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Vapor-phase growth and electrical conductivity of pure and impurity-doped ammonium halide crystals

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Ideal growth parameters for obtaining large transparent crystals of NH_4Cl and NH_4Br by vapor-phase technique are described. The electrical conductivity of such crystals and crystals grown from solution are reported. In pure NH_4Cl crystals two regions with slopes 1.26 and 0.8 eV are obtained in the $\log \sigma T$ vs $1/T$ plot. In impurity-doped NH_4Cl crystals a third region with slope 1.04 eV is also observed. In pure NH_4Br crystals two regions with slopes 1.06 and 0.66 eV are obtained.

INTRODUCTION

It is well known that single crystals of ammonium halides in cubic shape can be grown by slow evaporation of a solution containing ammonium halide and urea which acts as an aid for crystal growth. Experiments¹⁻³ like ir, NMR, x-ray diffraction, and density measurements have shown no presence of urea in crystals grown from solution within the experimental accuracy of these experiments. It has been recently reported that ammonium chloride can be grown by the vapor phase technique.⁴ The advantage of this method lies in the fact that since the crystals are grown in vacuum and no additive is present during the crystal growth process, the possible contamination of crystals with impurities and hydroxyl ions is eliminated. In this paper we report ideal growth conditions for growing NH_4Cl and NH_4Br crystals from the vapor phase and the electrical properties of such crystals. We also report suitable values of different growth parameters like ΔT —the temperature difference between the charge and the nucleation site, dx/dt —the pulling rate of the growth tube through

the furnace, and dT/dx —the temperature gradient along the growth zone.

CRYSTAL GROWTH

AR-grade British Drug House powders were used for growth of pure crystals. Pyrex for NH_4Cl and quartz for NH_4Br were used as growth tube materials. The growth tube was drawn to a bullet shape with a pointed tip at one end and a glass conduction rod was sealed to it. The tube was then filled with the charge (growth material) and another blocking tube was introduced at the other end as shown in Fig. 1(a). A space was left between the tip and the charge in the growth tube depending on the temperature profile in the furnace used. The diameter of the blocking tube was approximately 1 mm less than the inner diameter of the growth tube so that a small space was left between the two. The whole assembly was connected to a diffusion pump for evacuation and heated for 48 h, at 120 °C under vacuum. Under such conditions a vacuum $\sim 10^{-3}$ Torr was attained and the temperature was raised to a value such that the

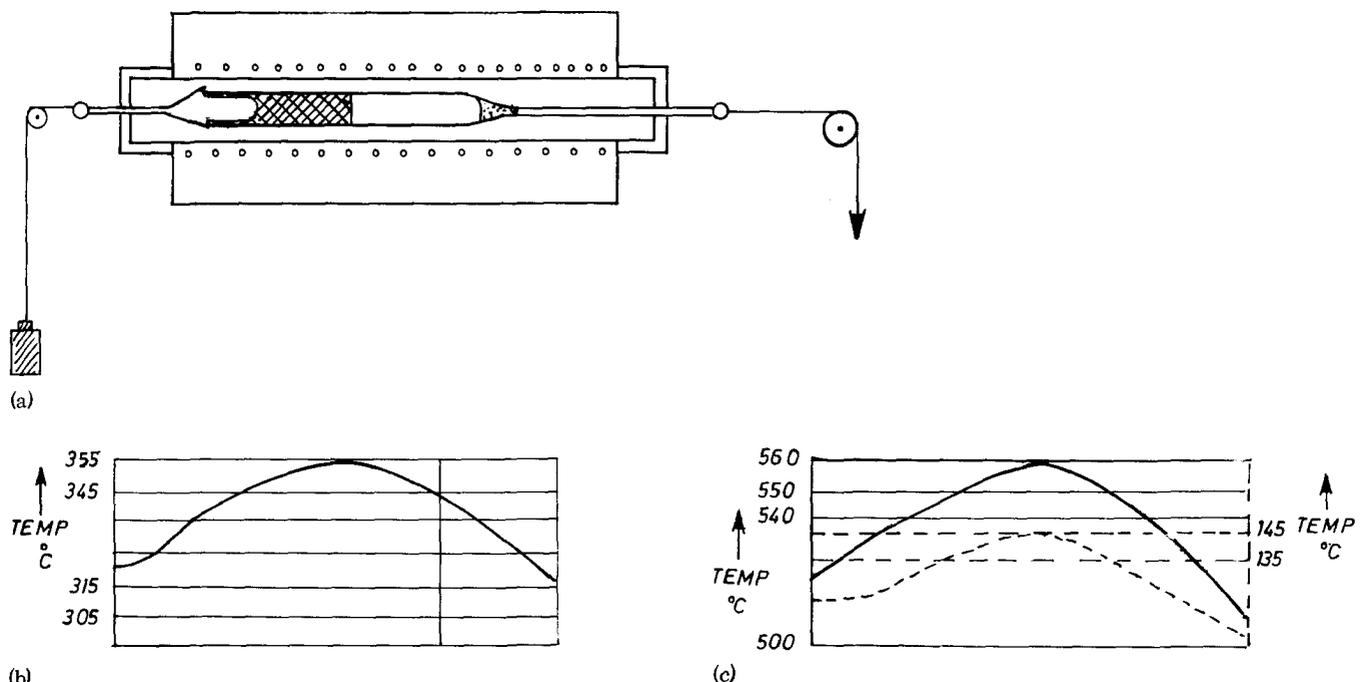


FIG. 1. (a) Experimental setup for crystal growth; (b) temperature gradient in the growth zone for NH_4Cl crystals; (c) temperature gradient in the growth zone for NH_4Br crystals. The dotted curve represents the temperature gradient during cooling near the phase transition temperature.

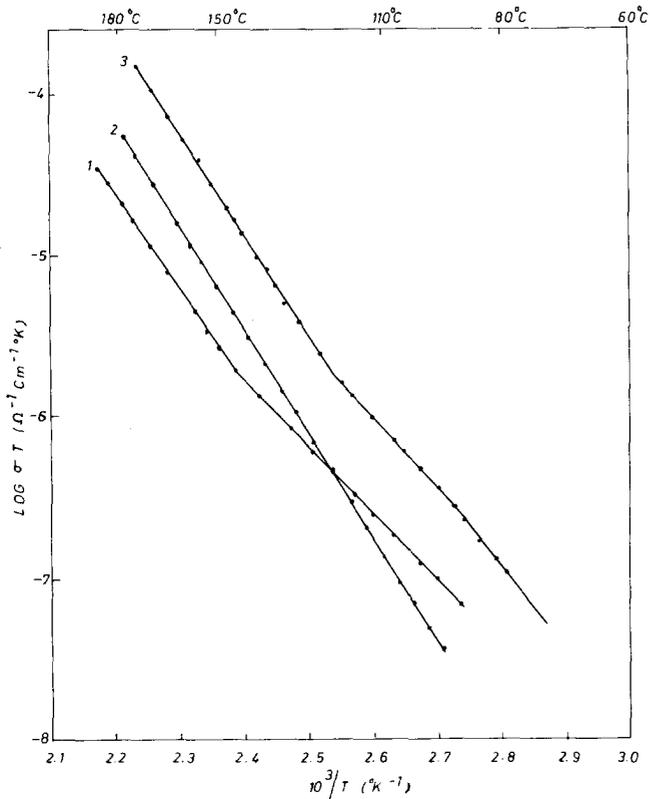


FIG. 2. Absolute electrical conductivity ($\log \sigma T$ vs $1/T$) plots: curve 1 for NH_4Cl vapor-grown crystals and curve 2 for solution grown NH_4Cl crystals. Curve 3 is the conductivity plot for Ni^{2+} -doped NH_4Cl crystals grown from solution.

charge condensed in the space between the growth and blocking tubes and the growth tube was self-sealed. This tube was then passed through the growth furnace. The tip of the tube was kept at the maximum temperature point in the growth zone for nearly 2 h so that any nucleation which could have deposited there by chance was removed. It was necessary, since the initial growth starts at the tip only and the presence of any microcrystallites would make the growth polycrystalline. The tip was then moved to the growth temperature point and the pulling was started. The nucleation starts at the tip which grows into a large single crystal as the tube moves slowly through the furnace. For pulling purposes two different arrangements, namely, the water-float method and the mechanical gear system, were used. The water-float system is both simple and does not produce any unwanted vibrations, but attaining a constant desired speed is a little difficult. To make the growth tube move only along the axis of the furnace two cover lids with holes in the center were put on the two sides of the muffle as shown in Fig. 1(a). For a smooth and continuous running of the growth tube through the furnace a small weight was added on the other side of the growth tube. This prevents sudden jumps which may be caused by the tension in the pulling wire. After the growth the crystals were slowly cooled to room temperature and the tube was broken to take out the crystals. The crystals were cylindrical in shape and the dimensions of the NH_4Cl crystals obtained were 0.8–1 cm diameter and 2–3 cm length, while those of the NH_4Br were 0.4–0.5 cm diameter and 1–2 cm length.

Fig. 1(b) shows the temperature gradient profile along the growth zone for NH_4Cl crystal growth. Best results were obtained with a nominal $\Delta T \sim 8\text{--}10^\circ\text{C}$. ΔT represents the difference between the temperature of the charge and the temperature at the tip of the growth tube at the time of nucleation. Various pulling rates were used but speeds between 1.2 and 1.5 cm a day were found to be most suitable. Higher pulling rates generally resulted in polycrystalline growth. For NH_4Br crystals the value of ΔT was found to be $\sim 15^\circ\text{C}$. The pulling rates were again 1.2–1.5 cm a day. NH_4Br has a phase transition at 138.5°C and the crystal breaks up into small fragments when cooled. To overcome this a modification was introduced. After the crystal growth, the temperature was reduced a little. The growth tube was pulled back to the starting point. The temperature was slowly lowered till the temperature profile was as shown in the dotted curve of Fig. 1(c). The tube was again pulled at the same rate. It was found that the crystals were not damaged during the phase transformation. Efforts to grow crystals still bigger in diameter did not succeed.

ELECTRICAL CONDUCTIVITY

The two opposite faces of the crystals were coated with Aquadag in addition to the platinum foils used to ensure good electrical contact with the measuring electrodes.

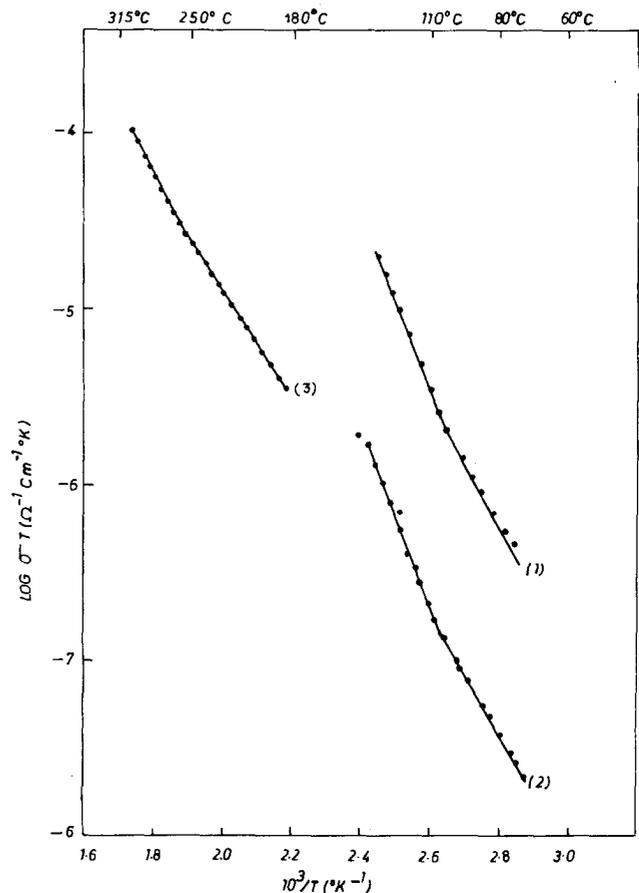


FIG. 3. Conductivity plot ($\log \sigma T$ vs $1/T$) for NH_4Br crystals. Curve 1 is for solution-grown NH_4Br crystals. Curves 2 and 3 are for vapor-grown crystals below and above the phase transformation at 140°C , respectively.

The measurements were done in vacuum using a GR 1644-A MΩ bridge. The crystals were heated at very slow rates and conductivity was measured at stabilized temperatures. A graph was plotted of $\log\sigma T$ vs $10^3/T$.

Earlier work^{1,2} on conductivity in solution-grown crystals has shown that divalent cations as well as divalent anions enhanced the conductivity by the same factor, thereby implying that both types of impurities make similar contributions to the conductivity. A mechanism of conduction which involves a proton transfer has been proposed but the energy parameters obtained and the interpretation of such values seem to be very different. Experiments on electrical conduction in vapor-grown crystals are reported in this paper for the first time.

Figure 2 shows the experimental results for various NH_4Cl crystals. Curve 1 is a plot of $\log\sigma T$ vs $1/T$ (absolute conductivity) for a crystal grown from vapor phase. There are two regions observed in these curves with slopes of 1.26 and 0.8 eV. Curve 2 is for $\log\sigma T$ vs $1/T$ for crystals grown from a solution containing urea. It can be seen from curves 1 and 2 that while the slopes of both curves are approximately equal at higher temperatures, the absolute conductivity is higher in solution-grown crystals than in vapor-grown crystals. This increase in absolute conductivity is rather difficult to explain. Extending the same physical picture as in alkali halides^{5,6} (we find no valid reasons to abandon this approach) we can interpret the two slopes in curve 1 as yielding $E_c + \frac{1}{2}W_s$ and E_c (E_c and W_s represent the activation energy for the migration of a positive ion vacancy and the energy of formation of a Schottky pair, respectively) which will give $E_c = 0.8$ eV and $W_s = 0.92$ eV. In both earlier papers on electrical conductivity of ammonium chloride crystals a proton transfer mechanism was postulated but the conventional interpretation of the slopes was used. There is a great deal of discrepancy between the values of W_s and E_c reported by these workers. Theoretical calculations^{7,8} for W_s and

E_c in ammonium halides show that W_s must be 1 eV which is in support of our experimental results and those reported earlier.¹ Curve 3 shows the effect of a large concentration of nickel (Ni^{2+}) impurity introduced through solution growth. In this case the extent of the extrinsic region is very much suppressed while a third region with a slope of 1.04 eV makes its appearance. If this is interpreted as conductivity due to the extrinsic associated region ($E_c + \frac{1}{2}W_s$) one would get a value of 0.48 eV for the binding energy of the impurity vacancy pair, which is of the right order.

Figure 3 shows the $\log\sigma T$ vs $1/T$ plot for NH_4Br crystals. Curve 1 is for solution-grown and curve 2 is for vapor-phase-grown crystals. There is a phase transformation at $\sim 138^\circ\text{C}$. Below 140°C the conductivity plot shows two regions with slopes of 1.06 and 0.66 eV. These slopes may be interpreted as giving $E_c + \frac{1}{2}W_s$ and E_c which gives $E_c = 0.66$ eV and $W_s = 0.80$ eV. Theoretical calculations give a value ~ 1.171 eV for W_s in NH_4Br . The two regions above 140°C probably represent the lower impurity regions as in the case of alkali halides. Measurements above 300°C were not successful due to increased vapor pressure which caused boil-off of material to occur, thus degrading the sample. However, impurity-doped crystals would yield more information about these regions.

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