

## Surface Free Energy of Fluorite and Apatite Crystals

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Specific surface free energy (SSFE) is significant value to explain the morphology of crystal. The relationship between SSFE and growth length of crystal face is considered to be proportional, which is known as Wulff's relationship, and well accepted for thermodynamic interpretation of crystal growth theoretically. Though Wulff's relationship is well accepted for theoretical analysis, experimental measurement of SSFE for crystal face is very few. According to Young's equation, SSFE of solid face can be introduced from contact angle of liquid on the solid face, and we observed SSFE of some crystals, for example, apatite[1], ruby[2], and quartz[3]. However, the SSFEs of crystal face have wide distribution even for a flat face of the crystal. Such wide distribution of observed SSFE was considered to result from steps on the crystal face. In this work, we observed SSFE of natural fluorite crystal. Natural fluorite crystal was cut and polished for (100), (110), and (111) faces. SSFE can be separated to dispersion component which results from van der Waals force and polar components which results from interaction between permanent dipole moments. The polar component of SSFEs on (100) and (111) faces were smaller than have large rate of dispersion component of than that on (110) face, because (100) and (111) faces are polarized face. Although the SSFE of real crystal is calculated from macroscopic value such as contact angles of liquid droplets, the SSFE reflects microscopic surface structure such as steps and the ionic morphology of the crystal face. We also observed SSFEs of apatite and fluorite crystals in order to demonstrate the effect of steps on the SSFE. Contact angle of water and formamide droplet on crystal face was observed using digital camera. SSFE was calculated using Fowkes approximation and Wu's harmonic mean equations. Though the crystals we experimentally obtained were growth form, the relationship between SSFE and the growth rate was almost proportional, which looks to satisfy Wulff's relationship qualitatively.

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