

X-ray analysis and ice nucleating behaviour of the AgI-CuI-KI system

S. SIVANESAN, K. BASKAR, R. GOBINATHAN, P. RAMASAMY
Crystal Growth Centre, Anna University, Madras 25, India

M. PALANISAMY
Guru Nanak College, Madras 32, India

Lattice parameter calculations and ice nucleation studies for the AgI-CuI-KI system are reported. Using the vacuum fusion method, samples of different compositions were prepared. The formation of cubic solid solution for these samples was confirmed by X-ray diffractograms. It was found that the solid solution of AgI, CuI and KI having the mol% composition of 60:20:20 has the highest nucleation temperature, -1.70°C , far greater than the nucleating temperature of pure AgI, CuI and KI.

1. Introduction

Various types of mechanism are involved in heterogeneous nucleation of ice from supercooled water. This heterogeneous nucleation is essentially a surface phenomenon and it is discussed from the view points of (i) size, (ii) polarizability, (iii) surface charge, (iv) hydrophilic sites (groups of foreign ions) in the midst of a hydrophobic surface, (v) adsorption sites on the substrate and (vi) lattice similarity between ice and the nucleating substance (lattice misfit). The above factors play a major role in the determination of threshold temperature. However, the most essential requirements for an efficient ice nucleant are hexagonal crystalline symmetry and lattice parameters reasonably close to those of ice [1]. Also, the effectiveness of the solid solutions as nucleation catalysts increases with decreasing mismatch between the basal plane of ice and the (111) plane of the cubic solid solutions [2].

Silver iodide particles serve as an effective substrate for ice nucleation. The similarity between the lattice structure of AgI and that of ice is probably the essential factor which makes it a good catalyst [3-5]. In the case of coherent nucleation catalysis, it is established that the structure of the growing crystal and the substrate on which it grows have a close resemblance to each other [6]. The supercooling temperature of ice nucleation of AgI substrate was -2.5°C .

Edwards *et al.* [7] observed the growth of ice at some specific sites present on the surface of AgI. Hence a fraction of the particles sizes activated the nucleation and the activity was proportional to the particle surface area at any given temperature [8, 9]. Moreover the ice nucleating ability of AgI has been found to be improved when bromine atoms replace some iodine atoms in the lattice, thereby decreasing the misfit [10]. AgI and CuI solid solutions have been tested for decreasing the mismatch between their lattice parameters and that of ice in order to increase the nucleating capability [2]. Recently, solid solutions

of AgI, AgBr and CuI were prepared to improve further the nucleation temperature of ice [11]. The main interest was to see whether in such a system the supercooling did reach a minimum at zero lattice misfit with ice. These materials are found to form continuous solid solutions throughout their different compositions.

It has been established that the KI-AgI system forms a stable compound between incongruent melting points 253 and 38°C [12]. But the most recent phase diagram of the system by Nakahara and Sakate [13] shows a continuous solid solution for the system. Mention must also be made here that the complex hygroscopic nucleating aerosols, $2\text{Ag} \cdot \text{KI}$, display efficiency at -7°C [14]. AgI and CuI form a continuous solid solution throughout the entire composition range [2]. However, in the case of KI and CuI system, only one intermediate compound, KCu_4I_5 , which is stable between 257°C and its incongruent melting point 332°C , is formed [12]. When the compound is cooled below 257°C , it disproportionates to KI and CuI. Thus, in the AgI, CuI and KI system, two combinations are found to form continuous solid solutions. Therefore, with the strong expectations of the formation of ternary solid solutions of AgI, CuI and KI, the authors carried out the preparation of the solid solutions of AgI, CuI and KI for the ice nucleation studies. In our quest for a substitute for AgI, this is yet another attempt to find a better ice nucleant.

2. Experimental procedure

2.1. Preparation of the sample

Silver iodide was carefully prepared by reacting KI with AgNO_3 in a dust-free dark room in our laboratory, particularly during the night. All the reactants used were only Analar grade samples (99.99%). High-purity (99.99%) commercially available copper iodide and potassium iodide were used.

Keeping the mol% silver iodide at a particular

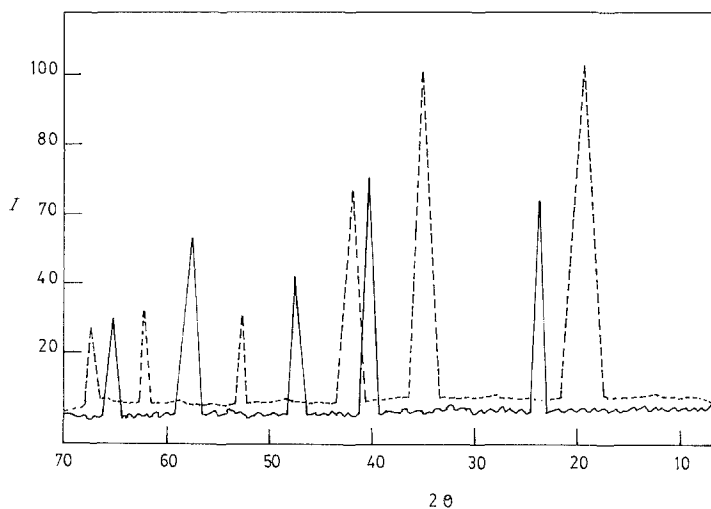


Figure 1 X-ray diffractograms for the 60:20:20 mol% combination of a "mixture" and "fusion" of the AgI-CuI-KI system: (---) mixture, (—) fusion.

value for one composition (say 60%) the remaining percentage (40%) was equally shared between CuI and KI (20% + 20%). Starting from 90 mol% AgI, the powders were intimately mixed to various molar compositions, with a gradual reduction of AgI by 10 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 wk. Later the specimens were powdered and carefully sieved into uniform sized particles ($97\ \mu\text{m}$) using clean stainless steel meshes. The above procedure was uniformly adopted for all the samples tested in this study.

2.2. X-ray analysis

X-ray powder diffractograms were taken for the source materials (AgI, CuI and KI) and every composition of the system. X-ray diffractograms have been obtained using Reich Seifert X-ray powder diffractometer, with $\text{CuK}\alpha$ target, nickel-foil filter and quartz α monochromator. The scanning was done at the rate of 1°min^{-1} . The spectrum for the mixture (60:20:20 mol%) and fusions of AgI-CuI-KI were taken (Fig.1) to confirm whether the present system forms a solid solution. In order to check the dependability of our source materials for preparing the fusion samples, we took separate X-ray powder diffractograms for AgI, CuI and KI. The lattice parameters of CuI and KI were calculated on the basis of cubic symmetry and that of AgI on the basis of hexagonal symmetry.

2.3. Ice-nucleation studies

The freezing nucleation method employed for the measurement of freezing temperatures was the same size as that of Vonnegut and Chessin [10], Gobinathan and Ramasamy [15,16] and Palanisamy *et al.* [11]. The stock suspensions can be prepared by suspending 100 mg in 100 ml triple distilled water. Each sample was stirred well and about 0.25 ml was taken in 20 similar well-cleaned 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 which can be cooled at a rate of $0.10^{\circ}\text{Cmin}^{-1}$. The same cooling rate was maintained for all the samples. On visual observation of the emerging ice crystals, the freezing temperature was measured with a Beckmann thermometer to an accuracy of 0.01°C . For each sample, four runs were made, and hence each nucleation temperature was the median of 20 observations with a fluctuation of $\pm 0.6^{\circ}\text{C}$. The experiments were repeated three times.

3. Results

Table I gives the lattice parameter of the source materials used in the present study. X-ray diffractograms of the AgI-CuI-KI system reveal the formation of cubic solid solutions with new lines (Fig.1). It is observed that the new lines are gradually shifted as the composition is changed. Because the ternary system used in the present study is a new type, lattice parameter comparison was impossible.

The ice-nucleation study revealed that the 60:20:20 mol% combination has the highest nucleation temperature, of -1.70°C . It is also observed that the first two samples have not revealed much variation in their nucleation temperature from the parent material in spite of considerable change in their percentage of misfit. But there is a considerable fall in the nucleation temperature with increase in misfit strain as the composition of AgI is decreased beyond the above combination.

4. Discussion

The close agreement between the calculated values and the literature values of the lattice parameter of the source materials testifies to the quality of the material and the accuracy of the method of calculation (Table I).

TABLE I Lattice parameter of the source materials (AgI, KI and CuI)

Sample	Lattice parameter (nm)	
	Literature	Calculated
AgI	0.458	0.458
CuI	0.606	0.607
KI	0.707	0.705

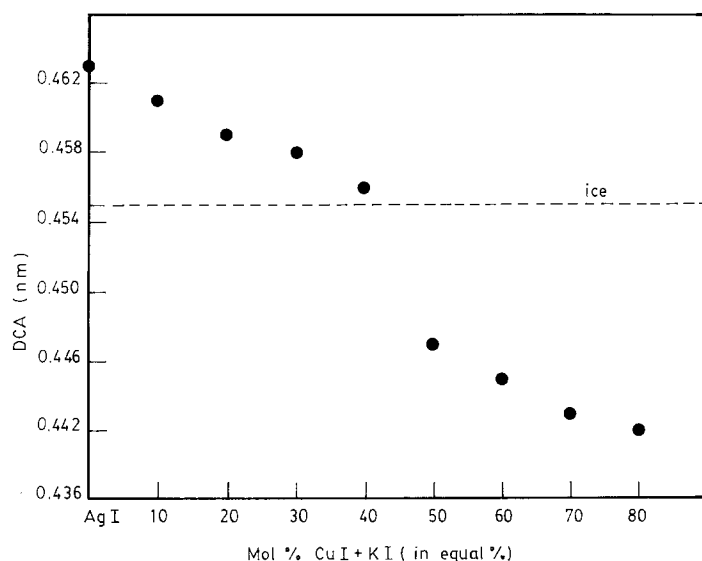


Figure 2 Distance of closest approach (DCA) of AgI-CuI-KI solid solutions as a function of composition.

As already reported, the AgI-CuI and AgI-KI [2, 17] systems form cubic solid solutions at room temperature. Therefore, it is natural to expect the formation of cubic solid solutions also in the case of AgI-KI-CuI. As anticipated, the X-ray diffractograms reveal the formation of cubic solid solutions. It is also verified that the *d*-spacings of AgI, KI and CuI systems do not resemble either the AgI-CuI or the AgI-KI system. This is also additional evidence for the formation of a new series of solid solutions differing from their parent materials as well as the binary solid solutions of the constituents. A careful analysis of X-ray diffractogram for the (60:20:20) mol % mixture of AgI-CuI-KI and the fused samples of the same composition of the materials has been carried out. In the mixture diagram all the lines of the source materials are present. In the fusion sample the parent lines are found to be absent with the presence of new lines.

The results of the lattice parameter measurements are given in Table II and the data are plotted in Fig. 2. It is noted that the addition of KI and CuI in equal mol % with AgI has really brought about a gradual reduction in the lattice parameter of AgI. Accordingly, the misfit strain with ice has decreased with an ultimate increase in the ice-nucleating ability of AgI: CuI: KI. The present study also confirms the concept that the lower the misfit, the higher is the nucleation temperature [2, 11].

The misfit strain has been calculated using the standard relation

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

where a_1 and a_0 are the distances of the closest approach of the nucleant and ice, respectively. The distance of the closest approach refers to the average distance of the atoms in the lattice and is represented by a $2^{1/2}/2$ for cubic system (a being the lattice parameter) while it is the lattice spacing in the basal plane in the hexagonal system.

Careful observation of previous work [2, 10, 11] gives an idea of the effective percentage combination of the materials for ice nucleation. In the case of the AgI-AgBr system, 25 mol % AgBr with AgI, and in the AgI-CuI system 25 mol % CuI with AgI, have produced the highest nucleation temperature, whereas in the case of the AgI-AgBr-CuI system, AgBr and CuI each of 25 mol % have been added with AgI to have a greater influence on the ice-forming capacity of this system. Interestingly enough, in the present case the enhanced nucleation temperature for the system is also found to be for the combination of 60:20:20 mol % AgI: CuI: KI.

Fig. 3 indicates the observed nucleation temperature as a function of composition for the samples listed in the Table II. The temperature indicated in each trial is the median of 20 observations with a fluctuation of $\pm 0.6^\circ\text{C}$.

TABLE II Lattice parameter of the AgI-CuI-KI solid solutions

Sample no.	Mol %			Lattice parameter a_1 (nm)	DCA a_0 (nm)	Misfit (%)
	AgI	CuI	KI			
Ice	-	-	-	0.451	0.451	0.0
-	100	-	-	0.459	0.459	1.47
1	90	5	5	0.646	0.457	1.25
2	80	10	10	0.644	0.455	0.81
3	70	15	15	0.642	0.454	0.59
4	60	20	20	0.639	0.452	0.14
5	50	25	25	0.627	0.443	-1.85
6	40	30	30	0.623	0.441	-2.29
7	30	35	35	0.621	0.439	-2.74
8	20	40	40	0.619	0.438	-2.96

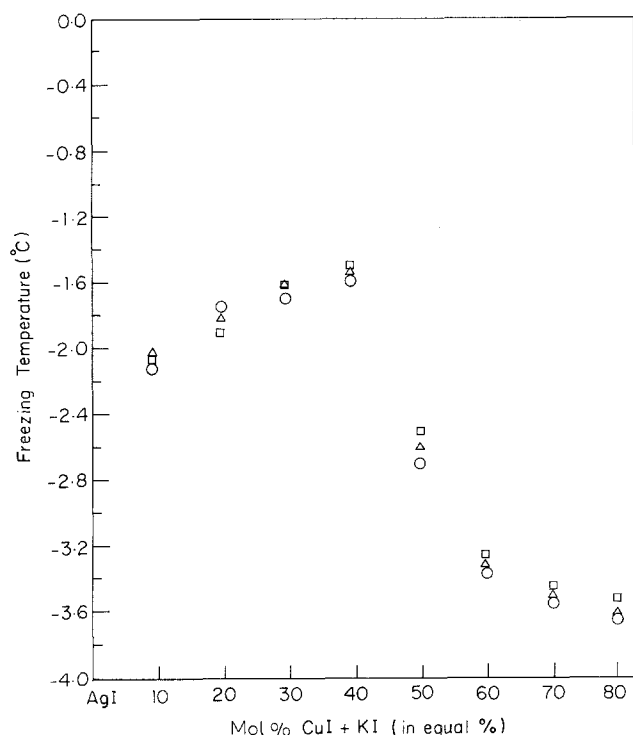


Figure 3 Freezing temperature as a function of composition of AgI-CuI-KI fusion nuclei. (Δ) trial I, (\square) trial II and (\circ) trial III.

The nucleation temperature is found to be very close to that of silver iodide for low mol % combination of CuI and KI. As the mol % combination of these materials is increased, one can expect a reduction in the lattice parameters resulting in the formation of solid solutions, because the ionic radius of the Cu^+ ion (0.096 nm) is smaller than that of the Ag^+ ion (0.126 nm) while that of the K^+ ion (0.133 nm) is slightly higher than that of silver iodide [18]. Therefore, the AgI lattice contracts by the substitution of Cu^+ and K^+ ions. This is evident from the fact that the lattice parameter of the resulting solid solutions gradually decreases as the concentration of Cu^+ and K^+ ions are equally increased. Fig. 2 shows the variation of the distance of the closest approach of AgI-CuI-KI solid solutions with composition. The dotted line corresponds to ice. Fig. 2 is a plot of the distance of closest approach of the samples determined from their lattice spacings and that of ice for their respective compositions.

The addition of CuI and KI has brought the modification in the lattice constant of AgI to a closer match to that of ice. Hence a corresponding enhancement in the nucleation temperature is observed. But it is not comparable to that of the previous results obtained for our AgI-AgBr-CuI system [11]. It is logical to expect the material AgI-AgBr-CuI (50:25:25) with the very low misfit of 0.05% to nucleate at an enhanced temperature. It should also be mentioned here that the activity of the AgI-CuI-KI system is not only less than that of the AgI-AgBr-CuI system but also slowly decreases with time. This is due to the addition of KI with AgI and CuI. It is also observed that the solid solutions of AgI-CuI-KI exhibit a slightly hygroscopic nature. This property may perhaps be a factor in the decreased nucleation activity of the system.

5. Conclusion

The formation of continuous solid solutions of the AgI-CuI-KI system has been established by the X-ray powder diffractograms. As the percentage of CuI and KI is increased, a gradual change in the lattice parameter of AgI is observed. The present study clearly supports the fact that the lower the misfit strain, the higher is the ice-nucleation temperature.

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