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Effects of Impurity Atomic Ions on Salt Nanocrystal Structures

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Summary

Incorporation of impurity ions such as potassium and bromide ions into sodium chloride crystals is one of the problems in the production of highly pure salt from seawater. Several studies were reported concerning to effects of impurity ions in the salt crystal growth. However, there was no report of molecular-level study on salt nanocrystals so far. In the present study, we have examined how the extent of incorporation of Br^- impurity ion into NaCl nanocrystal ions depends on the nanocrystal size and how the nanocrystal structures are changed by incorporation, by using ion mobility mass spectrometry combined with theoretical calculation.

In the experiment, we firstly assigned structures of pure sodium chloride nanocrystal ions $Na_nCl_{n-1}^+$ with n = 3 - 14. As a result, all structures were found to be almost the same with those of $Na_nF_{n-1}^+$ and $Na_nI_{n-1}^+$ reported previously by the authors. In particular, cage-like structures were assigned for n = 7 and 10, whereas rock-salt-like, face-centered-cubic structures were attributed to other sizes. Next, Br^--incorporated salt nanocrystal ions $Na_nCl_{n-1-k}Br_k^+$ were produced and detected up to k = 3. Among these nanocrystal ions with impurities, we examined the probability of incorporation of one Br^- ion as a function of cluster size n, by plotting the intensity ratios between the ions $Na_nCl_{n-2}Br^+$/ $Na_nCl_{n-1}^+$ normalized by the number of halogen sites. From the experiment, we found that the probabilities were lower than the value expected from the supplied halogen concentration ratio, i.e., the Br^- ion was found to be less incorporated than Cl^- to the nanocrystals. This result is consistent with the calculation result that the exchange reaction $Na_nCl_{n-1}^+ + Br^- \rightarrow Na_nCl_{n-2}Br^+ + Cl^-$ is endothermic for all sizes examined in the present study. The detailed structure assignments are now under study for the nanocrystal ions with Br^- impurity ions.