Studies of the phase diagram of sodium chloride at high temperatures and pressures produced by femtosecond laser pulses

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Abstract. On the basis of a set of critical parameters, we construct and study the phase diagram of sodium chloride at sufficiently high temperatures and pressures.

Analysis of phenomena in materials irradiated by ultrashort laser pulses can be performed on the basis of phase diagrams. For example, processes induced by femtosecond laser pulses in aluminum, copper and gold are considered in [1, 2], [3, 4] and [5], respectively.

The present study was conducted to construct and study the phase diagram of sodium chloride at sufficiently high temperatures and pressures.

To construct the phase diagram, we need information on the critical parameters of the material of interest: critical pressure $p_k$, critical temperature $T_k$, critical density $\rho_k$ and critical molar volume $V_{\mu k}$.

In literature, there is a great deal of data on critical parameters of several metals [6] and compounds [7], but little reliable information is available on the critical parameters of sodium chloride.

We constructed a phase diagram (figure 1) based on a set of critical parameters [8]:

$$T_k = 4700 \text{ K}, \quad p_k = 136 \text{ MPa}, \quad V_{\mu k} = 0.108 \text{ m}^3/\text{kmol}, \quad \rho_k = 540 \text{ kg/m}^3.$$  (1)

The values of the critical parameters (1) are in the same range as the critical parameters of other materials [6].

The phase diagram was constructed in accordance with physical characteristics and thermal parameters of different phases of sodium chloride, which were determined based on [7, 9, 10].

As reference points we used the density of crystals at normal atmospheric pressure, 2165 kg/m$^3$ [7], and the density of liquid sodium chloride at the melting temperature at normal atmospheric pressure 1516 kg/m$^3$ [10], which allow plotting the curve of melting and variation in crystal density with temperature on the phase diagram. The binodal constructed based on the critical parameters (1) better matches the melting curve compared to other estimates of the critical parameters of sodium chloride [8].

The phase diagram of sodium chloride allows us to consider ultrafast processes induced by effects of ultrashort laser pulses on the ionic crystal [11], including lattice heating in the surface layer [12], phase transitions driven by strong shock waves, absorption of incident laser light, etc.
Figure 1. The density-versus-temperature phase diagram of sodium chloride. Stable state region (homogeneous system): 1—gas, 2—liquid, 3—solid, 4—crystal; stable state region (heterogeneous systems): 5—solid and gas, 6—liquid and gas, 7—solid and liquid; metastable states: 8—supercooled gas, 9—superheated liquid, 10—solid, 11—solid and liquid; phase boundaries: a—binodal, b—spinodal; TK—critical point.

The region of strong shock effects was set based on the calculated ablation pressures $p_a$ on the surface of sodium chloride.

The ablation pressures were calculated by different formulas.
1. Formula given in [13]:

$$p_a[kbar] = 4.8 \times 10^{-4}(I[W/cm^2])^{1/2},$$  \hspace{1cm} (2)

where $I$ is laser intensity.

2. Scaling-based calculations [14, 15]:

$$p_a[Mbar] = 12(I[W/cm^2]10^{-14})^{2/3}(\lambda[\mu m])^{-2/3}. \hspace{1cm} (3)$$

3. Formula discussed in [16]:

$$p_a[kbar] = 2.6 \times 10^{-4}(I[W/cm^2])^{1/2}. \hspace{1cm} (4)$$

The chosen value $p_a = 3$ Mbar is reached: by (2) when $I = 3.9 \times 10^{13}$ W/cm$^2$, by (3) when $I = 1.5 \times 10^{13}$ W/cm$^2$, by (4) when $I = 13.3 \times 10^{13}$ W/cm$^2$. 


Figure 2. Critical electric field intensity as a function of inverse pulse duration in case of sodium chloride damage; approximation by five straight lines with different angular coefficients $K$: 1, 2—breakdown thresholds for nanosecond electric pulses, 3—breakdown thresholds for nanosecond laser pulses, 4—breakdown thresholds for picosecond laser pulses, 5—breakdown thresholds for picosecond and femtosecond laser pulses.

This high pressure is of great interest, since $p_a$ above 1 Mbar on the surface of sodium chloride may cause insulator transition to metallic state [17].

In this state, sodium chloride has a number of unusual properties [18].

The lower value of pressures on the surface of sodium chloride can be estimated from the critical intensity of laser radiation, which leads to radiation damage of the ionic crystal.

Information on the breakdown threshold of sodium chloride by nanosecond and picosecond laser pulses can be found in [19, 20], and on the radiation damage by femtosecond laser pulses, in our experimental studies [11].

Based on these studies, we analyzed the dependence of the breakdown threshold $E$ of sodium chloride on laser pulse duration $\tau$ in the nanosecond, picosecond and femtosecond range $\tau$. The graphs constructed (figure 2) showed that the breakdown thresholds can be approximated by three straight lines with different angular coefficients:

$$K = \frac{\lg E_2[V/cm] - \lg E_1[V/cm]}{\lg(1/\tau_2[s]) - \lg(1/\tau_1[s])}. \quad (5)$$

Figure 2 (for comparison) also presents data on the breakdown threshold of sodium chloride for nanosecond electric pulses taken from [21].

Figure 2 shows that the dependence of the laser-induced breakdown threshold on pulse duration in sodium chloride can be approximated by a number of straight lines with different angular coefficients. One can distinguish three regions with different values of $K$. The boundaries of these regions for sodium chloride are located at 0.8 ns and 30 ps.

The numerical values of $K$ for laser-induced breakdown are shown in table 1.

It turned out that the radiation strength of ionic crystals irradiated by nanosecond laser pulses is in a reasonably close agreement with the breakdown threshold of the same crystals exposed to short electric pulses of nanosecond duration (table 2).
Table 1. Laser-induced breakdown thresholds of sodium chloride.

| $\tau$ | $10 \text{ ns} \geq \tau \geq 800 \text{ ns}$ | $800 \text{ ps} > \tau \geq 30 \text{ ps}$ | $30 \text{ ps} > \tau \geq 80 \text{ fs}$ |
|-------|----------------------------------|----------------------------------|----------------------------------|
| $K$   | $0.32 \pm 0.02$                  | $0.107 \pm 0.005$               | $0.40 \pm 0.02$                  |

Table 2. Laser-induced breakdown thresholds of ionic crystals.

| Crystal | NaCl   | KI       |
|---------|--------|---------|
| $\tau$ | $10 \text{ ns} \geq \tau \geq 800 \text{ ps}$ | $8 \text{ ns} \geq \tau \geq 2.5 \text{ ns}$ |
| $K$    | $0.32 \pm 0.02$                  | $0.30 \pm 0.02$                  |

Table 3. Thresholds of the breakdown by short electric pulses.

| Crystal | NaCl   | KI       |
|---------|--------|---------|
| $\tau$ | $200 \text{ ns} \geq \tau \geq 40 \text{ ns}$ | $300 \text{ ns} \geq \tau \geq 30 \text{ ns}$ |
| $K$    | $0.34 \pm 0.02$                  | $0.30 \pm 0.02$                  |

However, as evidenced by figure 2, there is no complete agreement between laser-induced and electric breakdown thresholds of sodium chloride (lines 3 and 4, respectively). The laser-induced breakdown thresholds are lower.

According to [11], the critical intensity of laser radiation with a duration of 80 fs for sodium chloride is $I = 1.6 \times 10^{13} \text{ W/cm}^2$, which, when recalculated by formula (2), gives $p_a = 1.9 \text{ Mbar}$.

The emergence of optical quantum generators emitting femtosecond laser pulses made it possible to address many questions of radiation/matter interaction at a fundamentally different level. Ultrashort laser pulse durations enabled reaching the terawatt power level. Terawatt lasers led to the development of the physics of high and ultrahigh radiation fields closely related to the physics of extreme states of matter.

Experiments on the terawatt femtosecond chromium forsterite laser facility (figure 3) were carried out at the Laser Femtosecond Complex of the Joint Institute for High Temperatures, Russian Academy of Sciences [22].

We studied surface effects of $p$-polarized laser light with a wavelength of 1240 nm.

We used microscopic imaging of the test surface. The image of the crystal surface was recorded by a CCD-camera. The monitoring system enabled surface imaging before, during (with a delay of 0.5 ns) and after irradiation.

In case of short laser pulses, the pulse duration can be shorter than the time needed for the light-to-heat energy conversion. Thus, heating of the crystal lattice and other thermal processes occur as late as upon completion of the laser pulse.

Consideration of thermal effects is complicated by the need to analyze them on time scales that are orders of magnitude greater than the duration of a short laser pulse. It is necessary for understanding the details of the physical processes.

The generally accepted surface damage mechanism in transparent solids for femtosecond laser pulses is ablation. If the ablation threshold is exceeded, part of the melt moves away leaving a
damage spot on the test surface. Figures 4 and 5 show photographs of the surface of sodium chloride before and during irradiation, respectively. As can be seen in figures 4 and 5, femtosecond laser pulses produce a spot of liquid phase on the surface of the crystal of sodium chloride.

The experimentally observed solid-liquid phase transition on the surface of the sodium chloride crystal exposed to the femtosecond laser pulse was considered based on the phase diagram obtained using the energy balance and the Gibbs–Helmholtz equations.

Analysis of the processes in the phase diagram showed that the peak temperature (during isochoric heating) is followed by relaxation, the stage of phase trajectory transition to a binodal. Since the entropy in metastable states has a relative maximum, while the Gibbs potential has a relative minimum [23], the transition to the binodal should pass along the adiabat described by the equation $VT^3 = \text{const}$. Coupled solution of this equation and the equation of binodal of
sodium chloride allows us to calculate of the end point of the phase trajectory on the binodal, from which the recovery to the initial state begins.

To describe the solid–liquid phase transition observed in sodium chloride crystals exposed to ultrashort laser pulses, we established by the phase trajectory in the phase diagram (figure 1) of this ionic compound.

The result of the analysis is shown in figure 6.

Thus, based on the phase diagram of sodium chloride in the range of relatively high temperatures and pressures, we studied possible phase transitions induced by intense short laser pulses and made some quantitative evaluation of the processes under consideration.
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