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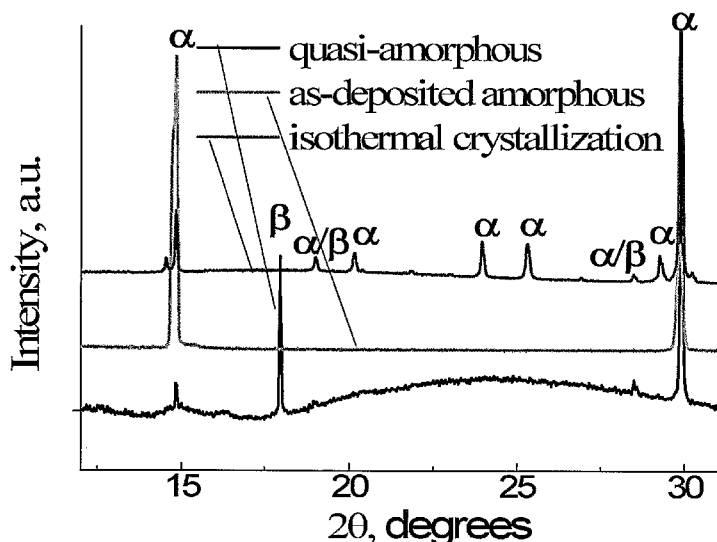


Fig. 2E

(57) Abstract: The present invention discloses a method for producing a polar crystal phase of a substance comprising: interacting a solution containing the substance material with a surface of a film having pyroelectric properties, for a certain period of time predefined to be sufficient to induce nucleation of at least one crystal of the substance material; applying a temperature change to the film enabling creation of an electric charge on the surface of the film, thereby creating a local electric field in the vicinity of the surface of the film, the electric field affecting the at least one crystal formed at the surface of the film to become oriented in accordance with the film surface, leading to the formation of the polar crystal.



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CRYSTALLIZATION OF POLAR CRYSTAL

FIELD OF THE INVENTION

The present invention relates generally to the process of crystallization of polar crystal and to the controlling of the process of crystal nucleation.

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BACKGROUND OF THE INVENTION

25 Crystallization is the (natural or artificial) process of formation of solid crystals precipitating from a solution or melt. The crystallization process consists of two major events, nucleation and crystal growth. Nucleation is the step where the solute molecules start to gather into clusters that become stable under the current operating conditions. These stable clusters constitute the
30 nuclei. However when the clusters are not stable, they redissolve. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Such

critical size is dictated by the operating conditions (temperature, supersaturation, etc.). It is at the stage of nucleation that the atoms arrange in a defined and periodic manner that defines the crystal structure. It should be noted that "*crystal structure*" refers to the relative arrangement of the atoms, not to the macroscopic properties of the crystal (size and shape), although those are a result of the internal crystal structure. The crystal growth is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Many compounds have the ability to crystallize with different crystal structures, a phenomenon called *polymorphism*. Each polymorph is in fact a different thermodynamic solid state and crystal polymorphs of the same compound exhibit different physical properties, such as dissolution rate, shape (angles between facets and facet growth rates), melting point, etc. For this reason, polymorphism plays a central role in different fields of science, for example for the preparation of drugs of required bio-availability, or polar crystals that display unique opto-electronic properties [1]. However, the process of crystallization is still done by trial or by empirical methods. Experimental knowledge of crystal nucleation in various molecular systems may be achieved employing tailor-made auxiliaries. The control and behavior of polymorphic crystallization may be understood at the molecular level through the interplay between inhibitor, solvent, solute, crystal and layer lattice energies, as well as surface layer structures. With respect to promotion of crystal nucleation, it may be achieved by Langmuir monolayers at the air-aqueous solution interface, acting as a templating agent.

In particular, specific proteins can control the various processes of ice nucleation such as bio-mineralization or freezing of supercooled water; their actions having an impact on the frost sensitivity of plants, the winter survival of certain insects, and even on weather systems in cold climate. The ability to control freezing temperature of supercooled water with auxiliaries, which promote or suppress ice nucleation, provides a critical factor in a variety of areas such as survival of ectothermic animals, cryo-preservation of cells and tissues, prevention of the freezing of crops, cloud seeding and snow making to

mention but a few. It should be noted that the condition in which a solution remains liquid below its phase transition temperature is termed supercooling. As an aqueous solution is cooled further below its freezing point, the extent of supercooling increases. In the absence of intervention, the water molecules in the solution, at a point usually no more than 15°C below the freezing point, spontaneously crystallize, and pure water precipitates as ice.

From a practical point of view, solid surfaces are the most useful templates for heterogeneous crystal nucleation and often may induce the precipitating of a desired polymorph, yet the mechanisms via which these templates operate are not fully understood. Generally, a crystallographic fit of the template to the grown crystal has been shown to induce oriented growth, which is usually called *crystal epitaxy*. Electric fields have been shown to affect the early stages of crystal nucleation, as for instance, by illumination of supersaturated solutions of polar molecules such as urea or glycine [2, 3, 5].

GENERAL DESCRIPTION

There is a need in the art in controlling crystallization processes and in inducing crystallization of polar crystals. The present invention enables the use of the surface of materials having pyroelectric properties as auxiliaries for crystallization. In particular, according to the teachings of the present invention, materials having pyroelectric properties operate as useful templates for inducing the nucleation of polar crystal phase by virtue of the electric charge that is created on their surfaces upon application of a temperature gradient (e.g. cooling) in the course of the process of crystallization. It should be noted that materials having pyroelectric properties may be made from a natural pyroelectric material or may be made by processing of a non-pyroelectric material inducing pyroelectric properties.

Therefore, there is provided a method for producing a polar crystal phase of a substance comprising: interacting a solution containing the substance material with a surface of a film having pyroelectric properties for a certain period of time predefined to be sufficient to induce the nucleation of at

least one crystal of the substance material ; applying a temperature change to the film enabling creation of an electric charge on the surface of the film, thereby creating a local electric field in the vicinity of the surface of the film; the electric field affecting the at least one crystal formed at the surface of the film to become oriented in accordance with the film surface, leading to the formation of the polar crystal.

In some embodiments, the electric field affects one or more properties of the polar crystal being formed. The electric field may affect a phase transition temperature of the polar crystal.

In some embodiments, the solution is an aqueous solution. The method may comprise applying the temperature change to the film to create a positive electric charge on the surface of the film, thereby affecting at least one property of the polar crystal being formed. The positive electric charge on the surface of the film induces a phase transition consisting of freezing of the aqueous solution and promotes ice nucleation.

Alternatively, the method comprises applying a temperature change to the film to create a negative electric charge on the surface of the film, thereby affecting at least one property of the polar crystal being formed. The negative electric charge on the surface of the film may induce a phase transition consisting of reduction of freezing temperature of the aqueous solution and retards ice nucleation.

In some embodiments, the method may be used for production of supercooled water, the electric charge on the surface of the film inducing a phase transition consisting of reduction of freezing temperature of the aqueous solution.

In some embodiments, the method comprises providing an inorganic, *quasi*-amorphous oxide film of a metal, mixture of metals or semiconducting element; and interacting the solution with the surface of the *quasi*-amorphous film.

In some embodiments, applying the temperature change comprises applying a mechanical strain to the film enabling the creation of the electric charge on the surface of the film.

The *quasi*-amorphous film may be at least one of the followings film:
5 SrTiO₃, BaTiO₃ and BaZrO₃. The *quasi*-amorphous film may be deposited on a silicon substrate. The polar crystal phase may be a polymorph crystal (e.g. meta-stable).

In some embodiments, the polar polymorph is a polar β -polymorph of glycine.

10 Some features of the invention are illustrated by two model systems: the induced crystallization of a meta-stable polar β -polymorph of glycine and the catalyzed freezing of supercooled drops of water, as performed on the pyroelectric *quasi*-amorphous films of SrTiO₃. It should be understood that amorphous films of SrTiO₃, BaTiO₃ and BaZrO₃ deposited on a silicon
15 substrate pulled though a steep temperature gradient, do not crystallize but form a pyroelectric and piezoelectric phase, called *quasi*-amorphous (a compound which is a non-crystalline ionic solid having a macroscopic polarization). An example of such material is an inorganic, *quasi*-amorphous oxide compound of a metal, mixture of metals or semiconducting element, in
20 particular having the formula $(A_xB_{1-x})_pO_n$. Here, A and B are independently selected from transitions metals, elements of Group IVA of the periodic table, alkali metals, alkali earth metals and rare earth metals; x has values of between 0 to 1; p is an integer having the values 1, 2 or 3; and n is an integer having the value of 1, 2, 3 or 4. Preferably, A is a transition metal or an element of Group
25 IVA of the periodic table; x is 1 and p is 2. More preferably, the compound is selected from SiO₂ and TiO₂.

The above materials and their pyroelectric properties are disclosed in the patent publication no. WO07144892 assigned to the same assignee of the present patent application and incorporated herein by reference.

30 Transformation of the amorphous into the *quasi*-amorphous phase does not cause change of composition and slightly reduces the roughness of the

amorphous films film from which they were prepared. For example from <0.5 nm/(100) μm^2 to <0.3 nm/(100) μm^2 , respectively or from $4 \text{ \AA}/(1 \times 1 \text{ } \mu\text{m}^2)$ to $8 \text{ \AA}/(1 \times 1 \text{ } \mu\text{m}^2)$ [15-17]. The transformation from amorphous to *quasi*-amorphous phase gives ability in separating the influence of the epitaxy effect, if any, from that of the local electric field developed by the pyroelectric surface in the vicinity thereof, where amorphous films work as almost ideal "zero field" reference. Under the influence of a temperature change, no electric charge is created on the surface of amorphous films and therefore no electric field is created. Therefore, to isolate the influence of the epitaxial effects from the effects of the electric charge, two materials (amorphous and *quasi*-amorphous) of the same chemical composition and having a very similar surface morphology have been investigated.

Furthermore, since the surface charge appears at the surface of pyroelectric materials in response to a mechanical strain e.g. temperature variation, crystallization in isothermal conditions provides an additional reference to compare surface with and without surface charge i.e. amorphous and *quasi*-amorphous surfaces. The inventors of the present invention have found that although the charge is neutralized by the ions adsorbed from the environment, the influence of the charge is sufficient to promote the nucleation of polar crystals. More specifically, although charges developing at the surface of the pyroelectric materials are neutralized within the time scale of msec to sec, depending on the environment, once the temperature becomes constant, the local electric field in the vicinity of the pyroelectric surfaces may reach hundreds of kV/cm, which is more than sufficient to affect the orientation of polar molecules.

Among the compounds found to form *quasi*-amorphous phases, those of SrTiO_3 have the highest pyroelectric coefficient [4], $10^{-8} \text{ C}/(\text{cm}^2 \cdot \text{K})$. In vacuum, the local electric field on a surface of pyroelectric may be very large. For instance, a material with a pyroelectric coefficient of $\alpha = 10^{-8} \text{ C}/(\text{cm}^2 \cdot \text{K})$ in response to a temperature change of $\Delta T = 1 \text{ K}$ develops the surface charge of

$q = 10^{-8} \text{ C/cm}^2 \approx 5 \cdot 10^{10} \text{ electron/cm}^2$ and an electric field of $E_p = q/\epsilon_0 > 0.1 \text{ MV/cm}$.

In air and water, this electric field is quickly screened out by the adsorption of ions. Even the cleanest water contains about 10^{14} ions (H^+ and OH^-) per cm^3 . Therefore, in pure water, at the distance of the screening length (Debye length L_D) of $\approx 1 \text{ }\mu\text{m}$, the electric field is completely screened. Within this layer, the electric field decreases from E_p/ϵ at the surface, to zero at the distance of L_D from the surface ($\epsilon=81$ is a dielectric constant of water). The time necessary for screening can be estimated as $\tau = L_D^2/D \approx 0.01 \text{ sec}$, where D is a diffusion coefficient of ions $D(\text{H}^+) \approx 10^{-10} \text{ cm}^2/\text{s}$ (for $D(\text{OH}^-) \approx 0.5 \cdot 10^{-10} \text{ cm}^2/\text{s}$). After the time τ , the electric field is concentrated within the screening layer (often called in electrochemistry double layer). The electric field within this layer persists as long as the charge at the surface is not removed by a chemical reaction. Therefore, the surfaces of pyroelectric materials are useful to promote crystallization of polar crystals.

In some embodiments, the solution interacting with the surface of the *quasi*-amorphous film, for a period of time sufficient to induce the nucleation of at least one crystal, is an aqueous solution.

As described above, although ice melts and water freezes under equilibrium conditions at 0°C , water can be super-cooled under homogeneous conditions in a clean environment down to -40°C without freezing. The influence of an electric field on the freezing temperature of super-cooled water (electro-freezing) is of topical importance in the living and inanimate worlds. There are a number of studies dating back to 1861, indicating that in the presence of an electric field, a transformation of a liquid into a crystalline solid may be observed for a narrow range of density and temperature on a time scale of a few hundred picoseconds, so called electro-freezing. This effect is attributed to the ability of the electric field to induce the formation of ice-like nuclei. In particular, electro-freezing of ice has been reported near charged metallic electrodes [12], or on dielectric surfaces charged by mechanical friction [13]. However, by using these techniques the effect of the electric field

cannot be isolated because SuperCooled Water (SCW) freezes at non-charged metallic surfaces close to the melting point as a result of binding of the water molecules to highly conductive surfaces, epitaxy and mirror charge effect [14]. The inventors have found a way to isolate the influence of the electric field by
5 using pyro-electric materials. They have also found that water freezes differently on positively and negatively charged surfaces of pyroelectric materials.

According to another broad aspect of the present invention, there is also provided, a method for freezing supercooled water. The method comprises
10 interacting an aqueous solution with the surface of a film having pyroelectric properties for a certain period of time predefined sufficient to induce the nucleation of at least one ice crystal; and; applying a temperature change to the film enabling the creation of an electric charge on the surface of the film; thereby creating a local electric field in the vicinity of the surface of the film;
15 the electric field affecting the water molecules of the aqueous solution formed at the surface of the film to become organized into structures clusters enabling the condensation and freezing into a polar ice state.

In some embodiments, the electric field affects one or more properties of the ice state being formed. The electric field may affect a phase transition
20 temperature of the ice state.

In some embodiments, the method comprises applying a temperature change to the film to create a positive electric charge on the surface of the film, thereby affecting at least one property of the ice state being formed. The positive electric charge on the surface of the film may induce a phase transition
25 consisting of freezing of the aqueous solution and promotes ice nucleation.

Alternatively, the method comprises applying a temperature change to the film to create a negative electric charge on the surface of the film, thereby affecting at least one property of the ice state being formed. The negative electric charge on the surface of the film may induce a phase transition
30 consisting of reduction of freezing temperature of the aqueous solution.

The method for freezing supercooled water may comprise providing an inorganic, *quasi*-amorphous oxide film of a metal, mixture of metals or semiconducting element; and interacting the solution with the surface of the *quasi*-amorphous film.

5 In some embodiments, the temperature change comprises a mechanical strain enabling the creation of an electric charge on the surface of the film.

In some embodiments, the polar ice state is a polar ice polymorph (e.g. hexagonal ice polymorph).

10 In other embodiments, the aqueous solution is supercooled enabling the freezing of supercooled water.

In some embodiments, the method of the present invention enables the elevation of the temperature of water freezing.

15 In some embodiments, the local electric field created in the vicinity of the surface of the *quasi*-amorphous film provides a positively charged surface inducing ice nucleation.

In other embodiments, the local electric field created in the vicinity of the surface of the *quasi*-amorphous film provides a negatively charged surface reducing the temperature of water freezing.

20 BRIEF DESCRIPTION OF THE FIGURES

In order to understand the invention and to see how it may be implemented in practice, preferred embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawing, in which

25 **Fig. 1A** illustrates the α -form of glycine;

Fig. 1B illustrates the polar β -polymorph of glycine;

Figs. 2A-2C illustrate the crystal growth of glycine on the surface of the *quasi*-amorphous (2A-2B) and amorphous (2C) films of SrTiO_3 examined by optical microscope;

Fig. 2D illustrates an optical microscopy image of a glycine solution droplet with a crystal of α -glycine grown at the air-water interface and crystal of β -glycine attached to the surface;

Fig. 2E represents the X-ray power diffraction spectra of glycine crystals grown on the surface of amorphous and *quasi*-amorphous films upon cooling and under isothermal conditions in a Bragg-Brentano mode;

Figs. 3A-3B illustrate the alignment of the COO^- groups of glycine facilitating the growth of the crystal along the b -axis, viewed along the a -axis (**Fig. 3A**) and along the b -axis (**Fig. 3B**); and;

Figs. 4A-4B illustrate electric fields induced by surface charge on a pyroelectric plate without depolarizing the charges (**4A**) and by external depolarization of charges (**4B**);

Fig. 4C illustrates the creation of an external electric field produced by a change in temperature on a pyroelectric plate;

Fig. 4D illustrates the packing arrangement of a pyroelectric LiTaO_3 crystal parallel to the polar (Z -axis);

Figs. 5A-5B illustrate powder diffraction patterns of ice crystals on LiTaO_3 surfaces;

Fig. 6A illustrate water molecules freezed on a charged surface of *quasi*-amorphous film of SrTiO_3 as ordered nuclei of ice; **Figs. 6B-6D** illustrate the freezing of water droplets on the surface of the *quasi*-amorphous and amorphous) films of SrTiO_3 at various temperatures during cooling: **Fig. 6B** at -4°C , **Fig. 6C** at -11°C and **Fig. 6D** at -12°C .

25 DETAILED DESCRIPTION OF EMBODIMENTS

In the present invention, inorganic amorphous and *quasi*-amorphous oxide films of a metal, mixture of metals or semiconducting element, such as SrTiO_3 are used to induce crystallization of a polar crystal phase and for the catalysis of freezing of supercooled water.

Glycine is known to form at least three different polymorphs under different conditions. In particular, Glycine is trimorphic at atmospheric pressure. The alpha form (α -form) spontaneously nucleates from neutral aqueous solution. Another form, known as the gamma form (γ -form), is formed from acidic or basic aqueous solutions. The γ -form is characterized by a different morphology of needle-shaped crystals. In pure water, at the isoelectric point of glycine pH~6, glycine is in the α -form (centrosymmetric space group $P2_1/n$) that precipitates via a mechanism involving centrosymmetric pairs of glycine molecule [6]. The polar phase γ (non centrosymmetric space group $P3_1$ or $P3_2$) is a thermodynamically stable phase at room temperature [7]. It crystallizes from aqueous solutions of high and low pH, if the aqueous solutions are irradiated with a plane polarized laser light [2].

Reference is made to **Fig. 1A** illustrating the packing arrangement of glycine in the α -form viewed along the crystallographic a -axis. The polar β -polymorph illustrated in **Fig. 1B** (non centrosymmetric space group $P2_1$) [8] is the least stable one, and it converts either to the α - or the γ -forms, the transformation to α -form being much accelerated by water vapor/liquid [7, 9-11]. It is obtained when grown in aqueous solutions containing methanol or ethanol where the latter inhibit the formation of either α or γ -polymorphs [6, 7].

In the present invention, droplets of 5 μ l of solution of glycine (25 % w/w) have been deposited on the surfaces of amorphous and *quasi*-amorphous films of SrTiO_3 at 40°C in an isothermal bath and then cooled in parallel down to +4°C at a rate of 2°C/min.

Reference is made to **Figs. 2A-2D** illustrating β -polymorph glycine crystals growth on the surface of the *quasi*-amorphous (**2A-2B**) and α -polymorph glycine crystals growth on the surface of the amorphous (**2C**) films of SrTiO_3 examined by optical microscope. It should be noted that although, not detectable visually, the crystals grown on the surface of the *quasi*-amorphous film contain small amount of the α -polymorph which are produced at the air-

solution interface. The vertical dimensions of the image **Fig. 2A** and **Fig. 2C** is 1 mm and of **Fig. 2B** is 100 μm .

As illustrated in **Fig. 2C**, on the reference amorphous film, the precipitation of the α -form of glycine is observed. In contrast, on the surface of the *quasi*-amorphous films, only the needle-like crystals of the polar β -form are observed (**Figs. 2A, 2B**).

Reference is made to **Fig. 2D** illustrating an optical microscopy image of a glycine solution droplet with a crystal of α -glycine grown at the air-water interface (dark rhomb at the top of the droplet) and crystal of β -glycine attached to the surface (long needle-like transparent crystals). It has been observed that the crystals growing at the air-water interface, far from the influence of the local electric field of the pyroelectric surface, are found to be of the α -form.

Reference is made to **Fig. 2E** illustrating an X-ray power diffraction spectra of the glycine crystals grown on the surface of amorphous and *quasi*-amorphous films upon cooling and under isothermal conditions measured by a Bragg-Brentano diffractometer. The X-ray power diffraction pattern represents the intensity of the films as function of 2θ , where 2θ is the angle between the incident beam and the scattered beam. A very strong Bragg peak at (001) is observed (at $2\theta=17.94^\circ$) indicating that the needle-like β -form crystals grow with their *b*-axis parallel to the surface of the film. Moreover, the least thermodynamically stable polar β -polymorph appears only at the surface of the *quasi*-amorphous films upon cooling, which are the conditions at which the surface is charged. Although the β -polymorph undergoes phase transition to the α - and γ -forms [7, 9-11], on the surface of the pyroelectric *quasi*-amorphous film, the crystals remain stable in the open air six weeks after their crystallization. The same experiments were performed by depositing drops of glycine solution at 24°C and growing the crystals isothermally, such that no charge develops on the surface of the *quasi*-amorphous films. α -polymorph

crystals were formed at the surface of both films (*quasi*-amorphous films without presence of electric charge and amorphous film).

Under the influence of the uncompensated positive charge that develops on the surface of the pyroelectric *quasi*-amorphous film upon cooling, the
5 COO⁻ groups of glycine, being isolated molecules or clusters, are attached to the surface and align parallel to the film surface, leading to the formation of the β -polymorph. Such alignment facilitates the growth of the needles along the *b*-axis of the crystals parallel to the surface of the film, as shown schematically in **Figs. 3A-3B**. In particular, **Fig. 3A** illustrates the alignment of the glycine
10 molecules on the positively charged surface as correlated to the packing arrangement of the β -polymorph viewed along the crystallographic *a*-axis and **Fig. 3B** illustrates the same viewed along the crystallographic *b*- axis.

As related above, pyro-electric materials are insulators but the charge on their surface can be manipulated. In case of polar materials, upon cooling or
15 heating, the surfaces of a pyroelectric plate cut perpendicular to the polar axis develop equal but opposite charges. The sign of the charge at a given surface is defined by the sense of polarity of the crystal and can be either positive or negative, depending whether the material is cooled down or warmed up. The charge induced by change in temperature dissipates within a few minutes due
20 to leakage through and/or around the plate. However, as long as the temperature continues to vary, the charge at the surface persists.

In this connection, reference is made to **Fig. 4A** illustrating a pyroelectric plate in which an electric field shown by grey arrows is induced by spontaneous polarization (surface charge) without compensating charges (e.g.
25 by depolarization). The electric field is confined to the interior of the crystal. The pyroelectric plate is unsupported and the induced surface charges operate as a parallel plate capacitor in which the electric field is confined to the plate interior. **Fig. 4B** illustrates the spontaneous polarization at equilibrium, compensated by external (depolarization) charge. Change in temperature
30 changes the spontaneous polarization and induces electric field inside the

crystal (similar to **Fig. 4A**). After a few minutes, the “excess” charge dissipates and the equilibrium reestablishes itself.

However, if one of the surfaces is connected to a conductor then its charge would be redistributed immediately and the direction of the electric field would depend on the conductor’s configuration.

Fig. 4C illustrates a set-up in which the pyroelectric plate is placed in a metal cylinder. In this configuration, a change in temperature produces an *external* electric field because the “excess” charge of the bottom side redistributes immediately; whereas the charge at the top side requires much longer equilibration time. The top surface of the plate becomes charged with respect to the walls of the container with the electric field perpendicular to the surface. The charge density, σ , generated at the surface as a result of some temperature change, for instance $\Delta T = 10\text{ K}$, is given by $\sigma = \alpha \cdot \Delta T = 2.3 \cdot 10^{-7} \text{ C/cm}^2$, where $\alpha = 2.3 \cdot 10^{-8} \text{ C/(cm}^2 \cdot \text{K)}$ is the pyroelectric coefficient of LiTaO_3 . Although, only a very small fraction of this charge, $f \ll 1$, is redistributed to the external conductor, the induced electric field can be very strong. For instance if $f = 10\%$ (as estimated for this specific configuration), the electric field is about $E \approx f \cdot \sigma / (\epsilon \cdot \epsilon_0) = 320 \text{ kV/cm}$, where ϵ_0 is the dielectric permittivity of vacuum and $\epsilon = 81$ is the dielectric permittivity of water. The fraction of the charge transferred to the conductor is defined by the equivalent capacitances of the pyroelectric crystal and the conductor. Since, water has a finite conductivity; the electric field decays (is screened) over $\approx 0.8 \text{ }\mu\text{m}$ (the Debye length for pure water). Since this distance is much larger than the size of a water molecule, the electric field generated in the vicinity of a pyroelectric surface is expected to align the polar water molecules and assemble them in supra-molecular clusters. The external electric field can be switched on and off by controlling the charge flow to the container. Accordingly, the effect of the electric field on the freezing of SCW can be compared with and without the induced electric field in either direction on the same surface.

Fig. 4D illustrates the projection of a packing arrangement of a pyroelectric LiTaO₃ crystal parallel to the polar (Z-axis), on (100) plane. The direction (001) called Z^+ (up) and the direction (00 $\bar{1}$) called Z^- (down) are not equivalent. Upon cooling, these surfaces develop positive and negative charge
 5 respectively. Therefore, the present invention enables to achieve a startling difference in the freezing temperature of SCW between the positively and negatively charged surfaces.

Four types of specimens (4 of each type, 8×8 mm) were prepared from the same (001) 3" diameter, 0.5 mm thick LiTaO₃ wafer (so-called Z-cut
 10 wafer). As illustrated in the figure, the specimens had either (001) or (00 $\bar{1}$) surface left uncoated and the opposite surface coated either by 200 nm of Cr (henceforth called Z_{field}^+ and Z_{field}^- respectively), or by 500 nm of Al₂O₃ (henceforth called $Z_{No\ field}^+$ and $Z_{No\ field}^-$ respectively). The specimens were placed exposing the uncoated surface in a copper cylinder with freshly polished inner
 15 surfaces mounted in a temperature controlled ($\pm 0.1^\circ\text{C}$) stage. The presence of the Cr layer at the bottom surface of the Z_{field}^+ and Z_{field}^- specimens assured good contact to the polished copper and facilitated charge distribution, whereas the insulating layer of Al₂O₃ obstructed charge flow. Consequently Z_{field}^+ and Z_{field}^- specimens develop an electric field at their top surface whereas $Z_{No\ field}^+$ and $Z_{No\ field}^-$
 20 specimens do not. The specimens were cooled in a room with $45\pm 5\%$ humidity at the rate of $2^\circ\text{C}/\text{min}$ down from $+24^\circ\text{C}$ until the condensation of small (≈ 0.1 mm) droplets was achieved. Further cooling froze the water and the freezing temperature was detected ($\pm 0.5^\circ\text{C}$) by observing the droplets with an optical microscope and by detecting the heat released during freezing. The setup has a
 25 relatively small thermal mass ($< 30\text{ J/K}$) and it is constantly cooled by a cold finger with liquid nitrogen. The control over the temperature is achieved by a computer-driven electrical heater. Due to the small thermal mass of the setup, freezing of the droplets releases sufficient amount of heat that the time-temperature dependence deviates from the programmed $2^\circ\text{C}/\text{min}$ and shows a
 30 constant temperature for 3-7 sec. During this period, the power consumption of

the heater drops by 10-15%. Recording both the temperature vs. time and the power consumption vs. time permits very accurate determination of the freezing point. To ensure reproducibility, prior to each experiment the top surface of the specimens was cleaned by low-pressure (0.5 mbar) oxygen plasma. The contact angle at room temperature was 7 ± 1 degrees for all LiTaO₃ samples (without surface charge). The orientation of the ice crystals was deduced from the X-ray diffraction acquired with a diffractometer.

Water droplets freeze at -12.5 ± 3 °C at surfaces (001) and (00 $\bar{1}$) without electric field (specimens $Z_{No\ field}^+$ and $Z_{No\ field}^-$). In contrast, the freezing-temperature on the specimens that develop electric field (Z_{field}^+ and Z_{field}^-) differs dramatically from each other and from the surfaces without field. Water droplets freeze at -7 ± 1 °C at the positively charged surface (Z_{field}^+ specimens), whereas at the negatively charged surface (specimens Z_{field}^-), water freezes at -18 ± 1 °C. The inventors have found that the freezing starts at the air/water interface, at which the electric field is much smaller than at the solid/water interfaces. Furthermore, if the water droplets are kept for 3-10 min at -11 °C on a Z_{field}^- specimen, they do not freeze. However, the 3-10 min. time period was found experimentally to be sufficient for the negative charge to dissipate. Thereafter, heating of the specimen (2 °C/min) from -11 to -8 °C produces a small but positive charge at the surface, which induces immediate freezing. Thus on a pyroelectric surface of Z_{field}^- specimens water freezing can be induced by heating, because it creates a positive charge at the (00 $\bar{1}$)-surface of LiTaO₃. These findings indicate that a positively charged surface promotes water freezing, while a negatively charged surface retards it, irrespective whether the crystallization occurs either on the (00 $\bar{1}$) or (001) surface.

Therefore, positively charged surfaces of the pyro-electric LiTaO₃ crystals and the SrTiO₃ thin films promote ice nucleation, whereas the same surfaces when negatively charged reduce the freezing temperature. Accordingly, droplets of water cooled down on a negatively charged LiTaO₃ surface and remaining liquid at -11 °C freeze immediately by heating this

surface to -8°C , as a result of the replacement of the negative surface charge by a positive one.

To provide additional insight, a specular X-ray diffraction (XRD) patterns of the ice polycrystals was measured. Powder X-ray diffraction studies demonstrates that the freezing on the positively charged surface starts at the solid-water interface, whereas on a negatively charged surface ice nucleation starts at the air-water interface. After nucleation, the droplet converts into a mixture of water and ice at 0°C , which is in contact with the surface of the LiTaO₃ crystal through which the heat is taken away. At 0°C , formation of new nuclei may occur only on the growing ice crystals (secondary nucleation), whereas nucleation at the surface of the LiTaO₃ at 0°C does not occur at all, otherwise the supercooling would not be possible to achieve. Therefore, the ice crystals formed grown on the crystal surface are expected to bare the information about the primary nuclei.

In this connection, reference is made to **Fig. 5A** representing powder diffraction patterns of ice crystals on LiTaO₃ surfaces. The freezing points of SCW are indicated on the graphs. Graphs **A-D** are $\theta-2\theta$ scans with an inclination angle $\phi=0^{\circ}$. In particular, graph **A** represents $Z_{No\ field}^{+}$ and $Z_{No\ field}^{-}$ specimens; graph **B** Z_{field}^{+} specimen; graph **C** Z_{field}^{-} specimen; graph **D** Z_{field}^{-} specimen which was kept at -11°C for 10 min without water drops freezing and then heating ($2^{\circ}\text{C}/\text{min}$) from -11 to -8°C resulted in freezing. Graph **E** represents the standard powder diffraction pattern of ice.

Fig. 5B represents powder diffraction patterns of ice crystals on LiTaO₃ surfaces. In particular, graph **F** represents a rocking curve of the $Z_{No\ field}^{+}$ specimen of the (002) peak. Graph **G** represents $\theta-2\theta$ scan of Z_{field}^{+} specimen with an inclination angle $\phi=7^{\circ}\text{C}$. Graph **H** represents a rocking curve of the Z_{field}^{-} specimen of the (002) peak. Graph **I** represents a rocking curve of the Z_{field}^{+} specimen of the (002) peak. Graph **J** represents a rocking curve of the Z_{field}^{+} specimen of the (100) peak.

As observed in graph A, the (XRD) patterns for $Z_{No\ field}^{+}$ and $Z_{No\ field}^{-}$ are almost indistinguishable which implies absence of epitaxial effects specific to either surface. The intensity of the (002) diffraction peak is at least 5 times larger than (100), (101) and (102) peaks. Furthermore, as illustrated in graph F, the rocking curve of the dominant (002) peak has a maximum around the inclination angle $\phi = \theta - \theta_{Bragg} = 0$. It should be noted that the inclination angle, ϕ , is the angle between the surface normal and the x-ray scattering vector in a $\theta - 2\theta$ scan, which indicates that the crystallites are aligned with (002) direction (*c*-axis of ice) perpendicular to the surface. This strongly suggests that the nucleation started at the LiTaO₃ crystal surface with their basal (001) face attached to the solid surface.

The XRD data represented by graphs B and C shows that the orientations of the ice crystals produced on the Z_{field}^{+} and Z_{field}^{-} specimens are completely different from each other and from those of the uncharged surfaces (graph A). The (100) and the (002) diffraction peaks are dominant in the case of Z_{field}^{+} as illustrated in graph B.

The $\theta - 2\theta$ XRD scans of the crystals do not show significant differences as a function of the inclination angle, ϕ ($\phi = 0^\circ$, graph B and $\phi = 7^\circ$, graph G). The XRD patterns are quite close to a randomly oriented set of ice crystals as shown in graph E. In addition, the intensity of the (002) diffraction peak does not change significantly as a function of the inclination angle as shown in graph I, which supports the conclusion drawn from graph B and G that, most of the crystals on Z_{field}^{+} surface are randomly oriented. However, the rocking curve of the (100) peak graph J indicates that there is a small population of crystals that are almost perfectly oriented with (100) direction perpendicular to the surface. In addition, there is a range of inclination angles $\phi = -4...+2^\circ$, with no crystals having this orientation. Presence of such an isolated population of crystallites suggests that this specific population was nucleated in the vicinity of a flat surface that served as a template. The only flat surface of the droplet is that of the LiTaO₃ crystal.

The XRD patterns of the ice crystals grown at the negatively charged surface of the Z_{field}^- specimens exhibit a very prominent feature indicating the source of their nucleation, as shown in graph C. The (002) diffraction peak is much wider but does not show a skew. Furthermore, the rocking curve of this peak shows two broad maxima in graph H, which implies that the nucleation took place on a curved surface, which is close but not parallel to the surface of the specimen, i.e., at the air- water interface as illustrated in Fig. 6D. Consequently, the nucleation occurs neither in the vicinity of the negatively charged $LiTaO_3$ surface nor in the bulk of the droplets, where the rate of nucleation is 10^{10} times slower in comparison to the air/water interface [14].

The XRD pattern of the ice crystals produced by the positively charged surface of the $00\bar{1}$ face (the charge-reversal experiment, graph D) indicates that the orientations of the crystals are almost random and very close to those found when the crystals were grown on the Z_{field}^+ specimen, which supports the conclusion that a positive charge at the $LiTaO_3$ surface strongly facilitates ice nucleation.

Similar differences in the temperature of ice nucleation are found when water freezing is performed on positively and negatively charged *quasi*-amorphous pyroelectric thin films. The SCW freezing experiments were performed with four types of 60 nm thick pyroelectric films of $SrTiO_3$ 7×12 mm: 1) those deposited on bare highly conductive (degenerate) (001) Si substrate (specimens QA_{field}^+). These specimens develop positive charge on the surface of $SrTiO_3$ upon cooling; 2) those deposited on 100 nm thick layer of conductive buffer ($SrRuO_3$) on highly conductive Si (specimens QA_{field}^-). These specimens develop negative charge on the surface of $SrTiO_3$ upon cooling; 3) those deposited on 50 nm thick insulating SiO_2 layer on Si (specimens $QA_{no\ field}^+$) and (4) those $SrTiO_3$ films on highly conductive Si that were intentionally left amorphous and non-pyroelectric (specimen $A_{no\ field}$). The specimens $QA_{no\ field}^+$ and $A_{no\ field}$ do not develop charge at their surface in response to temperature change.

The QA_{field}^+ , QA_{field}^- , $QA_{no\ field}^+$ and $A_{no\ field}$ films exhibit substantial differences in the freezing temperature but similar to those of $LaTiO_3$. Water droplets freeze at -4 ± 1 °C on the QA_{field}^+ specimens, whereas on both $QA_{no\ field}^+$ and $A_{no\ field}$ films water freezes at -12 ± 4 °C. On the QA_{field}^- specimens, water froze only at -
 5 19 ± 3 °C. The monitoring of ice nucleation on the QA_{field}^+ and that the amorphous $A_{no\ field}$ is shown in **Figs. 6B-6D**.

Therefore, water molecules orient their oxygen atoms with their lone electron pairs towards a positively charged surface, whereas water molecules orient their hydrogen atoms towards a negatively charged surface. Since the
 10 electron density and the geometry of the lone electron pairs of oxygen is very different from that of the two hydrogens, the water molecules self-assemble and interact differently with the surfaces of opposite charge.

As related above, *quasi*-amorphous pyroelectric films of $SrTiO_3$ can also be used to induce water freezing.. Hexagonal ice packs in the centrosymmetric
 15 space group $P6_3/mmc$ being proton-disordered. The crystal is polar along the c -axis on the assumption that there is no proton-disorder within the plane perpendicular to this axis.

Reference is made to **Fig. 6A**, illustrating water molecules freezed on the charged surface of *quasi*-amorphous film of $SrTiO_3$ as ordered nuclei of
 20 hexagonal ice. The water molecules loose their polarity only at a later stage of crystal growth. The freezing of water yield a crystalline powder; in variance to the single β -glycine crystals shown above, the anticipated orientation of the ice crystals induced at the nucleation stage is not preserved. Therefore, assuming proton-ordered along the c -axis, a nucleation of hexagonal ice can be obtained
 25 on a positively charged surface of the pyroelectric films of $SrTiO_3$.

The local electric field developed by the pyroelectric surface in the vicinity thereof organizes the water molecules into structured clusters that facilitate the freezing of supercooled water. However, it should be noted that the charge of the polar crystals is cancelled by adsorbed ions when exposed to the

environment. Therefore, the present invention also provides a build up of charge as a result of the cooling of the crystals.

Reference is made to **Figs. 6B-6D** illustrating the freezing of water droplets on the surface of the *quasi*-amorphous (bottom) and amorphous (top) films of SrTiO₃ (100 nm thickness grown on Si) at various temperatures during cooling: **Fig. 6B** at -4 °C, **Fig. 6C** at -11°C and **Fig. 6D** at -12 °C. It has been observed that the water droplets freeze at higher temperatures on the surface of pyroelectric *quasi*-amorphous films of SrTiO₃ than on the surface of amorphous SrTiO₃ films. The *quasi*-amorphous (polar) and amorphous (non polar) films are placed at random into a thermal bath and cooled down at a rate of 2°C/min. Water condensation from the ambient is first observed at 14°C. Upon cooling, water condensation continues and the droplets coalesce into larger drops and then freeze in a hexagonal ice polymorph. The freezing of the drops on the *quasi*-amorphous (pyroelectric) thin films occurs at -4°C, whereas at the surface of the amorphous (non-polar) films the drops froze at -12°C. The vertical dimension of all images is 1 mm. The space between the samples is an air gap.

Therefore, using the teachings of the present invention, pyroelectric materials promote the growth of polar crystals. Since both, the amorphous and *quasi*-amorphous films have the same chemical composition and almost the same morphology, epitaxy processes can be completely eliminated, which explicitly implies that the local electric field developed by the pyroelectric surface in the vicinity thereof affects the orientation of the glycine and the water molecules in the vicinity of the charged surface. Old films contaminated by adsorbing contaminants from the environment do not catalyze ice nucleation. It should be noted that the use of glycine for the experimental portion of this specification is for illustrative purposes only, as it is clear to one of ordinary skill in the art that the procedure and results disclosed and claimed in this specification can be performed for other compounds with polymorphs without undue experimentation.

CLAIMS:

1. A method for producing a polar crystal phase of a substance comprising:

interacting a solution containing the substance material with a surface of a film having pyroelectric properties, for a certain period of time predefined to be sufficient to induce nucleation of at least one crystal of said substance material;

applying a temperature change to said film enabling creation of an electric charge on the surface of said film, thereby creating a local electric field in the vicinity of the surface of said film, said electric field affecting said at least one crystal formed at the surface of said film to become oriented in accordance with the film surface, leading to the formation of the polar crystal.

2. The method of claim 1, wherein said electric field affects one or more properties of the polar crystal being formed.

3. The method of claim 2, wherein said electric field affects a phase transition temperature of the polar crystal.

4. The method of any one of claims 1 to 3, wherein said solution is an aqueous solution.

5. The method of any one of claims 1 to 4, comprising applying said temperature change to said film to create a positive electric charge on the surface of said film, thereby affecting at least one property of the polar crystal being formed.

6. The method of claim 5, wherein the positive electric charge on the surface of said film induces a phase transition consisting of freezing of said aqueous solution and promotes ice nucleation.

7. The method of any one of claims 1 to 4, comprising applying a temperature change to said film to create a negative electric charge on the surface of said film, thereby affecting at least one property of the polar crystal being formed.

8. The method of claim 7, wherein the negative electric charge on the surface of said film inducing a phase transition consisting of reduction of freezing temperature of said aqueous solution and retards ice nucleation.

9. The method of any one of claims 4 to 8, for production of supercooled water, the electric charge on the surface of said film inducing a phase transition consisting of reduction of freezing temperature of said aqueous solution.

10. The method of any one of claims 1 to 9, comprising providing an inorganic, *quasi*-amorphous oxide film of a metal, mixture of metals or semiconducting element; and interacting said solution with the surface of said *quasi*-amorphous film.

11. The method of claim 10, wherein said applying of the temperature change comprises applying a mechanical strain to said film enabling the creation of the electric charge on the surface of said film.

12. The method of claims 10 or 11, wherein said *quasi*-amorphous film is at least one of the followings film: SrTiO₃, BaTiO₃ and BaZrO₃.

13. The method of any one of claims 10-12, wherein said *quasi*-amorphous film is deposited on a silicon substrate.

14. The method of any one of claims 1 to 13, wherein the polar crystal is a polymorph crystal.

15. The method of claim 14, wherein the polymorph crystal is meta-stable.

16. The method of any one of claims 1 to 15, wherein the polar crystal is a polar β -polymorph of glycine.

17. A method for freezing supercooled water comprising:
interacting an aqueous solution with the surface of a film having pyroelectric properties for a certain period of time predefined to be sufficient to induce the nucleation of at least one ice crystal; and;
applying a temperature change to said film enabling the creation of an electric charge on the surface of said film; thereby creating a local electric field in the vicinity of the surface of said film; said electric field affecting

water molecules of said aqueous solution to become organized into structures clusters, enabling the condensation and freezing into a polar ice state.

18. The method of claim 17, wherein said electric field affects one or
5 more properties of the ice state being formed.

19. The method of claim 18, wherein said electric field affects a phase transition temperature of the ice state.

20. The method of any one of claims 17 to 19, comprising applying a temperature change to said film to create a positive electric charge on the
10 surface of said film, thereby affecting at least one property of the ice state being formed.

21. The method of claim 20, wherein the positive electric charge on the surface of said film induces a phase transition consisting of freezing of said aqueous solution and promotes ice nucleation.

15 22. The method any one of claims 17 to 19, comprising applying a temperature change to said film to create a negative electric charge on the surface of said film, thereby affecting at least one property of the ice state being formed.

23. The method of claim 22, wherein the negative electric charge on
20 the surface of said film inducing a phase transition consisting of reduction of freezing temperature of said aqueous solution.

24. The method of any one of claims 17 to 23, comprising providing an inorganic, *quasi*-amorphous oxide film of a metal, mixture of metals or semiconducting element; and interacting said solution with the surface of said
25 *quasi*-amorphous film.

25. The method of claim 24, wherein said temperature change comprises a mechanical strain enabling the creation of an electric charge on the surface of said film..

26. The method of claim 24 or 25, wherein said *quasi*-amorphous
30 film is at least one of the followings film: SrTiO₃, BaTiO₃ and BaZrO₃.

27. The method of any one of claims 24 to 26, wherein said *quasi*-amorphous film is deposited on a silicon substrate.

28. The method of any one of Claims 24 to 27, wherein said polar ice is in the hexagonal polymorph form.

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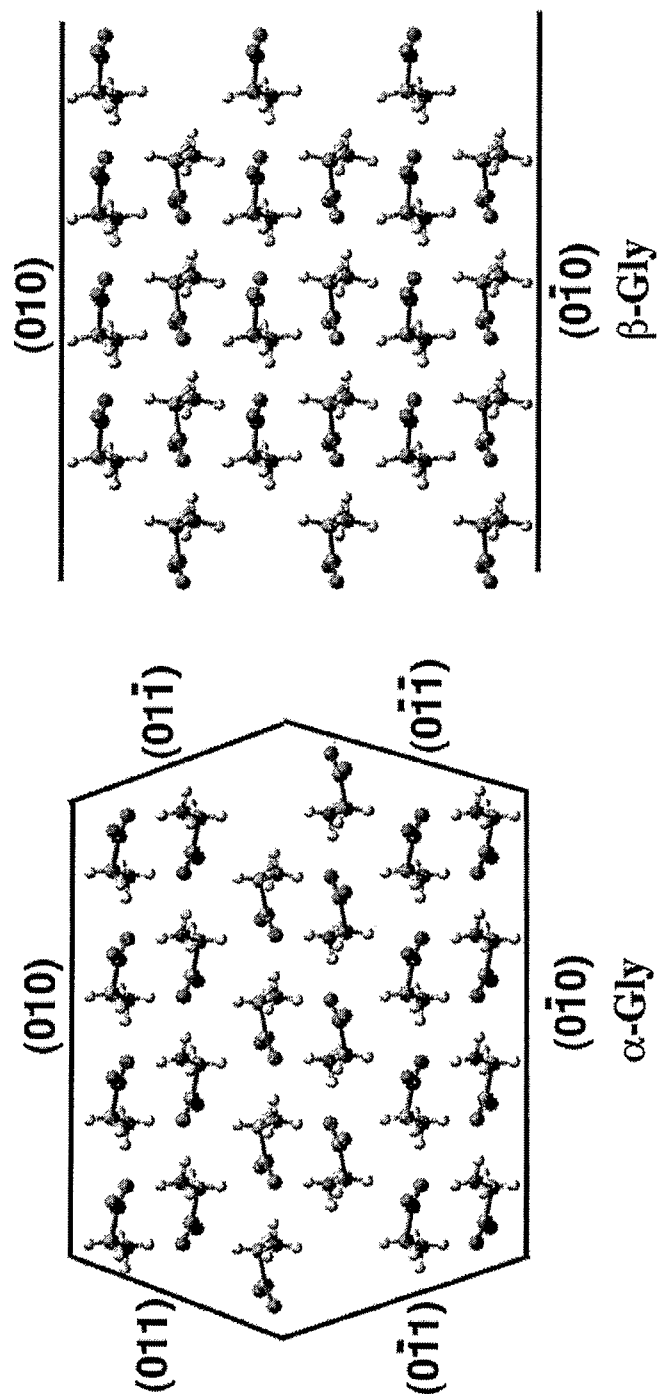


Fig.1A

Fig.1B

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Fig. 2A

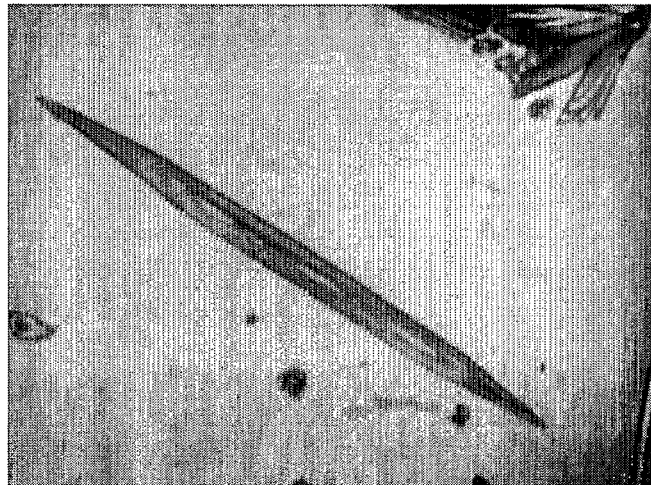


Fig. 2B

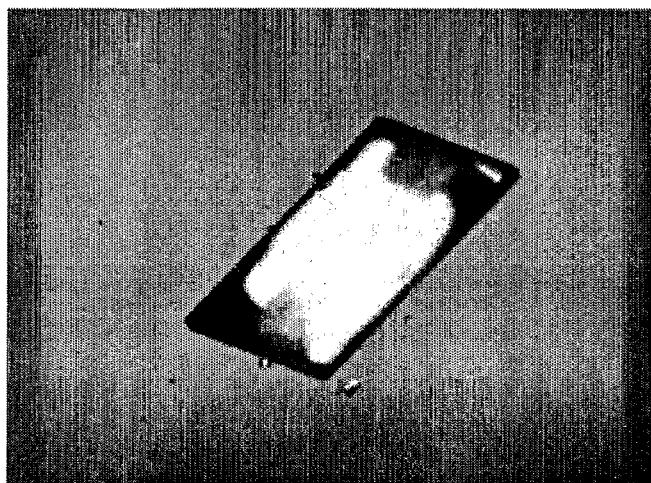


Fig. 2C

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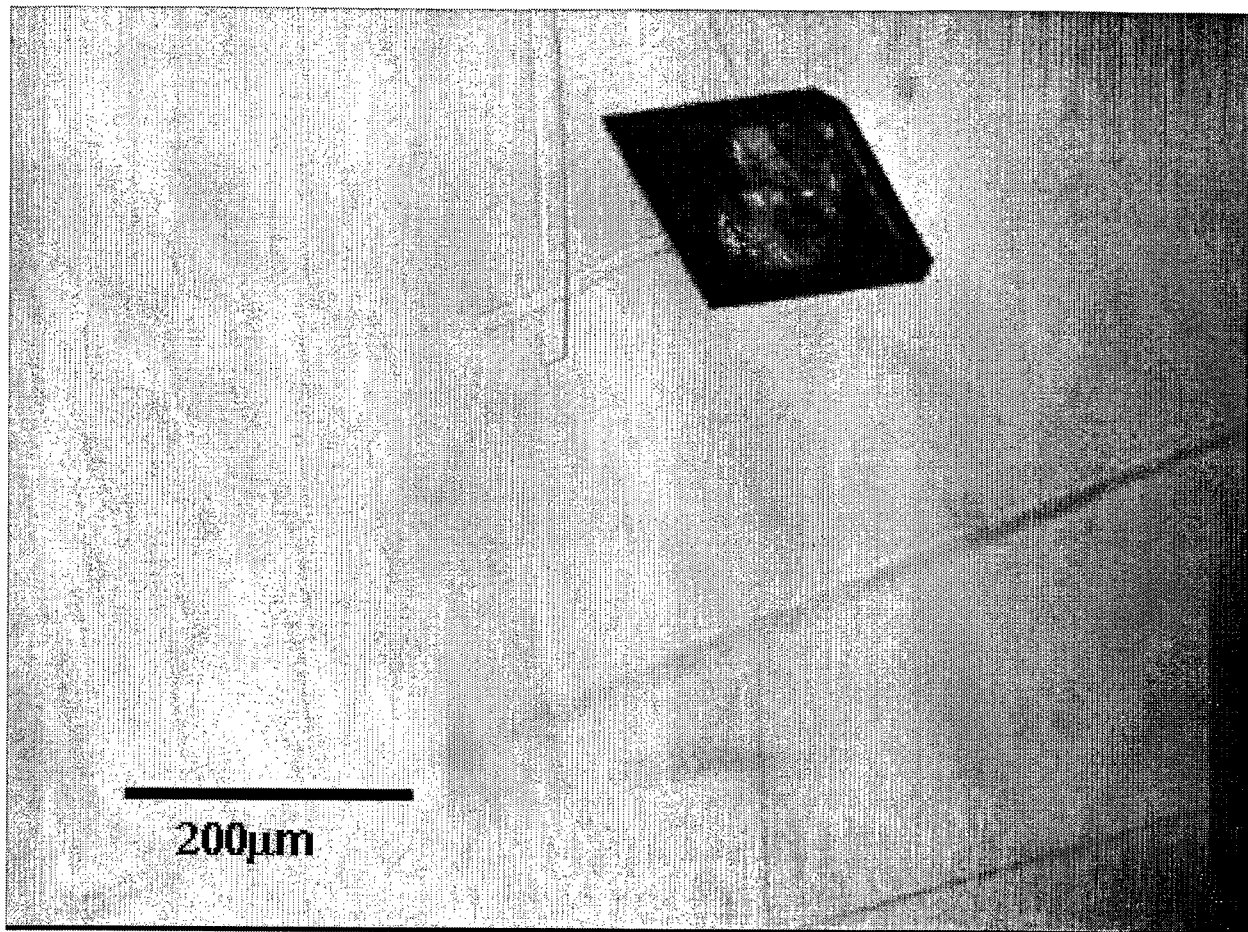


Fig. 2D

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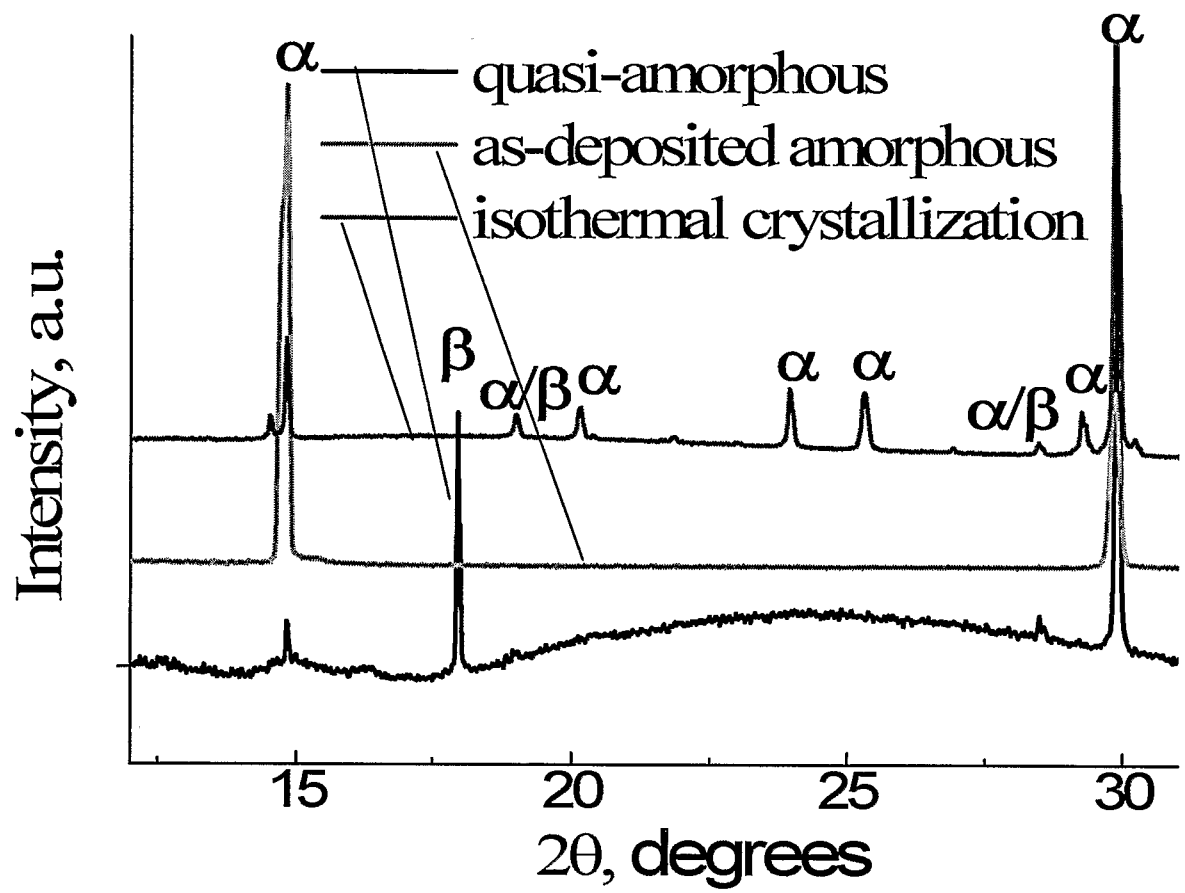


Fig. 2E

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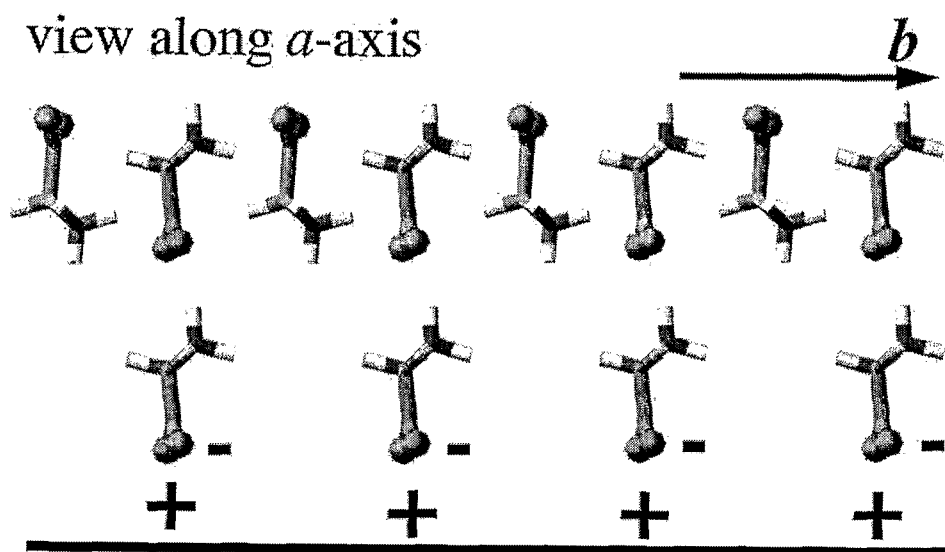


Fig. 3A

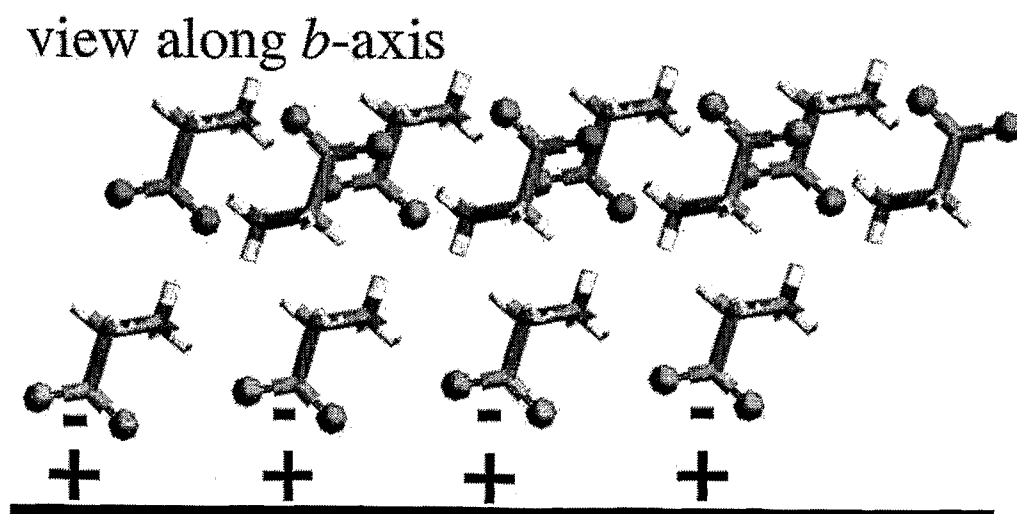


Fig. 3B

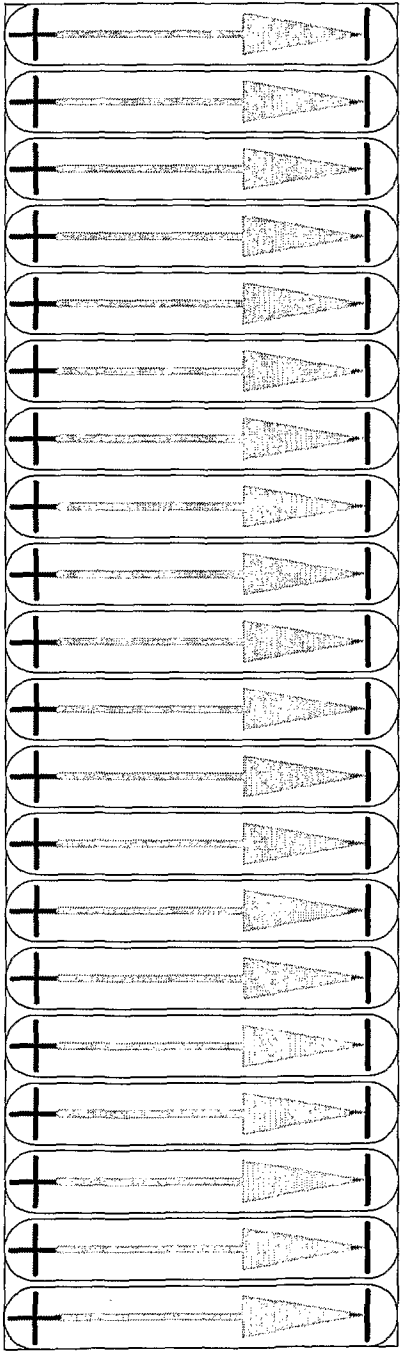


Fig. 4A

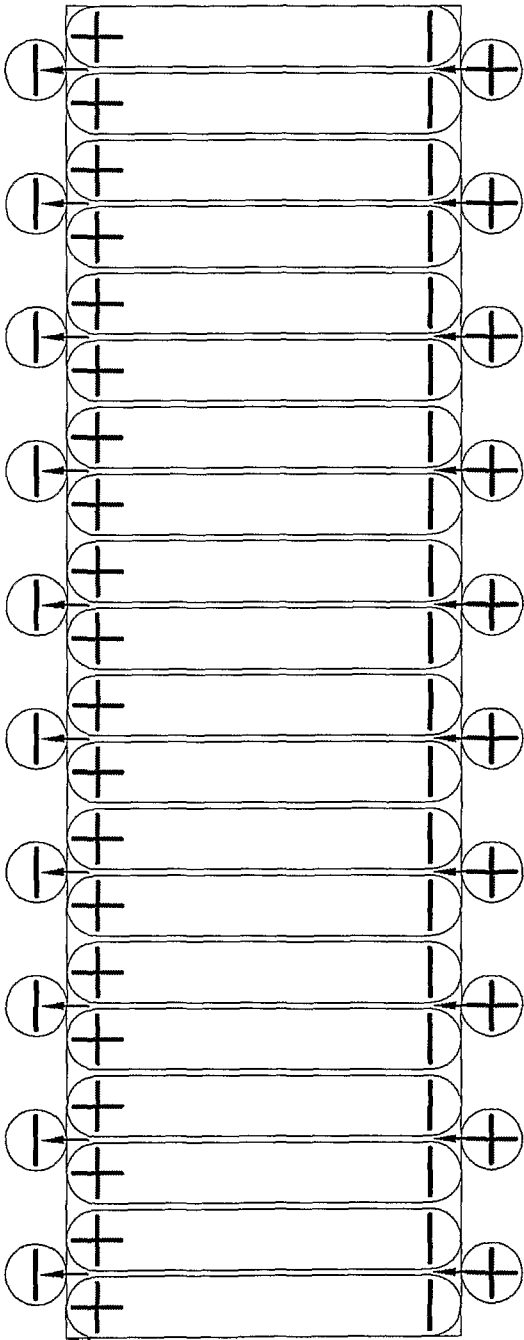


Fig. 4B

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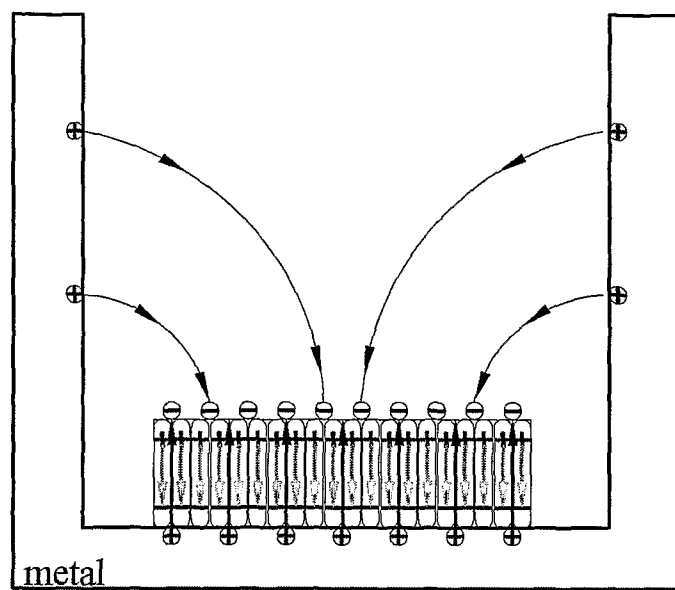


Fig. 4C

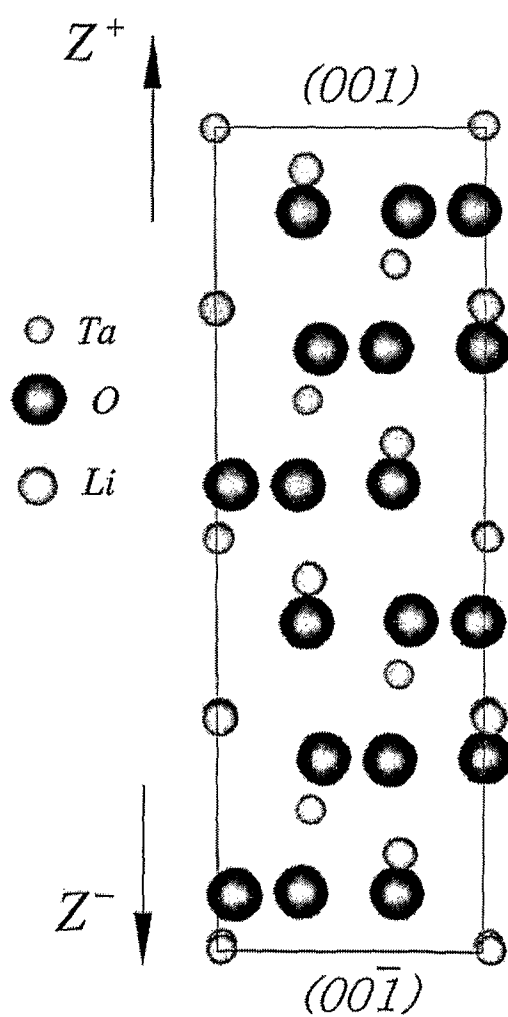


Fig. 4D

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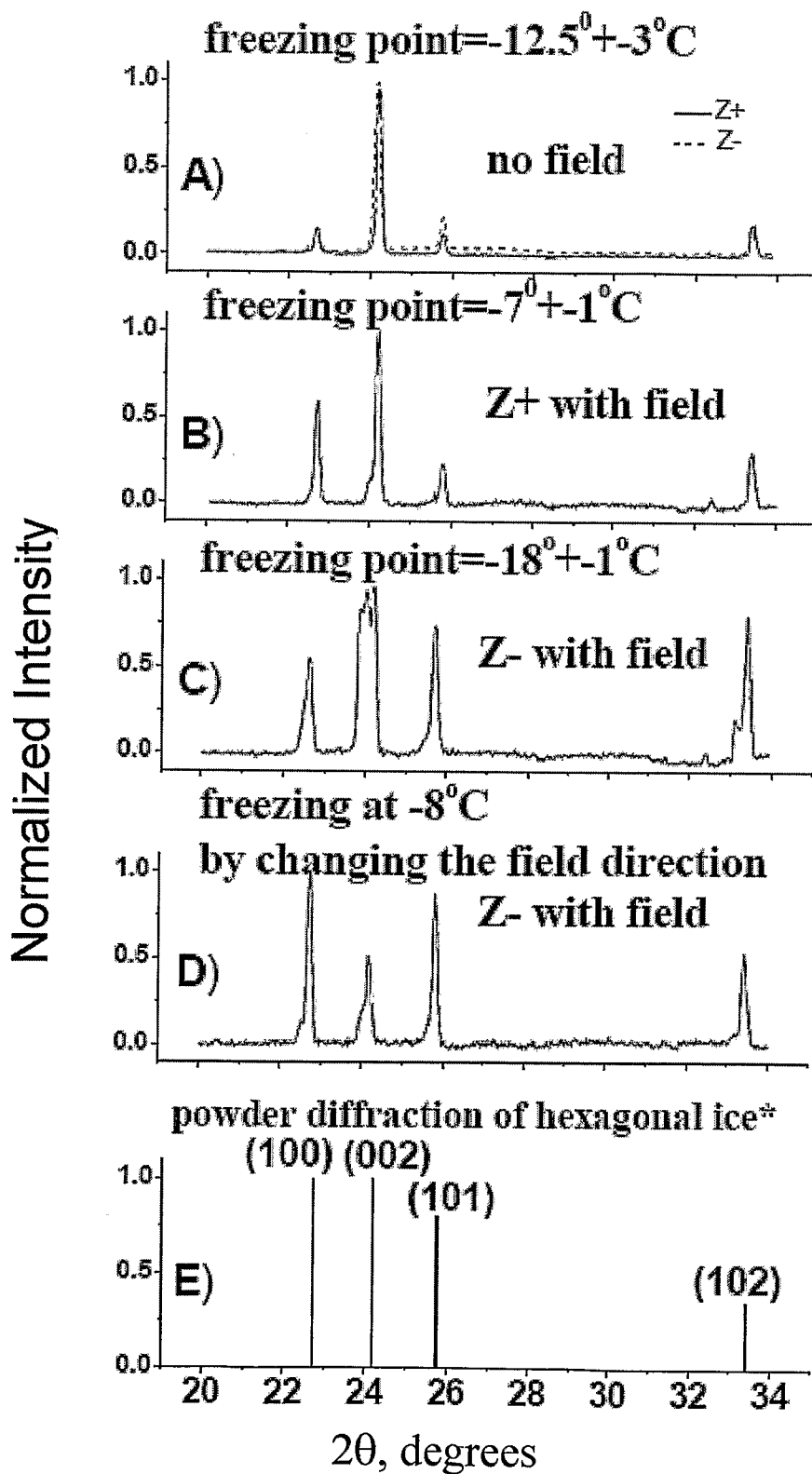


Fig. 5A

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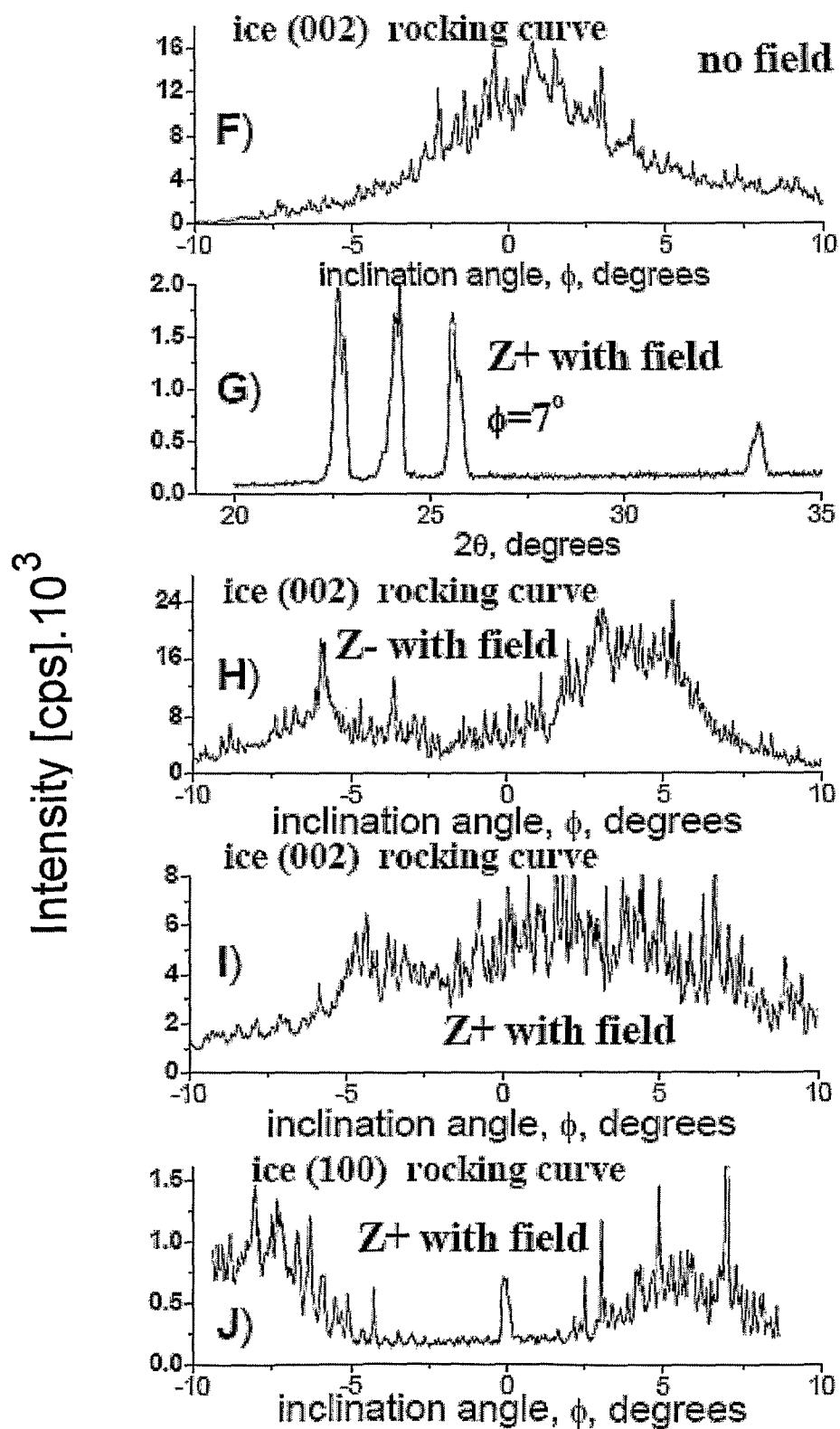


Fig. 5B

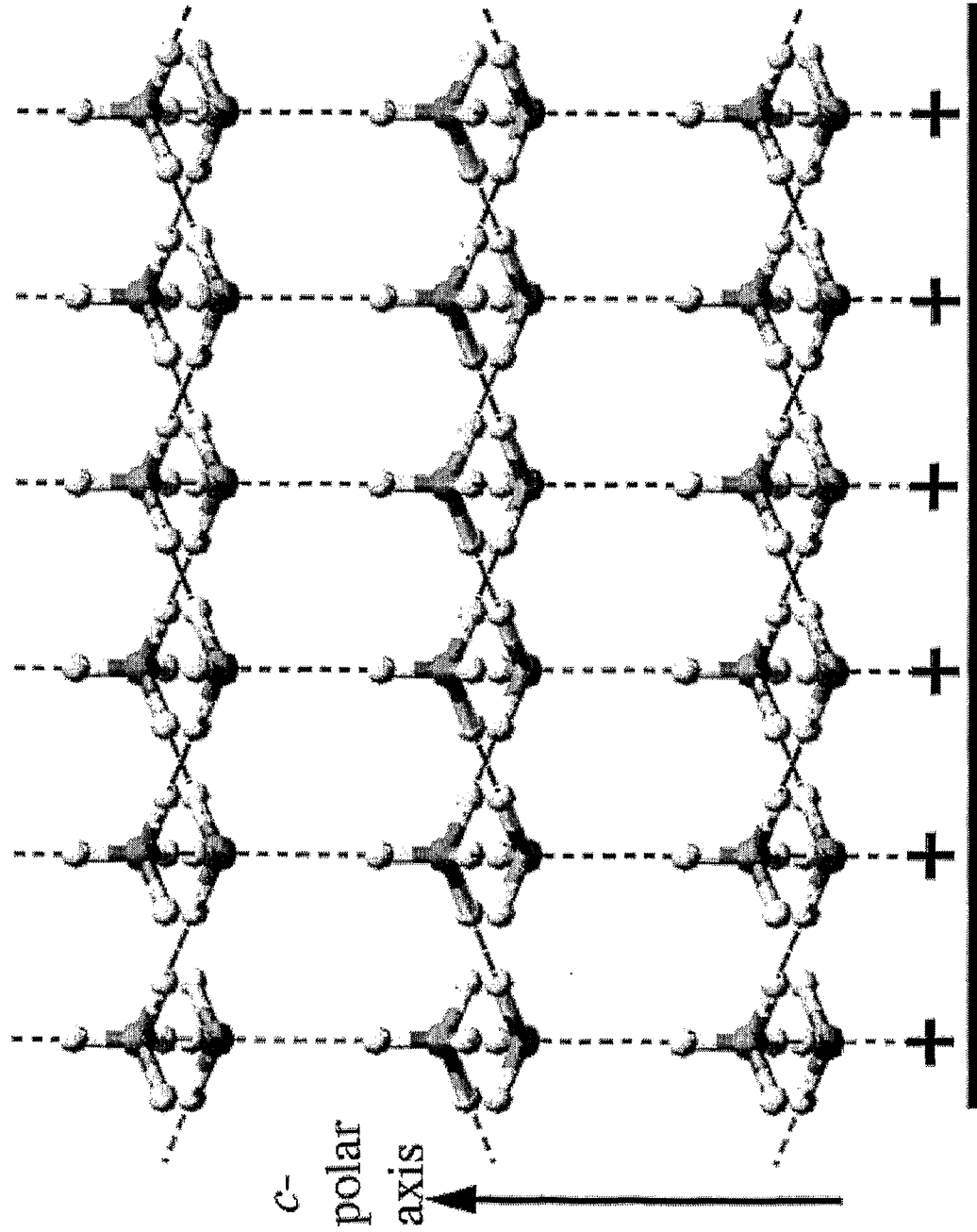


Fig. 6A

11/12

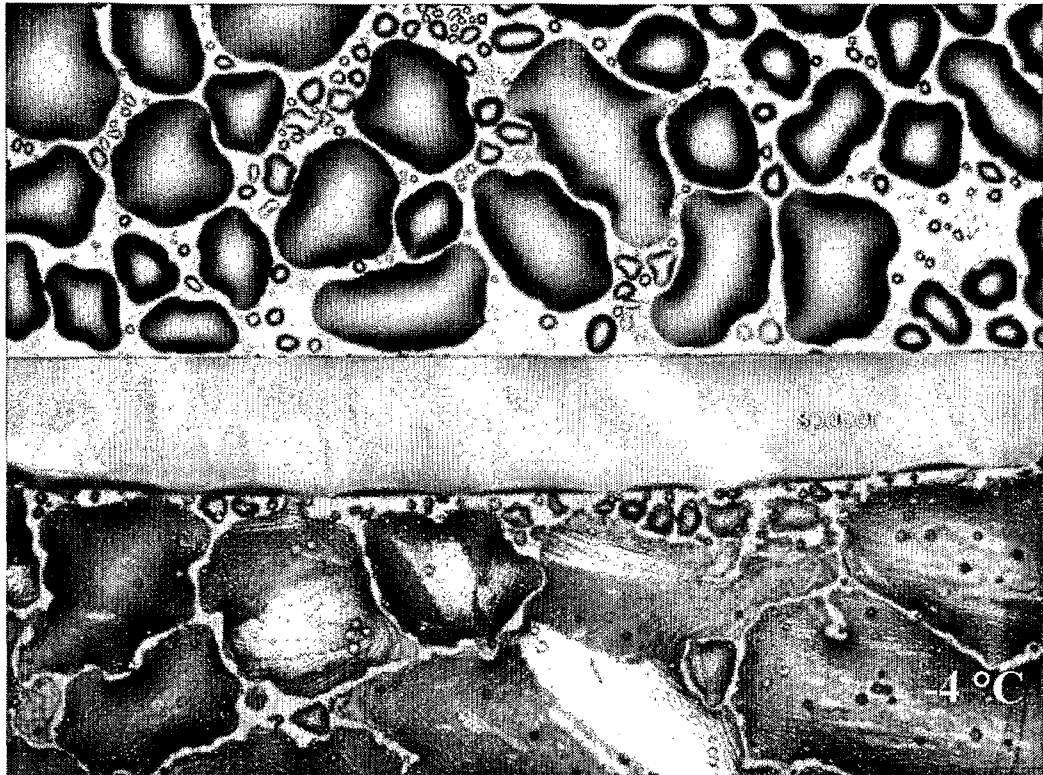


Fig. 6B

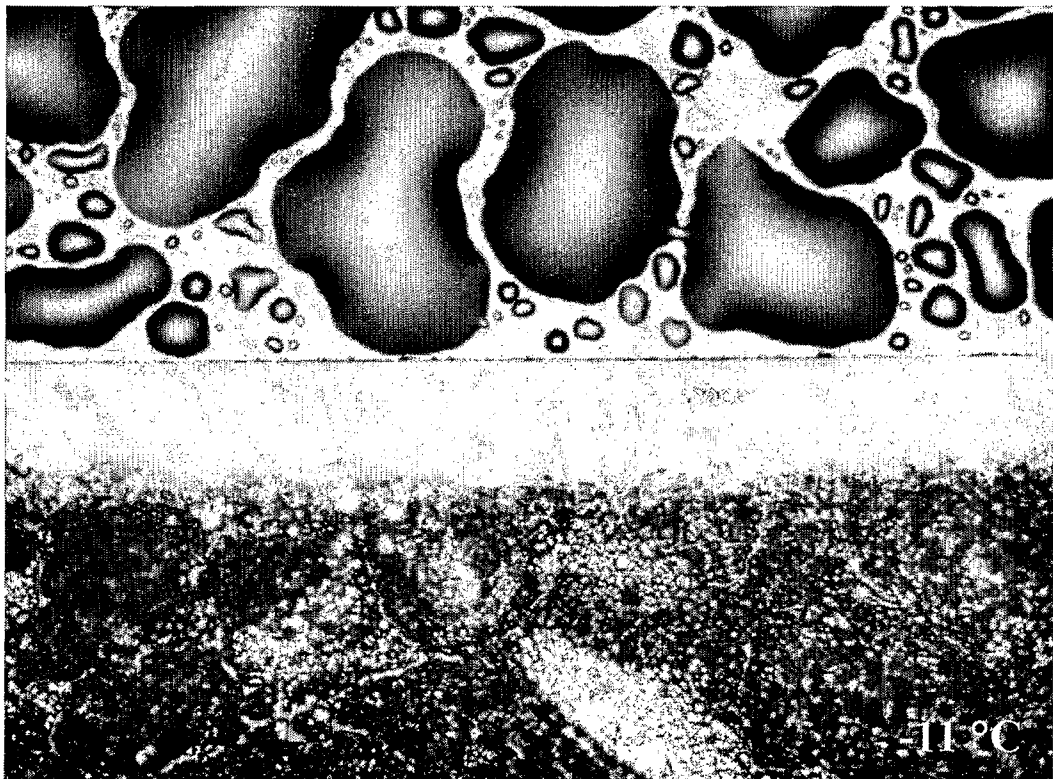


Fig. 6C

12/12

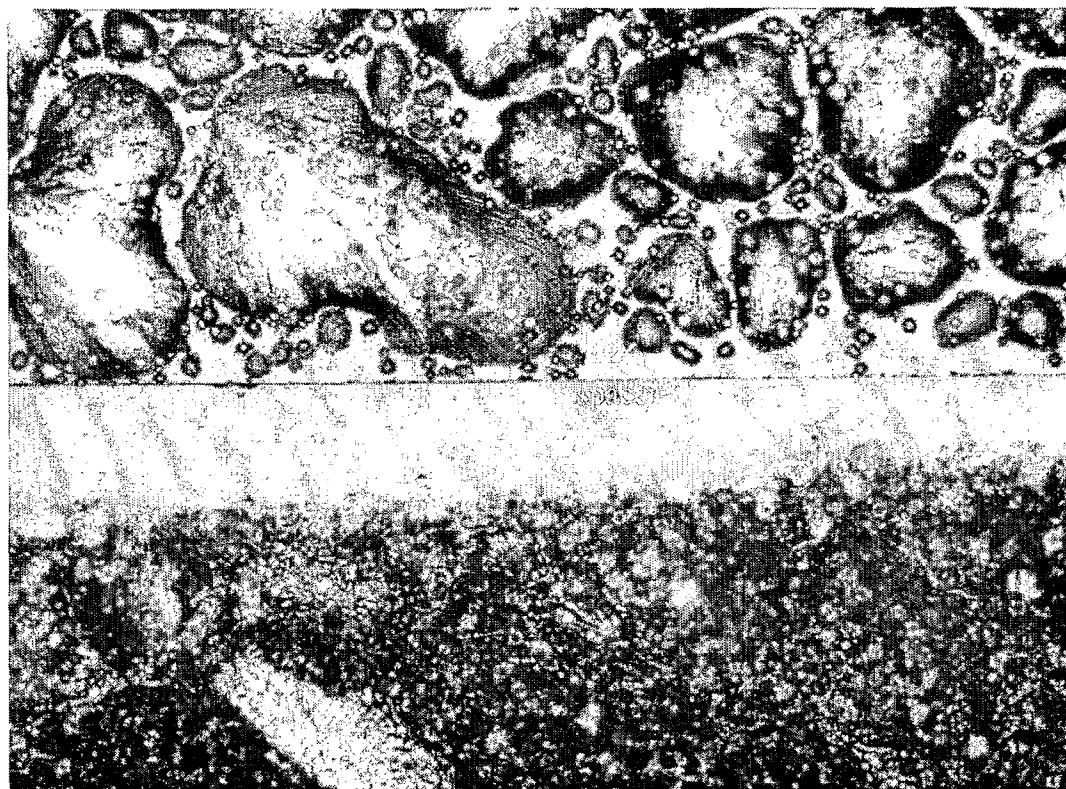


Fig.6D