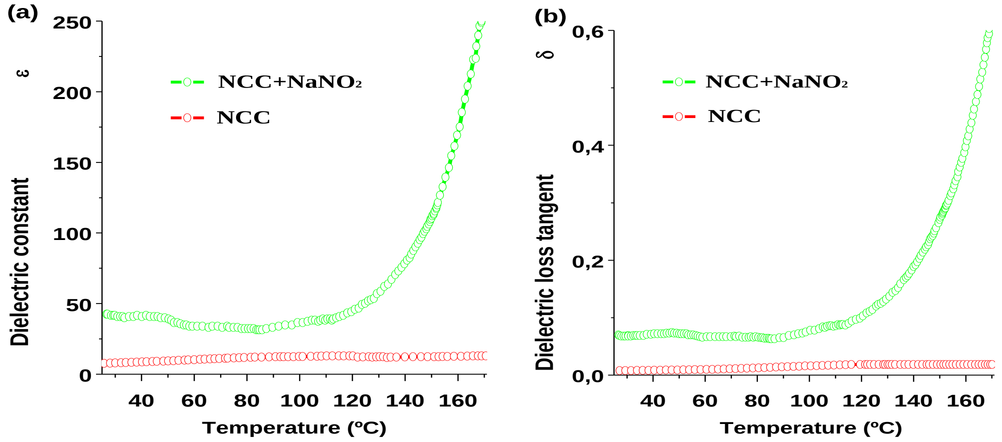

Figure 2. Temperature dependences of dielectric constant (a) and dielectric loss tangent (b) for NCC+$NaNO_2$ composite and NCC matrix.

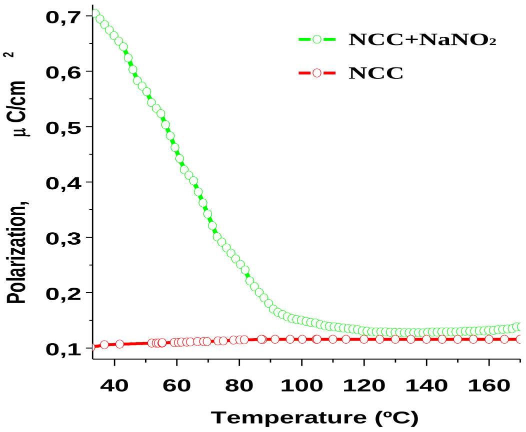

Figure 3. Temperature dependences of polarization for NCC+$NaNO_2$ composite and NCC matrix.

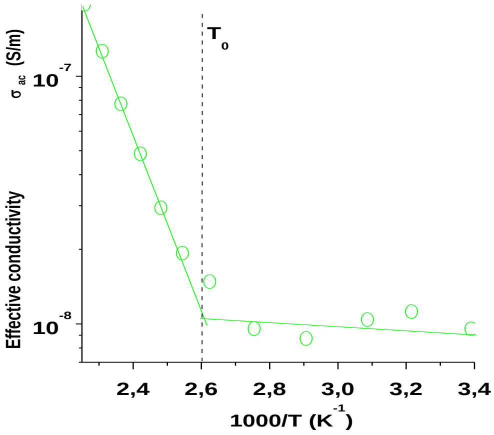

Figure 4. Dependence of conductivity on the reciprocal of temperature for NCC+$NaNO_2$composite.

Due to the lack of a typical peak of *ε(T)* for phase transition in $NaNO_2$ particles embedded into NCC matrix in the studied temperature range, we should carry out additional experiments related to the change of polarization values and conductivity with changing temperature as represented in Fig. 3 and Fig. 4 respectively. Ferroelectricity in NCC+$NaNO_2$ composite becomes more pronounced in the temperature dependence of polarization *P(T)* (Fig. 3). It is clearly seen in Fig. 2 that the values of polarization in the composite NCC+$NaNO_2$ decreases with increasing temperature in the interval from 35 ºC to about 110 ºC, but not reach to zero as always seen in single crystals of ferroelectrics at phase transition temperature [13]. These values decrease up to a certain value (~ 0.12 $\mu C/cm^2$) and practically remain unchanged with a further increase of temperature. The possible existence of phase transition in the composite NCC+$NaNO_2$ is also indicated by the dependence of effective conductivity σ_{ac} on the reciprocal of temperature, which was found from the data of dielectric loss:

$$\sigma_{ac} = \omega\varepsilon_0\varepsilon' tg\delta \qquad (1)$$

where $\omega=2\pi f$ – the angular frequency of an applied field, ε_0 – vacuum permittivity, ε' – the real part of complex dielectric permittivity, *tgδ* – dielectric loss tangent.

As seen in Fig. 4, a fracture of $\sigma_{ac}(1/T)$ was observed at temperature 110 °C. It should be noted that the similar anomaly is always observed for the bulk of $NaNO_2$ at phase transition temperature, for which the dependence of effective conductivity on the reciprocal temperature is determined by the formula [17,18]:

$$\sigma_{ac} = \begin{cases} \sigma_1 + \sigma_{01}\exp(-\frac{U_1}{kT}) \quad at \quad T < T_C \\ \sigma_2 + \sigma_{02}\exp(-\frac{U_2}{kT}) \quad at \quad T > T_C \end{cases} \tag{2}$$

where k - Boltzman constant, σ_{01} and σ_{02} – constants, σ_1 and σ_2 – non-activation types of conductivity, U_1 and U_2 – activation energy in ferroelectric ($T<T_c$) and paraelectric ($T>T_c$) phases respectively. In the case of single crystals of $NaNO_2$, the values of activation energy U of conductivity decrease in the ferroelectric-to- paraelectric phase transition [17,18].

Thus, despite the absence of the typical maximum for the phase transition in NCC+$NaNO_2$ composite in the temperature dependence of dielectric constant $\varepsilon(T)$, the decrease of polarization with increasing temperature up to a minimum value at 110 °C, and also the presence of a fracture of effective conductivity at the same temperature can be considered as an evidence of the presence of phase transition in the composite NCC+$NaNO_2$ at temperature 110 °C, i.e. lower than the phase transition temperature in the massif $NaNO_2$ (T_c = +164 °C).

The second one practically plays a leading role in all cases of embedding ferroelectric particles into pores. The influence of interaction between TGS nanoparticles embedded into pores on phase transition in TGS can be describded by using the expansion of free energy in accordance with Landau-Ginzburg-Devonshire theory [19], where the quantity of polarization plays the role of order parameter. In this regard, we consider TGS nanoparticles arranged in NCC matrix at similar distances from each other. In this case, the Gibbs free energy of the system from nanoparticles can be written as the sum of the energy of nanoparticles and their binding energy. Landau-Ginzburg-Devonshire expansion for the free energy density of a heterogeneous system includes not only different orders of the order parameter, but also derivatives of the order parameter with respect to coordinates. In the case of an ideal isotropic system, the first derivatives of order parameter can be included in the expansion only in the form of a scalar combination $(\mathrm{grad}P)^2$, and therefore, it can be written in the general form as follows [19]:

$$F(P(\mathbf{r}),T) = \frac{1}{2}\alpha(T)P^2(\mathbf{r}) + \frac{1}{4}\beta P^4(\mathbf{r}) + \frac{1}{4}\gamma P^6 + \frac{1}{2}\delta(\mathrm{grad}P(\mathbf{r}))^2 - EP, \tag{3}$$

where the constant δ characterizes the degree of heterogeneity of polarization. Thus, the free energy of the system of ferroelectric particles (in the absence of external electric fields) can be written as the sum of energies of TGS particles and dipole-dipole interaction between them (W_{dd}):

$$F = \sum_i \int_V \left(\frac{1}{2}\alpha P_i^2 + \frac{1}{4}\beta P_i^4 + \frac{1}{2}\delta(\nabla P_i)^2 \right) dV_i + W_{dd}. \tag{4}$$

According to [21] when considering the interaction between electric dipoles in a polarized medium, we must take into account the difference between the field acting on a dipole and the macroscopic electric field. This difference leads to the fact that the intrinsic dipole moments do not directly contribute to the energy of dipole-dipole interaction, but their effective values $\mathbf{p}^*$:

$$W_{dd} = \sum_{i,j} \int_V \int_V \left[\frac{\mathbf{p}_i^* \mathbf{p}_j^*}{r_{ij}^3} - \frac{3(\mathbf{r}_{ij}\mathbf{p}_i^*)(\mathbf{r}_{ij}\mathbf{p}_j^*)}{r_{ij}^5} \right] dV_i dV_j = \sum_i \mathbf{p}_i^* \mathbf{E}_i^*, \tag{5}$$

where V_i, V_j are volumes of TGS particles, r_{ij} is extrapolation length, which is determined by the distance between particles in the composite, $\mathbf{E}^*$ is effective field acting on i^{th} dipole from the nearest neighbors.

It follows from equation (5) that the phase transition temperature $\tilde{T}_o$ of the system of bound particles is determined by [22]:

$$\tilde{T}_\text{o} = T_\text{o} - \frac{1}{\alpha_\text{o}} W_{dd} = T_\text{o} - \frac{1}{\alpha_\text{o}} \sum_i \mathbf{p}_i^* \mathbf{E}_i^*, \tag{6}$$

where T_o is the phase transition temperature in the bulk of ferroelectric.

The energy of dipole-dipole interaction W_{dd} depending on the arrangement and orientation of dipole moments of particles in neighboring pores can have both positive and negative values. However, on the basis of general physical considerations we can conclude that dipole moments of TGS particles in neighboring pores are oriented so that their fields can be compensated by each other, i.e. $W_{dd} < 0$ and the dipole-dipole interaction reduces the free energy of each particle. The latter leads to the increase in ferroelectric phase transition temperature in an ensemble of interacting particles as compared to those for an insulated small particle [23].

Moreover, the shift of phase transition temperature for the NCC+TGS composite to higher temperatures as compared to the bulk of TGS may be related also to the presence of hydrogen bonds in the matrix and ferroelectric inclusion. These bonds fix the polarization in the contact region of components in the composite and tighten it to the range of higher temperatures.

The small values of dielectric constant for the NCC+TGS composite with the matrix from nanocrystalline cellulose in comparison with the composites based on other nanoporous matrices such as Al_2O_3, silica and glass with triglycine sulfate are most likely related to the strong interaction between TGS nanoparticles and NCC matrix, decreasing polarization near contact region and hampering the reorientation of dipole moments in TGS crystallites in the composite. Another reason could be a low degree of filling cellulose by triglycine sulfate.

The observed smearing of the phase transition is obviously conditioned by the nonsimultaneous phase transition in different TGS crystallites in the composite and by a native nanochannel diameter dispersion in the initial NCC matrix and its nonuniform filling with TGS nanocrystals.

The decrease of phase transition temperature in nanoparticles of $NaNO_2$ can be associated with the absence of strong chemical interaction of NCC matrix with the embedded material due to the compact molecular structure of sodium nitrite [13,24] together with the simultaneous influence of tilting polarization created by the depolarization field due to the accumulation of bound charges at the surface of nanoparticles.

The sharp rise in the dielectric constant with increasing temperature can be related to the rapid increase of the melting phase proportion in the nanoparticles and to the appearance of high-mobility ions Na^+ here.

4 CONCLUSIONS

The study showed a significant influence of the matrix of nanosrytalline cellulose on properties of hydrogen-containing triglycine sulfate nanoparticles embedded into this matrix as compared to those of non-hydrogen-containing sodium nitrite. The shift of phase transition temperature of these nanoparticles to higher temperatures is related to the dipole-dipole interaction between themselves in the case of sodium nitrite as well as the interaction between the matrix and TGS inclusion fixing the polarization in the ferroelectric inclusion due to hydrogen-bond system. The smearing of phase transition is conditioned by the nanochannel diameter dispersion in the initial NCC matrix and its nonuniform filling with TGS nanocrystals. A mathematical expansion based on Landau-Ginzburg-Devonshire theory was used to explain the obtained results. The specified causes leading to the changes in electrophysical properties of the studied nanocomposites can be considered as an effective way to practically control useful properties of materials for electronic engineering.

ACKNOWLEDGMENT

The study was supported by Russian Science Foundation, Project N 14-12-00583.

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Received on April 26 – 2017

Revised on October 24 – 2017