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Ice nucleation activity of PbI_2–CdI_2 system

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The ability of a solid substrate to induce ice nucleation in supercooled water depends on a number of factors. There is a tendency for the more effective nucleant to possess hexagonal crystalline symmetry and lattice parameters reasonably close to those of ice. The present study was undertaken in an effort to decrease the mismatch between ice and lead iodide and thereby improve the nucleating behaviour of lead iodide. For this purpose lead iodide has been considered. PbI_2 and CdI_2 were added in different molar ratios and fused at 430° C. An X-ray diffractogram of each combination was taken, and an ice nucleation study was made with finely powdered samples of each combination The nucleation temperature at 50:50% combination of PbI_2 and CdI_2 has the highest nucleation temperature of $-2.35°$ C. Other combinations have also revealed nucleation temperatures higher than that of pure PbI_2 and CdI_2. The causes for the activity have been discussed.

1. Introduction

Heterogeneous nucleation is a surface phenomenon. Therefore, any prediction of nucleating ability must consider the detailed physics of the surface. The factors which determine the threshold temperature of a nucleant are: (1) the surface charge; (2) the hydrophilicity; (3) the polarizability; and (4) the size. These criteria have been established in a qualitative way to predict which materials are good nucleating agents for ice. The most obvious requirement is that there must be some surface which is similar to the arrangement of the oxygen atoms in an ice crystal. The growth of crystal on the above substrate is called epitaxial growth.

Interest in the epitaxy of ice on foreign substances stems mainly from the ability of crystals of certain natural minerals and some inorganic compounds to nucleate supercooled water and to initiate ice-crystal formation in clouds of supercooled water droplets. In order to obtain a better understanding of the mechanism, Turnbull and Vonnegut [1] examined how the catalytic potency of a heterogeneity is affected by its structural relationship with the forming crystal. This theory predicts that the order of potency of various catalysts will be inversely proportional to the atomic disregistry with the certain low index planes of the forming crystal.

Mason and Hallett [2, 3] and Mason and Maybank [4] tested the nucleating ability of finely dispersed aerosols, in both diffusion and mixing cloud chambers. They found that although there is a tendency for the more effective nucleant to possess hexagonal crystalline symmetry and lattice parameters reasonably close to those of ice, there are also exceptions. For a number of substances which nucleate at temperatures above $-15°$ C, it is possible to find a low index face on which the atomic spacings differ from those either in the basal plane or prism faces of ice by not more than 12%.

Ice nucleation on a foreign substrate may be regarded as an oriented overgrowth of ice on this substrate. It is quite reasonable to assume that this overgrowth is facilitated by having the atoms, ions or molecules which make up the crystallographic lattice of the substrate, exhibit a geometric arrangement which is as close as possible to that of the water molecules in some low-index plane of ice. In this manner atomic matching across the interface between ice and the substrate particle may be achieved.

It has been shown by Chessin and Vonnegut [5] that the addition of silver bromide to silver iodide causes a significant decrease in the lattice spacings of the host silver iodide. They showed that a significant improvement in the nucleation ability occurred as the average distance of the atoms in the (1 1 1) plane of AgI–AgBr solid solutions approaches that in the basal plane of the crystalline ice [6].

Later, Chessin *et al.* [7] found that the lattice parameters of the continuous solid solutions of AgI and CuI vary in a regular way from those of pure AgI to those of pure CuI. The effectiveness of the solid solutions as nucleation catalysts increases with decreasing mismatch between the basal plane of ice and the (1 1 1) plane of cubic solid solutions [8].

Lead iodide is also an effective ice nucleant with a nucleation temperature of − 6° C. There is specific variation, such as lattice fit, between lead iodide and silver iodide. Silver iodide with a higher basal misfit (1.4%) has lower supercooling whereas lead iodide with lower misfit has higher supercooling. This is attributed to the fact that it is the prism face rather than the basal face which is active as the nucleus [9]. It is known that the prism misfit of PbI_2 (3.6%) is greater than prism misfit (1.6%) of AgI. The oriented overgrowth of ice upon the lead iodide has been studied by quite a few workers [10–13]. So far no attempt has been made to improve the nucleation temperature of PbI_2 by changing its lattice spacing by partial substitution with substances of an iso-structural nature. The present study was undertaken in an effort to decrease the mismatch between ice and lead iodide and thereby improve the ice nucleating behaviour of lead iodide. For this purpose cadmium iodide has been considered. The ionic radius of Cd^{2+} is 0.097 nm which is comparable to the ionic size of Pb^{2+} (0.12 nm). The addition of CdI_2 with PbI_2 in different molar ratios may result in the formation of a new compound reducing the prism misfit with ice. With this intention the author has carried out this work.

Cadmium iodide with a hexagonal crystal structure has unit cell dimensions $a = 0.425$ nm and $c = 1.380$ nm. Cadmium iodide has a layer structure, being built up by stacking molecular CdI_2 sheets in various close packed arrangements, each consisting of a layer of cadmium ions sandwiched between two close packed layers of iodine atoms. The close packed iodine layers occupy the various A, B or C position in the stack. A close packed arrangement of this kind is usually expected to result in a trigonal symmetry which is actually found to be the case for all the cadmium iodide polytypes with known structure [14].

The 2H polytype of lead iodide belongs to the CdI_2 type of structure. It is hexagonal in crystal structure with the lattice constant $a = 0.456$ nm and $c = 0.698$ nm. The structure is characterized by an octahedral coordination of the cations and by anion–anion contacts along certain directions which allows the structure to be viewed as layer-like. The iodine atoms are located in almost perfect hexagonal close packing. The lead-to-iodine distance is 0.322 nm and the interlayer iodine–iodine separation is 0.421 nm. These distances are about 5% smaller than the sum of the corresponding ionic radii, from this stand point the crystal can be viewed as a hexagonal close packing of iodine ions with small lead ions interlaced between them [15]. Therefore, it is expected that the fusion of these two layer structured crystals above their melting point may result in the formation of a continuous solid because of the common factors mentioned above.

3. Experimental details

3.1. Preparation of the samples

Lead iodide was prepared by precipitation from aqueous solutions of analar grade potassium iodide and lead nitrate in the laboratory itself. The other source material used was the commercially available LR grade cadmium iodide.

Because the first trials of fused samples of PbI_2 and CdI_2 revealed a grey deposit on the top surface of the sample, cadmium iodide was purified by melting it in a vacuum-sealed test tube. After quenching, it was found that a grey impurity deposit had formed on the surface of cadmium iodide. This was removed. Again the powdered cadmium iodide was sealed and melted. Thus the impurity was completely removed. The powders of lead iodide and cadmium iodide were then intimately mixed in different molar ratios from 10 to 90 and sealed off in a glass tube of vacuum of 10^{-5} torr. The specimens were heated to a temperature approximately 20° C above the melting point of lead iodide, 410° C, which is higher than that of cadmium iodide. This procedure was adopted in the absence of a phase diagram for the combination of these two salts. The fused salts were ground to a powder in a mortar and pestle. All specimens were again vacuum sealed and annealed at 150° C for 2 h to ensure the formation of a new compound. The annealed samples of the present

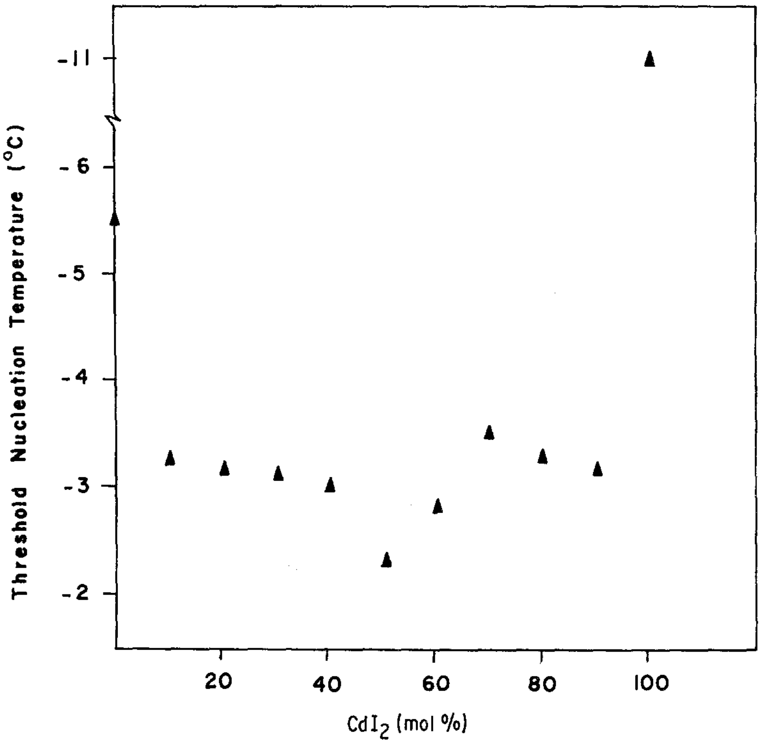

Figure 1 Threshold nucleation temperature as a function of composition.

study were ground into fine powder and sieved into uniform size particles by mesh No. 270.

3.2. X-ray diffractograms

X-ray diffractograms were taken in a Philips X-generator model 1140. Since the source materials are hexagonal in structure, all the powder lines could be indexed on the basis of a hexagonal system. Lines caused by the source materials were present along with new lines in the first set of samples prepared. The compound was then prepared again and the annealing time was increased to 12 h. In the second set of samples lines caused by the source materials were also observed in all combinations except the 50:50 mol% combination. This reveals the presence of a new compound in the mixture in all combinations except 50:50 mol%.

3.3. Ice nucleation studies

The freezing nucleation method employed for tests reported here is that of our earlier studies [16–18]. 100 mg finely powdered particles were suspended in 100 ml double distilled water. The suspended particles were stirred well and 0.25 m of this sample was taken in test tubes of 10 mm diameter and 100 mm length. The samples were tested with five test tubes in each run. The freezing temperatures were measured by introducing the test tubes to a vigorously stirred cooling bath which was cooled at a rate of about 0.10° C min^{-1}. The experiment was performed four times, resulting in 20 observations of nucleation temperatures with a variation of ± 0.4° C.

4. Results

The results of the lattice parameter measurements reveal that a new compound has been formed with the lattice dimensions of $a = 0.497\,58$ nm and $c = 0.696\,58$ nm in the 50:50 mol% combination of PbI_2 and CdI_2. The presence of the new lines, as well as the lines due to the parent materials, reveal that all other combinations are the mixtures of the new compound and the parent materials. Unfortunately, no work is available on the formation of a new compound with PbI_2 and CdI_2 and structural determination to check the above quantities. Therefore, comparison of the lattice parameter determination with earlier works is not possible.

The nucleation study has revealed that the nucleation temperatures show only a slight variation for all other combinations from that of the 50:50 mol% combination of PbI_2 and CdI_2 (Fig. 1). The lattice parameter determination of the other combinations with the new lines alone shows a large variation in the unit cell dimensions from that of 50:50 mol % combination.

5. Discussion

The decrease in the supercooling necessary to produce freezing reaches a maximum for 50% combination. The nucleation temperature at 50% combination is − 2.35° C, which is far greater than − 5.5° C and − 11° C for pure PbI_2 and CdI_2, respectively. For other combinations a higher nucleation temperature is also observed. The low nucleation temperature of − 11.0° C is not surprising, since CdI_2 is a highly soluble salt.

The measurements of nucleation temperature for the 50% combination can be compared with the prediction of the coherent nucleation theory [1]. The amount of supercooling necessary for nucleation should vary with the square of the disregistry between the crystal lattices defined as

$$\delta = \frac{a_2 - a_1}{a_1}$$

where a_1 and a_2 are the lattices of the ice and catalyst. Lead iodide is accepted to be a poorer nucleating material for ice crystals than silver iodide [19]. This is due to the fact that the misfit for ice on the prism face is greater than the basal face of lead iodide. Therefore, the percentage of misfit is calculated by the modified equation:

$$\delta = \frac{1}{2}\left(\frac{a_2 - a_1}{a_1} + \frac{c_2 - c_1}{c_1}\right) \times 100,$$

where a_1 and c_1 are the lattice parameters of ice and a_2 and c_2 are the lattice parameters of the nucleating material. The basal misfit of the 50 mol % combination is found to be 10% whereas the prism misfit is 7.7%. These misfit percentages are certainly higher than the basal and prism misfits of pure PbI_2 of 0.5% and 3.6%, respectively. Despite its higher percentage of misfit, the 50% combination exhibited higher nucleation activity. Hence despite the obvious importance of the crystallographic properties of a substrate to its ice nucleability, no clear correlation can be established between ice nucleation threshold and the crystal symmetry of the present PbI_2–CdI_2 combination.

The higher nucleation activity of PbI_2–CdI_2 system can be explained on the basis of active sites. Since all the combinations have a higher nucleation activity, there must be a common factor which controls the activity. The active site must be the factor for the improved nucleation activity of PbI_2–CdI_2 system. The X-ray diffractograms have clearly indicated the presence of a number of new lines along with the lines due to the parent materials. This is the evidence for the presence of a solid solution of PbI_2 and CdI_2.

Experiments with AgI and numerous other substances show that the region surrounding active sites should have a hydrophobic character for the surface to exhibit a high ice nucleation efficiency [19–21]. The active site is represented by a foreign atom or ion (or a group of foreign atoms or ions). This active site, surrounded by a relatively hydrophobic surface, behaves as a hydrophilic centre. In the present case, Cd^{2+} ions with smaller ionic radius can very easily fit into the lattice of PbI_2 and hence can act as hydrophilic starting centres in a hydrophobic surface. The growth of an ice embryo is facilitated by surface diffusion of weakly adsorbed molecules near the active site. The adsorbed water molecules orient themselves in the ice-like structure. As more and more water molecules aggregate, the energy of the interface will be minimized enabling the critical ice embryo to grow.

6. Conclusions

This work was started in an attempt to improve the prism misfit of lead iodide. Contrary to expectation, the formation of a continuous solid solution of PbI_2 and CdI_2 was not obtained. However, the nucleation study has revealed that the cadmium ions have acted as active centres to improve the nucleation activity to − 2.35° C.

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