CONTRIBUTION TO THE VIEW HELD ON MICROHARDNESS OF ALKALI HALIDES

By

J. SÁRKÖZI, A. TÓTH and J. L. KISS

Department of Experimental Physics, Technical University, Budapest

(Received December 15, 1971)

Presented by Prof. Dr. J. MÁTRAI-ZEMPLÉN

Methods of hardness measurements have much improved in the recent decades. Progress is mainly in the more exact processes of measurements and in the detection of testing errors. A far less success was achieved by relating the values of hardness obtained by the different methods. This is not surprising if we consider that the hardness number obtained by the different methods of measurements (e.g. wearing out, scratching, different types of micro-indentation, etc.) are not necessarily related to the same fundamental physical properties of the material. The material does not deform to the same degree in the different methods of measurement and so it has a different measure of hardening. In spite of all these difficulties, hardness tests are widely implemented because of their many advantages. Establishment of a relationship between the principal physical properties and the hardness number of the material would be of much help.

Many experimental results prove that the cation impurity increases the hardness of alkali halide crystals. The authors attribute the increased hardness to the interaction between the dislocation and the multiple point defects caused by doping [1, 2].

The objective of the present work was to investigate this question.

Experiments and results

The samples were cleft from NaCl single crystals containing different contaminations. Three groups of samples can be considered in view of contamination, such as: extremely pure (impurity is less than 10^{-5} mol %); purposefully doped (a known quantity of cation impurity given to the extremely pure basic material); and nominally pure ones. The single crystals in the first two groups were grown by Bridgman's method from a specially purified basic material.* The crystals were free of anion impurity because of the conditions of growth [3].

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* Also here we want to accentuate our thanks to R. VOSZKA, senior lecturer to the Biophysical Institute at the University of Medical Sciences, Budapest, for placing at our disposal the samples of extreme purity as well as the ones purposefully doped with cation after the purification.

The nominally pure crystals were grown from a pro analysi basic material by the Kyropoulos method, and so they contained, besides the usual cation impurity mainly, anion and oxygen contaminations as well.

We cleaved uniform samples of $5 \times 5 \times 1$ mm^3 size from crystals that were tempered beforehand in air at 650 °C. Heat treatment in nitrogen atmosphere did cause no change of importance in the quantities measured.

The point defect structure of samples with the given rate of impurity was changed by quenching from an elevated temperature to room temperature [4] at such a speed that the concentration of the dislocation increased but slightly.

The Vickers microhardness value was chosen to characterize the hardness of the quenched crystals. In order to have information for the interaction between point defects and dislocations we also examined the length of "rosetta" appearing after a selective etching — around the indenter [5].

a) *The Vickers microhardness test*

Microhardness was measured at room temperature on samples prepared as indicated above by a Hanemann D32 microhardness tester that was set up on a Zeiss NEOPHOT microscope. Most tests applied a load of 4 p., and the microhardness value was calculated as an average of 40 indentations. Loading was interpreted vs. diameter of impression and the rule by MOTT [6]. $P = ad^n$ was proved where P is the load, d is the indentation diameter, a and n are the structure sensitive coefficients. According to the investigations, both the a value and the microhardness value H_v obtained at a load of 4 p show the same trends of changing as a function of quenching temperature, and this is why the microhardness value obtained at an indentation of 4 p is used in the present study for characterizing the mechanical properties of crystals.

In Fig. 1 the microhardness as a function of quenching temperature is shown for four crystals differring by both impurity concentration and contamination.

Study of the curves has led to some unambiguous conclusions.

1. It can be ascertained that the Ca type divalent cation impurity creates a maximum in the microhardness (H_v) vs. quenching temperature (T_q) function, at about the quenching temperature of 300 °C (curve 1 in Fig. 1).

2. The presence of Tl as monovalent impurity in the crystal lattice makes a peak in the $H_v - T_q$ curve at about 500 °C (Fig. 1 curve 2).

3. If the mono- and the divalent cation impurities are present together in the (nominally pure) crystal lattice then both maxima develop, indicating that they exert their effect independently of the microhardness (Fig. 2).

4. For quenching temperatures over 600 °C, the microhardness increases independently of impurity contents (See Figs 1 and 2).

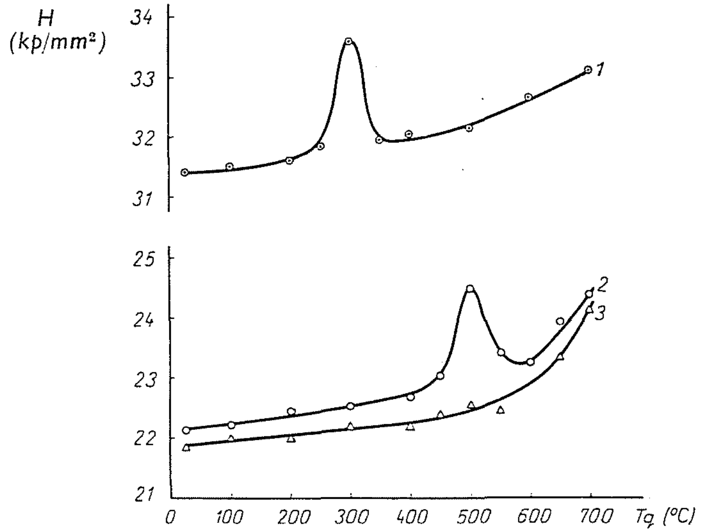

Fig. 1. Microhardness of quenched NaCl samples as a function of the quenching temperature. Impurity contents of the samples: 1 — 0.1 mol% $CaCl_2$, 2 — 0.1 mol% TlCl, 3 — extremely pure

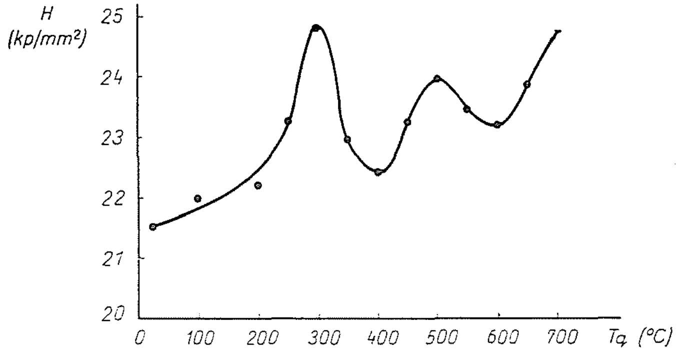

Fig. 2. The microhardness of a nominally pure quenched NaCl sample as a function of quenching temperature

b) *Measurement of "rosetta" length*

Saskolskaya and coworkers demonstrated that the length of the so-called "dislocation-rosetta" might be characteristic of the hardness of alkali halide crystals. According to a later work [8] they have also measured the "rosetta" length on quenched LiF samples containing Mg contamination. The measurements proved the close dependence of "rosetta" length upon the quenching temperature. We arrived at a similar conclusion for quenched NaCl samples with different rates of impurity. Tests were made according to [5].

A typical series of test results is seen in Fig. 3. The quenching temperature is plotted on the horizontal axis; as for the vertical one the relation of diagonal "rosetta" length is depicted so that we gained on quenched and unquenched samples of the same material. The "rosettas" were produced by a load of 4 p.

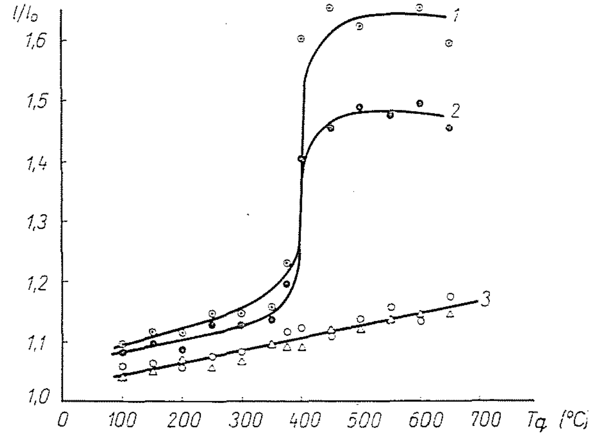

Fig. 3. Relative rosetta lengths on quenched NaCl samples as a function of the quenching temperature. Impurity contents of the samples: 1 — 0.1 mol% $CaCl_2$, 2 — nominally pure, 3 — extremely pure and 0.1 mol% TlCl

It is highly conspicuous at once that the "rosetta" lengths greatly change with the quenching temperature on samples with impurity of two valencies (curves 1 and 2 in Fig. 3). The rosetta lengths slightly react to tempering in samples made of an extremely pure basic material or a material doped with a monovalent cation (curve 3 in Fig. 3), and only a slow rise can be observed with increasing the quenching temperature. "Rosetta" lengths for samples contaminated with Ca^{++} show a very sharp change in growth at about a quenching temperature of 400 °C. Curves of a similar trend were obtained when "rosetta" lengths were measured at a constant indentation diameter.

Discussion

The microhardness value, like other hardness characteristics presents the material's resistance to plastic deformation. Consequently, hardness is in close connection with the process of plastic deformation, thus, first and foremost the plastic deformation has to be the point of scientific investigation.

To generate a plastic deformation — as it is well known — dislocations have to develop and propagate.

A great majority of research workers explain the change of hardness of the crystals by the change of energy demand for the dislocations to propagate. For example FLEISHER's [2] interpretation for hardening upon divalent cation impurities, is that hardening is due to dislocations caught on complexes. PRATT gives a similar explanation for his experimental results [9].

Nevertheless, our present results might permit to draw the conclusion that the foregoing interpretation can only be applied for hardness maxima formed at 300 °C, and that is unambiguously connected with the divalent cation impurity (Fig. 1 curve 1). The braking of dislocations caused by the "complexes" appears by the small lengths of the "rosettas" and in the microhardness higher values. When at a temperature over 300 °C the disintegration of complexes begins [10], the relative scale lengths of the "rosettas" increase (Curves 1 and 2 in Fig. 3), and the microhardness value decreases.

The microhardness and the "rosetta" length curves' progress at higher quenching temperature ranges already points to the undecisive importance of dislocation braking in the hardness values. This is proved for example by the fact that no influence of monovalent cation impurity at the scale of the "rosetta" lengths (that might be the characteristic for dislocation braking) can be observed (curve 3 in Fig. 3), while it can very well be observed in the microhardness (curve 2 in Fig. 1). This is also confirmed by the phenomenon how the quenching — over 600 °C — increases the crystals' microhardness irrespective of their contamination (Fig. 1 and Fig. 2), while no intrinsic change was observed at the "rosetta" lengths scale.

From the foregoing we might draw the conclusion that in the hardness value another factor might play a rôle in addition to the braking of dislocations, i.e. the process of generation of dislocation concomitant of plastic deformation. Changes in the process of generation and multiplication of dislocations might much affect hardness values, and, at the same time, these changes do not necessarily appear in the length of "rosetta" [11].

There are observations pointing out the importance of point defects for the formation and multiplication mechanism of dislocations [12, 13]. In our case it is easily conceivable that a tempering at about 500 °C creates a condition for the monovalent contamination which has a braking effect upon dislocation multiplication. Condensed vacancies might play the same role in crystals quenched from a temperature over 600 °C.

Available data do not permit even a qualitative picture about the correlation between the generation of dislocations and the hardness value, thus, this is only to indicate the likelihood of phenomena.

Summary

The microhardness of quenched NaCl crystals extremely pure, nominally pure (containing both anion and cation impurities) and doped purposefully with monovalent and divalent cation, was investigated as a function of quenching temperature. It was observed that the microhardness of crystals quenched from a given temperature increased upon the effect of contamination present in the lattice. The explanation is connected with the generation mechanism of dislocations.

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József Sárközi
András Tóth
Dr. József Kiss
Budapest XI., Budafoki u. 8, Hungary