Amino-acid Based Ferroelectric Nanocomposites from Glycine Sodium Nitrate and Nanodispersed Silicon Dioxide: Preparation, Structure and Electrophysical Properties

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For the first time, the nanocomposites from glycine sodium nitrate (GSN) and nanoparticles of silicon dioxide (nSiO2) have been synthesized using a slow evaporation technique. Observed that the optimal content of nSiO2 was estimated as 16.7 wt.%, any deviation from which affected the growth of GSN crystals in the composite, phase transition temperature, dielectric constant, and characteristics of dielectric hysteresis loops. All the anomalies will be thoroughly explained with the evidence of structural data of X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

Keywords: glycine sodium nitrate, silicon dioxide, phase transition, amino acids, ferroelectricity.

1. INTRODUCTION

The ferroelectric materials containing amino acids in general and glycine in particular (triglycine sulfate [1 – 4], glycine sodium nitrate [5], glycine silver nitrate [6], glycine phosphate [7], etc.) have been widely applied in biosensors, infrared sensors, NLO, memories [4, 8, 9] due to their good mechanical and electrical stability, wide transparency and high sensitivity. In this context, glycine sodium nitrate (GSN) is known as a semi-organic compound from sodium nitrate and glycine which create hydrogen bonds between donor carboxylic acid (COOH) and accepter amino (NH2) [5], resulting in the formation of valuable electro-optic properties for NLO applications. From our point of view, the current applications of GSN are not commensurate with its potential. Indeed, some primary properties of GSN are even better than those of triglycine sulfate (TGS) such as the considerably high spontaneous polarization $P_s \sim 1 \mu \text{C/cm}^2$ with a small coercive field $(E_c \sim 5 \text{kV/cm})$ at room temperature, the higher Curie point of $T_c \sim 56 \degree \text{C}$ in comparison with 49 $\degree \text{C}$ of TGS [5]. While TGS characteristics have been regularly adjusted to meet new practical requirements by combining with other materials or adopting appropriate substances, GSN has been of little interest. As far as we are concerned, there have been no works dedicated to the improvement of primary GSN properties. GSN is mostly applied in the form of as-grown single crystals. In today's science and technology era, it is rare to use pristine material in practice. In this regard, improving GSN electrophysical properties is necessary to expand not only our fundamental understanding, but also the scope for new applications.

In the present work, nanoparticles of silicon dioxide (nSiO2) were utilized to synthesize a composite with GSN. Silicon dioxide has been found in several applications in the role of a good insulator with high thermal and electrical stability [10 – 13]. Especially, at the nanoscale level, it has large specific surface areas that enhance the interactive ability with other components. In this study, different compositions (weight ratios) of nSiO2 and GSN will be considered to evaluate the influence of nSiO2 on structures as well as the electrophysical properties of GSN.

2. SAMPLES SYNTHESIS AND EXPERIMENTAL TECHNIQUES

The procedure for the preparation of nSiO2/GSN nanocomposite is illustrated in Fig. 1 using the slow evaporation technique. Firstly, the two starting materials of glycine and NaNO3 with a mole ratio of 1:1 were dissolved into deionized water to get a saturated solution at room temperature. After 2 h of stirring using a magnetic stir in a closed bottle, nanoparticles of silicon dioxide stored in the form of hydrosol ranged in size of 20 – 200 nm [14] were added so that the mass ratio of nSiO2:glycine + NaNO3 was of 0.1:1, 0.2:1, 1:1 and 3:1. All substances were mixed by the stirrer for 1h, then the mixture was kept at 20 $\degree \text{C}$ to slowly evaporate for about 40 days. Finally, a fresh mixture was obtained, taken out, dried at 100 $\degree \text{C}$ for 2 h to remove residual water and pressed into circle samples with a radius

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of 2 mm and a thickness of 1 mm. A silver glue was applied on a large surface to make electrodes for dielectric measurements. For comparison, the crystals of GSN were also synthesized through the same procedure.

Before measuring dielectric characteristics, the structures of nSiO2/GSN nanocomposite samples were carefully investigated using X-ray diffraction (Rigaku Ultima IV) and Fourier-transform infrared spectroscopy (Bruker Tensor 37, USA). For testing electrophysical properties, a silver conductive paste (7440-22-4-Sigma-Aldrich) was applied on the sample surfaces. The ferroelectric/ferroelectric phase transition was observed on the spectra of dielectric constant (GW Instek LCR-821 meter) from 30 – 110 °C, while the relaxation features were conducted in the range of 1 – 107 Hz on an impedance gain/phase analyzer (Solartron-1260A, UK). Besides, the switching characteristics of the composite were taken on a Precision LC tester (Radiant Technology, Korea).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Structure features

For GSN which is mostly applied in practice in the form of single crystals, the quality of the crystalline structure is one of the most important criteria considered to confirm the success of a preparation process. In our case with the participation of nSiO2, the results could be very different from the pure samples, and therefore the crystalline structure of the synthesized composite must be checked more carefully. According to the exported XRD patterns (Fig. 2), the obtained GSN crystals were reliable with several characteristic peaks at 20 = 13.97° (-201), 18.18° (110), 19.49° (-111), 22.24° (002), 23.09° (-311), 25.04° (-402), 26.15° (310), 28.31° (400), 31.82° (202), 33.88° (311), 34.42° (-313), 36.49° (220) and 39.56° (-220) which are in good agreement with those reported in literature [5, 15]. It is worth to note that our experiments and reported works [5, 15] showed a high sensitivity of crystalline structure to synthesis conditions. In this regard, there were differences in XRD patterns observed by the authors. In our case, all main peaks of GSN were detected. In the presence of nSiO2 in the structures, the crystallinity degree decreased, even though the positions of peaks were not moved (Fig. 2). For samples with nSiO2:GSN of 0.2:1 or lower nSiO2 content, most of the GSN peaks were obtained (Fig. 2 b). However, at higher than 75 % of nSiO2, the crystalline structure might be not formed with only a few small peaks in the XRD pattern (Fig. 2). Likely, the nSiO2 disturbed the growth of GSN crystals.

Fig. 1. Scheme for preparation of nSiO2/GSN nanocomposite

![Diagram of preparation process](image)

Fig. 2. a – XRD patterns; b – FTIR spectra of nSiO2, GSN and the composites at different compositions

![Graphs showing XRD and FTIR spectra](image)
of GSN peaks. The wavenumber of 528 cm\(^{-1}\) seems to be originated from free glycine [20] that is probably left over after synthesis because of not combining with NaNO\(_3\) to form GSN. This is in good agreement with the decreased crystallinity observed in XRD patterns toward high-nSiO\(_2\)-content samples.

### 3.2. Phase transition

Phase transition plays a leading role in most the applications in electronics using ferroelectric-based materials. In our experiments, the phase transition for the composite was investigated by measuring the dependences of dielectric constant \(\varepsilon\) on temperature \(T\) from 30 to 100 °C (Fig. 3). Observing that \(\varepsilon(T)\) has peaks at 60.2, 63.8 and 69.2 °C for samples of nSiO\(_2\):GSN = 0.2:1, 1:1 and 3:1, respectively. In other words, in the presence of nSiO\(_2\), the phase transition temperature was higher than that of pure GSN (\(T_c = 56 °C\) [5]). Besides, the higher the nSiO\(_2\) content was, the greater the phase transition temperature obtained (Fig. 3). This was good because the ferroelectric phase was expanded. However, for the composite samples with high nSiO\(_2\) content, the values of dielectric constant sharply dropped (< 40) when nSiO\(_2\) content was higher than 50 % as seen in the inset of Fig. 3. According to our experiments, the highest \(\varepsilon\) might reach 1000 at nSiO\(_2\):GSN = 0.2:1 and this composition can be considered optimal. The explanation for that will be given in detail in this paper.

![Fig. 3. The results for phase transition testing for composite samples containing different nSiO\(_2\) content](image)

### 3.3. Switching properties

Switching properties characterizing the reversal of polarized molecules, groups of molecules or domains are very important when applying ferroelectrics in practice. Besides, clarifying their switching properties may help to figure out the behaviors of structural elements in materials [21]. The above structural analysis (XRD, FTIR) and phase transition indicated that the composite samples with the increased nSiO\(_2\) content were of lower quality. To confirm once again this conclusion, the switching features for the synthesized composite were also investigated as presented in Fig. 4. Firstly, it is worth to emphasize that the dielectric hysteresis loop for pure crystals of GSN obtained in our preparation process has a similar shape to that reported in the literature [5]. Besides, the values of saturated polarization (\(P_s = 0.96 \mu\text{C/cm}^2\)), remnant polarization (\(P_r = 0.83 \mu\text{C/cm}^2\)) and coercive field (\(E_c = 3.28 \text{kV/cm}\)) at room temperature (Table 1) were comparable with the published data [5]. When combined with nSiO\(_2\), the decrease in \(P_s\), \(P_r\) and the increase in \(E_c\) were detected (Table 1). The P-E loops gradually lost the characteristic shape with increasing nSiO\(_2\) content (Fig. 4). This anomaly seems to be consistent with those of XRD, FTIR and \(\varepsilon(T)\) described above. According to our experiments, samples with the weight ratio of nSiO\(_2\):GSN = 0.2:1 can be considered as optimal because any deviation from that led to unexpected consequences. Indeed, the higher nSiO\(_2\) content might reduce the dielectric constant (Fig. 3) and hinder the switching process (Fig. 4), while the lower nSiO\(_2\) content resulted in the reduction of phase transition temperature (Fig. 3).

![Fig. 4. P-E hysteresis loops for pure GSN and composite samples with different compositions at room temperature and 1 kHz](image)

### 3.4. Frequency response of nSiO\(_2\)/GSN composite

Because the frequency is related to the reversal speed of the external electric field that directly affects the behavior of charged groups in materials, analyzing electrophysical parameters at different frequencies is valuable to explore the structure as well as ferroelectricity of ferroelectric-based compounds. The samples of optimal nSiO\(_2\):GSN = 0.2:1 were chosen for these experiments. The results are shown in Fig. 5 in the form of frequency dependences of the real \(\varepsilon'\) (Fig. 5 a) and the imaginary \(\varepsilon''\) (Fig. 5 b) permittivity at different temperatures in the polar phase (\(T < T_c = 60.2 °C\)). Obviously, at each temperature, the increase in frequency led to the monotonic decrease in \(\varepsilon'\) (Fig. 5 a) that is in good agreement with those of pure GSN crystals [5]. However, in the dependences of \(\varepsilon''(f)\) (Fig. 5 b), a deviation from the reported pure GSN was found with the appearance of a peak. Noted [22] that the presence of peaks on \(\varepsilon''(f)\) at frequencies of \(10 – 10^7\) Hz was also observed in TGS which belongs to

<table>
<thead>
<tr>
<th>Composite samples</th>
<th>(P_s), (\mu\text{C/cm}^2)</th>
<th>(P_r), (\mu\text{C/cm}^2)</th>
<th>(E_c), \text{kV/cm}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure GSN</td>
<td>0.96</td>
<td>0.83</td>
<td>3.28</td>
</tr>
<tr>
<td>nSiO(_2):GSN = 0.2:1</td>
<td>0.86</td>
<td>0.73</td>
<td>3.94</td>
</tr>
<tr>
<td>nSiO(_2):GSN = 1:1</td>
<td>0.35</td>
<td>0.13</td>
<td>2.69</td>
</tr>
<tr>
<td>nSiO(_2):GSN = 3:1</td>
<td>0.12</td>
<td>0.05</td>
<td>2.07</td>
</tr>
</tbody>
</table>

![Table 1. The values of \(P_s\), \(P_r\), \(E_c\) for the composite at different compositions](image)
the glycine-containing ferroelectric family as GSN. This peak shifted toward higher frequencies at higher temperatures (Fig. 5 b), indicating the activation nature of the relaxation process. The relaxation time $\tau$ can be calculated from the relaxation frequencies $f_r$ taken at the peaks by $\tau=1/2\pi f_r$.

The dependences of relaxation time on inverse temperature are presented in Fig. 6. Apparently, there were two relaxation processes corresponding to two activation energies of 1.52 and 2.57 eV observed at $10 - 10^7$ Hz in the ferroelectric phase of nSiO$_2$/GSN.

3.5. Discussion

Firstly, the obtained results allow us to conclude that the use of nSiO$_2$ content higher than the weight ratio of 0.2:1 or 16.7 wt.% may cause several consequences as the drop of $\varepsilon$ (Fig. 3) and $P_s$ (Fig. 4), as well as the distortion of the dielectric P-E hysteresis (Fig. 4). The reason for that might be related to the presence of nSiO$_2$ that hindered the contact between glycine and NaNO$_3$ during the growth of crystals evidenced by the lack of peaks in the XRD pattern (Fig. 2 a) and the rise of free glycine left over in FTIR spectra (Fig. 2 b), resulting to the shrinking of GSN volume in the synthesized samples. Consequently, the ferroelectricity of the composite showed less clearly. Notably, regardless of whether the free glycine is left over or not, the addition of the dielectric component of nSiO$_2$ indisputably reduces the GSN volume and therefore the ferroelectricity becomes weaker. Commonly, the change of electrophysical parameters gradually occurs during heating in the polar phase [1, 2]. Likely, the main reason in our case was not associated with that due to the sudden drop of $\varepsilon$ and $P_s$.

When increasing nSiO$_2$ content, the observed increase in phase transition temperature $T_c$ (Fig. 2) and coercive field $E_c$ (Fig. 3) might be referred to the stronger interaction between nSiO$_2$ nanoparticles and GSN crystals through hydrogen bonds due to residual water. Indeed, the residual water molecules can be completely removed from nSiO$_2$ at higher than 500 °C [18], while the synthesized samples were heated up to 100 °C. If this assumption was true, the polar phase of GSN became more stable and turned into the paraelectric phase at higher temperatures. At the same time, the greater number of nSiO$_2$ nanoparticles surrounding GSN crystals could create a stronger interaction, leading to the difficulty in moving domain walls i.e. to the rise of $E_c$.

The appearance of maxima in $\varepsilon''(f)$ can be understood because the interaction between nSiO$_2$ nanoparticles and GSN crystals could cause the increase in viscosity for that the relaxation frequencies $f_m$ can be estimated as follows [1]:

$$f_m = \frac{1}{\eta D},$$

where $\eta$ is the viscosity coefficient and $D$ is the width of domains. With increasing temperature, the viscosity decreased, leading to an increase in relaxation frequencies (Fig. 5 b).

The activation energies of 1.52 and 2.57 eV are significantly higher than those reported in the literature for pure GSN [5]. Known [5, 23] that the activation energy of proton transfer in glycine zwitterion as for GSN is about 0.69 eV. It allows us to assume that there was the contribution of hydrogen bonds to potential barriers. In this regard, the decrease in $E_c$ from 2.57 to 1.52 eV might be referred to less stable hydrogen bonds with increasing temperature.
4. CONCLUSIONS

The study successfully estimated the optimal content of silicon dioxide nanoparticles for preparation of composite with glycine sodium nitrate as 16.7 wt.%. At which the phase transition point increased by 4.2 °C while the dielectric constant and spontaneous polarization slightly decreased. The higher nSiO₂ content might inhibit the growth of GSN crystals, resulting in a sharp decrease in dielectric constant and spontaneous polarization, as well as the distortion of dielectric hysteresis loops. Besides, the increased nSiO₂ may strengthen the growth of GSN crystals, resulting in a sharp decrease in dielectric constant and spontaneous polarization, as well as the distortion of dielectric hysteresis loops. The obtained results provide a considerably simple but effective approach for improving the properties of the amino-acid based ferroelectric family.

REFERENCES


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