Effect of Lattice Energy Mismatch on the Relative Mass Peak Intensities of Mixed Alkali Halide Nanocrystals

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The relative mass peak intensity distribution of the $[M_{14-n}A_nI_{13}]^+$ mixed alkali halide nanocrystals containing a "magic" number of 14 metal cations (M and A) and 13 iodide anions is examined. These nanocrystals were generated through sputtering of mixed solid alkali halides using fast atom bombardment and analyzed by use of a double-focusing sector field mass spectrometer. The mass peak intensities of mixed cluster ions composed of two different metals relative to the "pure" nanocrystals (containing one or the other metal) are compared for two types of mixed cluster ions: one with small lattice energy mismatch, i.e., $[Rb_{14-n}K_nI_{13}]^+$ cluster ions, and the other type with large lattice energy mismatch, i.e., $[Cs_{14-n}A_nI_{13}]^+$ cluster ions where A is either Na, K, or Rb. In contrast to what was previously[1] found for clusters with small energy mismatch in which the rate of *formation* (which depends on the possible number of isomers that each mixed cluster ion can have) determines the relative intensities of mass peaks, the rate of *evaporation* (i.e., the cluster instability) determines the relative mass peak intensities in salts with relatively large lattice energy mismatch. These results are consistent with our previously proposed kinetic model for the formation and decay of these clusters.

Introduction

The study of the physical properties of atomic and molecular nanocrystals forms an interface between the domain of solid state physics and that of molecular physics.[2] A knowledge of the properties of nanocrystals is particularly significant in the areas of catalysis, photography, crystal growth, astrophysics, and many others.[2] From a study of nanocrystals, we can learn how crystals form and grow and how the crystalline bulk properties evolve as the size of a cluster increases [3] and equally important, the stability and dynamics of these important materials themselves can be understood.

Alkali halide crystals are considered as typical ionic systems. These crystals have all the properties inherent to ionic systems such as high melting and boiling points, very low conductivity, and high solubility in polar solvents.[4] A simple size-independent, two-body interatomic electrostatic potential, attributable to the closed-shell nature of the electronic configurations of the positively charged alkali and negatively charged halide ions, easily gives about 90% of the binding energies of alkali halide compounds.[3,4] Because of their elementary electronic properties, the alkali halide crystals and gas phase molecules were treated theoretically as early as 1920.[5]

For the above reasons, nanocrystals of alkali halides have been also extensively studied both theoretically and experimentally. Campana et al.[6] studied CsI cluster ions of the type $[M_nX_{n-1}]^+$ (for n values up to 70) which were generated by xenon ion bombardment and detected by a secondary ion mass spectrometer. The mass spectra of these cluster ions showed an irregularity in their relative abundance, indicating the presence of "local maxima" at $n = 14$, 23, 38, and 63. These n values are called the "magic numbers" and are attributed to the formation of $3 \times 3 \times 3$, $3 \times 3 \times 5$, $3 \times 5 \times 5$, and $5 \times 5 \times 5$ cuboid structures.[7,8] These ions are relatively stable, and their stability diminishes the rate of their decomposition prior to detection; hence, they have more intense mass spectral peaks.

Many theoretical treatments such as self-consistent-field theory[9] and the bond-breaking model[10] have been used to provide structures and to explain the presence of magic numbers in alkali halide cluster ions. A direct determination of the structure is not possible; however, Martin[2] used total energy calculations to determine the most stable structures of $[Na_nCl_{n-1}]^+$ cluster ions ($n = 1-18$). For $n = 14$, one of the magic numbers, he found a $3 \times 3 \times 3$ simple cubic (rock salt) lattice structure. In this structure, Cl^- ions occupy the single interior site of the lattice and each of the 12 edges, whereas the Na^+ ions occupy the six faces and the eight vertex sites.[11] Similar calculations by others[12,13] and more recent semiempirical and ab initio self-consistent-field calculations[14] confirmed Martin's work.

It is known that most alkali halides such as NaCl, NaI, NaF, KF, KI, and KCl crystallize into fcc structures, whereas bulk CsCl and CsI form a body-centered-cubic (bcc) lattice.[15] However, the mass spectra of all alkali halides show the same magic numbers, indicating that the nature of binding differences which lead to distinct structures in the condensed phase is insignificant in the cluster size regime.[3] In addition, calculations of total binding energies for alkali halide clusters by many groups[3,16−20] show that all of these clusters acquire simple cubic structures irrespective of their bulk crystalline structures.

The structure and relative yield of small mixed alkali halide clusters have also been examined. Diefenbach and Martin[3] found that small cluster ions of mixed alkali halides are stable even for compositions that do not form solid solutions in the condensed phase (e.g., NaI and CsI). Using the polarizable ion model, they calculated the total energies and the corresponding geometry of these clusters. It was found that mixed clusters with ions of comparable sizes (e.g., Rb^+, Cs^+) give the most stable structures.

In an effort to examine the effect of defects on the formation and stability of nanocrystals, we have studied the formation of mixed alkali halides with a general formula of $[M_{14-n}A_nI_{13}]^+$, where M and A are different alkali metal ions. There are a "magic" number of 14 metals and 13 iodides in these cluster ions. We have previously[1] studied the mass spectral distribution of peak intensities of mixed RbI and KI cluster ions formed

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through fast atom bombardment. The bulk lattice energies of KI and RbI are very similar (150 and 145 kcal/mol, respectively).[21] It was found that the maximum of relative mass peak intensities occur at $n = 7$. This observation was explained assuming that the rate of cluster evaporation is independent of n, due to similar lattice energies. The variation in the distribution of peak intensities was proposed to be determined by the rate of formation which itself depended on the number of configurations that each mixed cluster could have (i.e., its number of isomers). The maximum number of configurations for the mixed alkali halide clusters of the type $[M_{14-n}A_nI_{13}]^+$ occurs at $n = 7$, which is the cluster found to have the maximum mass peak intensity.

In this paper, we compare the previous results with the case of mixed clusters of salts that have large bulk lattice energy differences. Specifically, we consider mixed clusters of the type $[Cs_{14-n}A_nI_{13}]^+$ where A is either Na, K, or Rb. These cluster ions are formed from mixtures of CsI and either NaI, KI, or RbI. The observed relative mass peak intensity distribution for each type of mixed salt cluster is found to be explained if the rate of evaporation (which is a direct measure of the cluster instability) rather than the rate of formation (condensation from smaller units) determines the mass peak intensity of each cluster.

Experimental Section

The mass spectra of the mixed alkali halide nanocrystals of the type $[Rb_nK_{14-n}I_{13}]^+$ and $[Cs_{14-n}A_nI_{13}]^+$ for $n = 0-14$ were obtained by the use of a VG Analytical ZAB-SE (Ion Tech Ltd., Teddington, Middlesex, UK) reverse geometry mass spectrometer fitted with a fast atom (Xe) bombardment gun. The details of the experiment have been published previously.[22] Briefly, an unsaturated solution of equal molar ratio of the pairs NaI + CsI, KI + CsI, RbI + CsI, and KI + RbI was prepared in distilled water and placed on the probe tip. The water was dried off, leaving mixed crystals on the tip. Cluster ions were prepared by the bombardment of the mixed solids by an 8 keV Xe atom gun. An acceleration voltage of 8 keV was applied to the cations to extract them from the source. The accelerating ions were analyzed with the magnetic sector in conjunction with the electric sector and detected by a conversion dynode followed by electron multiplier. The pressure in the acceleration region was kept at $\sim 5 \times 10^{-6}$ Torr and in the analyzer at $\sim 5 \times 10^{-8}$ Torr. We collected three sets of 200 scans on three different days to ensure reproducibility.

Results

Small Mismatch of Lattice Energies. As mentioned earlier, bulk crystalline KI and RbI compounds have similar lattice structures (fcc) and similar lattice energies (−149.9 and −144.9 kcal/mol, respectively).[21] To study the formation of mixed nanocrystals of these two compounds, we prepared an unsaturated mixed solution of them which was subsequently dried to form a mixed crystal. The mixed crystal was used in fast atom bombardment mass spectrometry to generate the mixed cluster ions of the type $[Rb_nK_{14-n}I_{13}]^+$ ($n = 0-14$). For the observed spectrum, we calculated the mass spectral intensity distribution of these clusters by calculating the fraction (F_k) of ions observed for the kth mixed cluster ion having an intensity I_k in the mass spectrum. The following equation was used:

$$F_k = (I_k/\sum_{n=0}^{14} I_k) \times 100 \qquad (1)$$

A "bimodal" distribution for the probability distribution of these cluster ions centered near $n = 7$ was obtained and is shown in Figure 1. These results suggested that more nanocrystal ions are detected with nearly comparable number of RbI and KI molecules.

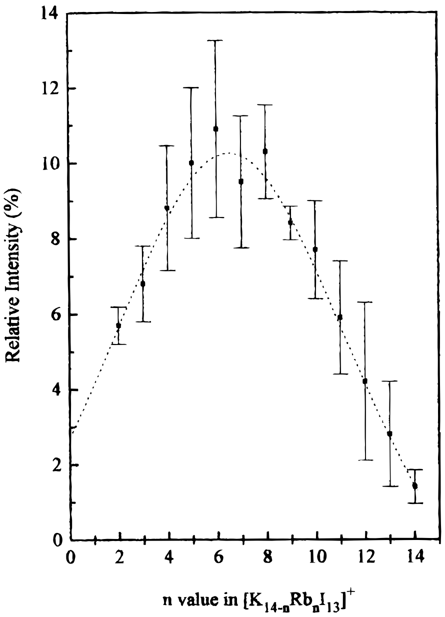

Figure 1. Calculated relative intensities of mixed nanocrystals of $[Rb_nK_{14-n}I_{13}]^+$ for $n = 0-14$. The relative intensities were normalized with respect to the total sum of all the intensities of individual ions using eq 1 of the text.

Large Mismatch of Lattice Energies. In order to study the effect of introducing "defects" into a nanocrystal $[Cs_nI_{n-1}]^+$, we selected to study mixed cluster ions of the general formula of $[Cs_{14-n}A_nI_{13}]^+$ with A = Na, K, or Rb. The values of n were varied from 0 to 14. These ions were prepared by atom bombardment of equal molar ratios of CsI and either of NaI, KI, or RbI solutions, as explained in the Experimental Section.

The mass spectral distribution of intensities for the cationic nanocrystals were calculated using eq 4 of the previous section. For cations of the form $[Cs_{14-n}A_nI_{13}]^+$, the peak intensities were normalized with respect to the intensity of the "pure" $[Cs_{14}I_{13}]^+$ for $7 \geq n \geq 0$ and with respect to the intensity of $[A_{14}I_{13}]^+$ for $14 \geq n \geq 7$. The intensities of the two "pure" clusters are not similar due to the difference in their stability. For example, the intensity of $[Cs_9K_5I_{13}]^+$ was normalized with respect to $[Cs_{14}I_{13}]^+$ as if the lattice were a "pure" lattice of cesium iodide with five potassium "defects".

Figure 2 shows the logarithm of the relative intensities of the cationic mixed nanocrystals plotted against n values. The intensities of Rb-substituted CsI cluster ions show higher intensities than those of the pure $[Cs_{14}I_{13}]^+$ and $[Rb_{14}I_{13}]^+$ ions for the $[Cs_{13}Rb_1I_{13}]^+$, $[Cs_{12}Rb_2I_{13}]^+$, and $[Cs_1Rb_{13}I_{13}]^+$. In other words, replacement of up to two Rb atoms for Cs atoms produces more mixed cluster ions than the parent ion. Similarly, substitution of a Cs atom in a "pure" Rb lattice gives more mixed clusters as evidenced by its higher mass spectral intensity. However, as the number of foreign atoms in the "pure" lattices of cesium iodide or rubidium iodide increases beyond two, the peak intensities dramatically decrease. Indeed, for $n = 5-8$, we observed no peaks at all.

In cases of Na and K substitution into the lattice of cesium iodide ($n < 7$) and substitution of Cs in the potassium iodide or sodium iodide lattices ($n > 7$), the intensities decrease by an order of magnitude as soon as the first foreign atom is introduced. As K atoms replace the Cs atoms in the lattice, we observed no mixed K−Cs−I cluster ions for n values of 4−11,

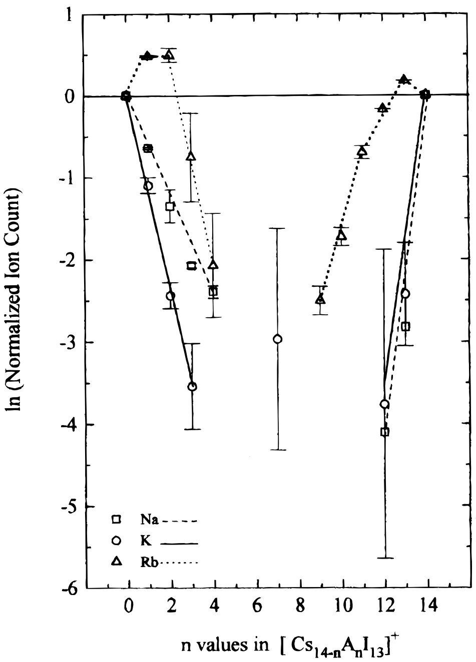

Figure 2. Calculated relative intensities of mixed nanocrystals of $[Cs_{n-14}A_nI_{13}]^+$ where A is either Na (squares), K (circles), or Rb (triangles). The intensities are plotted as ln(ion counts) against n. The intensities were normalized with respect to $[Cs_{14}I_{13}]^+$ for $n \leq 7$ and with respect to $[A_{14}I_{13}]^+$ for $n > 7$ (cf. the text).

with the exception of $n = 7$ which showed a peak with a large uncertainty in its intensity. Sodium substitution for Cs atoms in the lattice occurred only for $n = 1-4$ and $9-13$. The intensities of these ions were larger than the corresponding K-substituted peaks but smaller than Rb-substituted peaks. Therefore, the tendency of alkali metals forming mixed lattices of $[Cs_{14-n}A_nI_{13}]^+$ was found to be Rb > Na > K.

Discussion

Simple Kinetic Model for Mixed Nanocrystals Formation. We previously[1] proposed a simple kinetic model for the formation of mixed alkali halide nanocrystals. In that model, we assumed that these nanocrystals are formed rapidly from the collisions between the atoms and ions which are produced initially through sputtering of the solid surface. The rapid formation of these nanocrystals is followed by cooling processes resulting from the different channels of evaporation (unimolecular decomposition).

It is assumed that the nanocrystals under study are formed by the heterogeneous nucleation in which a metal cation seeds the rapid nucleation of a nanocrystal by attracting halide molecules. This would require a certain number of collisions, Z_k, to form a nanocrystal of a fixed composition and arrangement (i.e., a certain isomer). If one assumes that a nanocrystal of a certain composition (a fixed value of n, say k) requires Z_k number of collisions, then the number of nanocrystal ions formed from the nucleation process, N_k^{formed}, is written as

$$N_k^{\text{formed}} \approx N_k^{\text{isom}} e^{-Z_k C_k} \tag{2}$$

We may assume that the number of collisions required to form any one of the configurations of any of the 15 nanocrystals is the same, if the collisions are sticky (i.e., C_nZ_n is the same for any isomer of the 15 different clusters). This allows us to write eq 2 as

$$N_k^{\text{formed}} \approx K N_k^{\text{isom}} \tag{3}$$

where the constant K is equal to $K'e^{-C_kZ_k}$.

In the above model, the mass peak intensity of a "magic" mixed crystal of a certain composition, say $[A_kM_{14-k}I_{13}]^+$, was assumed to result from a rapid nucleation due to sticky collisions between constituting ions and molecules. Evaporation of a monomer of MI (or AI) from the next larger clusters, such as $[A_{k+1}M_{14-k}I_{14}]^+$, was also assumed to give rise to the $[A_kM_{14-k}I_{13}]^+$ clusters. Evaporative cooling of the latter would result in its disappearance. Setting up a steady-state equation, the intensity (or the number) of steady-state cluster ions is found to be given by

$$I_{k,13} \approx K_{13} N_{k,13}^{\text{isom}}/\rho_{k,13} \tag{4}$$

where K_{13} and $\rho_{k,13}$ are the rate constant of formation (due to collisions) and the rate constant of evaporation of the cluster in question, respectively.

For clusters of similar lattice energies, $\rho_{k,13}$ is assumed to be independent of the cluster composition; it is the same for any value of k. Since the collisions were assumed to be sticky, then K_{13} is constant for clusters with the same number of molecules, be it MI or AI. Then the intensity $I_{k,13}$ in eq 4 depends only on the number of isomers that a certain composition of the mixed cluster may possess, namely $N_{k,13}^{\text{isom}}$. This is found to be in agreement with our results shown in the previous publication.[1]

In the present case, the mass peak intensity depends on the ratio $N_{k,13}^{\text{isom}}/\rho_{k,13}$ in eq 4. As the energy mismatch becomes significant, the mixed cluster becomes unstable with respect to its dissociation products. Since it is known that the reverse activation energy for the evaporation process from alkali halide clusters is zero,[22] this leads to a reduction in the activation energy of the evaporation process which becomes equal to the difference in the thermodynamic internal energies of the mixed cluster and its dissociation (evaporation) products. As the mixed cluster becomes unstable, the activation energy for its dissociation decreases. The more substitution is made into the "pure" cluster, the more unstable the resulting mixed cluster becomes toward evaporation. This explains our observation in Figure 2, showing that the relative mass peak intensity is highest toward "pure" clusters of one salt or the other; it decreases as the number of foreign atoms increases and has a minimum in the middle. It is interesting that the Rb−Cs−I mixture shows a small maximum toward the two extremes (n =1 and 13). This could be explained by the interplay between an increase in the formation of the number of isomers (and thus more clusters of the same mass) as a molecule of one salt is added to another and a simultaneous increase in evaporation rate due to the instability of the mixed nanocrystals.

It is expected that the stability of an ionic nanocluster of a certain structure and fixed number of positive and negative ions depends on the packing of these ions. Nanoclusters with the maximum attraction between the oppositely charged ions and minimum repulsion between the similarly charged ions are undoubtedly the most stable clusters. This depends on the packing of the cluster. The dissolution of a few molecules of one salt into the lattice of another one would disrupt the periodic packing of the ionic cluster, which in turn increases the internal energy and its subsequent instability.

The instability introduced by adding impurity molecules depends on the mismatch in the lattice energies and thus of the radii of the host and guest molecules. The radii mismatch between K^+ and Rb^+ is only 0.15 Å, while that between Cs^+ and K^+ and between Cs^+ and Na^+ is 0.36 and 0.74 Å, respectively. At the temperature of these clusters, a mismatch of 0.15 Å does not give rise to a large difference in the internal energy and thus to the dissociation energy of the cluster upon mixing. On the other hand, a mismatch in the radii of Cs^+-K^+(0.36 Å) or Cs^+-Na^+ (0.74 Å) cause such a large change in the internal energy to make the mixed clusters unstable with respect to their dissociation products.

In summary, we would like to emphasize that our kinetic model, which was detailed previously,[1] can account for both cases of mixed alkali halide cluster ions where the mismatch of bulk lattice energies of the constituting salts is large or small. In the case of small mismatch of bulk lattice energies, the rate of cooling is independent of composition, and thus the rate of formation (which depends on the number of isomers formed for a certain mixed composition) of the mixed nanocrystals dictates the observed distribution of relative mass intensities of these cluster ions. In the case of large mismatch of bulk lattice energies, it is the rate of evaporation (i.e., the relative stability of the mixed nanoclusters) that is the dominating factor in determining the relative mass intensities of the ions.

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