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Grain boundary properties of ice doped with small concentrations of potassium chloride (KCl)

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Abstract

The grain boundary (GB) migration rate was studied in ice bicrystals obtained from 1 to 10 $\mu\text{mol l}^{-1}$ (0.02 to 0.2 ppm) potassium chloride (KCl) water solutions and annealed at temperatures above -20°C for 170 days. GB mobility was determined as a function of annealing temperature and solute concentration. The GB mobility values obtained show a systematic dependence on the solute concentration. For the first time, it was observed in ice that small concentrations of impurity decrease the GB mobility, as occurs in other materials. The results also indicate possible changes of the GB structure in the annealing temperature range studied.

1. Introduction

The mobility and structure of ice grain boundaries (GBs) are of special interest in glaciology and the physics of clouds. Glaciers are formed from the accumulation and compaction of falling snow and they provide one of the most important records of past climate. The crystalline structure of glaciers is related to different physical processes like sintering, recrystallization and grain growth. The study of these processes is extremely important in understanding the ice cores and the climate changes inferred from them. Glaciers contain different types of impurities, with concentrations that depend on their location and depth, typical values being about 1 $\mu\text{mol l}^{-1}$ [1]. Ice particles present in clouds, for example hail, ice crystals and snow, are actively involved in all the microphysical processes occurring in clouds. Clouds are the most efficient machines for the capture and transport of atmospheric pollutants. Impurities are captured on the ice particle surface and then diffused into the bulk, so the knowledge of the surface and GB structure of ice is critical in understanding these phenomena. Impurities contained in ice cloud particles are widely dispersed, ranging from a few $\mu\text{mol l}^{-1}$ up to 10^3 or $10^4 \mu\text{mol l}^{-1}$ [2].

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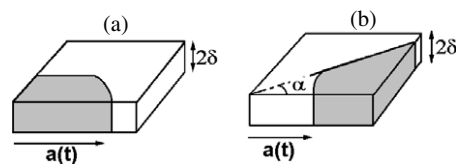


Figure 1. Grain boundary configurations.

In most materials, small amounts of impurities have a great influence on the GB mobility and structure. However, few experimental studies have been carried out in ice to investigate the effect of impurities on GB motion. Jellinek and Gouda [3] made experiments with thin ice sheets doped with $10^4 \mu\text{mol l}^{-1}$ of NaCl. They found that, below -10.5°C , the grain growth rate was smaller than that of pure ice, while the contrary was true for larger temperatures. Achával *et al* [4] performed grain growth experiments using cylindrical polycrystalline ice samples obtained from pure water and a water solution of NaCl, NH_4OH and HF with concentrations ranging from 10^2 to $10^5 \mu\text{mol l}^{-1}$ and annealing temperatures in the range -2 to -16°C . These authors found that impurities increase the GB migration rate, and they associated this behaviour with a change in the GB structure produced by the solute atoms. The above papers presented experiments performed with a large amount of impurities; for low concentrations of impurities, Alley *et al* [5, 6] presented a theoretical analysis of how impurities can modify GB motion occurring in glacial ice and concluded that NaCl in concentrations of $1 \mu\text{mol l}^{-1}$ can reduce the ice GB migration rate at -54°C (the NaCl eutectic point is -20°C).

It is known that solubility in ice is very low, and the values reported in the literature are scarce and widely dispersed. For instance, the values reported for HCl solubility at temperatures above -20°C are between 10^4 and $1 \mu\text{mol l}^{-1}$ [7, 8]. At present, many glaciologists consider that the traces of impurities are exclusively in the GBs and in triple junctions. For temperatures above the eutectic point the acid solutions are expected to form a system of veins along triple junctions, i.e. it is thought that the concentration of impurities at the boundary are high enough to produce a GB wetting phase transition. In these cases the impurities may raise the GB mobility and thus accelerate the GB velocity, as was observed in aluminium doped with Ga or Pb [9].

The purpose of the present work is to study the influence of very low impurity concentrations on ice GB structure and mobility, in order to establish if impurities always increase the ice GB mobility at temperatures above the eutectic point. This study was performed by following the GB time evolution on ice bicrystalline samples doped with small concentrations of KCl and annealed at temperatures between -5 and -20°C (the eutectic temperature of KCl is -10.7°C).

2. Summary of GB migration theory

We outline here the basic GB migration theory used in the present study to obtain the mobility of a GB following its time evolution. A complete description of this theory is given in a previous work [10].

For bicrystalline samples that have one of the initial configurations shown in figure 1, the GBs move driven by a capillary force combined with the effect of a superficial groove, which can be formed on the intersection of the free surface of the sample and the GB by surface or vapour diffusion or by evaporation. In this case, the GB experiences a drag force provided by the growing groove, and its movement is of a spasmodic type [11], i.e. the GB migration rate

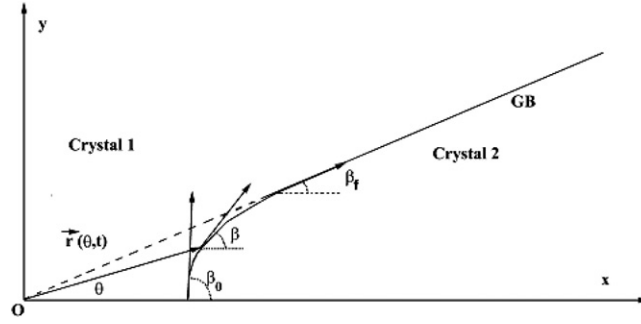


Figure 2. GB characteristic variables for the configurations shown in figure 1.

continually decreases until the GB movement completely stops. Later on, if the GB is able to leave the superficial groove behind, a new stage of the GB movement begins, being similar to the previous one. As seen in figure 2, $r(\theta, t)$ describes the shape of the GBs at time t . Defining $a(t) = r(0, t)$ as the GB displacement, it can be shown [10] that during the aforementioned consecutive stages

$$a^2(t) - a^2(0) = 2\overline{M\gamma_{gb}^{eff}} FH(t/t_{crit}) \quad (1)$$

with

$$\overline{M\gamma_{gb}^{eff}} = \frac{\int_{\beta_f}^{\beta_o} M\gamma_{gb}^{eff} d\beta}{\beta_o - \beta_f}, \quad \gamma_{bg}^{eff} = \gamma_{bg} + \frac{\partial^2 \gamma_{bg}}{\partial \beta^2}$$

$$F = \frac{R^2(0)(\beta_o - \beta_f)}{\int_0^{\theta_m} R^2(\theta) d\theta}, \quad \text{and} \quad H(t/t_{crit}) = \int_0^t \frac{dt'}{1 + (t'/t_{crit})^n}. \quad (2)$$

γ_{bg} and M are the GB surface energy and mobility, respectively, β is the GB inclination and $t_{crit} = (\delta \cdot c/M)^{1/n}$, with 2δ the dimension of the sample in the direction perpendicular to the GB motion and c and n constants that depend on the mechanisms involved in the groove formation. $n = 3/4, 2/3$ and $1/2$ for the mechanisms of surface diffusion, gas diffusion and evaporation condensation, respectively. β_o and β_f correspond to $\theta = 0$ and $\theta = \theta_m$, respectively. For the geometric configurations shown in figure 1, the GB time evolution is such that the GB preserves its shape, i.e. $r(\theta, t)$ can be expressed as stationary part, $R(\theta)$, times a time evolution part, $T(t)$. From equation (2) it can be seen that the shape factor F is proportional to the reciprocal of the area swept by the vector radius $R(\theta)$ measured in units of $R(0)$.

From equation (1), it can be shown that for $t \ll t_{crit}$

$$a^2(t) - a^2(0) \cong 2\overline{M\gamma_{gb}^{eff}} Ft. \quad (3)$$

From this equation, the mean effective mobility, $\overline{M\gamma_{gb}^{eff}}$, can be obtained if F and $a(t)$ are experimentally determined. Note that F can be obtained from equation (2) measuring at any time t $r(\theta, t)$ and $r(0, t)$.

3. Experimental details

The GB migration rate was studied in ice bicrystals obtained from 1 to 10 $\mu\text{mol l}^{-1}$ (0.02 to 0.2 ppm) potassium chloride (KCl) water solutions, annealed for 170 days at $-5, -10, -15$ and -20°C .

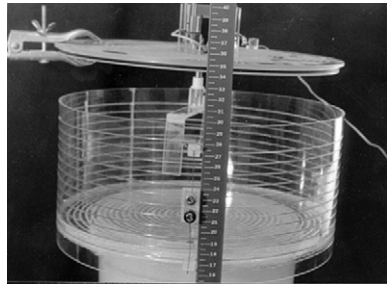


Figure 3. Cell used to grow ice doped bicrystals.

The bicrystalline samples used have one of the initial configurations shown in figure 1. During annealing, samples were left inside a hermetic and transparent box filled with silicone oil. In this way a superficial wedge (groove) was formed on the intersection of the free surface and the GB only by surface diffusion.

The bicrystals were grown following a similar procedure to that described by Nasello *et al* [12]. Initially, a bicrystalline seed was obtained with $\langle 10\bar{1}0 \rangle / 60^\circ$ orientation. Then, the doped bicrystalline samples were grown using the cell shown in figure 3, which was placed inside a freezer at -16°C . A bicrystalline seed of approximately $1\text{ cm} \times 1\text{ cm}$ in size was fused to the brass bar at the bottom of the cell, which was in thermal contact with the freezer. The cell was filled with 2 l of 0.02 and 0.2 ppm KCl water solution (1 and $10\ \mu\text{mol l}^{-1}$) prepared with Milli Q water (impurity concentration smaller than 0.02 ppm). The walls of the cell were heated so the heat of freezing could flow only through the brass rod. The liquid inside the cell was continuously stirred in order to maintain the solute concentration in the ice–water interface constant. In this way, after two days, semi-spheres of bicrystalline ice were obtained of approximately 3 cm in radius. The solute concentration of the resulting ice was measured using a ICP-MS (inductively coupled plasma mass spectrometry) technique, employing a Thermo X-7 equipment of 462 W power, which can detect a K concentration above 0.03 ppb. The mean potassium bicrystal concentrations obtained were 0.03 times the original ones.

From the bicrystals, samples of $1\text{ cm} \times 1\text{ cm} \times 0.5\text{ cm}$, with the configurations shown in figure 1, were obtained by polishing the surface sample with a microtome placed in a cold room. Immediately after the samples were prepared they were introduced in a transparent acrylic box filled with silicone oil and placed inside boxes at constant temperatures.

In order to determine $a(t)$ and F values, photographs of each sample viewed between crossed Polaroids were taken at time intervals of approximately 24 h, using a camera attached to a microscope. This process was carried out over approximately six months. When the GB was not perpendicular to the surface of the sample, pictures of the up and the down faces of the samples were taken. These photographs were analysed separately to obtain $a(t)$ and F values, and each group of results was designated as either ‘up’ or ‘down’ respectively.

4. Results

4.1. Temporary evolution of the GB displacement a

Figures 4(a)–(d) show the values of $a^2(t) - a^2(0)/2F$ versus t corresponding to samples annealed at -5 , -10 , -15 and -20°C . In these figures the values corresponding to the up and down surfaces of two samples (c , c^+) are distinguished. c and c^+ correspond, respectively, to bicrystals obtained from 1 to $10\ \mu\text{mol l}^{-1}$ (0.02 to 0.2 ppm) KCl water solutions.

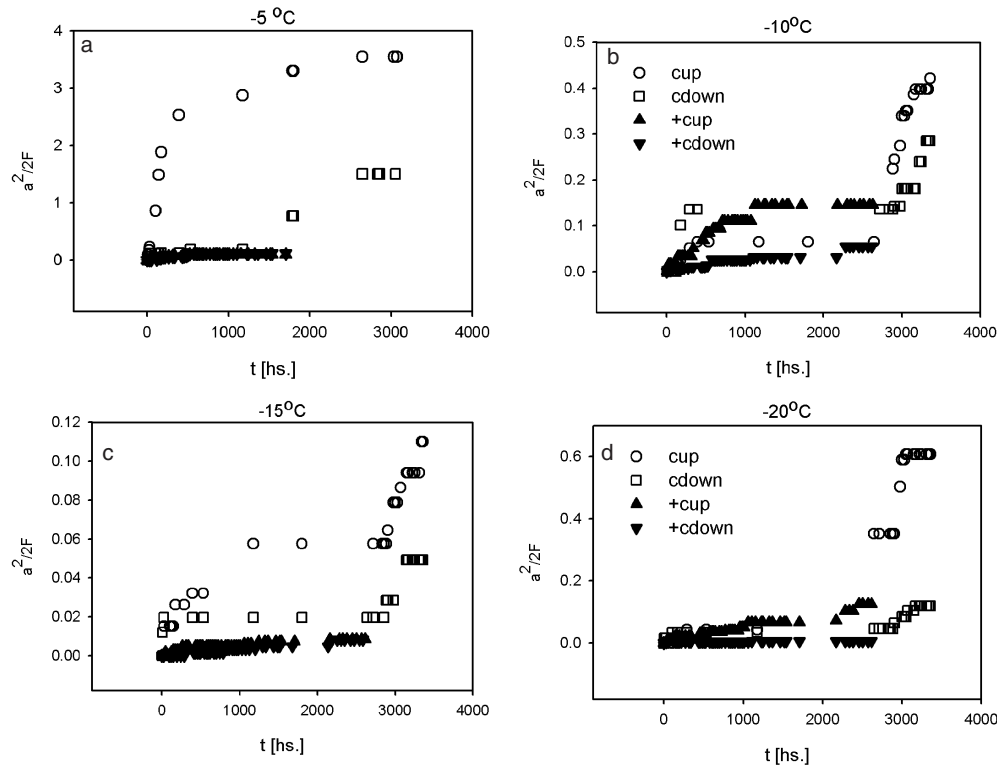


Figure 4. Squared values of the grain boundary displacement a , measured in mm^2 and scaled by the shape factor F , as a function of the annealing time. In the figures, up and down refer to the values obtained from the two boundary intersections with the main surface samples, and c and $\pm c$ refer to bicrystals obtained from the 1 and 10 $\mu\text{mol l}^{-1}$ water solution. Figures (a)–(d) correspond to the different studied annealed temperatures.

In these figures we can see that, on average, GBs corresponding to the c^+ samples move more slowly than the others. Also, it can be seen that GBs are continuously dragged until $t \sim 2500$ h, after which they begin a more rapid movement again. So, as predicted by the theory, two stages of a spasmodic movement are clearly observed.

4.2. Temperature dependence of the doped ice GB mobility

To analyse the effect of solute concentration on GB mobility, the initial slope of the $a^2(t) - a^2(0)/2F$ versus t plot was determined for each sample and stage. According to equation (2), this slope gives us $\overline{M\gamma_{\text{gb}}^{\text{eff}}}$. Figure 5 shows the $\overline{M\gamma_{\text{gb}}^{\text{eff}}}$ mean values obtained for the c and c^+ samples respectively. In this figure, the following features are observed. (a) The values corresponding to c samples are greater than those corresponding to c^+ samples. On average, it is found that $\overline{M\gamma_{\text{gb } c}^{\text{eff}}}/\overline{M\gamma_{\text{gb } c^+}^{\text{eff}}} \cong 0.1$, where $\overline{M\gamma_{\text{gb } c}^{\text{eff}}}$ and $\overline{M\gamma_{\text{gb } c^+}^{\text{eff}}}$ correspond to the $\overline{M\gamma_{\text{gb}}^{\text{eff}}}$ values of the c and c^+ samples respectively, i.e. the GB mobility increases by approximately one order of magnitude when the solute concentration decreases by the same order. (b) The $\overline{M\gamma_{\text{gb}}^{\text{eff}}}$ mean values do not decrease gradually with temperature in the whole temperature range studied, i.e. they cannot be represented by only one thermally activated behaviour. Indeed, the values corresponding to $T = -20^\circ\text{C}$ are greater than those corresponding to $T = -15^\circ\text{C}$. However,

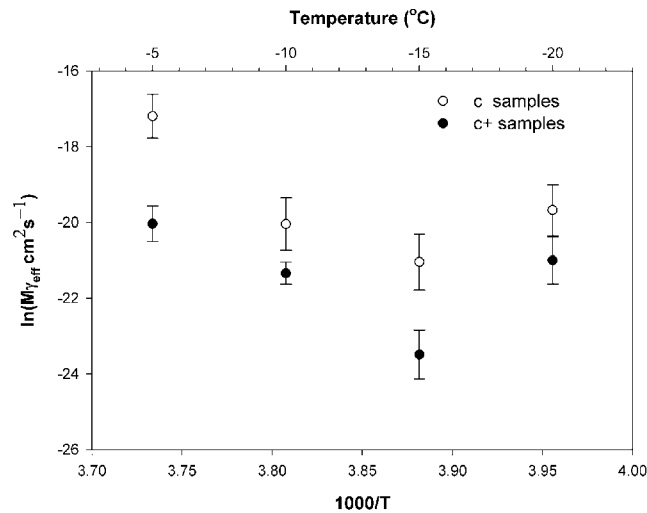


Figure 5. Temperature dependence of the mean values of the effective grain boundary mobility M_{gb}^{eff} for the bicrystals obtained from 1 to 10 $\mu\text{mol l}^{-1}$ (0.02 to 0.2 ppm) KCl water solutions, respectively (c and c⁺ samples).

for temperatures above or similar to -15°C , the GB mobilities obtained in the present work for c and c⁺ samples could be represented by a thermally activated process with an activation energy of ~ 1.3 eV. In agreement with that observed for Al by Molodov *et al* [13], this activation energy value is greater than that obtained for pure ice, which is 0.53 eV [12].

5. Discussion

It is common knowledge that, in most materials, impurities have a great influence on GB mobility and structure. In the case of small solute impurity concentrations, the theories developed predict a decrease of one order of magnitude in GB mobility when the GB solute concentration increases by the same order [14–17]. On the other hand, when solute concentrations are high enough to produce the melting of the GB, the doped GBs can move more quickly than pure ones, as was observed in aluminium doped with Ga or Pb [9].

The results presented in figure 5 show that in the whole range of temperatures studied the GB mobility approximately decreases by one order of magnitude when the KCl concentration changes from 1 to 10 $\mu\text{mol l}^{-1}$, in a qualitative agreement with the aforementioned theories for small concentrations. Then, for the first time, the present results experimentally show that, at very low solute concentrations and high annealing temperatures, impurities in ice, as in other materials, slow the GB movement down. Also, these results indicate that the concentration of impurities used in the present work are not high enough to produce melting of the GBs.

The remarkable increase of the GB migration rate when the temperature changes from -15 to -20°C shown in figure 5 is similar to results observed in tin by Gostein and Shvindlerman [18]. According to these authors, in tin the GB structure changes from a disordered type to a strongly ordered type when the temperature decreases. An ordered structure favours a decrease in GB solute concentration which, in agreement with the theories mentioned above [14–17], can produce an increase of the GB migration rate when the GB changes its structure at lower temperatures.

The increase in migration rate observed in figure 5 could then be attributed to a change in the ice GB structure from a non-ordered structure to a more structured one. In ice this change can be easily argued. In fact, it is known that the ice surface behaves as a quasi-liquid structure at temperatures near the melting point [19], a behaviour that could be extended to GBs [20]. On the other hand, as soluble impurities reduce the freezing point of ice, the quasi-liquid characteristics of ice GBs with low impurity concentrations would be favoured. Then, figure 5 could indicate that a doped ice GB would have a quasi-liquid characteristic at temperatures above or equal to -15°C and a more ordered structure at lower temperatures.

6. Summary

In this work we investigated the GB structure and mobility of ice grown from 1 to $10\ \mu\text{mol l}^{-1}$ (0.02 to 0.2 ppm) potassium chloride (KCl) water solutions. Our main result was that at low solute concentrations the ice GB mobility increases by around one order of magnitude when the solute concentration decreases by the same order. This behaviour, similar to that observed in other materials and different from that previously observed for ice at higher solute concentrations, was related to the fact that GB melting could not take place in ice at low solute concentrations and at temperatures above the eutectic point.

Another remarkable result was that in spite of a systematic decrease in mobility with temperature, an increase in mobility was observed for samples annealed at -20°C . Based on this observation we inferred that, for the samples studied, the ice GB structure could change from a disordered quasi-liquid structure at high temperatures to a more ordered structure at lower temperatures.

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