Dispersion and Polar Component of Specific Surface Free Energy of NaCl(100), KCl(100), and KBr(100) Single Crystal Surfaces

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Abstract

Contact angle of ethylene glycol and formamide on (100) faces of NaCl, KCl, and KBr single crystal was measured, and the specific surface free energy (SSFE) was calculated. Dispersion component of the SSFE was 90.57, 93.78, and 99.52 mN\(\cdot\)m\(^{-1}\) for NaCl, KCl, and KBr, respectively. Polar component of the SSFE was 1.05, 0.65, and 0.45 mN\(\cdot\)m\(^{-1}\) for NaCl, KCl, and KBr. Such a large ratio of dispersion component of SSFE results from the neutrality of the crystal surface of alkali halide. Lattice component of alkali halide is 780, 717 and 689 kJ\(\cdot\)mol\(^{-1}\) for NaCl, KCl, and KBr. The larger lattice enthalpy decreases dispersion component, and increases polar component of the SSFE. The larger lattice enthalpy is considered to enhance the rumpling of the crystal surface more strongly, and such rumpling is considered to decrease the neutrality of the crystal surface.

Keywords

Component, Specific Surface Free Energy, Crystal Growth, Mineral Salt, Morphology

1. Introduction

The relationship between the specific surface free energy (SSFE) and the contact angle of a liquid is shown by Young’s equation [1]:

\[ \gamma_s + \gamma_{SL} \cos \theta = \gamma_L \]  

\(\gamma_s\) is the SSFE of the solid, \(\gamma_{SL}\) is the interfacial tension between the solid and the liquid, and \(\gamma_L\) is

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the surface tension of the liquid. Because there are two unknown parameters $\gamma_S$ and $\gamma_{SL}$ in Equation (1), we cannot introduce $\gamma_S$ from a single contact angle, $\theta$, only. In order to evaluate the SSFE from the contact angle of liquid, several models are proposed [2]-[6]. For example, Fowkes [5] proposed that the surface tension could be described as a sum of the dispersion component and the polar component as,

$$\gamma_S = \gamma_S^d + \gamma_S^p$$

(2)

where $\gamma_S^d$ and $\gamma_S^p$ are the dispersion and polar components of SSFE of the solid, and introduced the following equations of harmonic mean:

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 4 \left( \frac{\gamma_{LV}^d \gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p \gamma_S^p}{\gamma_{LV}^p + \gamma_S^p} \right)$$

(3)

where $\gamma_{LV}^d$ and $\gamma_{LV}^p$ are dispersion and polar component of the surface tension of the liquid, respectively. The values of $\gamma_S$ can be obtained from $\theta$ as

$$\gamma_{LV} (1 + \cos \theta) = 4 \left( \frac{\gamma_{LV}^d \gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p \gamma_S^p}{\gamma_{LV}^p + \gamma_S^p} \right)$$

(4)

This equation is widely accepted for studies of the SSFE of polymer surfaces [2]. We adopted this established experimental method to determine the SSFE of some inorganic crystals, ruby [7], quartz [8], and apatite [9], using contact angle of liquid droplet. In this work, we are studying alkali halide crystals, and discussing the detailed meaning of SSFE of crystal, especially dispersion and polar components of SSFE.

2. Experimental

Three kinds of synthetic alkali halide single crystals, NaCl, KCl, and KBr from Furu-Uchi Chemicals were used as sample crystals. Each alkali halide crystal was cleaved using sharp edge of a knife and (100) surface was prepared. Droplet of formamide or ethylene glycol was dropped on the cleaved face of each crystal using micro-pipette. The droplets sized ~0.1 mm$^3$ were observed using digital camera with a magnifying lens. We took more than 40 photographs for each crystal face and used the photographs in which the boundary between the liquid and solid was clearly recognized the contact angles of the droplets were measured manually using printed photographs.

3. Results and Discussion

Average and standard deviation of contact angles of ethylene glycol and formamide on NaCl, KCl, and KBr are summarized in Table 1.

The contact angles of liquids on alkali halide crystal are much smaller than those on inorganic oxide crystals [10]. The values of dispersion and polar component of the SSFE can be calculated from the contact angle of liquids using Equation (4). The dispersion and polar components of ethylene glycol are 30.1 and 17.6 mN/m$^{-1}$, and those of formamide are 39.5 and 18.7 mN/m$^{-1}$ [2].

Calculated SSFE of NaCl, KCl, and KBr and dispersion and polar components of them are summarized in Table 2. In our previous research, we did not discuss the dispersion and polar component separately, but we discussed summed SSFE only [7]-[9].

Table 1. Average and standard deviation of the contact angles of ethylene glycol ($\theta_E$) and formamide ($\theta_F$) on (100) face of NaCl, KCl, and KBr.

<table>
<thead>
<tr>
<th>Alkali halide</th>
<th>$\theta_E$</th>
<th>$\theta_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>$12.20^\circ \pm 1.72^\circ$</td>
<td>$16.56^\circ \pm 2.36^\circ$</td>
</tr>
<tr>
<td>KCl</td>
<td>$16.21^\circ \pm 2.30^\circ$</td>
<td>$18.29^\circ \pm 3.13^\circ$</td>
</tr>
<tr>
<td>KBr</td>
<td>$12.98^\circ \pm 1.52^\circ$</td>
<td>$13.25^\circ \pm 2.28^\circ$</td>
</tr>
</tbody>
</table>
Here we re-calculated $\gamma_S^d$ and $\gamma_S^p$ for CaCO$_3$, Ba$_5$Cl(PO$_4$)$_3$, SiO$_2$, and Al$_2$O$_3$ using former data. For inorganic oxide materials, the value of dispersion and polar component is close. On the other hand, dispersion component for alkali halides is much larger than the polar component of the SSFE. The ratio of $\gamma^d$ and $\gamma^p$ is almost even for inorganic oxides, but $\gamma^d$ of alkali halide is very large and $\gamma^p$ is very small.

Polar component of SSFE is caused by the potential energy of interaction between two permanent dipoles. On the other hand, the dispersion component results from interaction between two induced dipoles. On (100) face of these alkali halide crystals, same number of anion and cation arrange alternately, which compose neutral surface as shown in Figure 1(a). Therefore, interaction between induced-dipoles is dominant and the dipole-dipole interaction should be subordinate.

The relationship between dispersion component of SSFE and lattice enthalpy was compared as shown in Figure 2, and the polar components of SSFE are also compared with lattice enthalpy as shown in Figure 3. The lattice enthalpy for NaCl, KCl, and KBr is 787, 717, and 689 kJ mol$^{-1}$, respectively [11].

![Figure 1. Neutral surface of NaCl (a) and rumpled surface (b).](image)

![Figure 2. Dispersion component of the SSFE of NaCl, KCl, and KBr, as a function of lattice enthalpy.](image)

<table>
<thead>
<tr>
<th>Crystals</th>
<th>$\gamma_S^d$</th>
<th>$\gamma_S^p$</th>
<th>$\gamma_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>90.57 ± 3.05</td>
<td>1.05 ± 0.14</td>
<td>91.62 ± 3.19</td>
</tr>
<tr>
<td>KCl</td>
<td>93.78 ± 3.88</td>
<td>0.65 ± 0.11</td>
<td>93.12 ± 3.99</td>
</tr>
<tr>
<td>KBr</td>
<td>99.52 ± 2.27</td>
<td>0.45 ± 0.06</td>
<td>99.96 ± 2.26</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>18</td>
<td>30</td>
<td>48</td>
</tr>
<tr>
<td>Ba$_5$Cl(PO$_4$)$_3$</td>
<td>22</td>
<td>28</td>
<td>50</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>23</td>
<td>35</td>
<td>58</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>31</td>
<td>25</td>
<td>56</td>
</tr>
</tbody>
</table>

Table 2. Specific surface free energy (SSFE) and dispersion and polar components of that on (100) face of NaCl, KCl, and KBr. The SSFE of some inorganic oxide re-calculated from our former experimental results are show in the bottom. The values have 5% - 10% fluctuation depending on individual samples of inorganic oxide crystals.
The larger lattice enthalpy causes the smaller dispersion component of SSFE. The larger enthalpy causes the larger value of polar component of the SSFE of each alkali halide crystal. Though the potential energy for each ion in the alkali halide crystal is symmetric, the potential for the surface ions is asymmetric. The ions are attracted inside of the crystal, which caused the rumpling of the crystal surface. The structure of crystal surface of NaCl, KCl, and KBr is studied by Vogt and Weiss using LEED, and reported that the rumpling of the first layer ($\Delta$) are 0.007, 0.003, and 0.002 nm for NaCl, KCl, and KBr, respectively [12] [13]. The crystal with the larger lattice enthalpy has the larger rumpling. As shown in Figure 1(b), the surface of alkali halide is neutral, but the rumpling of the crystal face decreases the neutrality, and the surface became a little polar. NaCl crystal has the largest lattice enthalpy and the largest rumpling. Therefore, NaCl has the largest ratio of polar component and the smallest dispersion component. On the other hand, KBr has the smallest lattice enthalpy and the smallest rumpling, and KBr has the smallest rate of polar component and largest dispersion component.

4. Conclusions

The dispersion component of SSFE is much larger than the polar component for alkali halide, because the surface of alkali halide is neutral and less polarized. The larger lattice enthalpy causes the smaller dispersion and larger polar component of the SSFE, because rumpling decreases the neutrality and increases the polarity of the surface of alkali halide.

Although contact angle of liquid on crystal surface is macroscopic value as we can see by our naked eye, the contact angle of liquid includes microscopic information such as atomic scale roughness of the crystal surface.

References


