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X-ray diffraction and ice nucleation studies of AgI–AgBr–CuI system

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Lattice parameter calculations and ice nucleation studies for the AgI–AgBr–CuI system are reported in this study. Thirteen samples of different molar compositions were prepared by vacuum fusion. The X-ray powder diffractograms of these samples revealed the formation of cubic solid solutions of the above system. It is found that the 50:25:25 mol % composition of AgI, AgBr and CuI, has the highest nucleation temperature of −0.48° C, which is far greater than −2.53 and −2.26° C for pure AgI and CuI, respectively.

1. Introduction

Heterogeneous nucleation of ice from supercooled water can take place by a variety of mechanisms depending upon system variables and the exact nature of the nucleant surface involved. Theoretical studies and experimental measurements have determined that the ice nucleating ability of a particle is dependent upon its size and its ability to act as a condensation nucleus in addition to other physical and chemical factors.

It is found from experiments [1] that a good ice-forming nucleus is one that is relatively large and water insoluble, has crystallographic properties similar to those of ice and has at its surface emanating bonds that are similar in nature to the O–H–O bond in ice. During the process of ice formation, the nucleus seems to act both as a condensation nucleus in initiating the condensation of water molecules and simultaneously as a crystallization nucleus in initiating the crystallization of the condensed water [2].

It has also been observed that ice nucleation is induced by epitaxial growth from a surface crystal structure similar to that of ice [3]. This epitaxial growth often occurs with considerable mismatch between the growing crystal lattice and the seed lattice in which case the interfacial binding must provide sufficient energy to sustain elastic distortions of one or both crystals.

It is reported [3–5] that the epitaxial catalysis is improved by modifications which bring the lattice constant of the nucleant to a closer match with that of ice. A theory of nucleation catalysis based on the elastic distortion has predicted that a substance having a smaller lattice mismatch would be an even better nucleus [6]. Then for a substrate whose misfit with ice crystal is extremely small in one direction and the matching density is high, the association of water molecules takes place first in one direction. Also, when a misfit exists, both crystal surfaces deform, depending on the interaction and rigidities. If the substrate is soft, the deformation appears mostly in it and the surface free energy of the interface between ice and substrate will be reduced, a favourable condition for nucleation [7].

Royer [8] suggested that in the case of oriented overgrowth, the distances between the corresponding bricks of upper layer of the host crystal and the lower layer of the guest crystal must be approximately equal, if the molecules of the guest crystal, after adsorption, are to have their normal lattice spacing. The difference between these distances should not exceed 12% on average. Apart from this, no other similarity between the lattice structure is needed.

Silver iodide has been recognized as an effective ice nucleant. Its efficiency in ice nucleation is chiefly attributed to its hexagonal crystal structure, similar to that of ice [9]. The lattice constant of silver iodide is 1.55% larger than that of ice. This accounts for the 2.5° C supercooling that is necessary to freeze water in the presence of silver iodide.

Gravenhorst and Corrin [10] found that highly purified silver iodide, having a low-water solubility and a low mismatch with ice, has an unexpectedly poor ice-forming capacity. However, its nucleating ability can be greatly improved by creating hydrophilic centres or structural imperfections on addition of impurity of salt ions [11–13].

Later Ramachandra Murty and Ramana Murty [14] observed that the nucleation temperature of silver iodide was affected to varying degrees by the addition of different soluble salts, depending upon the polarizability of the cations. However, it seems rather inevitable that though the effect of chemistry of nucleants such as AgI comes into play, lattice matching is still an important factor in ice nucleation [7]. Hence, it would be more interesting to study the effect of decreasing the lattice misfit by decreasing the lattice parameter of silver iodide. This can be done conveniently by forming a series of terminal solid solutions [15, 16].

It is evident that the AgI–AgBr system forms two terminal solid solutions at room temperature, with a large miscibility gap between them [17]. Hence, Chessin and Vonnegut [18] have studied the AgI–AgBr system by forming their co-precipitates. Since the bromine atom is smaller then the iodine atom, they expected that the addition of AgBr with AgI would reduce the lattice spacing in the AgI lattice. From the ice

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nucleation studies of Vonnegut and Chessin [4], it is noted that the 30:70 mol % combination of AgI and AgBr has the highest nucleation temperature of about −1.25° C.

Later Chessin *et al.* [17] were interested in a system which exhibited complete solid solubility. Their main interest was to see whether, in such a system, the supercooling did reach a minimum at zero lattice misfit with ice. So they chose the AgI–CuI system, which was found to form continuous solid solutions throughout their different compositions. It was found that the effectiveness of the solid solutions as nucleation catalysts increased with decreasing mismatch between the basal plane of ice and the (1 1 1) plane of the cubic solid solutions.

It is obvious that the cubic AgBr, when added to the hexagonal AgI, forms a cubic AgI–AgBr solid solution. In a similar way, the addition of CuI with AgI also forms a cubic AgI–CuI solid solution. Therefore, we have carried out the present work to determine the impact of the ternary AgI–AgBr–CuI system on the ice nucleation temperature, despite the fact that no phase diagram of the above system is available.

2. Experimental details

2.1. Preparation of the samples

Silver iodide and silver bromide were carefully prepared by reacting potassium iodide with silver nitrate and potassium bromide with silver nitrate, respectively, in the dark room of our laboratory, especially during the night. All the reactants taken were only analar grade samples (99.95% purity). High-purity (99.95%), commercially available copper iodide, CuI, was used. The quallity of the source materials was ensured by analysing their respective X-ray powder diffractograms.

In order to have a better understanding of the ice nucleating mechanism of the system in hand, we began experimenting with the AgI–CuI system. The samples were prepared exactly in the same molar compositions by vacuum fusion, as was done by Chessin *et al.* [17]. X-ray analysis and ice nucleation studies were carried out. After comparing our results, which agreed very closely with their data, the AgI–AgBr–CuI system was also investigated.

Keeping the mol % silver iodide at a particular value for one composition (say 70%), the remaining percentage (30%) was equally shared between AgBr and CuI (15% + 15%). Starting from 95 mol % AgI, the powders were intimately mixed to various molar compositions, with a gradual reduction of AgI by 5 mol % in each composition. Then they were taken in Corning glass crucibles and vacuum sealed under a pressure of 10^{-5} torr. They were melted and the melts were kept for 72 h and then quenched to room temperature. The fused samples were ground into fine powder in an agate mortar and pestle. They were again sealed off under the same vacuum (10^{-5} torr) and annealed at 200° C for 2 weeks. Later all the specimens were powdered and carefully sieved into uniform sized particles (50 μm) using stainless steel meshes (nos. 300 and 350). The above procedure was uniformly adopted in all the systems tested.

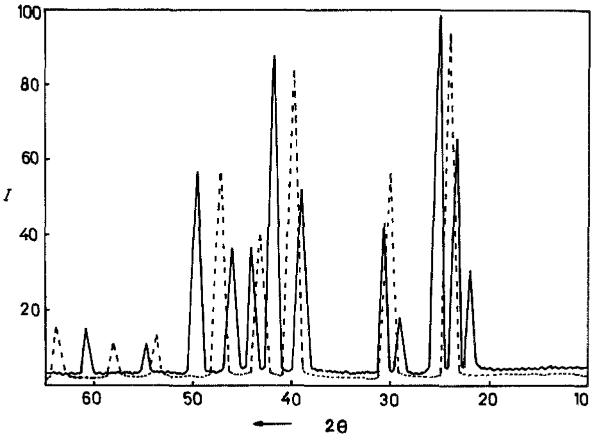

Figure 1 X-ray diffractograms for the 50:25:25 mol % combination of "mixture" and "fusion" of the AgI–AgBr–CuI system. —— mixture; ----- fusion. *I*, intensity; *θ*, angle of diffraction.

2.2. X-ray analysis

X-ray powder diffractograms were taken for the source materials (AgI, AgBr and CuI) and for each and every composition of the systems employing Cu*Kα* radiation in a "Reich Seifert" X-ray powder diffractometer in our laboratory. A nickel-foil filter was used to minimize the Cu*Kβ* radiation; a quartz monochromator was also employed. Scanning was carried out at 1°min^{-1} in 2θ. X-ray diffractograms for the 50:25:25: mol % "mixture" and "fusions" of AgI–AgBr–CuI were taken (Fig. 1) to make sure whether the present system forms a solid solution. The lattice parameters of AgBr and CuI were calculated on the basis of cubic symmetry and that of AgI on the basis of hexagonal symmetry.

2.3. Ice nucleation studies

The method employed for the measurement of freezing temperatures was the same as that of Vonnegut and Chessin [4] and Gobinathan and Ramasamy [19, 20]. The samples were prepared by suspending 100 mg in 100 ml triple distilled water. Each sample was well-stirred and about 0.25 ml was placed in 20 similar test tubes of length 100 mm and diameter 10 mm. After careful airtight closure of the test tubes, five of them were introduced into a vigorously stirred cooling bath, in a single run. The bath was cooled at a rate of $0.10^\circ \text{C min}^{-1}$, which was maintained constant throughout the work. On visual observation of the emerging ice crystals, the freezing temperature was measured with a Beckmann thermometer to within an accuracy of 0.01° C. Four runs were made for each sample and hence, each nucleation temperature was the median of 20 observations with a fluctuation of ±0.3° C. The experiment was repeated three times.

3. Results

Table I gives an idea of the reliability of the source materials used in this study. The X-ray diffractograms reveal the formation of cubic solid solutions with new lines. These new lines are found to be gradually shifted, as the composition is changed. Owing to the non-availability of any previous data in literature on this system, the structural determination and data comparison become impossible.

TABLE I Lattice parameters of the source materials (AgI, AgBr and CuI)

Sample	Lattice parameter (nm)	
	Literature	Calculated
AgI	0.458 34	0.458 63
AgBr	0.577 05	0.577 54
CuI	0.606 03	0.606 61

The ice nucleation study has revealed that the 50:25:25 mol % combination has the highest nucleation temperature. Among the thirteen samples examined, the last seven are found to have only a slight variation in nucleation temperature from that of 50:25:25 combination.

4. Discussion

The close agreement between the calculated values and literature values of the lattice parameters of AgI, AgBr and CuI (Table I) testifies the quality and dependability of the source materials used, as well as the precision of the measurements made. This also paves the way for a meaningful comparison of the results obtained by their usage.

It is reported [17, 18] that the "AgI–CuI" and "AgI–AgBr" systems form cubic solid solutions at room temperature. Hence, it is expected that the AgI–AgBr–CuI system may also form cubic solid solutions. As anticipated, the X-ray diffractograms of all the samples have revealed this fact. For instance, a careful analysis of the X-ray diffractograms (Fig. 1) for the 50:25:25 mol % "mixture" of AgI–AgBr–CuI and for the "fused" sample of the same composition of the above materials has made known the formation of an entirely new compound. In the "mixture" diagram, all the parent lines of the source materials are present. In the fusion sample diagram, the parent lines are found to be absent with the presence of new lines.

Gobinathan and Ramasamy [21] have reported that the size and the polarizability of the nucleant are some of the important factors in the determination of its ice nucleation temperature. On account of this, uniform sized particles (50 μm) have been used throughout this study to avoid any difficulty at any stage, in the interpretation of results.

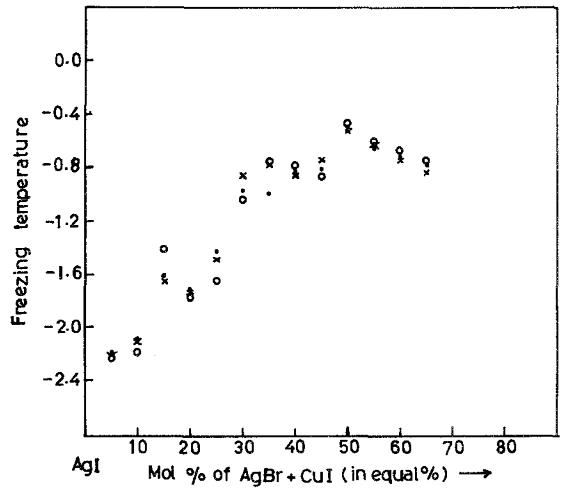

Figure 2 Freezing temperature as a function of composition of AgI–AgBr–CuI fusion nuclei. ●, × and ○ represent trials I, II and III, respectively.

The results of the lattice parameter measurements are given in Table II and the data are plotted in Figs. 2 to 4. It is noted that the addition of AgBr and CuI in equal mol % with AgI has really brought about a marked improvement in the gradual reduction of the lattice constant of AgI, except for the 4th sample. Consequently, the lattice misfit with ice has decreased with an ultimate increase in the ice nucleating ability of the system. The lower the misfit, the higher is the nucleation temperature. This is more evident from our experimental findings.

Lattice misfit δ with ice has been calculated by using the relation,

$$\delta = \frac{a_1 - a_0}{a_0}$$

where a_1 and a_0 are the distances of closest approach of the nucleant and ice, respectively. The distance of closest approach (DCA) refers to the average distance of closest approach of the atoms in the lattice and is represented by $a\sqrt{2}/2$, for the cubic system (a being the lattice parameter), while it is the lattice spacing in the basal plane in the hexagonal system. The misfit expresses the difference between the atomic spacings in the close-packed plane (1 1 1 plane) in the cubic system and the basal plane of ice lattice.

TABLE II Lattice parameters of the AgI–AgBr–CuI solid solutions

Sample no.	Mole (%)			Lattice parameter a (nm)	DCA a_1 (nm)	Misfit δ (%)
	AgI	AgBr	CuI			
–	100	–	–	0.458 63	0.458 63	1.6129
Ice	–	–	–	0.451 35	0.451 35	0.0
1	95	2.5	2.5	0.648 30	0.458 41	1.5642
2	90	5.0	5.0	0.648 07	0.458 25	1.5287
3	85	7.5	7.5	0.647 15	0.457 60	1.3847
4	80	10.0	10.0	0.647 38	0.457 76	1.4202
5	75	12.5	12.5	0.646 92	0.457 44	1.3492
6	70	15.0	15.0	0.645 11	0.456 16	1.0657
7	65	17.5	17.5	0.643 53	0.455 04	0.8175
8	60	20.0	20.0	0.641 53	0.453 62	0.5029
9	55	22.5	22.5	0.640 20	0.452 68	0.2947
10	50	25.0	25.0	0.638 65	0.451 59	0.0532
11	45	27.5	27.5	0.637 13	0.450 51	−0.1861
12	40	30.0	30.0	0.634 75	0.448 83	−0.5583
13	35	32.5	32.5	0.632 61	0.447 31	−0.8951

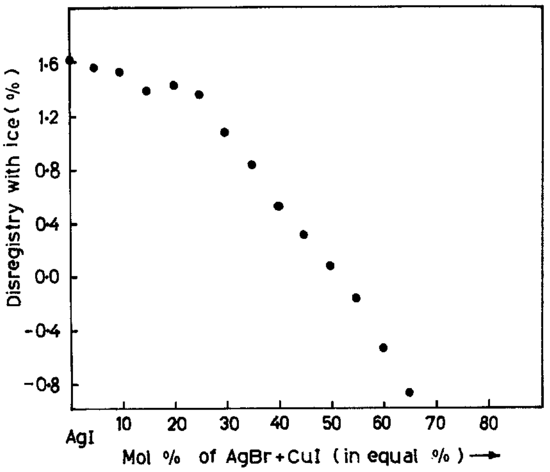

Figure 3 Disregistry of the AgI–AgBr–CuI solid solutions with respect to ice as a function of composition.

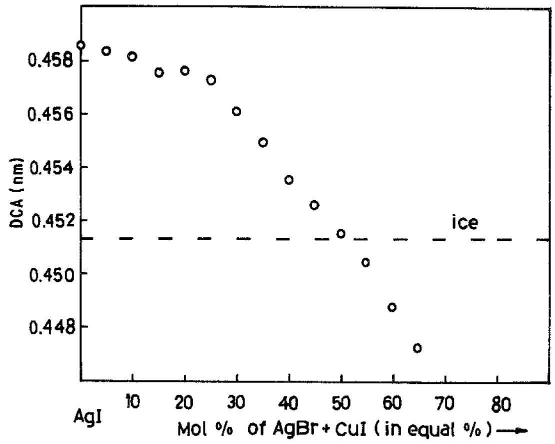

Figure 4 Distance of closest approach (DCA) of AgI–AgBr–CuI solid solutions as a function of composition.

The authors have carefully observed from the previous works [4, 17, 18] that either the addition of nearly 25 to 30 mol % AgBr with AgI or the addition of nearly 25 mol % CuI with AgI has produced the highest nucleation temperature, in each case. Hence, it is logically expected that the 50:25:25 mol % combination of AgI, AgBr and CuI may have a greater influence on the ice forming capacity of the system. This expectation is found to be true from the results.

Fig. 2 indicates the observed threshold nucleation temperature, the highest temperature at which nucleation starts, as a function of composition for the samples listed in Table II. From Fig. 2, one may really judge and appreciate the reproducibility of the results. The highest nucleation temperature for the 50:25:25 combination is −0.48° C, which is far greater than −2.53 and −2.26° C for pure AgI and CuI, respectively.

Fig. 3 is a plot of the disregistry of the samples, determined from their lattice spacings and that of ice, and their respective compositions. Fig. 4 shows the variation of the distance of closest approach of AgI–AgBr–CuI solid solutions with composition. The dotted line corresponds to ice.

It is reported [4] that 100% AgBr has been a poor ice nucleant because of its smaller lattice constant (9%) to that of ice. However, it should be mentioned that in the present study, 100% AgBr has a nucleation temperature of −2.8° C, despite having a large misfit with ice. The reason for this activity is not immediately clear, except that it works very well in all other aspects of the investigation.

A qualitative explanation can be given for the efficient nucleation activity of the present system. It is pointed out [22] that AgBr (NaCl type) dissolves AgI up to 30 mol % at 25° C and the hexagonal AgI dissolves only approximately 4 to 5 mol % AgBr at 25° C. Since the radius of the Br^- ion is smaller than the radius of the I^- ion, the AgI lattice contracts on substituting Br^- ions. Hence, the addition of AgBr with AgI causes an appreciable reduction in the lattice misfit of the host silver iodide with ice.

The distribution of ice nucleation active sites in varying numbers on the surface of ice-forming nuclei has been proposed by Zettlemoyer and co-workers [5, 13, 23, 24] and Corrin and co-workers [25–28]. This active site is represented by a foreign atom or ion (or a group of atoms or ions). When it is surrounded by a relatively hydrophobic surface, it behaves as a hydrophilic centre. It is known that AgI and CuI have similar physico-chemical properties. It is more likely that Cu^+ ions are possible due to the replacement of I^- ions from CuI, by the Br^- ions. A mixture of cations of different sizes, such as Ag^+ and Cu^+, will become ordered among different sets of sites, due to the influence of ionic size upon preferred location. Such related variations in site preference for different monovalent cations have also been reported in the β-alumina structure [29, 30]. In the present case, Cu^+ ions with smaller ionic radius can very well fit into the AgI lattice and act as hydrophilic starting centres in a hydrophobic surface. This situation would be more conducive for more and more water molecules to aggregate. Among these associated molecular chains, an interaction at their sides triggers a "zipper-like" action with the help of short-range potential fields, thereby minimizing the interfacial energy and facilitating nucleation as has been suggested by Fukuta [7].

The reason for the significant nucleation activity of the system can also be explained on the basis of the polarizability of the atoms. As the water molecule is polar, the binding is essentially electrostatic. Therefore, it could be expected that the ice nucleation would be preferred on materials, having highly polarizable atoms [31]. However, the nucleation activity will be affected differently by the addition of CuI to the AgI system, depending upon the polarization power of the cation. Since the radius of the cation Cu^+ is smaller (0.096 nm), the polarizing power of the Cu^+ is very high. Hence, the addition of CuI with AgI would definitely improve the ice forming capacity of silver iodide. Thus, due to the combined activity of AgBr and CuI, the nucleating efficiency of AgI has been greatly improved. The activity is more enhanced in the case of the 50:25:25 combination. The experimental results fully support the above statement.

5. Conclusions

The formation of cubic solid solutions is observed from the X-ray diffractograms of the present system. A marked decrease in the lattice spacings of the solid solutions, due to the addition of AgBr and CuI with AgI, has also been noticed. Thus the nucleating efficiency of the system, as a whole, has been greatly improved.

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