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Surface recrystallization in calcium-doped NaCl crystals

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Exposure of cleavage surfaces of calcium-doped NaCl to water vapour produced surface recrystallization at sites from which condensed water had evaporated. The crystals, initially stable in air, became hygroscopic following further recrystallization. Examination of the habit, properties and growth conditions of these crystals pointed to an interaction between moisture and calcium that resulted in hydrated calcium chloride. This interaction proceeds much more rapidly along grain boundaries in NaCl bicrystals. In general, the calcium in NaCl separates out into second-phase in a crystal cooled to room temperature, and any subsequent exposure to moisture produces erosive attack of the matrix adjacent to precipitates, resulting in a macroscopically defective substructure.

1. Introduction

A freshly cleaved surface of NaCl undergoes physical and chemical attack when exposed to air, primarily as a consequence of atmospheric moisture. Controlled exposure to water vapour pressure, p, for a number of hours has shown that the surface reaches a stable reversible adsorption state at relative pressures $p/p_0 < 0.76$, where p_0 is the vapour pressure of water at room temperature [1, 2], while prolonged exposure causes water molecules to penetrate into the crystalline lattice [3]. At $p/p_0 = 0.76$, which corresponds to the vapour pressure of a saturated NaCl solution, liquid water condenses on the surface and progressively dissolves away the substrate.

The physical condition of the crystal is found to affect behaviour, water adsorbing preferentially onto surface microsteps [1] and penetrating further into specimens that have been plastically deformed [4]. It is also known that growth and dissolution of an NaCl surface in contact with aqueous solution is affected by trace impurities in the solution [5], but little work has been done to tell us whether residual impurities in the crystal have any influence on surface solubility. In principle, such an influence could be considerable since surface attack initiates at defects, and the point-defect properties of NaCl in the low-temperature extrinsic region are controlled by residual impurities that form aggregates of hydrophilic salts.

One impurity that merits attention is calcium, since this has a distribution coefficient of unity for the residual quantities that remain in NaCl crystals [6], making it the major divalent cation impurity responsible for extrinsic vacancy concentration in nominally pure crystals. At high temperatures this impurity remains in solid solution [7], but as the crystal is cooled to room temperature it separates out into phases based on $CaCl_2$ [8], which is a deliquescent salt that forms hydrates that are also deliquescent [9]. The presence of such impurity on a freshly cleaved surface can only assist attack by ambient moisture. It has been noted [10] that crystalline deposits accumulate on the surface of a NaCl crystal exposed to fluctuations in relative humidity, such as those occurring in the normal laboratory atmosphere, and it is presumed that such deposits result from alternating dissolution and recrystallization of the surface. The present work reports on surface recrystallization, following surface dissolution, that derives directly from calcium impurity in the solid substrate.

2. Experimental details

The observed recrystallization was first noted following exposure to water vapour of a doped (250 ppm Ca^{2+}) NaCl crystal on which measure-

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ments of surface potential were being carried out. This prompted a systematic investigation using the simplest apparatus that could be constructed to direct a controlled flow of water vapour across a crystal surface. Dry nitrogen, controlled by a stop-cock, was passed through distilled water and the moist outflow was directed parallel to the sample surface by means of a glass tube. The sample was placed on the stage of an optical microscope and the effects produced were observed directly. A single whiff of moist nitrogen (2 to 3 sec duration) was sufficient to produce surface water droplets, which usually evaporated within a few seconds, but repeated exposure to water vapour gave rise to small regions on the surface that continued to absorb moisture from the atmosphere, and under these circumstances it was necessary to control such deliquescence by maintaining a stream of dry nitrogen over the surface. All observations were at room temperature.

A specimen surface several cm^2 in extent was obtained by cleavage in air of ingots pulled from the melt under dry nitrogen. Doped ingots were obtained by adding nominal $CaCl_2.2H_2O$ to the starting material, which was then progressively heated under vacuum in the growth chamber in order to drive off water. After growth the ingots were cooled to room temperature over a period of approximately 1 day. The calcium impurity content of the specimens was obtained by emission spectroscopy.

3. Surface observations

The initial whiff of water vapour produced erosion of cleavage steps on the surface and left tiny round plateaux or hollows in the regions where water droplets condensed and then evaporated. These regions, especially plateaux, where where recrystallization patterns were observed to form, but most regions from which water droplets evaporated, produced no recrystallization whatsoever, the total number of regions containing patterns occupying only a minute fraction of the total surface area. A few extended flows (~ 10 sec each) of moist nitrogen were sufficient to bring out all the recrystallization obtainable on any one surface, further exposure changing neither the amount nor the location of recrystallization. Each exposure, however, caused dissolution of the surface crystals produced previously.

General observations were as follows.

(i) Recrystallization patterns were observed on specimens in which calcium impurity content was of the order of 50, 100, 150 and 250 ppm, but they were not detected on undoped nominally pure single crystals. The number of evaporated droplet regions containing surface crystals increased with calcium inpurity content; for the specimen doped to 250 ppm they covered approximately 1% of the sample surface area.

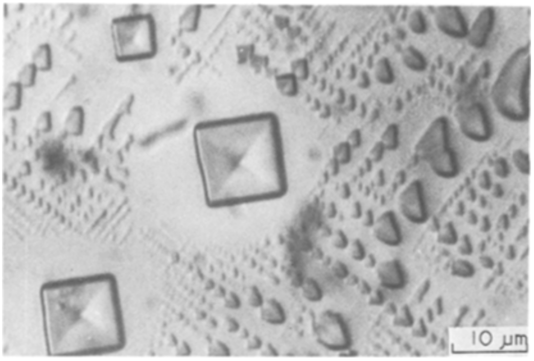

Figure 1 Pseudosquare and chevron-shaped crystals on (0 0 1) substrate surface doped to 150 ppm Ca^{2+}. The arrowhead direction of the chevrons and the diagonals of the square are aligned along ⟨1 1 0⟩.

(ii) Recrystallization was localized. After three or four extended squirts of moist nitrogen, a maximum in the number of regions was obtained, at locations that were not changed by further exposure.

(iii) The surface crystals had a variety of habits, ranging from "squares" and chevrons (Fig. 1) to various forms of cross (Fig. 2a, b). However, the basic structure of each shape, such as the diagonals of the squares and the arms of the crosses, was almost invariably aligned along the ⟨1 1 0⟩ crystalline directions of the substrate. (There is a ⟨0 1 0⟩ cross in Fig. 2a.) The shapes thus appear as different modes of a common form of crystallization. The square crystals were often irregular, and are better described as "pseudosquares".

(iv) Interferometric microscopy determined that the observed shapes were relief figures standing proud of the surface, although the configuration of light and dark shadows in the micrographs sometimes give rise to the optical illusion that the reliefs are sunken pits. The square crystals were hopper-shaped, with a depression at their centre.

(v) Variations in the rate of evaporation of the water droplets, obtained by controlling a flow of dry nitrogen that formed the atmosphere over the sample surface, changed the shape of the crystals

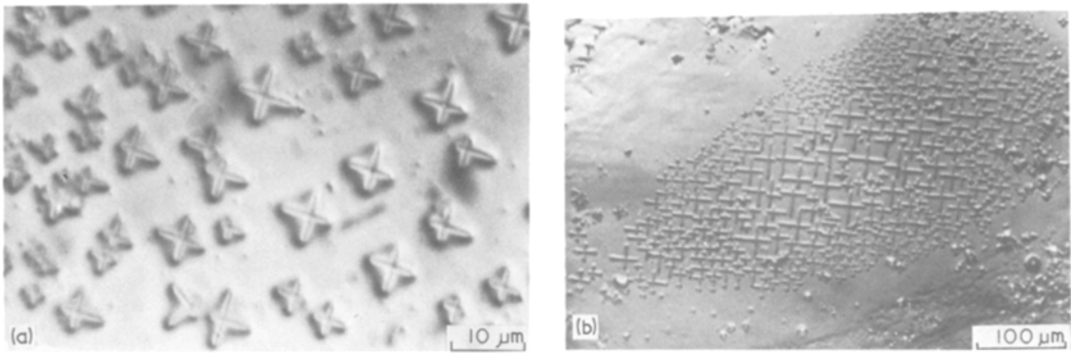

Figure 2 (a) Crystal crosses aligned in ⟨1 1 0⟩ directions on (0 0 1) substrate doped to 150 ppm Ca^{2+}. Note ⟨0 1 0⟩ cross near bottom margin. (b) A "graveyard" of narrow-armed crosses on (0 0 1) substrate doped to 250 ppm Ca^{2+}, observed in hollow after fast evaporation.

produced at any given location. In general, square crystals as in Fig. 1 were formed by slow evaporation, while a faster rate produced crosses (Fig. 2). In Fig. 3, which shows a plateau left by a water droplet, rapid evaporation has produced narrow fingers and crosses near the plateau edge while larger rosettes and pseudosquares appear near the centre where evaporation was slower.

(vi) In general, the crystals were hygroscopic, water vapour condensing preferentially near crystals rather than elsewhere on the substrate. However, the crystals formed when water vapour made initial contact with a freshly cleaved surface, and which were usually square or chevron shaped, were stable in the presence of atmospheric moisture, whereas later crystals formed after a number of exposures to vapour were actively deliquescent and could be observed only by being kept under a surrounding flow of dry nitrogen. A few seconds' exposure to air caused rapid deterioration. The crystals formed under these latter more hygroscopic conditions were usually in the form of narrow fingers or crosses.

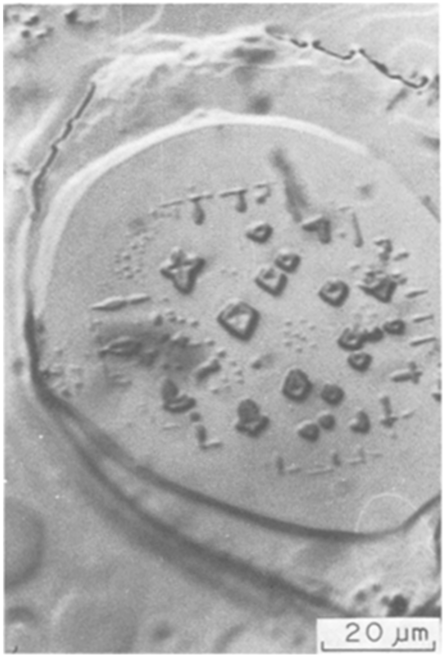

Figure 3 Crystals sited centrally on plateau left by evaporating water droplet. Rapid evaporation near periphery has formed small crystals, while slower evaporation produces larger pseudosquares near centre. 150 ppm Ca^{2+}.

(vii) The few plateaux containing recrystallization patterns were not visibly different from the many that did not, the formation of the crystals deriving solely from the local concentration of soluble impurity. This is demonstrated in Fig. 4, which shows a plateau on which a water droplet spilled over the edge onto the surrounding etched surface before evaporating. Recrystallization patterns normally form centrally on a plateau (see Fig. 3), but in Fig. 4 the patterns appear where the water has flowed, showing that a dissolved component has moved in solution.

4. Nature of the recrystallization process

4.1. Surface behaviour

The absence of recrystallization on undoped substrates, plus the systematic increase with doping, shows that surface crystals are a consequence of the added calcium impurity and not simply a form of recrystallized NaCl. NaCl does not crystallize easily from pure solution [11], and when it does it extends laterally over the substrate in thin (0 0 1) growth layers [12], so that dissolution and recrystallization on an undoped NaCl surface gives irregularly contoured surface domains [1]. Such a

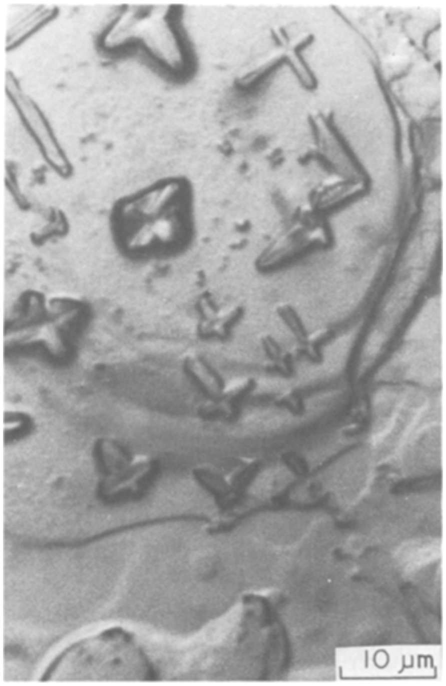

Figure 4 Plateau region, 150 ppm Ca^{2+}. The crystals outside the plateau rim in the lower half of picture were formed from constituents carried in water that overflowed this rim.

process, which gives the plateaux and the surrounding "orange peel" surface etch seen in Figs. 3 and 4, cannot form surface excrescences. Certain contaminants in solution assist crystallization of NaCl, but calcium is not one of these [11], not even when such growth proceeds by adsorption at a surface [5], so we are not dealing with NaCl crystal habit promoted by the presence of impurity.

The structure and composition of the surface crystals could not be determined by electron diffraction, owing to the overall fragility and hygroscopicity of the surface, but it was noted that stripping an acetylcellulose coating from the surface removed the square crystals, but left the crosses firmly bonded to the substrate. In transmitted light the centres of the extracted crystals were bright and scintillating, which indicates that the square crystals grew outwards from a central nucleus rather than directly onto the substrate. NaCl substrates are known to impart a common ⟨1 1 0⟩ recrystallization texture to different types of overlying crystal. Thus, solution growth of NaCl onto NaCl [13] produced ⟨1 1 0⟩ fingers which, at higher supersaturations, spread outwards into sheets that were not bonded to the substrate, similar to the observations for pseudosquare crystals. However, deposition of polyethylene onto NaCl [14] produced ⟨1 1 0⟩ rosettes similar to those seen in Figs. 3 and 4, while crystallization of polypropylene also resulted in ⟨1 1 0⟩ orientations of growth [15]. Thus, surface crystal shape is determined, not by composition or equilibrium crystal habit, but by substrate properties and growth kinetics [5], so that the same compound can appear in a range of different shapes. The variety of shapes seen in close proximity on the plateau of Fig. 3 can, therefore, be attributed to the same crystallizing constituents, while the bare patches around the large square crystals in Fig. 1 indicate that nearby impurity has gone to extend the squares whereas the same impurity further away appears as ⟨1 1 0⟩ crystalline pimples and fingers.

The hygroscopicity noted in Section 3(vi) identifies calcium chloride as a compound formed from the crystallizing impurity [9]. The equilibrium room temperature composition would be $CaCl_2.6H_2O$, which is highly deliquescent [9], and it was in fact found that successive exposures to water vapour led to ⟨1 1 0⟩ crystalline fingers that required protection from ambient moisture. However, closer observation showed that ambient moisture condensed onto the substrate around the crystals rather than directly onto the crystals themselves, and it has already been noted that the crystals that emerged when a freshly cleaved surface was exposed to water vapour were stable in air. Since calcium chloride has high aqueous solubility and since successive recrystallization is an accepted means of purification, the progressive increase in hygroscopicity must be attributed to the production of increasingly pure crystals of calcium chloride. It follows that the crystals formed initially contained a stabilizing component, presumably NaCl, and also that slow evaporation favoured incorporation of this component.

The existence of stable crystals formed from a combination of $CaCl_2$, NaCl and water was observed in other circumstances. An NaCl ingot, doped with a nominal 100 ppm of calcium and stored for 2 years, were found upon cleavage to contain small pseudosquare crystals, similar to those at the centre of Fig. 3, within a surface layer 2 mm thick. These crystals were observed immediately on cleavage (without exposure to water vapour) and were unaffected by ambient moisture. A calculation from the expression for the diffusion length, $(Dt)^{1/2}$, of the diffusion coefficient D of the species that had diffused at room temperature into the surface layers during storage time t yielded the value $2 \times 10^{-14}\,\mathrm{m^2\,sec^{-1}}$, which is a large value that is consistent with the limited data on the diffusion coefficient of water, that in KCl at 200° C, for example, being $10^{-11}\,\mathrm{m^2\,sec^{-1}}$ [16]. In further observations, direct evidence of the role of water comes from recrystallization produced by residual impurity segregated to grain boundaries. Calcium is a common residual impurity in analytically pure NaCl, with an average concentration of approximately 10 ppm. When specimens were cut from nominally pure bicrystal ingots, cracked along the boundary and exposed to water vapour, a few small stable pseudosquare crystals were observed to form on the boundary surface. This is consistent with boundary segregation of residual calcium [17]. The cracked boundaries sometimes contained observable preformed precipitates, identified by their strong deliquescence as calcium chloride. Ambient moisture condensed onto these precipitates to form spreading droplets which, when allowed to stand on the substrate, produced small recrystallization pseudosquares along the liquid rim of the droplet.

It is important to note the sparseness of recrystallization regions. They covered 1% of substrate surface when doping level was 250 ppm, but since only part of each region is covered by crystals, and since there are fewer calcium sites in the surface crystals than cation sites in an equal volume of substrate, an order of magnitude estimate for the local calcium concentration needed to produce recrystallization comes out as no more than 0.1%, assuming this impurity level extends over most of each recrystallization region. It is possible to obtain this extra local impurity in the host lattice by macrosegregation, but such impurity will inevitably separate out at low temperatures into a local accumulation of second-phase precipitates. However, the high concentration of impurity within precipitates is necessary in order to explain recrystallization. It is known that the decrease in calcium solid solubility with temperature produces several forms of $CaCl_2$ precipitate [8], that precipitates in lightly doped NaCl (10 ppm Ca^{2+}) nucleate heterogeneously at grain boundaries and dislocations [18], and that precipitate segregation adjacent to a grain boundary in nominally pure NaCl (calcium content 10 ppm) can extend over macroscopic distances of many microns [17, 19]. It follows that the combined effect of the decrease in solid solubility with temperature, compositional inhomogeneity during crystal growth, impurity segregation to line and surface defects, and heterogeneous nucleation of second phase creates a network of precipitates along a substructure within the specimen. Homogenizing treatments (anneal followed by quench) fail to eliminate this substructure [20], since when precipitation starts up again at lower temperature most precipitates reform at the sites they occupied previously. Hence, the specimen becomes imbued with a semi-permanent substructure, and those parts of the substructure containing a high density of deliquescent calcium chloride precipitates are the incipient recrystallization centres that await only the introduction of water in order to be activated.

4.2. Grain-boundary observations

Precipitates accumulate more readily on a grain boundary than within the single-crystal matrix, which explains why recrystallization in nominally pure specimens (10 ppm Ca^{2+}) was encountered on cracked-open grain boundaries but not on cleavage surfaces in single crystals. However, a cleavage surface at right angles to the grain-boundary plane in a nominally pure bicrystal has only a small chance of intersecting one of the sparsely distributed recrystallization regions. One of these chance encounters is shown in Fig. 5. Exposure to water vapour of this surface was seen through the microscope to produce a sequence of crystalline crosses along the boundary, but the highly deliquescent nature of the boundary region made

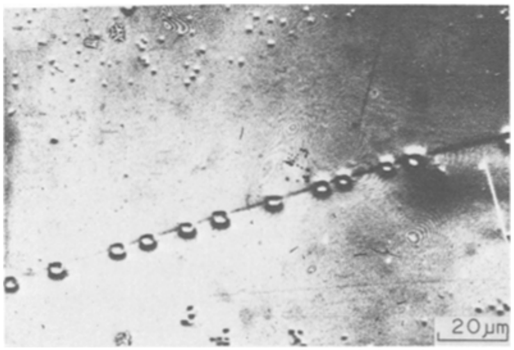

Figure 5 A (0 0 1) surface cleaved perpendicular to ⟨0 0 1⟩ axis of 5° tilt boundary in a nominally pure NaCl bicrystal. The sequence of loops represents water that has condensed around crystals formed along the dark line of the boundary sloping across the picture.

it difficult to capture this event by microphotography. The micrograph in Fig. 5 has been processed to reduce background "noise" and to highlight the recrystallization features represented by the sequence of "squashed hoops". Each of these is a raised lip of water completely surrounding a crystal cross (not visible) that will be shortly overwhelmed by further condensation of ambient moisture.

The existence of deliquescent water-soluble components in selected parts of a grain boundary was also encountered during the sectioning by wet-string water-saw [21] of bicrystal ingots containing 20° tilt boundaries. The ingots were pulled under dry nitrogen from a melt of analytically pure salt. Water penetrated into particular segments of these boundaries in the growth direction with a rapidity (several $\mathrm{cm\,h^{-1}}$) that would be difficult to explain unless water were eroding a preferentially soluble path, such as that provided by a string of calcium chloride precipitates. The existence of strings of precipitates of residual impurity in the growth direction was postulated in earlier experiments to explain "growth spines" observed in the electrodecoration of grain boundaries [22].

5. Conclusions

The conclusion that the surface crystals are a form of $CaCl_2$ hydrate that is stable in air in the presence of calcium-doped alkali halide leads one to expect that similar crystals should form on cleavage faces of other calcium-doped alkali halide crystals. Preliminary experiments confirm that this is so, with calcium-doped KCl and KBr substrates showing all the features reported in Section 3 for surface recrystallization on NaCl.

The finding that calcium impurity is an important factor in the susceptibility of alkali halide crystals to attack by moisture reinforces an earlier observation [3] that calcium impurity increases water solubility at low temperatures. The dissolved water diffuses into the lattice as H_2O molecules [3], giving rise to defect equilibria additional to the simple ones used to explain bulk transport in the pure lattice. The reaction between the water molecule and the calcium ion that is usually invoked to explain the decrease in extrinsic conductivity produced by ambient moisture is the formation of calcium hydroxide [23, 24]. The present work, however, indicates that the reaction that takes place at room temperature between water and calcium ions in the chloride phase is hydration of the chloride, and hence any discussion of properties that are influenced by a water–calcium interaction, up to the temperature (~ 170° C) at which hydrates decompose at ambient pressure into anhydrous $CaCl_2$ [9], must take the possibility of hydration into account.

Solid state recrystallization demands rearrangement of lattice ions. In the present instance, water molecules can reach a $CaCl_2$ particle by interstitial diffusion [3], but the large accretion of water involved in the structural transformation to $CaCl_2.6H_2O$ requires removal of matrix ions from lattice sites adjacent to the particle. The ease with which this occurs depends on how fast diffusion takes place at the low temperatures at which hydration is possible. These temperatures are below 200° C. The diffusion coefficient of water at 200° C is about $10^{-11}\,\mathrm{m^2\,sec^{-1}}$ [16], whereas extrapolated values for the self-diffusion coefficient of sodium are $< 10^{-17}\,\mathrm{m^2\,sec^{-1}}$ [17], while those for chlorine are even smaller. Hence, water molecules can diffuse in much more rapidly than matrix ions diffuse out, which has two effects: (i) the rate of recrystallization is not limited by the availability of water molecules, (ii) the local increase in stress produced by excess water ensures that recrystallization takes place preferentially at grain boundaries. The lattice diffusion coefficients of sodium and chlorine are so small, in fact, that the timescale of a normal laboratory experiment is insufficient to allow the recrystallization that takes place inside a single crystal to be observed (note the 2 year storage time for recrystallization noted in Section 4.1). Diffusion along grain boundaries and subgrain boundaries, however, is orders of magnitude more rapid, especially when lattice structure alongside the boundary interface has been broken up by impurity precipitates; hence hydration and recrystallization takes place much more quickly along boundaries. A consequence is that the semi-permanent substructure imprinted into a crystal lattice by impurity precipitation is made more gross by exposure to moisture, owing to the removal of matrix ions on sites adjacent to precipitates in order to accommodate water of crystallization.

The development of a macroscopic substructure in grain boundaries should become most noticeable on reheating the crystal to 200° C, when the water of crystallization is driven off, either back into the ambient or interstitially into the matrix lattice, leaving behind a network of enlarged cavities around initial precipitation centres, and it was noted in earlier experiments in which bicrystal specimens were held many hours at 200 to 250° C that a distribution of cavities corresponding to grain-boundary precipitation was electrodecorated with colloidal silver [22]. The observed cavities were larger than was needed simply to accommodate residual impurity precipitates, and it is possible that the enlarged cavity size resulted from hydration of calcium chloride particles. What is certain is that the grain-boundary structure presented by recrystallization is similar to that provided by electrodecoration. It was found that electrodecoration colloids formed along channels aligned in the direction of the tilt axis [22], so that cleavage at right angles to the tilt axis cut through the colloids lying in these channels and displayed them as a sequence of silver blobs along the boundary. This sequence exactly matches the sequence of hoops in Fig. 5, including a common value (~ 10 μm) for the spacing between crystals and between channels. Hence, the cavities filled with silver correspond exactly to the crystallization centres produced in the present work, and both are apparently a consequence of calcium chloride precipitates.

The present work shows that exposure to moisture of an alkali halide crystal containing residual hygroscopic impurity can introduce irreversible changes in specimen substructure. It follows that any measurement of a property that is dependent on substructure must either exclude the influence of moisture or determine how far it needs to be taken into account.

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