The paper presents findings on the characteristics of GaSe fourfold-expanded matrix with propolis and sodium nitrite (NaNO₂), intercalated in between matrix layers. The nature of changes of impedance frequency behavior, electric loss tangent, and dielectric permittivity under normal conditions, when illumination is applied, and in a constant magnetic field of synthesized intercalate GaSe < NaNO₂ > and bi-intercalate GaSe < NaNO₂ + Propolis > has been identified. The extraordinary effects have been obtained, indicating that clathrate GaSe < NaNO₂ > has immense values of photo- and magneto-capacitive effects while a current–voltage (I–V) characteristic of clathrate GaSe < NaNO₂ + Propolis > exhibits the hysteresis behavior typical of memristor structures. The memory effect related to pseudo-capacitive charge accumulation has been found and shown to be due to oxidation–reduction reactions.

**Keywords** Clathrate · Propolis · Photo-capacitive effect · Magneto-capacitive effect · Memristor effect

**Introduction**

The formation of heterostructured inorganic/inorganic, inorganic/organic and bio/inorganic clathrate compounds is attracting more and more attention of experts in all science domains. This interest results from a wide range of new properties that emerge in the said compounds. Along that way, a notable progress has been achieved in supramolecular chemistry. However, there are not so many published works focused on exploring physical properties of supramolecular complexes and their clathrate compounds. In terms of practical use, experimental results of semiconductor clathrates—such as phonon glass—which are one of the most promising thermoelectric materials demonstrate a vivid example (Beekman et al. 2015). A solution was practically found to the Slack hypothesis (Slack 1995, 1997) about the formation of structures in which loosely bound atoms can range in a limited volume, ensuring low thermal conductivity at high electrical conductivity (Shevelkov et al. 2011). As for other physical aspects of supramolecular host–guest ensembles, attention should be drawn above all the works on electronic structure calculations (Borsch et al. 2009) or excitation energy transfer systems (Ibrahim et al. 2002).

With an interest in clathrates, an issue of a size effect in such compounds, for example, the ferroelectric polarization behavior (Patent PCT BY 2000) when a critical size of ferroelectric domains and a change in the Curie temperature exist was brought to the foreground. This has been proved by the use of porous matrices whose typical pore size (Krohns et al. 2009; Hai et al. 2009; Fridkin 2006; Fokin et al. 2002; Vakhrushev et al. 2004; Baryshnikov et al. 2008; Tien et al. 2005 and associated references) is in a nanometer range. Thus, unlike the bulk material, NaNO₂ nanoparticles exhibited a temperature shift of a ferroelectric phase transition toward the low-temperature region at 18 K and a sharp increase in the permittivity from 10² to 10³, whereas the permittivity of nanocomposite SBA-15 < NaNO₂ > with a pore size of 52 Å was equivalent to 10³ (Murzina et al. 2007). The same is true for ammonium sulfate in pores of a molecular lattice matrix MCM-41 with the pore size of 40 Å (Tien et al. 2008). In this case, permittivity is considerably lower (for macrostructures, 235 versus 27). In a
mixed ferroelectric guest material $NaNO_2 + KNO_3$ intercalated in pores of MCM-41, the shift in the temperature of ferroelectric phase transition toward a high-temperature region was observed and the permittivity of nanocomposite MCM-41 $<NaNO_2 + KNO_3>$ simultaneously increased up to $10^4$ (Yadlovker et al. 2005). Recently, it was shown by the authors of this work that 2D nanostructured SmCl$_3$ in semiconductor GaSe matrix demonstrated spontaneously generated electromotive force of around 10 V at room temperature what is two orders higher if compare to known structures (Ivashchyshyn et al. 2021).

Understanding of regularities of ferroelectric behavior of encapsulated nanocomposites is far from complete. Undeniably, the physical properties of nanoparticles under conditions of a limited guest geometry greatly differ from the properties of corresponding bulk materials due to their quantum size effects and interaction with matrix walls. An examination of nanoconfinement-induced changes of material properties is essential to successfully apply nanocomposites based on porous matrices (Ptashnyk et al. 2018; Bishchaniuk et al. 2014). The noteworthy feature here is that a replacement of a dielectric matrix with a semiconductor one provides not only broader opportunities for variation of nanocomposites properties, but also gives rise to new unique phenomena and effects that appear. For example, a large shift of the Curie point toward low temperatures at 125 K is observed for InSe $<NaNO_2>$ as reported in Kurnaev (2005) and Grygorchak et al. (2017). Accordingly, charge accumulation at interfaces, which in turn is a quantum analog of an electrochemical battery, is attributable to GaSe $<NaNO_2 + FeSO_4>$.

**Experimental**

A photosensitive single-crystal gallium selenide (GaSe) was selected as a semiconductor quasi-2D matrix and sodium nitrite and propolis as a ferroelectric component and organic semiconductor, respectively.

The single-crystal GaSe grown by the Bridgman–Stockbarger method has a vividly expressed layered structure and p-type conductivity. The width of a bandgap is 2.02 eV as reported by optical data. As documented in Lies (1997), it is characterized by guest positions oriented perpendicular to the C crystallographic axis along of weak Van der Waals forces. Moreover, the single crystal shows high photosensitivity in the visible range of the spectrum.

The selection of sodium nitrite as a ferroelectric was based on its ability when melted to directly intercalate single crystals of gallium selenide due to Lewis base nature on nitrite ion. Propolis is being chosen as a biologically active organic substance that behaves similarly to a p-type semiconductor. It was also shown in Drapak et al. (2003, 2005) that electrical properties and a photosensitivity range of semiconductor/propolis structures are dependent on the phase of matter, on a method of its application onto semiconductor wafers and on the material of a wafer. As it was assumed in Drapak et al. (2004), despite an extremely complex chemical composition (Dontsov et al. 1992), the films of propolis exhibit a characteristic arrangement as in the case with some inorganic semiconductors that have a long-range arrangement. This assumption relies on good correlation between the activation energy for conductivity in investigated films and the bandgap in a certain temperature range (Drapak et al. 2004).

The formation of intercalated structure took place in two stages. At the first stage, sodium nitrite has been introduced into an initial matrix through the method of direct exposure of a semiconductor single crystal in its melt at a 300 °C temperature for 5–10 min. Because of an n-stage arrangement, the distance between the corresponding layers greatly increased (Ivashchyshyn et al. 2015). The intercalation lasted until the matrix GaSe expanded fourfold. At the second stage, the single-crystal GaSe intercalated with sodium nitrite was placed in a 10% alcohol solution of propolis for 24 h. Then, the sample was taken out and dried at the room temperature. The content of the guest component was monitored using precision gravimetric and chemical analyses.

Impedance measurements were made using AUTO-LAB measuring system (ECO CHEMIE, the Netherlands) equipped with FRA-2 and GpEs software in the direction of the crystallographic axis C in the frequency range of $10^3$–$10^6$ Hz. Uncertain points were filtered out with the Dirichlet-enhanced filter (Stoynov et al. 1991; Barsoukov et al. 2005). Frequency dependences of $Z$ complex-valued impedance were analyzed through the graph-analytical method using ZView 2.3 software (Scribner Associates). The approximation errors did not exceed 4%. The adequacy of plotted impedance models for a set of experimental data was confirmed by the completely random nature of frequency dependences of first-order residual differences (Stoynov et al. 1991; Barsoukov et al. 2005). The impedance dependences were measured under normal conditions, in a constant magnetic field of 2.75 kOe, and under illumination using a 65 W solar simulator (for the standard AM 1.5G solar spectrum, the total available power is 982 W/m$^2$) along the crystallographic axis C. This geometry of measurement was chosen to allow neglecting the Lorentz force.

The investigation of charge relaxation was carried out by means of thermally stimulated discharge method with linear heating in a temperature range of 240–350 K at a rate of 5 °C/min. The thermally stimulated discharge spectra were recorded in the mode of short-circuited contacts (Fig. 1).
Results and discussion

Conductive and polarization properties of GaSe expanded matrices were investigated and covered in Ivashchyshyn et al. (2015). This paper was aimed to examine the properties of clathrate GaSe<NaNO₂> with the bi-intercalated guest components. The purpose of this approach was to combine the properties of ferroelectric NaNO₂ and biologically active organic semiconductor propolis. Under this approach, such components, when placed into an inorganic semiconductor matrix with quasi-two-dimensional guest positions, were expected to yield characterizing properties of the formed structure.

As the intercalation took place in steps, the existing intercalates have been examined accordingly. First, the properties of intercalate GaSe<NaNO₂> were studied. Figure 2 shows the real part of the complex impedance as a function of the frequency (ReZ(ω)) under normal conditions and the classical behavior of ReZ(ω) was obtained. This behavior is frequency-independent over a wide range of 10⁻³–10³ Hz (curve 1 in Fig. 2). It should be noted that the introduction of NaNO₂ results in a sufficient increase in conductivity of 10³ times compared to the fourfold-expanded matrix (Ivashchyshyn et al. 2015). This is explained by an increase in the concentration of free charge carriers due to the introduction of a ferroelectric guest component into expanded layers. Impedance measurements in the constant magnetic field reveal a slight increase in resistance ReZ, as illustrated in the curve 2 (Fig. 2), which is most probably due to the Zeeman effect resulting in localization of free current carriers owing to redistribution of impurity levels above and below the Fermi level. A decreasing behavior of ReZ(ω) and its oscillation in the 1–20 Hz frequency range confers a more interesting result. In this case, oscillations may occur as a consequence of a certain state of an energy system where the condition of resonant quantum tunneling will be met. When illumination is applied, deformation of ReZ(ω) vividly intensifies and a frequency range in which it is seen extends to 1–10³ Hz (curve 3 in Fig. 2), indicating the phenomenon of quantum–mechanical resonance tunneling. Tunneling suggests that the frequency of an external electrical field that transfers localized charge carriers to higher energy levels in quantum wells thus meets the conditions of resonance tunneling through a set of potential barriers that divide quantum wells. Experimental observations show that the nonmonotonic character of such oscillations demonstrates nonideality of a N-barrier structure.

For a detailed analysis, let us consider the frequency behavior of an imaginary part (−ImZ(ω)) of the complex impedance as shown in Fig. 3. The presented dependences...
$-\text{Im}Z(\omega)$ demonstrate explicitly oscillations that occur when the constant magnetic field or illumination are applied to a sample separately (curve 2 and 3, respectively, in Fig. 3), confirming the above mechanisms of phenomena under investigation. In addition, there are clearly pronounced maxima in the high-frequency range. For measurements made under normal conditions, the maximum of dependence $-\text{Im}Z(\omega)$ is near $10^4$ Hz. When the constant magnetic field and illumination are applied, the maximum tends to shift toward the high-frequency region $-2.5 \times 10^3$ and $4 \times 10^3$ Hz, respectively, which corresponds to the bias in this region of dispersion decay $\text{Re}Z(\omega)$. This means that the applied constant magnetic field and illumination increase the effective relaxation time which account for the maximum in the distribution $\tau$.

Figure 4a shows the complex-valued impedance $Z$ of intercalate $\text{GaSe} < \text{NaNO}_2>$ in the form of a Nyquist diagram. In this case, the points represent measured values and the curve shows the model results of associated equivalent electrical circuits as demonstrated in Fig. 4b. When measurements are made under normal conditions, the Nyquist diagram represents a superposition of two semicircles shown as two R/C links when being plotted (equivalent electrical circuit 1 in Fig. 4b). The high-frequency link displays the transfer of electric charge through enlarged blocks of a semiconductor matrix and a low-frequency link—through enlarged and filled $\text{NaNO}_2$. When Under the influence of the constant magnetic field, the equivalent electrical circuit acquires a shape of the equivalent electrical circuit 2 as represented in Fig. 4b. The BCPE element (a finite element of the stationary phase) reflects how the current flows in a spatially confined region with complex conductivity. The CPE element (a capacitive element of the stationary phase) reflects the distributed capacitance stemming from the presence of vacancies or impurity defects that account for electronic conductivity at the room temperature. When illuminated, the impedance hodograph enters the IV quadrant of the complex plane. When being plotted, this plane is represented as an inductor (equivalent electrical circuit 3 in Fig. 4b). The physical nature of inductive behavior (this phenomenon is also called “negative capacitance”) in such structures is elaborated in Kostrobij et al. (2018).

The mechanism of the given “negative” photocapacitance is most likely associated with photon excitation of electrons out of occupied states below the Fermi level. In addition, this mechanism is related to the formation in this way of trapped centers for injected electrons that feature a relaxation time greater than the half-period of a sinusoidal signal.

The above-mentioned assumptions are confirmed by measured current of thermally stimulated discharge (Fig. 5). The dependence $I(T)$ strikingly shows a narrow-band character of an impurity energy spectrum with a homocharge relaxation.

Resulting effects and phenomena should be vividly reflected on the polarization characteristics of clathrate $\text{GaSe} < \text{NaNO}_2>$. Accordingly, the frequency behavior of permittivity shown in Fig. 6 was analyzed. For practical use of received results, the dependence $\varepsilon(\omega)$ is of interest in the frequency range where an electric loss tangent (tg$\delta(\omega)$) is

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**Fig. 4** a Nyquist diagrams are plotted in the direction perpendicular to the fourfold-expanded clathrate $\text{GaSe} < \text{NaNO}_2>$ measured under normal conditions (black), in the magnetic field (red), when illumination is applied (blue). b The equivalent electric circuit: (1) normal conditions, (2) magnetic field, (3) light

**Fig. 5** Spectra of thermally stimulated discharge for the fourfold-expanded clathrate $\text{GaSe} < \text{NaNO}_2>$. 

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less than 1 (inset to Fig. 6). Figure 6 and its inset show that \( \varepsilon \) starts to behave unusually once the following condition \( \tan \delta < 1 \) is met. Huge photo- and magneto-capacitive effects in the high-frequency range—\( \varepsilon_L/\varepsilon_D \approx 2000, \varepsilon_H/\varepsilon_0 \approx 40,000 \)—are attractive from the practical point of view. This structure acts like an ultra-sensitive capacitive sensor of the constant magnetic field and light and can be used for the fabrication of highly capacitive photo- and magneto-varicaps.

An appreciable increase in \( \varepsilon \), when illuminated, as reported in Žukowski et al. (2000) might take place due to additional polarization that occurs during hopping charge transfer. Formation or visualization of a photoelectric effect is most likely due to photo-induced multiply charged centers (Kurbanov et al. 2011). In fact, illumination of such substances leads to redistribution of charge carriers over discrete levels, polarization of certain centers, and change in the density of states (Anisimova et al. 2013). This, in turn, changes in permittivity give rise to the photodielectric effect. In variable electric fields, the photodielectric effect is characterized by a number of additional features because a complex spectrum of localized states is found to contribute to polarization processes of various energy levels depending on the field frequency and illumination.

In this case, a significant magneto-capacitive effect has been highly likely attributed to the Zeeman modification of an energy spectrum as well documented by the authors in Demin et al. (2006). This energy is followed by an increasing density of states near the Fermi level, which causes an increase both in the Maxwell–Wagner polarization and the additional one arising due to jumps of current carriers executed by localized states with energies close to the Fermi energy.

An increase in \( \text{Re}Z \) of two times and narrowing of the frequency range \( (10^{-2}–10 \text{ Hz}) \), curve 1 in Fig. 7) have been obtained at the next stage of intercalation of propolis into clathrate \( \text{GaSe} < \text{NaNO}_2 > \). Apparently, introduction of propolis causes an additional energy barrier for current to flow. However, the behavior of \( \text{Re}Z(\omega) \) remains the same. Oscillations (curve 2 and 3 in Fig. 7) that were inherent to clathrate \( \text{GaSe} < \text{NaNO}_2 > \) are observed, magnetosensitivity is found to slightly increase, and photosensitivity of \( \text{Re}Z \)—to decrease when the constant magnetic field and illumination are applied.

Figure 8 illustrates dependences of \( - \text{Im}Z(\omega) \). When measurements are made under normal conditions (curve 1 in Fig. 8), a shift of the maximum approaches the region of lower frequencies (140 Hz). Under the influence of the constant magnetic field, the maximum is shifted toward lower frequencies (90 Hz). It is noteworthy that this uncommon result, such as the shift of the main maximum toward higher frequencies (172 Hz) and visualization of an additional low-frequency maximum (172.2 Hz), is ascribed to illumination. This indicates that the light induces additional energy wells with the comparably longer relaxation time. Propolis, an organic semiconductor, could be the reason for the longer relaxation time.

Figure 9 demonstrates Nyquist diagrams plotted for clathrate \( \text{GaSe} < \text{NaNO}_2 + \text{Propolis} > \). As noted previously, the points represent measured values and the curve shows the model results of associated equivalent electrical circuits as demonstrated in Fig. 9b. Since the centers of the semicircles do not lie on the axis of X, the equivalent electrical circuits employ the capacitive element. It is important to note that the constant magnetic field (curve
in Fig. 9a) does not cause a horizontal line that has been typical for clathrate GaSe<br>NaNO2> (curve 2 in Fig. 4) to occur. The behavior of the Nyquist diagrams remains the same under both normal conditions and illumination. That is why a single-type equivalent electrical circuit is used for modeling (circuit 1 Fig. 9b). As in the previous case, illumination causes the impedance hodograph to enter the IV quadrant of the complex plane that is represented as the inductor (circuit 3 Fig. 9b).

To understand the changes in the impurity energy spectrum, currents of thermally stimulated discharge were measured after intercalation of propolis (Fig. 10). The energy spectrum has been shown to be transformed from narrow-band into quasi-continuous demonstrating several bands with deep traps. In addition, relaxation of homo- and hetero-charge takes place.

The corresponding changes in the energy spectrum slightly decrease the maximum value of ε, and, therefore, diminish high values of photo- and magneto-capacitance inherent to clathrate GaSe<br>NaNO2> (εL/εD ≈ 26, εH/ε0 ≈ 24). Low values of associated effects are proved to be the result of a change in the energy structure of impurity levels as evidenced by the dependence I(T) shown in Fig. 10.

For clathrate GaSe<br>NaNO2> + Propolis with bi-intercalate guest component, current−voltage (CV) characteristics assume an unusual form (Fig. 11). The hysteresis nature of the CV characteristic indicates a memristor effect. Since for clathrates GaSe<br>NaNO2>, the CV characteristics were linear, it is assumed that for clathrate GaSe<br>NaNO2> + Propolis propolis introduces oxygen vacancies that tend to migration after an external potential is applied. In this case, the mechanism of charge accumulation would be pseudo-capacitive in nature due to oxidation−reduction reactions (Kamble et al. 2018).

Fig. 8 Frequency dependences of the imaginary term of the specific impedance of GaSe<br>NaNO2> + Propolis measured under normal conditions (black), in the magnetic field (red), and when illumination is applied (blue)

Fig. 9 a Nyquist diagrams are plotted in the direction perpendicular to clathrate GaSe<br>NaNO2> + Propolis measured under normal conditions (black), in the magnetic field (red), and when illumination is applied (blue). b The equivalent electric circuit: (1) normal conditions and magnetic field, (2) light

Fig. 10 Spectra of thermally stimulated discharge for clathrate GaSe<br>NaNO2> + Propolis
Conclusions

1. Clathrate GaSe<\textit{NaNO}_2> with a bi-intercalate guest component has been first formed using a two-stage intercalation technology.

2. Introducing NaNO\textsubscript{2} between layers of the fourfold-expanded matrix GaSe at the first stage has proved to cause an increase in conductivity of \(10^3\) times in comparison to the initial expanded matrix.

3. For clathrate GaSe\textit{NaNO}_2, appreciable photo- and magneto-capacitive effects along with the value of electric loss tangent less than 1 are observed in the high-frequency range—\(\varepsilon_{\infty}/\varepsilon_D \approx 2000\), \(\varepsilon_{\infty}/\varepsilon_0 \approx 40,000\). The resulting structure could be used for the manufacture of highly sensitive and highly capacitive photo- and magneto-varicaps.

4. Introducing propolis into clathrate GaSe\textit{NaNO}_2 at the second stage causes a twofold decrease in conductivity and diminishment of photo- and magneto-capacitive effects.

5. For clathrate GaSe\textit{NaNO}_2+ Propolis, the I–V characteristic is found to feature the hysteresis behavior typical of the memristor effect. This compound could be used for the production of next-generation storage units.

Fig. 11 Cyclic voltammetry characteristic of GaSe\textit{NaNO}_2+ Propolis measured with 5 mV/s scan rate under normal conditions (black) and in magnetic field (red) and when illumination is applied (blue)

Declarations

Conflict of interest

The author V. Maksymych declares that he has no conflict of interest. The author F. Ivashchyshyn declares that he has no conflict of interest. The author D. Całus declares that he has no conflict of interest. The author A. Pidluzhna declares that she has no conflict of interest. The author M. Gała declares that he has no conflict of interest. The author P. Chabecki declares that he has no conflict of interest.

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