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Article

A new hybrid cold storage material

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SUMMARY
Transportation of biological samples, such as cryopreserved mammalian cells, at ultra-low temperature, has been critical for medical research and services. The general public has now recognized another vital role of ultra-low temperature transport due to its irreplaceable role in delivering various vaccines that can protect us from deadly viruses. This study focuses on the cold storage material to facilitate the low-temperature transportation of vaccines and other commodities such as seafood. Dry ice does not suffice for the long-range transport of these products to rural areas. We propose using a combination of dry ice and ethanol, which has a higher thermal capacity, thermal conductivity, and latent heat, to produce a much more sustainable cooling solid for an extended period of cold transportation. We performed a detailed analysis of the performance of this new cold solid material to examine the feasibility of using it for shipping vaccines. The calculations showed that the new substance's cold storage capacity is 47.6 percent higher than dry ice. Therefore, this new combined substance is more appropriate for ultra-low temperature transportation. It is a promising new cold storage technology. Furthermore, the unique cold storage material combination presents a more economical and environmentally friendly transport cooling solution.

INTRODUCTION
Pandemics are global challenges that society faces. However, the needed long-distance shipment of the vaccine presents a challenging task as some vaccines need to be shipped at low temperatures worldwide, including to far-away underdeveloped regions (1). Like many biological samples, such as cryopreserved mammalian cells, these vaccines must be kept at a minimum of -70°C (2). Conventionally, dry ice is used as the packages' cooling material due to its sublimation temperature of -78.5°C, lower cost compared to larger freezers, easy preparation process, and pollution-free transportation with no direct carbon dioxide emissions (3-5). Dry ice has been commonly used during ultra-low temperature transportation of medicines, biological agents, and foods based on these advantages. For example, hospitals and shipping companies utilize dry ice to transport and store various vaccines at present (6).

However, the use of dry ice alone for shipping vaccines has its drawbacks. First, dry ice is consumed quickly and is difficult to store because of its high sublimation rate. In a standard 50-quart cooler, 15 pounds of pure dry ice is exhausted in 24 hours (7). Thus, dry ice needs to be replenished every five days during the shipping of certain vaccines, which is not ideal during long-distance cold transportation. Second, the latent heat of dry ice phase change is insufficient to transport and store vaccines everywhere, such as to a distant remote area or countryside, due to its limited cold storage capacity. Finally, the heat-absorbing capability of dry ice is low, leading to a lower cold storage capability. Intensive heat in the surrounding environment may pass through the package and reach the vaccines, potentially thawing the vaccines during transportation (8).

Previous research on the use of dry ice for exceedingly low-temperature transportation focuses on improving the container. For example, reducing the sublimation rate of dry ice by covering the inner walls of the insulation package with a reflective layer such as aluminized mylar foil (9). Inexpensive cryogenic shipping containers have been created that can remain at less than −50°C for 72 to 96 hours while holding dry ice shipments (10). It has been found that powdered dry ice releases cold faster than block dry ice, and dry ice placed in the inner wall of the cold storage box performs better in heat transfer than dry ice placed in the middle of the cold storage box (11-12). The success of these efforts depends upon the effective cold storage material used in the container.

Thus, there is an urgent need to improve traditional dry ice as a phase change material (PCM) for cold storage, such as enhancing the latent heat rate of cold storage change and thermal conductivity (13). In previous studies, dry ice was mixed with liquid ethanol to create rapid cooling for cold baths (14). Some factors influencing dry ice phase transition, such as the specific surface area of dry ice, the ambient pressure, and the mixing ratio of dry ice and ethanol, were explored (15). However, the dry ice and ethanol mixture was only investigated at the liquid state and used solely for cold baths. Therefore, if dry ice is mixed with ethanol and cryogenic treatment is performed, a new, hybrid cold solid phase change material can be obtained.

The solid form of a dry ice and ethanol mixture is still relatively new, especially relating to vaccine and food transport, therefore, we hypothesized that the combination of dry ice and ethanol will produce a more sustainable cooling solid for cold transportation compared to pure dry ice. After comparing varying dry ice and ethanol ratios, we determined that a 50/50 proportion would create a more sustainable solid during the extended period of vaccine transportation. We analyzed the performance of this new material to investigate its feasibility and benefits for shipping vaccines through theoretical calculations. The results indicated that the cold storage performance of the new cold storage material combination is greater than that of dry ice, suggesting that dry ice and ethanol combined is a more effective cooling solid than dry ice alone. Therefore, the proposed combination of dry ice and ethanol presents as a new and more promising cold storage material for transporting vaccines as ethanol has a higher thermal capacity, latent heat, and thermal conductivity.

RESULTS

This study proposed a new cold storage material that combines both dry ice and ethanol. We hypothesized that this combination would produce a more sustainable cooling solid for cold transportation than dry ice alone. We used theoretical calculations based on ethanol's and dry ice's properties to compare the performance of the material combination versus dry ice alone.

We chose to combine ethanol and dry ice instead of only using dry ice to form a new hybrid cold material. Ethanol has several physical properties compared to dry ice at -78.5ºC (1.01 MPa), making it a good candidate for creating a new hybrid material (**Table 1**) (16-17). First, the latent heat of ethanol volatilization is 1,115 kJ/kg, which is more than double that of dry ice sublimation. This property indicates that the heat absorption during the volatilization of ethanol is two times larger than that of dry ice sublimation. Second, the thermal conductivity of ethanol is ten times higher than that of dry ice at 0.195 W/(m·K), implying that the energy storage rate for solid ethanol cold storage is much higher than that of dry ice. Third, the specific heat capacity of ethanol is 4.11 kJ/(kg·K), which is about five times the value of dry ice, suggesting that ethanol can absorb more 'invading' heat from the outside, which protects the vaccine better during shipping.

Next, we considered other substances such as ammonia or water. Ammonia has a solidification point around -100°C and is volatile. However, this material is poisonous (18). It is much easier to regulate a combustible substance, such as ethanol, than toxic ammonia. The solidification point of water is 0°C, which is not as effective for cooling. Finally, we compared the latent heat of dry ice and ethanol and dry ice and water as the percentage of water or ethanol increases (**Figure 1**). The latent heat of the combined ethanol and dry ice is much higher than the mixed water and dry ice when the percentage of ethanol is increased. Thus, ethanol can absorb more heat before the heat reaches the products.

Physical properties	Dry ice	Ethanol	Units
Latent heat of phase change	573	1115	kJ/kg
Thermal conductivity	0.011	0.195	W/(m·K)
Sublimation/evaporation temperature	-78.5 [23]	-114/78	°C
Specific heat capacity	0.8	4.11	kJ/(Kg·K)

Table 1. Physical properties of dry ice and ethanol at -78.5ºC, 1.01MPa.

Then, using theoretical calculations, we compared samples of pure dry ice and the new storage material combination of dry ice and ethanol with the same initial temperature, T0 (< -78.5ºC), and weight and obtained their cold storage capacities. We calculated the cold storage capacity of 1 kg of pure dry ice with an initial temperature of -80ºC by utilizing the properties in Table 2 and dividing the cooling process into two steps– heating to the sublimation point and sublimation (**Figure 2A**). The cold storage capacity was 574.2 kJ for pure dry ice.

To calculate the cold storage capacity of 1 kg of the new hybrid cold storage material at -80ºC, we divided the cooling process into three steps: heating to the phase change point, sublimation of the dry ice, and volatilization of the ethanol. We also used a proportion of 50 percent ethanol and 50 percent dry ice. We chose this proportion based on the analysis in **Figure 1** and the dry ice and ethanol properties shown in **Table 1**. The latent heat, thermal conductivity, and specific heat capacity of ethanol are much higher than those of dry ice (**Table 1**). Therefore, this indicates that ethanol has a better cold storage capacity than dry ice. In addition, adding ethanol can also decrease the rate of sublimation of dry ice because it can discharge the cold gradually during transportation as the rate of evaporation of ethanol is minimal, which is essential for the long-term shipment of the vaccine. The higher the ethanol ratio, the stronger the cold storage material (**Figure 3**). However, dry ice must exist in the new hybrid material due to ethanol's high flammability and difficulties revolving around ethanol at the solid state. With 50 percent ethanol, ethanol's superior qualities are utilized while drastically reducing its combustibility, as illustrated by the red dashed line in **Figure 3**. The cold storage capacity of a 50/50 combination of dry ice and ethanol is 847.45 kJ. These calculations show that the cooling capacity of the new cold storage material is 47.6% greater than that of pure dry ice of the same quantity and

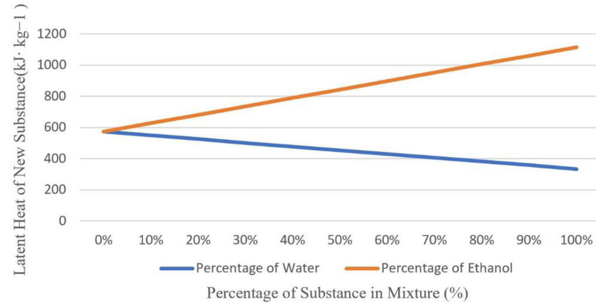

Figure 1. Comparison between latent heat of dry ice and ethanol and latent heat of water and dry ice. When the percentage of ethanol increases, the resulting substance of dry ice and ethanol's latent heat increases. When the percentage of water increases, the resulting substance of dry ice and water's latent heat decreases.

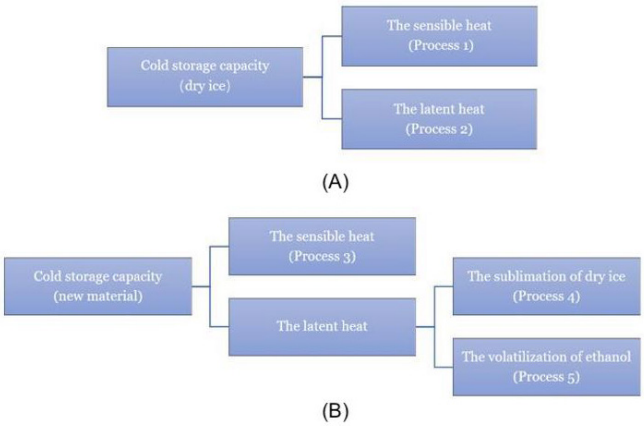

Figure 2. The different components of dry ice and the new cold storage material. (A) The components of dry ice. (B) The components for the new cold storage material.

initial temperature.

We also calculated the contributions of dry ice to the cooling strength from latent heat and sensible heat (**Figure 2A**). The latent heat took up most of the process at 573 kJ, providing 98.6% of the cooling. On the other hand, the sensible heat at 8 kJ provided only 1.3% of the cooling. In comparison, the results of the new storage material delineated that the sensible heat at 25 kJ contributes 2.2%, and the latent heat at 1,115 kJ yielded 97.8% (**Figure 2B**). Again, these results were obtained assuming there was 1 kg of the new substance, and the new substance increased/declined 10 K. The calculations showed that the latent heat takes up most of the process, with the sensible heat only providing a small portion in both cases. Thus, the latent heat must be greater for a substance to be more effective. Moreover, the new cold storage material's overall cooling capability is much higher.

To solve the problem of exceptionally low-temperature transportation, an efficient and reliable cold storage agent is required and a cold storage box with superior insulation performance is also needed. Therefore, the newly-introduced phase-change cold storage material is put inside the cold storage box to form a low-temperature environment for the vaccine. The heat leakage of the cold storage box and

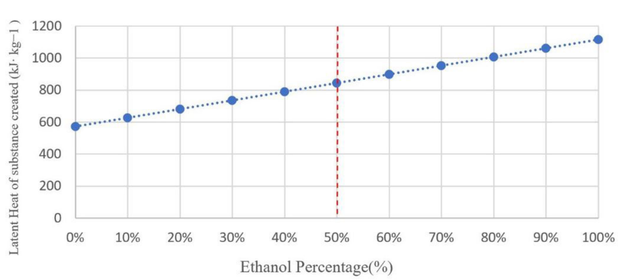

Figure 3. Effect of ethanol percentage on the latent heat of the new substance. When the percentage of ethanol increases, the latent heat of the new substance increases. The red dashed line indicates the point where ethanol's superior qualities are utilized in the new substance but reduce the combustibility of the substance.

resulting effective cold storage time were analyzed using theoretical calculations and found to be 26.41 W for both pure dry ice and the new combination of dry ice and ethanol.

Finally, we evaluated the performance of the cold storage materials. The cold chain transportation effective time of the pure dry ice per kilogram was about 6.04 hours, and that of the new cold storage material combination was about 8.91 hours. The analysis delineates that the cold storage time of the new material was 47.6 percent more than using pure dry ice. Therefore, combining dry ice with ethanol in the solid state is a more effective material for cold storage during transportation.

DISCUSSION

Dry ice and the newly created mixture of dry ice and ethanol are suitable for ultra-low temperature transportation due to their low phase transition temperature and high latent heat value. The theoretical calculations reveal that the cold storage performance of the new cold storage material is much better than that of dry ice. Calculations conducted using the box model delineate that the cold storage capacity and the cold chain transportation effective time of the new cold storage material is 47.8 percent more than that of dry ice. Thus, the new combination of ethanol and dry ice is a more suitable solution for cold transportation.

While our calculations show the combination of dry ice and ethanol to be a more effective cooling substance for long-distance transportation, we made assumptions such as neglecting thermal resistance during this research. As the results convey, the performance of the new material is calculated under ideal circumstances, so there may be slight deviations if the material were employed in real life.

Regarding the box calculations explained in the materials and methods section, there are some considerations regarding materials and spacing. As time progresses, the heat leakage increases. Thus, by minimizing heat leakage, transportation will be even more effective. Therefore, the outer layer material of the storage boxes is crucial. For example, if it were metal, which conducts heat quickly, the heat leakage increases. Thus, a material with low heat conductivity must be chosen. In addition, it is crucial to fill the storage box as much as possible to decrease the available area and distance, resulting in less space open for heat to leak in.

The next step is to test the feasibility of this new material in real-world conditions. In addition, the ideal proportions of ethanol and dry ice can be further investigated to create the most efficient material. We chose to use a 50/50 ratio of dry ice and ethanol to achieve the most significant benefit from ethanol's properties while reducing its combustibility (see **Figure 3**). However an alternative proportion may be superior.

This work suggests that the new cold storage material is a promising solution to the possible problems of cold storage technology, especially in the exceedingly low cold storage transportation field. This new phase change material is superior to pure dry ice for long-distance shipment because of its higher cold storage capacity and low rate of evaporation phase change. Compared to dry ice, it can store materials at colder temperatures and release the cold for a longer time than pure dry ice. In addition, ethanol is environmental-friendly, non-toxic, and cheaper in comparison. Exhibiting better economic value and reliability for cold chain transportation than dry ice, it has promising prospects in the transportation of seafood, medicines, biological agents, and other foods. Most importantly, it can avail in the critical transportation of vaccines during pandemics to secure the safety and reliability of the vaccines. Therefore, this new cold storage material is important in the future of all industries relating to the issue of cold transportation.

MATERIALS AND METHODS

Performance of pure dry ice

The entire cooling process was divided into two portions: heating to the sublimation point, T_1, (Process 1) and sublimation (Process 2) (**Figure 2A**). The physical properties of pure dry ice were measured by the specific heat capacity, C_0, and the latent heat of phase change, q_0. Moreover, the heat transfer of Process 1 is Q_1, and of Process 2 is Q_2. These physical properties of pure dry ice are given (**Table 2**) (19).
So, we have:

$$Q_1 = mC_0(T_1 - T_0) \quad [1]$$

$$Q_2 = mq_0 \quad [2]$$

The cold storage capacity, Q, is:

$$Q = Q_1 + Q_2 = mC_0(T_1 - T_0) + mq_0 \quad [3]$$

Through Equation [3], we analyzed the performance of pure dry ice.

Performance of the new hybrid cold storage materials

As no chemical reactions occur during the mixing of dry ice and ethanol, it was assumed that the thermal properties of dry ice and ethanol remain unchanged. The cooling process was divided into three portions: a) heating to the phase change point, T_2, (Process 3), b) sublimation of the dry ice (Process 4), and c) volatilization of the ethanol (Process 5) (**Figure 2B**).

The physical properties of the hybrid material include the latent heat of volatilization of ethanol, q_1, the specific heat capacity of new cold storage material, C_2, and the mass of the ethanol and dry ice, m, each contributing half. The heat change of Process 3, 4 and 5 are Q_3, Q_4, and Q_5. These physical properties are given (**Table 3**).
So, we have:

$$Q_3 = mC_1(T_2 - T_0) \quad [4]$$

$$Q_4 = 0.5mq_0 \quad [5]$$

$$Q_5 = 0.5mq_1 \quad [6]$$

The cooling storage capacity Q is:

$$Q = Q_3 + Q_4 + Q_5 = mC_1(T_2 - T_0) + 0.5mq_0 + 0.5mq_1 \quad [7]$$

Through Equation [7], we analyzed the performance of the new cold storage combination.

Then, the calculations for the contributions to the cooling strength from Process 1 (latent heat) and Process 2 (sensible heat) of dry ice were completed and compared (**Figure 2A**). These calculations were done assuming there was 1 kg of dry ice and the dry ice increased or declined 10 Kelvin (K).

Cold storage box analysis

A reliable cold storage box is also required for more efficient ultra cold transportation. The newly introduced phase-change cold storage material was put inside the cold storage box to form a low-temperature environment for the vaccine. The heat leakage of the cold storage box and resulting effective cold storage time were analyzed using theoretical calculations. A standard cold storage box commonly used today was selected, assuming the following. First, the ambient temperature was 15°C (±2°C). Second, the temperature in the cold storage box was below -70°C. Finally, the effective volume of the cold storage box was 10 L. The box's dimensions are given (**Table 4**).

The external dimensions of the cold storage box were 337 x 241 x 269 mm, and the internal dimensions were 275 x 185 x 216 mm. The shell and the liner were made of polyethylene, the thermal insulation material. The thermal conductivity of polyurethane, a polyethylene component, was about 0.0351 W/(m·K), and that of polyethylene was about 0.42 W/(m·K). The temperature zone can be equipped with a temperature monitor to measure the temperature changes.

To analyze the efficiency of the box, the dimensions of the box and quantity of phase change material (PCM) were kept as assumed (**Figure 4**). In addition, the following conditions were taken in the analysis (20-21). First, air, PCMs, and insulation material were isotropic. Second, thermal resistance was not considered. Finally, the phase change process of PCMs took place in a multi-phase coexistence zone at a specific temperature. Thus, the physical properties of PCMs were linear functions of temperature.

Properties	Symbol	Value	Units
Mass	m	1	kg
Specific heat capacity of the dry ice	C_0	0.8	$kJ \cdot kg^{-1} \cdot K^{-1}$
Initial temperature	T_0	193.15	K
Sublimation temperature of the dry ice	T_1	193.65	K
Latent heat of the dry ice	q_0	573	$kJ \cdot kg^{-1}$

Table 2. The values, symbols and units of the variables in the pure dry ice cooling process.

Properties	Symbol	Value	Units
Specific heat capacity of the material	C_1	2.3	$kJ \cdot kg^{-1} \cdot K^{-1}$
Sublimation temperature of the material	T_2	194.65	K
Latent heat of the material	q_1	1115	$kJ \cdot kg^{-1}$

Table 3. The values, symbols and units of the new cold storage material cooling process.

Dimensions	Value (mm)
Length	337
Width	241
Height	269

Table 4. The dimensions of the cold storage box.

The heat leakage of the cold storage box is shown below:

$$Q' = Q_{dis} + Q_{equip} \quad [8]$$

where *Q'* is the overall heat leakage of the cold storage box, Q_{dis} is the heat dissipation of the cold storage box, and Q_{equip} is the heat leakage of the equipment, if there are any.
As the cold storage material was placed between the liner and the insulator, Q_{dis} is mainly the heat dissipation through the liner, $Q_{\alpha 1}$, and the heat exchange between the outer layer of the box and the environment, $Q_{\alpha 2}$ (21).

$$Q_{dis} = Q_{a1} + Q_{a2} \quad [9]$$

$Q_{\alpha 1}$ relates to the convection of the inner space and the heat conduction of the liner, which can be approximated as a single-layer flat wall heat transfer process. The calculation was as follows:

$$Q_{a1} = K_{a1}A_1(t_1 - t_2) \quad [10]$$

Where A_1 represents the surface area of the liner, m^2, $A_1 = 0.3m^2$, t_1 is the temperature inside the cold storage box, *K*, and t_1 = 203.15 K, t_2 is the temperature of the cold storage material, K, and *t2* = 193.15 K, and K_{a1} is the heat transfer coefficient of the liner, *W/(m²·K)*.

$$K_{a1} = \frac{1}{\frac{1}{\alpha_1} + \frac{d_1}{\lambda_1}} \quad [11]$$

where α_1 represents the convection coefficient of heat transfer between the liner and the inside air, W/(m²·K) and α_1 = 1.1 W/(m²·K), d_1 represents the thickness of the liner, *m*, d_1 = 0.003 *m*, and λ_1 represents the thermal conductivity of the liner, *W/(m²·K)* and λ_1 = 0.42 *W/(m²·K)*.

Q_{a2} relates to the convection of the outer space of the box and the heat conduction of the insulator and the shell, which can be approximated as a multi-layer flat wall heat transfer process. Thus, we have:

$$Q_{a2} = K_{a2}A_2(t_3 - t_2) \quad [12]$$

where A_2 represents the surface area of the shell, m^2, A_2 = 0.47 m^2, t_3 represents the temperature outside the cold storage box, K, t_3 = 288.15 K, and K_{a2} represents the heat transfer coefficient of the outer layers, *W/(m²·K)*.

$$K_{a2} = \frac{1}{\frac{1}{\alpha_2} + \frac{d_2}{\lambda_2} + \frac{d_3}{\lambda_3}} \quad [13]$$

where α_2 represents the heat convection coefficient between the shell and the ambient air, *W/(m²·K)*, α_2 = 11 *W/(m²·K)*, d_2 represents the thickness of the insulator, *m*, d_2 = 0.057 m, λ_2 represents the thermal conductivity of the insulator, *W/(m²·K)*, λ_2 = 0.0351 W/(m2·K), d_3 represents the thickness of the shell, *m*, d_3 = 0.005 m, and λ_3 represents the thermal conductivity of the shell, *W/(m²·K)*, λ_3 = 0.42 *W/(m²·K)*.

Therefore, the Q_{dis} is:

$$Q_{dis} = [K_{a1}A_1(t_1 - t_2) + K_{a2}A_2(t_3 - t_2)] \quad [14]$$

The heat of equipment is the heat emitted by the lights or other equipment in the cold storage box during operation. In the present analysis, there is no heating equipment in the cold storage box, which means:

$$Q_{equip} = 0 \quad [15]$$

So, the overall heat leakage of the cold storage box *Q'* is:

$$Q' = Q_{dis} + Q_{equip} = [K_{a1}A_1(t_1 - t_2) + K_{a2}A_2(t_3 - t_2)] \quad [16]$$

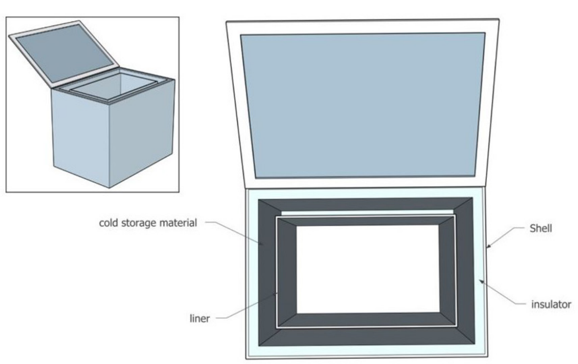

Figure 4. Structural diagram of the cold storage box.

The cold storage time

To evaluate the performance of cold storage materials, the cold chain transportation effective time, *t*, is introduced here (22):

$$t = \frac{Q}{Q'} \quad [17]$$

where Q represents the cold storage capacity of the material, *J*, and *Q'* represents the overall heat leakage of the cold storage box, *W*.

This effective time, *t*, was the length of time that cold storage materials of the same quality can maintain low temperatures in cold chain transportation. The greater the value of *t*, the better the cold storage performance of the material, and the better it was for long-distance cold chain transportation.

New cold solid matrial and its creation process

Based on a thoroughly investigated methodology of the cold liquid preparation of dry ice and ethanol, we created the cold solid material of dry ice and ethanol. To make 1.0 kg of this new cold solid (assuming ethanol's density as 800.0 kg/m3), 500 g of pure dry ice and 625 ml of absolute ethanol (mass ratio of dry ice and ethanol at around 1:1) was required. First, dry ice was processed into granules in a container, where 625 ml of absolute ethanol at room temperature was added gradually. Then, the dry ice-ethanol mixture was stirred to obtain a white emulsive material. Finally, the container with the cold liquid material was put in an exceedingly low-temperature freezer to freeze it below -80°C, where the material condensed into a solid state. This new cold solid material can be made using different ethanol concentrations in dry ice.

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