

Variation in morphology of silver bromide crystals in aqueous solution by first principles calculations

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Morphology of inorganic crystals in aqueous solutions can be controlled by varying reaction conditions such as acidity and solute concentration. Such changes in morphology could be explained by the variation of surface energies of different crystallographic planes. However, experimental information of surface energies is limited. In order to predict the morphology prior to experiments, the use of reliable theoretical methods is essential. In the present study, we have employed a DFT method to evaluate the surface energy as a function of solute concentration of the aqueous solution. AgBr was used as a model system, since reliable experimental data are available [1].

First principles calculations were performed using numerical basis functions as implemented in the DMol³ code [2]. The dnp (double numeric polarized) basis set with the cut-off of 6.5 Å was used. GGA-PBE was used as the exchange-correlation functional. The solvation effect was taken into account by the use of conductor-like screening model (COSMO). The atomic arrangements were fully optimized before the evaluation of the total energy. Three surfaces, i.e., (100), (110), and (111) were examined. Since (111) makes polar surfaces, four different models with different terminations/adsorption were examined. As for AgBr, they are (111)_{R_{Ag}}, (111)_{R_{Br}}, (111)_{Br}:H⁺, and (111)_{Ag}:OH⁻, where R_x denotes reconstructed surface model terminated by X-atoms (X=Ag, Br). (111)_X:Y means that the polar surface terminated by X-atoms are adsorbed by Y. (Y=H⁺, OH⁻). The reconstructed surface model was based on those published experimentally in MgO and NiO [3]. Surface slab models were sandwiched by vacuum layers with a thickness of 20 Å. The number of atoms in the supercells were 32 for (100) and (110) surface models, and 44 for (111) models excluding adsorbed atoms. Surface energy was obtained using the difference in total energies between the surface model and the bulk model. When the composition of the supercell model was non-stoichiometric, the surface energies were compensated by the use of corresponding chemical potentials obtained by using cluster model. Zero point energy and the pV term were ignored. Morphology of the Wulff equilibrium shape of crystals was drawn using GDIS code [4]. Similar set of calculations were made for NaBr for comparison.

FIG. 1(a) and (b) show the dependence of the surface energy as a function of pBr at the standard condition of pH=0, where pBr = $-\log C_{\text{Br}^-}$ and C_{Br^-} is the Br⁻ concentration in the aqueous solution. A general tendency of increase in surface energy in the order (100), (110), (111)_{R_{Br}} and (111)_{R_X} (X=Ag, Na) can be found. It is interesting to note that (111)_{Br}:H⁺ is lowest when pBr < 1.4 in AgBr. The stabilization is partly due to the use of pH=0 condition in the present case. The stability region of the (111)_{Br}:H⁺ contracts with the increase of pH. For example, it is stable only when pBr <

-6.6 at pH=8. The stability region of $(111)_{\text{Br}}:\text{H}^+$ went towards much lower pBr region in the case of NaBr. Wulff equilibrium shape can be computed using the surface energies. FIG. 2 shows the morphology map of AgBr with pH and pBr. With the decrease of both pH and pBr, the morphology changes from cubic to octahedral through tetradecahedral in between because of the stabilization of the $(111)_{\text{Br}}:\text{H}^+$ surface. In the case of NaBr, the Wulff equilibrium shape is cubic in similar ranges of pH and pBr as in FIG. 2. Such dependence of the morphology on pBr was experimentally reported for AgBr in aqueous solution [1]. The present result agrees with the experimental data only qualitatively. The stability region of the (111) surface by experiments was $\text{pBr} < 2$ at $\text{pH}=8$, which is wider than the results of the present study, i.e., $\text{pBr} < -8$ at $\text{pH}=8$. The disagreement may be ascribed to the presence of other adsorption species on the (111) surface at the high pH conditions. Temperature effects may also be partially responsible.

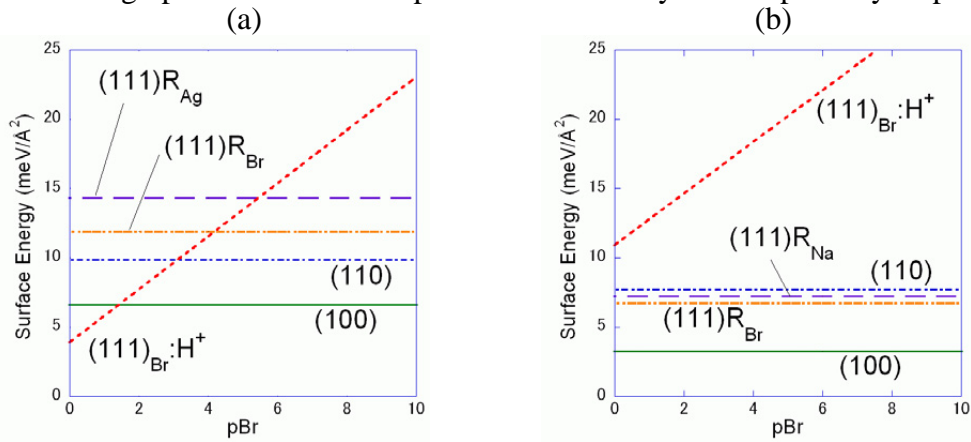


FIG. 1. The dependence of surface energy on pBr in aqueous solution (at pH=0) for (a) AgBr and (b) NaBr.

In summary we have attempted to reproduce the variation in morphology of AgBr with pBr and pH of the aqueous solution by first principles calculations. Solvation effects were taken into account by COSMO. The results are in qualitative agreement with the experimental data when H⁺ adsorption on the $(111)_{\text{Br}}$ -surface was taken into account. Factors such as other adsorption species should be considered to get better agreement with experimental results.

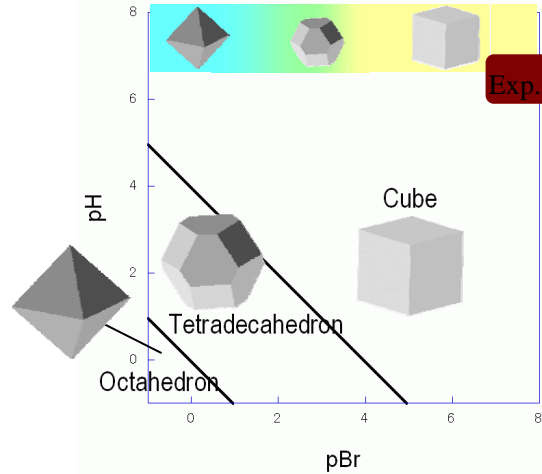


FIG. 2. Computed morphology map of AgBr in the aqueous solution.

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