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Mechanical strengthening and impurity precipitation behaviour for divalent cation-doped alkali halides*

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The yield stress of NaCl doped with Ca, Sr, Mn, Pb and Cd, KCl doped with Pb, and KBr doped with Sr and Pb, has been investigated as a function of the state of aggregation of the impurity. For all systems the yield-stress remains constant during isothermal annealing treatments if the impurity concentration is below a threshold value dependent on the material. At higher concentrations two opposite behaviours have been found. For systems where a coherent Suzuki phase has been detected (NaCl–Cd and NaCl–Mn) or is expected to occur (KCl–Pb, KBr–Pb and KBr–Sr) a marked softening is observed during annealing. On the other hand, a marked hardening appears for NaCl–Pb, NaCl–Ca and NaCl–Sr, where the stable dihalide phase has been shown to form. Mechanisms responsible for the reported behaviour are proposed and briefly discussed.

1. Introduction

It has been recently reported [1], that the hardening behaviour during thermal annealing after quenching is quite different for NaCl–Pb and KCl–Pb. In fact, the yield-stress of NaCl–Pb increases markedly with annealing time for concentrations equal to or greater than 15 ppm, whereas for KCl–Pb is remains constant, even for concentrations as high as 220 ppm. Furthermore, treatments apparently leading to Suzuki-phase precipitates in this material [2] do not induce, either, an observable change in yield-stress. This clear difference between both systems was interpreted in terms of a different aggregation behaviour of lead ions. Semicoherent precipitates seem to be rapidly formed for NaCl–Pb and lead to the incoherent phase $PbCl_2$ during high-temperature annealing [3–5], whereas aggregates and coherent precipitates (presumably Suzuki-phase like) are induced during annealing of KCl–Pb [2]. For both systems, the initial stages of aggregation (formation of dimers, trimers, etc.) do not cause any extra-hardening effect with regard to the isolated dipoles.

In addition to the above mentioned data for NaCl–Pb and KCl–Pb, some interesting data on the effect of impurity aggregation on yield-stress have also been published for other systems [6, 7]. Unfortunately, the available information is still very scarce and fragmentary. Moreover, the data have been usually discussed [8, 9] in terms of a simple aggregation model of dipoles into small aggregates (trimers, etc.) and the formation of well-defined precipitated phases has been ignored. Consequently, the influence of impurity precipitation of yield-stress behaviour has not been so far adequately considered.

In this paper, an attempt is made to extend the same type of experiments reported in [1], to other divalent cation-doped systems. The main emphasis has been laid on systems (e.g., NaCl–Cd and NaCl–Ca) where the aggregation and precipitation behaviour has been studied by other techniques [10–14] and a reasonable understanding

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of the precipitates formed during annealing is available. In fact, one of the objectives of this work is to elucidate the correlation between the nature of those precipitates and their effect on the yield-stress of alkali halide crystals.

2. Experimental procedure

The systems investigated included NaCl doped with Ca, Sr, Mn, and Cd, KCl doped with Pb and KBr doped with Sr and Pb. For all cases, concentrations in the crystal have been determined by atomic absorption spectrophotometry. The study has been performed for standard size samples (4 mm x 4 mm x 10 mm) as well as small-size samples (2 mm x 2 mm x 6 mm) for which quenching rates are higher. The results are similar, although the scatter of data-points is quite large for the latter case.

Quenching treatments were performed by heating the sample for 20 min at 450° C and then dropping it onto a copper block. The efficiency of this quenching rate for small-size samples has been checked as follows. For NaCl–Mn the broad EPR signal for aggregated manganese is eliminated for concentrations equal to or greater than 200 ppm; for NaCl–Pb the optical absorption bands associated with $PbCl_2$ precipitates disappear for concentrations of about 60 ppm and the ionic thermocurrent (ITC) spectra consists of the single band corresponding to isolated dipoles for this concentration. However, the situation for other systems and concentrations will depend on the detailed shape of the time–temperature–transformation diagrams and a definite prediction cannot be advanced because, perhaps for the higher concentrations, the hardness after quenching cannot correspond with that due to isolated dipoles.

Isothermal annealing treatments were carried out in the temperature range 20 to 200° C. Mechanical testing was always carried out at room-temperature (RT) using an Instron testing machine. In all cases the stress–strain curves showed the typical shape [15, 16]. Macroscopic yield-stress values were determined by the intersection of the extrapolation of the easy-glide stage with the linear elastic region.

3. Results

First, it has been ascertained that for low enough concentrations, below a certain threshold, depending on the material, all systems show a yield-stress which is independent of annealing time for all temperatures within the covered range. This is illustrated in Fig. 1 for NaCl–Mn (58 ppm) annealed at RT, where the evolution of the yield-stress with time is compared with the decrease in dipole concentration, as inferred from the EPR spectra. In the inset of Fig. 1, the dependence of yield stress with annealing time at RT, 100 and 200° C for other systems (NaCl–Ca, KBr-Sr, NaCl–Cd and KBr–Pb) is included. This result confirms that the formation of the first aggregates (dimers, trimers) for the *I–V* dipoles does not modify the yield-stress of the crystals with regard to the isolated dipoles, as concluded in the previous work [1].

For higher concentrations, where some type of precipitation is involved, the experimental data indicate that two opposite behaviours are found, depending on crystal specimens.

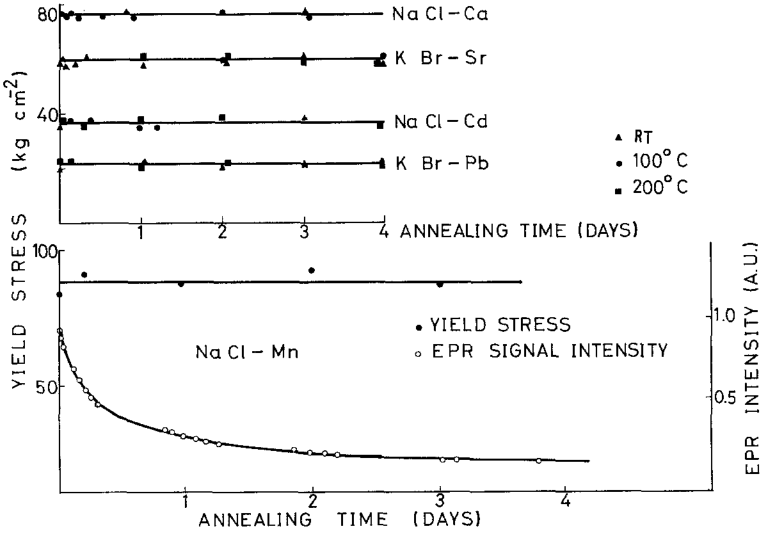

Figure 1 Dependence of the yield stress and EPR dipole signal with annealing time at RT for NaCl–Mn (37 ppm). In the inset, evolution of the yield stress at various temperatures for: NaCl–Ca (140 ppm), KBr–Sr (88 ppm), NaCl–Cd (37 ppm) and KBr–Pb (35 ppm).

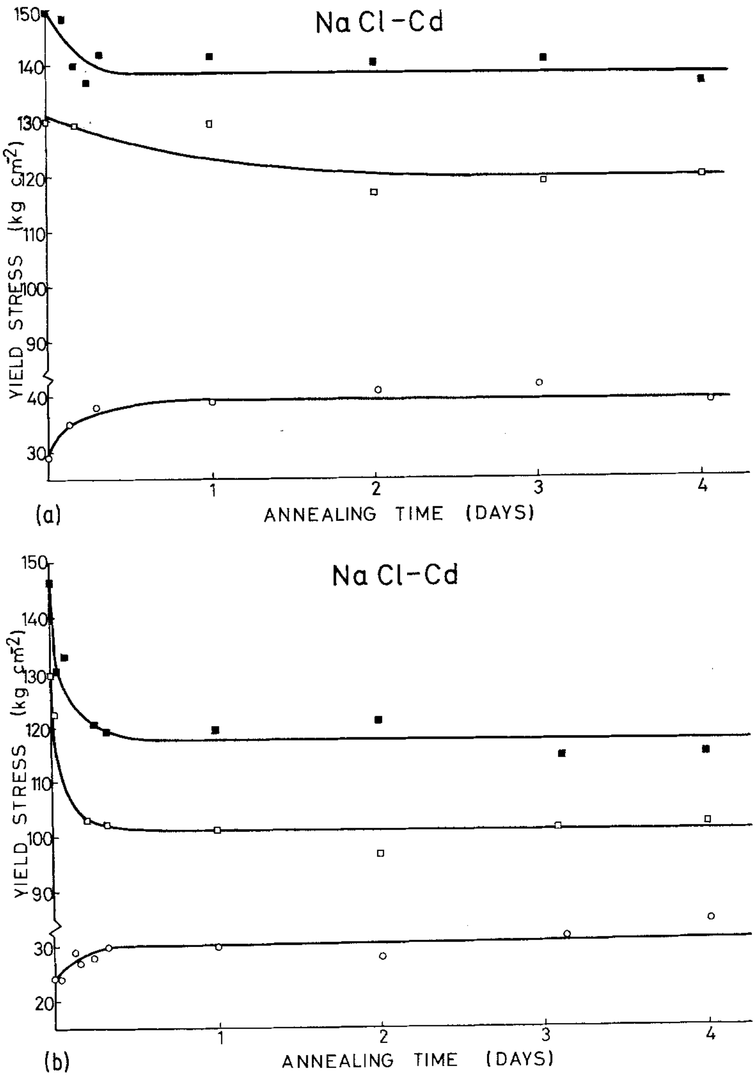

Figure 2 Dependence of the yield stress with annealing time at various concentrations: (■) 624 ppm, (□) 359 ppm and (○) 37 ppm for NaCl–Cd. (a) Room temperature and (b) 200° C.

3.1. NaCl–Cd, NaCl–Mn, KCl–Pb, KBr–Pb and KBr–Sr

For NaCl–Cd, where Suzuki-phase precipitates are unequivocally formed, the dependence of yield-stress on annealing time is given in Fig. 2. Fig. 2a shows the data corresponding to RT annealing and Fig. 2b shows the data for samples annealed at 200° C. At RT, the yield-stress remains constant or perhaps experiences a slight initial increase with time for the lower concentrations (37 ppm); whereas, for the higher concentrations it shows a definite decrease during the initial stages of annealing (~ 10 h). For longer annealing times, the yield-stress reaches a steady value in all cases. At 200° C, the situation is somewhat similar. Except for the lowest annealing, a marked initial softening of the crystal is observed, until a final steady value of yield stress is found, as for the RT case. The degree of softening is much higher for 200° C than for RT annealing. For 100° C annealing the observed behaviour is intermediate between that described for RT and 200° C.

The same basic behaviour is found for other systems: KBr–Pb, KBr–Sr and NaCl–Mn. Data on the evolution of the yield-stress with annealing time for KBr–Sr, containing various amounts of Sr, are shown in Fig. 3a and b, corresponding to RT and 200° C annealing, respectively. The results are quite similar to those described above for NaCl–Cd, although the decrease in yield-stress is, here, much more pronounced. A comparative plot of the effects of 200° C annealing on NaCl–Cd, KBr–Sr, KBr–Pb and NaCl–Mn crystals, with similar doping levels, is given in Fig. 4. The

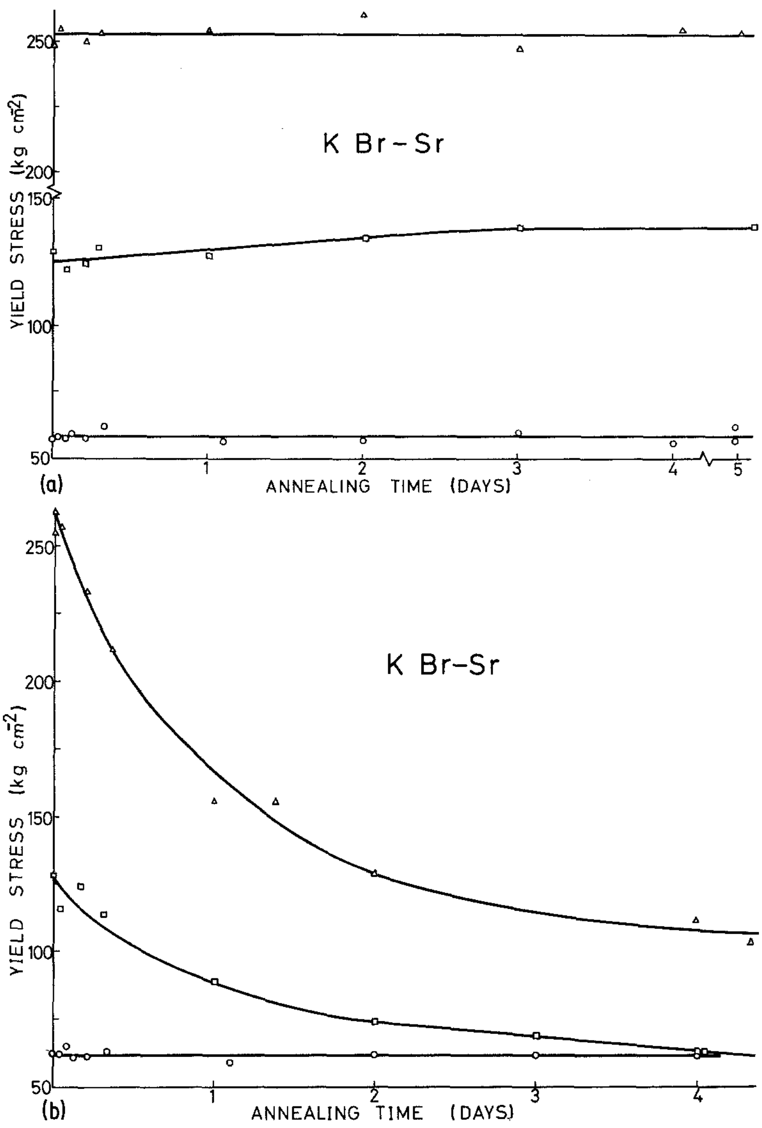

Figure 3 Dependence of the yield stress with annealing time at various concentrations: (△) 930 ppm, (□) 365 ppm and (○) 88 ppm, for KBr–Sr. (a) Room temperature and (b) 200° C.

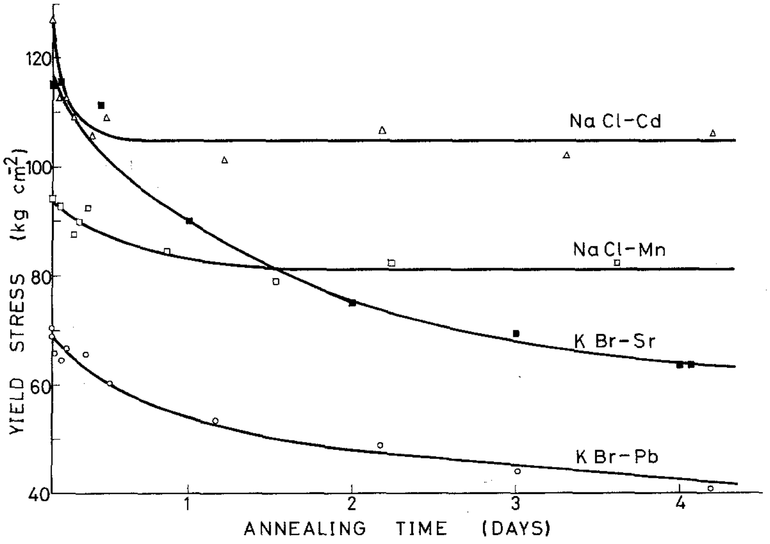

Figure 4 Comparative softening of the yield stress with annealing time at 200° C for: (△) NaCl–Cd (360 ppm), (□) NaCl–Mn (383 ppm), (■) KBr–Sr (365 ppm) and (○) KBr–Pb (132 ppm).

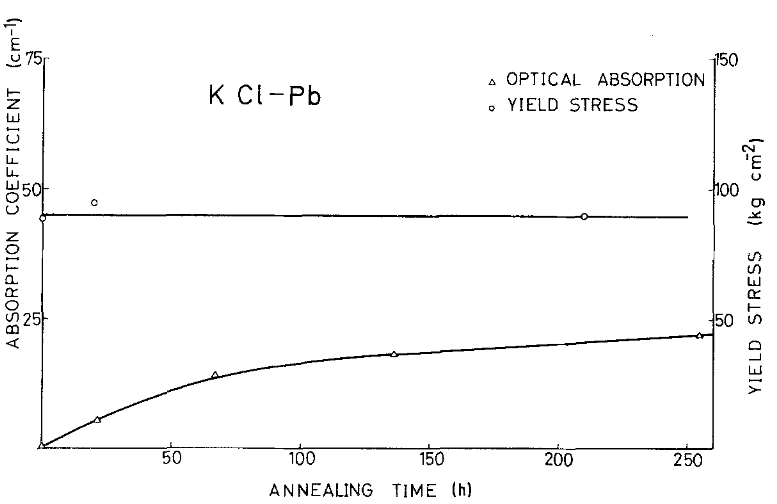

Figure 5 Comparison of the time dependence at RT of the yield stress and the height of the 280 nm absorption band for KCl–Pb (54 ppm).

"softening" effect is particularly small for NaCl–Mn which also presents some peculiar behaviour at 100° C, where some initial softening, followed by hardening has been observed. More work should be necessary on this system to clarify its behaviour. However, efficient migration of Mn to the crystal surface has been reported during heating [17] that may interfere with the aggregation process and be responsible for the complex yield-stress behaviour.

For KCl–Pb, some new optical data have now been obtained which allow for a meaningful comparison with the mechanical data described in [1]. As shown in Fig. 5, the yield-stress is constant during 200° C annealing, whereas an absorption band at 280 nm grows steadily with time at the cost of the A band of Pb^{2+}. At the same time, lead–vacancy dipoles decay with time, as revealed by dielectric loss and ITC techniques on a similarly doped sample [18]. In fact, the additional optical bands have been associated to Suzuki-phase precipitates [19], although direct evidence for this particular structure is not yet available.

For lead concentrations much higher (~ 3600 ppm) than those used previously, the yield-stress decreases with annealing time as commented above for NaCl–Cd, NaCl–Mn, KBr–Sr, and KBr–Pb.

3.2. NaCl–Ca, NaCl–Sr, NaCl–Pb

The data obtained for NaCl–Ca and NaCl–Sr, as well as those previously reported for NaCl–Pb, show an opposite behaviour to that corresponding to the materials included in Section 3.1. Fig. 6 illustrates the evolution of yield-stress with annealing time at 100° C for NaCl–Ca crystals containing various amounts of Ca. It is clear that a very marked hardening is obtained during annealing for concentrations above a certain threshold. Comparative data for NaCl–Pb, NaCl–Sr and NaCl–Ca

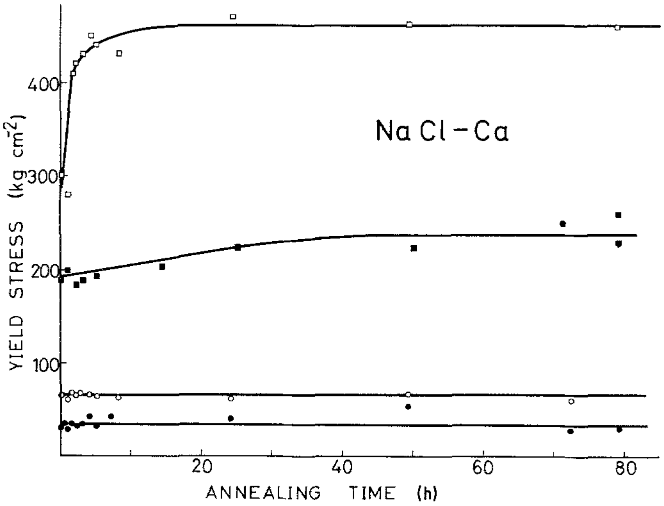

Figure 6 Dependence of the yield stress of NaCl–Ca with annealing time at 100° C for several concentrations: (□) 7400 ppm, (■) 2250 ppm, (○) 407 ppm and (●) 140 ppm.

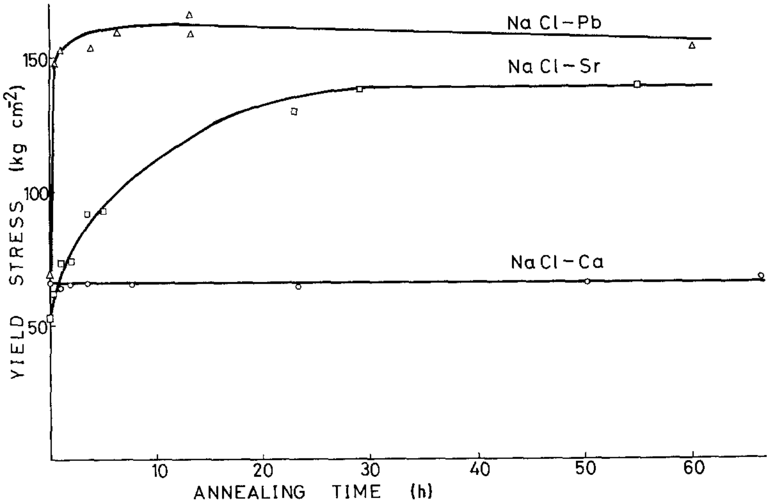

Figure 7 Dependence of the yield-stress with annealing time at 100° C for: (○) NaCl–Ca (140 ppm), (□) NaCl–Sr (150 ppm) and (△) NaCl–Pb (48 ppm).

are given in Fig. 7. At higher temperatures, the annealing-induced saturation hardening becomes smaller, as reported for NaCl–Pb. Data for NaCl–Sr are shown in Fig. 8. Above 175° C, practically no annealing-induced hardening is observed.

In order to gain a better insight into the obstacles responsible for the hardening in these materials, additional optical data have been obtained on NaCl–Pb, to be compared with the yield-stress data. In the previous work [1] it was concluded that some optical absorption bands develop during annealing at the cost of the A band, namely a complex band on its low-energy side (~ 286 nm) and another one at the high-energy side (~ 264 nm) appearing only during high temperature (100 to 200° C) annealing, attributed by several authors to $PbCl_2$ precipitates. It was then observed that the 286 nm band was associated to some intermediate centre in the precipitation process of $PbCl_2$, since, after an initial increase, it decreased to the benefit of the $PbCl_2$ band. Now the evolution of the yield-stress with annealing time has been compared with the growth of those optical bands. Fig. 9a shows the data for RT annealing and Fig. 9b shows the data for 200° C annealing. At RT, only the intermediate band (286 nm) develops and not the one associated with $PbCl_2$. The yield-stress increases in good correlation with the growth of that 286 nm optical band. At 200° C the initial rapid hardening is also associated with the growth of this intermediate band. For longer annealing times, where the 286 nm band decays to the benefit of the $PbCl_2$ band, a clear decrease in yield-stress is observed.

4. Discussion

Although it is not possible to give a detailed picture of the hardening (or softening) mech-

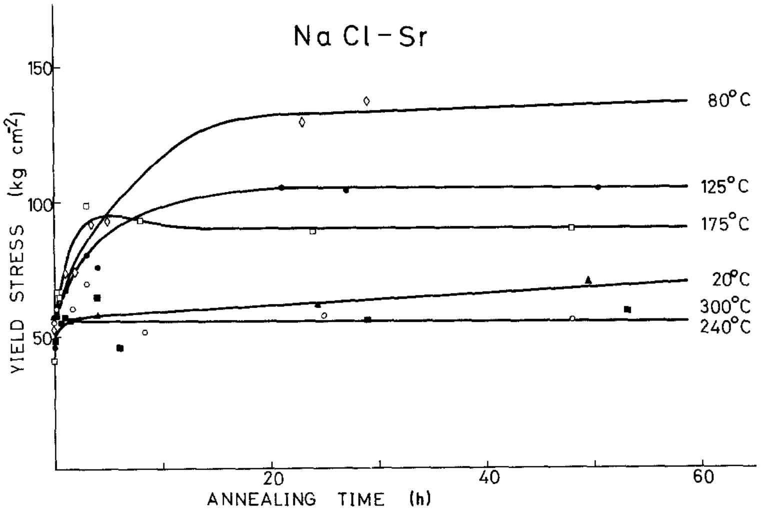

Figure 8 Dependence of the yield stress with annealing time for NaCl–Sr (150 ppm) at several annealing temperatures (RT to 300° C).

anisms operating in the various sytems, some general conclusions can be inferred from the data.

(a) The formation of small aggregates (dimers, trimers) from the isolated *I–V* dipoles does not induce any change in yield-stress for all the investigated systems. This conclusion is in accordance with that reported by Dryden *et al.* [6]. On the other hand, the changes in yield-stress observed by these authors for NaCl–Ca and LiF–Mg and attributed to the formation of larger aggregates are very likely related to the occurrence of precipitation processes, as discussed below.

The constancy of the yield-stresss, regardless of whether dipoles are isolated or forming small aggregates, appears more consistent with a Snoek-type [20] than with a Fleischer-type hardening mechanism [21]. In fact, the latter model would imply a yield-stress markedly dependent on aggregate configuration because of the differences in the associated stress-field, particularly in its axiality.

(b) For systems such as NaCl–Cd, where Suzuki-phase precipitates are formed, a clear softening of the material is observed during annealing for concentrations above a certain threshold. This behaviour could be attributed to the fact that these precipitates retain a high degree of coherence with the host lattice. In fact, one should presumably attribute the observed decrease in yield-stress to the increase in the interphase area between the precipitate and the crystal host associated with the cutting of the precipitates by the moving dislocations [22]. This mechanism predicts a yield-stress value which decreases on increasing precipitate size and, consequently, during annealing time. The amount of softening increases with annealing temperature, suggesting that the final size of the precipitates is correspondingly larger.

For the other systems where softening has also been observed, the simple criterion advanced by Lilley [23] suggests that Suzuki-phase precipitates are also expected since all $r_{2+}/r_{+} \leqslant 1.2$, where

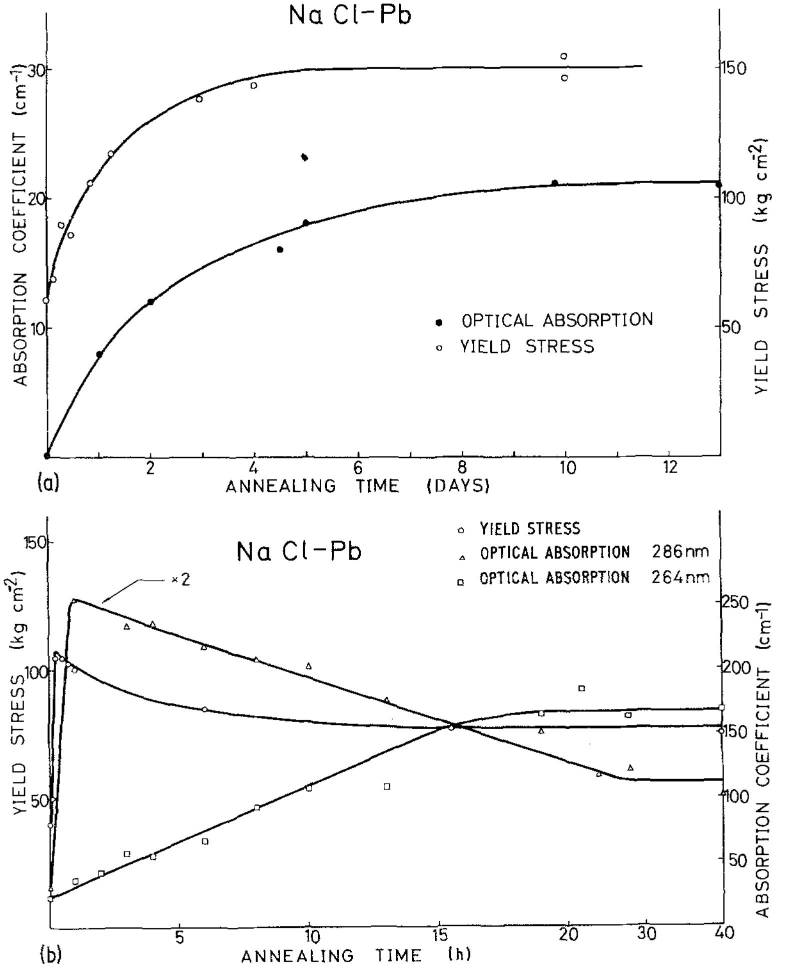

Figure 9 Comparison between the time evolution of the yield stress and optical absorption for NaCl–Pb (50 ppm). (a) Room temperature, ● optical absorption at 286 nm; (b) 200° C, △ optical absorption at 286 nm and □ optical absorption at 264 nm.

r_{2+} and r_+ are, respectively, the impurity and host cation radii. In summary, the softening appears to be a general effect associated with the Suzuki-phase or similarly coherent precipitates.

(c) For systems, such as NaCl–Ca, NaCl–Sr and NaCl–Pb, where the stable dihalide phase has been reported to occur, a definite hardening is observed at moderate annealing temperatures ($\leqslant 150^\circ$ C for NaCl–Pb and $\leqslant 100^\circ$ C for NaCl–Ca and NaCl–Sr). However, the new data on NaCl–Pb unequivocally show that the hardening observed at these lower temperatures is not associated with the stable phase but with some intermediate phases. The same conclusion would apply to NaCl–Ca, where X-ray studies have revealed that the phases formed below $\sim 100^\circ$ C, correspond to small plate-like structures, called the plate-zones, parallel to the $\{1\,1\,1\}$ and $\{3\,1\,0\}$ planes of the matrix lattice [10, 24]. These plate-zones posess a stoichiometry similar to that of $CaCl_2$, although retaining some degree of coherency with the matrix. At higher temperatures, the plate-zones (specifically the $\{1\,1\,1\}$) turn into the incoherent dihalide $CaCl_2$ phase. In both cases, NaCl–Ca and NaCl–Pb, the coherency of the intermediate phases should diminish during annealing because of the increasing precipitate size. This accounts for the initial hardening observed in the curves of Figs 6 and 9. On the other hand, the formation of the stable phase at longer annealing times is associated with a lower value of the yield-stress, which is particularly significant at the higher temperatures. This effect can be explained in terms of an Orowan-type mechanism for the overcoming of the incoherent dihalide precipitates by the moving dislocations [22].

Although the precipitation behaviour for NaCl–Sr is not so clearly established, the situation appears to be similar. In fact, intermediate rod-like precipitated phases have been reported during low-temperature annealing, which develop into $SrCl_2$ at higher temperatures. Furthermore, some very recent results on NaCl–Eu show the same behaviour and have been explained with a similar scheme [25].

As a summary, the correlation between the kind of mechanical response, the ratio r_{2+}/r_+ and the type of final precipitate formed or expected can be easily visualized in Table I. One may conclude that measurements of the variation of yield-stress with ageing time can be used to follow and qualitatively distinguish the type of precipitation behaviour in divalent cation-doped alkali halides.

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References

1. J. GARCÍA SOLE, C. ZALDO and F. AGULLÓ-LÓPEZ, *Phil. Mag. A* **41** (1980) 177.
2. R. CAPELLETTI, A. GAINOTTI and L. PARETI, Proceedings of the Symposium on Thermal and Photostimulated Currents in Insulation, October 1975, Dallas, edited by D. M. Smith (The Electrochemical Society, London, 1976).
3. A. BOHUM, J. DOLEJSI, M. SIMECKOVA and H. SVOBODOVA, *Z. Phys.* **243** (1971) 244.
4. J. L. PASCUAL, J. M. CABRERA and F. AGULLÓ-LÓPEZ, *Sol. Stat. Comm.* **19** (1976) 917.
5. L. MARCULESCU, *Phys. Stat. Sol. (b)* **80** (1977) 265.
6. J. S. DRYDEN, S. MORIMOTO and J. S. COOK, *Phil. Mag.* **12** (1965) 379.
7. W. G. JOHNSTON, *J. Appl. Phys.* **33** (1962) 2050.
8. A. I. SORS and E. LILLEY, *Phys. Stat. Sol. (a)* **32** (1975) 533.
9. C. W. A. NEWAY, R. P. HARRISON and P. L. PRATT, *Proc. Brit. Ceram. Soc.* **6** (1966) 305.
10. K. SUZUKI, *J. Phys. Soc. Japan* **10** (1955) 794.
11. *Idem, ibid.* **16** (1961) 67.
12. G. A. ANDREEV and V. A. KLIMOV, *Sov. Phys. Sol. Stat.* **16** (1975) 1926.
13. A. L. GUERRERO, E. P. BUTLER and P. L. PRATT, *J. de Physique Colloque C6* supplement au no. 7 **41** (1980) C6-363.

TABLE I Summary of materials, type of mechanical response, r_{2+}/r_+ and type of precipitate found

Material	Mechanical behaviour (above threshold concentration)	Ratio r_{2+}/r_+	Type of precipitate	Reference
NaCl–Mn	Softening	0.84	Suzuki-phase	[26, 27]
KBr–Sr	Softening	0.85	–	
KCl–Pb	Softening	0.90	Suzuki-phase?	[2]
KBr–Pb	Softening	0.90	–	
NaCl–Cd	Softening	1.02	Suzuki-phase	[11]
NaCl–Ca	Hardening	1.04	Dihalide	[10]
NaCl–Sr	Hardening	1.19	Dihalide	[8, 28]
NaCl–Pb	Hardening	1.26	Dihalide	[3, 4]

14. W. SPENGLER and R. KAISER, *Phys. Stat. Sol. (b)* **66** (1974) 107.
15. R. W. DAVIDGE and P. L. PRATT, *Phys. Stat. Sol.* **6** (1964) 759.
16. B. H. KEAR, C. E. SILVERSTONE and P. L. PRATT, *Proc. Brit. Ceram. Soc.* **6** (1966) 269.
17. E. PEDRERO, T. OCAÑA, A. GOMEZ and M. JOSE YACAMAN, *Thin Solid Films* **27** (1975) 149.
18. W. C. COLLINS and J. H. CRAWFORD, *J. Phys. Rev.* **4B** (1971) 3745.
19. P. G. BERTOLDI, R. CAPELLETTI, F. FERMI, M. MANFREDI and V. J. GRAVERIS, *J. de Physique. Colloque C6* no. 7 (1980) 367.
20. P. L. PRATT, R. CHANG and C. NEWEY, *Appl. Phys. Letts.* **3** (1963) 83.
21. R. L. FLEISCHER, *Acta Metall.* **9** (1961) 996.
22. P. HAASEN, "Physical Metallurgy" (Cambridge University Press, Cambridge, 1978) Chap. 14.
23. A. SORS and E. LILLEY, *Phys. Stat. Sol. (a)* **27** (1975) 469.
24. K. SUZUKI, *J. Phys. Soc. Japan* **13** (1958) 79.
25. F. J. LOPEZ, H. MURRIETA S., J. HERNANDEZ A. and J. RUBIO O., *Phys. Rev.* **22B** (1980) 6428.
26. J. A. CHAPMAN and E. LILLEY, *J. Mater. Sci.* **10** (1975) 1154.
27. D. L. KIRK, A. R. KAHN and P. L. PRATT, *J. Phys. D. Appl. Phys.* **8** (1975) 2013.
28. E. LAREDO and E. DARYTAGE, *J. Chem. Phys.* **53** (1970) 2214.

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