

## Melting properties of radiation-induced Na and Cl<sub>2</sub> precipitates in ultra-heavily irradiated NaCl

A. V. Sugonyako<sup>1</sup>, D. I. Vainshtein<sup>1</sup>, H. P. den Hartog<sup>1</sup>, A. A. Turkin<sup>2</sup>,  
and H. W. den Hartog<sup>\*,1</sup>

<sup>1</sup> Solid State Physics Laboratory, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

<sup>2</sup> National Science Center Kharkov Institute of Physics and Technology, 310108 Kharkov, Ukraine

Received 11 July 2004, revised 3 September 2004, accepted 17 September 2004

Published online 20 January 2005

PACS 61.46.+w, 82.50.Kx

Exposure of NaCl to high doses of ionizing radiation leads to the formation of nano-particles of metallic Na, very small chlorine precipitates, vacancy voids, and dislocations. A useful way to monitor the stage of the damage formation process is measuring the latent heat of melting of the Na-particles (~100°C) and chlorine precipitates (-101°C). In this paper we will present data, showing that for doses in the range of TRad (1010 Gy) the concentration of radiolytic Na may become very large. Even in pure samples, we have converted more than 20% of all NaCl molecules into metallic Na and chlorine, but often higher percentages can be achieved. In this paper we will present new data obtained for ultra-high irradiation doses and a first attempt will be made to understand the results.

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

### 1 Introduction

In the earliest stages of the irradiation primary F and H-centers dominate the defect production. The next stage is governed by the mobility and reaction rates of the above-mentioned defects, leading to: (i) annihilation of F and H-centers, (ii) production of aggregates (M, R and N centers), chlorine molecules and chlorine precipitates, and (iii) formation of defects associated with trace impurities. Subsequently isolated extended defects are formed, which are distributed randomly over the crystal. Extended defects of Cl-atoms have not been investigated in detail, because these precipitates can be studied only with a very few techniques. This is unfortunate, because chlorine nano-bubbles play a crucial role in advanced stages of radiolysis.

Apart from the above-mentioned defects also dislocations and vacancy voids are created [1]. The efforts in the 1970's and 1980's were made to explain the formation of damage in NaCl, but vacancy voids were not taken into account [2, 3]. The formation of voids is far from trivial, because radiolytic processes in NaCl take place in the halide sub-lattice. To create voids it is necessary to displace Na<sup>+</sup> ions and these displacements should be incorporated as natural steps in the process. We have proposed a new mechanism describing the formation of neutral vacancy voids [4] to explain the observations for heavily damaged NaCl.

Heavily irradiated NaCl samples may become unstable, and in some cases they even decompose explosively. This has been explained by interactions between Na-particles, chlorine precipitates and voids [5]. In some heavily irradiated NaCl:K appreciable differences may exist between the stored energy and the

\* Corresponding author: e-mail: [h.w.den.hartog@phys.rug.nl](mailto:h.w.den.hartog@phys.rug.nl), Phone: +3150-363-4789, Fax: +3150-363-4879

value expected on the basis of the concentrations of radiolytic Na and chlorine [6]. We assume that the lost stored energy is released during instantaneous reactions *after* measuring the LHM of Na at about 100 °C and *prior* to the stored energy measurement at 300–450 °C. Depending on the presence of small concentrations of impurities (a few 100 ppm) some materials showed a much milder behavior.

We will present results showing non-saturating behavior of pure and doped NaCl samples up to doses as high as  $10^{10}$  Gy ( $10^{12}$  Rad). In these samples new stages of damage formation are reached. It is remarkable that also in these extremely heavily damaged materials a few 100 ppm impurities affect the radiolysis decisively. In agreement with earlier results we have found at ultra-high doses a drastic reduction of the rate of production of radiation damage in NaCl samples due to doping with 400 ppm NaBr. On the other hand full saturation of the amount of damage in NaCl samples doped with only 400 ppm NaBr as a function of the dose, indicated by our earlier observations up to 1500 MGy, could not be confirmed, because between 1500 and  $10^4$  MGy a small but consistent increase of the amount of damage is observed. The reduced production of radiation damage due to NaBr, which has been found earlier, is confirmed in this investigation. This might have important applications in the development of radiation resistant overpack materials for storage of high-level nuclear waste.

The other samples did not show saturation up to  $10^4$  MGy. In some samples (including pure NaCl) the concentration of metallic Na can be higher than 20 at%. The following question should be dealt with: What is the reason why a sample accommodates more than 20% metallic Na plus the same amounts of chlorine and large numbers of electro-neutral vacancy voids. The observations for extremely heavily damaged samples suggest that in these materials entirely new stages of damage formation develop, which are characterized by dense and well-organized, structured ‘fabrics’ of: (i) Na-precipitates, (ii) Cl<sub>2</sub> nano-bubbles, (iii) dislocation loops, and (iv) vacancy voids.

## 2 Experimental results and discussion

The latent heat of melting of Na-precipitates and chlorine bubbles is measured by means of differential scanning calorimetry (DSC). We have observed a variety of latent heat peaks due to Na-precipitates. Some peaks are well defined (peaks 1 and 2, [7]) while sometimes they vary with the dose, dose rate, dopant, irradiation temperature, thermal treatment, etc. The latent heat curves for chlorine are well defined.

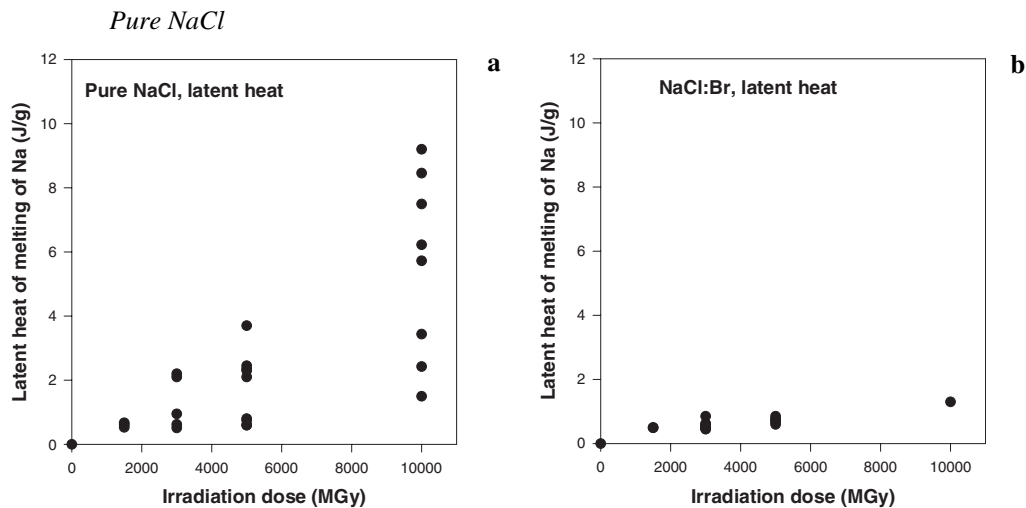


Fig. 1 Behavior of the LHM of Na as a function of the dose: a) in pure NaCl, b) in NaCl:Br.

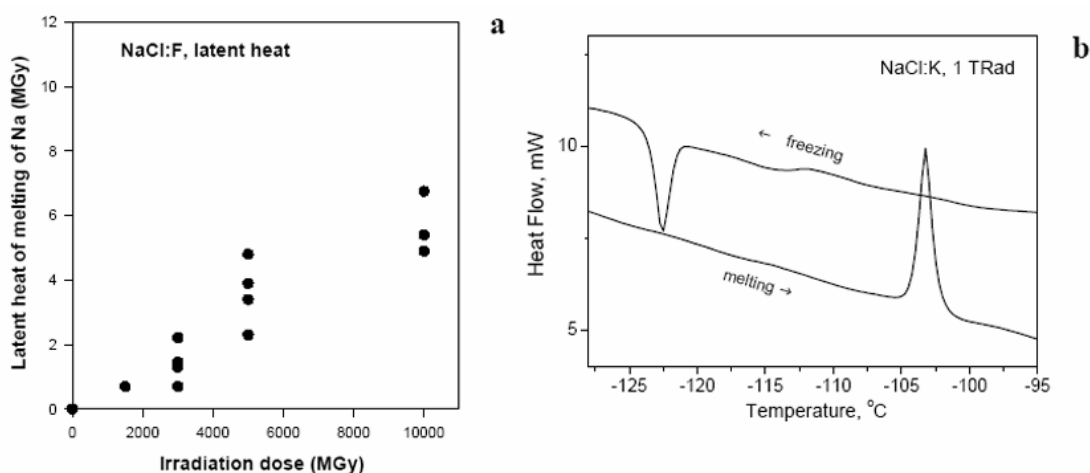
Up to 1500 MGy (150 GRad) the production of radiation damage as a function of the dose seems to saturate at values of the latent heat of melting (LHM) of Na of  $\sim 1$  J/g, or  $\sim 2.3$  at% Na and chlorine. In the present investigation we will focus our attention at the behavior radiolysis at ultra-high doses. In fig. 1a we show the results for the LHM of Na in pure NaCl. We note that beyond 1500 MGy the LHM of Na for pure NaCl scatters widely, whereas below 1500 MGy the scatter is moderate. At  $10^4$  MGy the scatter for pure NaCl is one order of magnitude! The scatter is related with specific properties of the pure NaCl samples, because for doped samples it is much smaller.

### 2.1 NaCl:400 ppm NaBr

NaBr impurities have a significant effect on the radiation resistance at ultra-high doses. Up to 1500 MGy the production of radiation damage is slightly smaller than for pure NaCl. Between 1500 and  $10^4$  MGy the difference between NaCl:Br and pure NaCl increases drastically with increasing dose. Whereas in the ultra-high dose range the resistance of pure NaCl to ionizing radiation decreases rapidly with increasing dose, NaCl:Br shows reasonable radiation resistance, although in these materials the amount of damage vs the dose does not saturate even at  $10^4$  MGy (Fig.1 b). Another feature is that for NaCl:NaBr samples the results are, in contrast with pure NaCl, consistent. Comparing NaCl:400ppmNaBr with pure NaCl, we observe, that at high doses small bromide concentrations have drastic effects on the damage production. The reason why the scatter is small for NaCl:Br compared with pure NaCl might be that the effects of other (minority) impurities are not observed. We conclude that the reduction of the damage is due to bromide ions.

### 2.2 NaCl: 1000 ppm NaF

In fig. 2a we have plotted the values of the LHM of Na, as a function of the dose. There is a significant scatter of the amount of damage in the different samples, which had been irradiated under the same conditions. However, compared with pure NaCl the results for NaCl:F are more consistent. The 'round' shape of the voids up to 1500 MGy suggests that the stability of these samples is rather high [5]. It is possible that the variations for NaCl:F are due to localized back reactions, because the dose is much higher than in our previous work. The variations for heavily damaged NaCl:F may also be due to: (i) variations of the impurity concentration or (ii) deformations of the samples during preparation, resulting in variations in the dislocation density, which affect the radiolysis process.

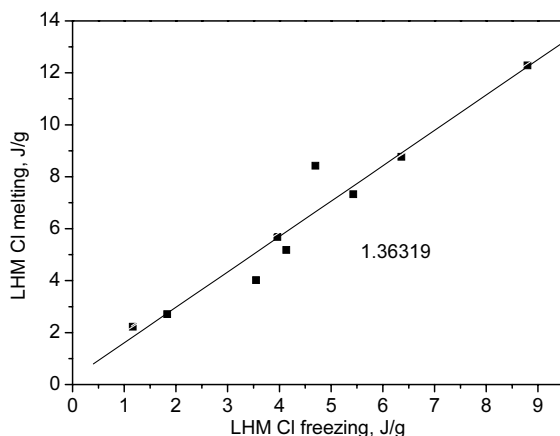


**Fig. 2** a) Behavior of the LHM of Na in NaCl:F as a function of the dose, b) latent heat of melting peak of chlorine during heating (LHM=9.16 J/g) and cooling (LHM=5.71 J/g).

### 2.3 Latent heat effects of Cl<sub>2</sub> bubbles

Chlorine precipitates have been detected by their LHM peak at  $-101$  °C, which coincides with the triple point of chlorine. In Fig. 2b we show the chlorine peak in NaCl:KCl during melting and freezing. With increasing damage the LHM peak increases and it is proportional to the LHM of Na only if the Cl<sub>2</sub> concentration is sufficiently high. The ratio of the LHM peaks should be constant, because equal numbers of chlorine and sodium atoms are produced. For samples with low damage percentages we often find far less melting chlorine than expected. This might be due to two reasons: (i) chlorine precipitates are appreciably smaller than Na nano-particles and (ii) like H and V<sub>k</sub>-centers chlorine atoms are bound covalently to the nearest chloride ions of the NaCl lattice. By increasing its surface area the precipitates gain energy; i.e. the precipitates are small and their melting properties might deviate from the bulk properties. The discrepancy between the Na and Cl<sub>2</sub> results can be reduced by annealing 30 min between 150 and 180°C, which does not lead to recombination of Na and Cl<sub>2</sub>. Although the amount of Na remains the same, we find a drastic increase of the LHM peak of chlorine. During annealing no extra chlorine atoms are produced. I.e. the increase of the LHM peak should be associated with chlorine atoms, which could not be observed in the ‘as irradiated’ samples. We assume that during annealing the chlorine molecules form larger precipitates, which contribute to the LHM peak.

For heavily damaged samples we have found large differences between the LHM of chlorine during heating or cooling. Although there were differences between details of the results, the total LHM of Na is the same for heating and cooling. Systematic experiments have been carried out to determine the ratio R of the LHM of chlorine during heating and cooling (Fig. 5). For the selection of samples used to construct Fig. 3 we find  $R = 1.36$ . For samples with low LHM values, R does not differ appreciably from 1, whereas for some of the most heavily damaged materials the ratio might be 2 or even larger. The reason for this behavior is *not* that a fraction of the chlorine atoms is ‘invisible’, as for low and moderately damaged samples. A linear relationship between the LHM of chlorine and Na is observed for samples with LHM of Na larger than  $\sim 1.5$  J/g (or  $\sim 3$  at% metallic Na) [8]. Below this concentration the LHM of chlorine is suppressed. The difference between the values of the LHM observed during heating and cooling is reproducible, which is in contrast with the behavior, expected with the assumption that a fraction of the chlorine atoms does not melt [8].



**Fig. 3** Ratio R of LHM values during heating (melting) and cooling (freezing) for a selection of comparable samples.

We have found appreciable differences in the position of the LHM peaks during heating and cooling (between 15 and 20 K), which may increase in some cases to 35 K. In the example of Fig. 2b it can be

seen, that the difference is about 20 K. The difference in position of the latent heat peak and the ratio of the LHM values obtained during heating and cooling seem to be connected with each other.

Both the different location and the differences of the LHM values during heating and cooling can be explained by assuming that there are high pressures in the chlorine bubbles. We assume that during *heating* at the melting temperature the surrounding lattice is forced to accommodate the increased volume, whereas during cooling the decreased volume is followed by a slow relaxation, which does not contribute to the LHM. Using the ratio 1.36 (Fig. 3) we find for the internal pressure of the chlorine bubbles a few kBar, which is well above the critical pressure of chlorine (76.1 bar). This explains why we have not been able to detect the liquid-vapor transition.

**Acknowledgements** This study has been supported by NWO-NATO NB 67-316 and by STCU (grant # 1761).

## References

- [1] H. W. den Hartog, D. I. Vainshtein, V. I. Dubinko, and A. A. Turkin, Nucl. Instrum. Methods in Phys. Res. B **191**, 168 (2002).
- [2] U. Jain and A.B. Lidiard, Philos. Mag. **35**, 245 (1977).
- [3] G. van Opbroek and H.W. den Hartog, J. Phys. C: Solid State Phys. **18**, 257-268 (1985).
- [4] V. I. Dubinko, A. A. Turkin, D. I. Vainshtein, and H. W. den Hartog, J. Nucl. Mater. **289**, 86-95 (2001).
- [5] A. A. Turkin, V. I. Dubinko, D. I. Vainshtein, and H. W. den Hartog, J. Phys. C: Condens. Matter **13**, 203 (2001).
- [6] D.I. Vainshtein and H.W. den Hartog, Radiat. Eff. Defects Solids **152**, 23-37 (2000).
- [7] J. Seinen, J.R.W. Weerkamp, J.C. Groote, and H.W. den Hartog, Phys. Rev. B **50**, 9793 (1994).
- [8] D.I. Vainshtein, H.W. den Hartog, V.I. Dubinko, and A.A. Turkin, Radiat. Eff. Defects Solids **156**, 51-57 (2001).