

## Discussion

### *Comments on "Mechanical strengthening and impurity precipitation behaviour for divalent cation-doped alkali halides"*

Recently Zaldo *et al.* [1] reported on the influence of the clustering of divalent metal impurity-cation vacancy dipoles on the critical yield stress of alkali halide crystals. They investigated different systems and generalized their mechanical behaviour by classifying all crystals into two groups depending on the ratio of the ionic radii of the impurity ion and the host cation. An important representative of the systems with the mentioned ratio  $> 1.0$  forming no Suzuki-phase is NaCl–Ca. In addition to the measurements and citations in [1] a number of relevant results already exists, e.g. [2–7] which were used for a more detailed interpretation than that given in [1]. In the article of Zaldo *et al.* [1] three main conclusions were derived with respect to this kind of crystals. (a) The formation of dipole aggregates as dimers, trimers etc. is not followed by a change of the yield stress. This fact is preferentially attributed to a Snoek-type interaction. (b) The crystals will be hardened at low temperatures (for NaCl–Ca, e.g.  $T \leq 100^\circ\text{C}$ ), if metastable intermediate phases (plate-like structures parallel  $\{111\}$  and  $\{310\}$  planes) are formed during precipitation, because of the diminishing coherency with increasing precipitate size. (c) At higher temperatures (about  $200^\circ\text{C}$  for NaCl–Pb) the plate zones (especially the  $\{111\}$  one) are transformed into the stable incoherent dihalide  $\text{CaCl}_2$  phase connected with a decreasing yield stress which is explained by an Orowan-type mechanism for overcoming the incoherent dihalide precipitates by the dislocations.

The measurements [2–7] mentioned above agree with the experimental results in [1] concerning the mechanical behaviour, but some differences exist with respect to their interpretation, originating especially from the information of other simultaneously applied methods used in addition to the mechanical one.

It was shown quantitatively by an analysis of the dipole decay during isothermal annealing in the temperature range between room temperature and  $100^\circ\text{C}$  that a dimer kinetics including a back reaction is sufficient to describe the aggregation

process for lower Ca-concentrations in NaCl crystals [2]. In [3] simultaneously with the yield stress the dipole decay was measured for the NaCl–Ca crystals and no change of the yield stress was found for low doped crystals at intermediate annealing times. In accordance with [1] and [2] this behaviour was explained by the formation of small dipole aggregates, but contrary to [1] the unaltered yield stress could be attributed to a competition of the Snoek-type interaction originating in the reorientation of the dipoles and the Fleischer-type interaction caused by the overcoming of fixed point obstacles (e.g. dimers). By a quantitative analysis it was shown that the superposition of the two interactions just leads to a constant value of the yield stress in the regions of the dipole concentration attainable experimentally by isothermal annealing [3].

The annealing of higher doped NaCl–Ca crystals already leads to precipitations at temperatures of about  $100^\circ\text{C}$ , as it was shown by a mathematical analysis of NMR and dielectric loss measurements [4]. A simultaneously performed measurement of dipole decay and yield stress in this range [3, 5] showed an increase of the yield stress in accordance with Zaldo *et al.* [1] at temperatures  $\leq 100^\circ\text{C}$  and a decrease at temperatures of about  $200^\circ\text{C}$  [5], analogous to the behaviour of the NaCl–Pb crystals observed by [1]. X-ray diffraction photographs of a very high doped crystal (7000 ppm Ca) yielded two characteristically distinct patterns [6]. In the light of extensive investigations carried out recently [5] extended to very high annealing times ( $> 1000\text{h}$ ) this result must be interpreted in the following way. The Laue pattern in the reference state (quenching down from  $600^\circ\text{C}$ ) is caused by  $\{310\}$  plate-like precipitations. These are formed during the cooling process, probably in the temperature region at about  $75^\circ\text{C}$ . The impossibility of the formation of a crystal containing only dipoles at room temperature by a  $600^\circ\text{C}$  annealing was shown for calcium concentrations  $> 500\text{ppm}$  by a direct measurement of the dielectric loss [7]. The number of  $\{310\}$  precipitations grow during annealing at temperatures  $\leq 100^\circ\text{C}$  and therefore the yield stress increases. If all dipoles are incorporated in  $\{310\}$  precipitations and the annealing treatment is continued (overaging experiments)

the precipitates grow further (Ostwald ripening) yielding to a decrease of the yield stress in accordance with the Orowan mechanism.

The annealing at 200°C produced a Laue pattern [6] characteristically for the {1 1 1} structure, that means, the {3 1 0} precipitates of the reference state are transformed to the {1 1 1} ones leading to a decrease of the yield stress because the interaction strength of the {1 1 1} ones is smaller than that of the {3 1 0} ones due to a better coherency. It was impossible to find any reflexes originating on the dihalide CaCl<sub>2</sub> phase, as was observed by Suzuki [8] for a crystal doped with 10 000 ppm Ca. Obviously the calcium concentration is too low to form the dihalide precipitation. But the interpretation given here including also the X-ray diffraction results can also explain consistently the results of Zaldo *et al.* [1].

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