Soft and deformable hydrated salt crystals under deliquescence

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Crystals are usually identified by their geometrical shape with flat faces reflecting the highly ordered microscopic structure which strongly impact the mechanical and physical properties of the crystal. Among these properties, inorganic salts due to their ionic structure and solubility of ions in water are in principle hygroscopic. The latter remains very important in a wide range of applications such as the stability of pharmaceutical formulations, stability of food ingredients and in Earth and atmospheric science. By combining different microscopy and spectroscopy techniques, we show that natural inorganic salt hydrates (i.e salts which contain water molecules in a definite ratio as an integral part of the crystalline structure) such as sodium sulfate decahydrate (Na₂SO₄ • 10H₂O) and magnesium sulfate hexahydrate (MgSO₄ • 6H₂O) can behave remarkably differently at their deliquescence point: instead of keeping the faceted shape and staying hard while absorbing moisture from the air, they become soft, deformable and lose their facets. Defects at the surface can heal at a speed much faster than the deliquescence rate by the mechanism of visco-capillary flow over the surface. This behavior appears to be related to the number of water molecules present in the crystalline structure and their mobility and makes that microcrystals simultaneously behave crystalline like in the core bulk and liquid-like at the surface. In addition, when the relative humidity is decreased below the deliquescence point, unfaceted soft hydrated crystals become rigid and facets grow again over time. We also show that the soft and deformable state is completely absent for the anhydrous salts such as sodium chloride (NaCl) and sodium sulfate thenardite (Na2SO4); Our findings provides new insights on the properties of hydrated salts crystals which are abundant on earth and have also been detected in other planets such as Mars. In controlled environment, by optimizing their performance with improved control over their geometry and size, they can have potential applications such as thermal energy storage, where the key parameter is the relative humidity instead of the temperature.

Reference

[1] Rozeline Wijnhorst, Menno Demmenie, Etienne Jambon-Puillet, Freek Ariese, Daniel Bonn, Noushine Shahidzadeh, Softness of Hydrated salt crystals under deliquescence, Nature Communications, accepted, in press 2023.