Plastic Crystals and Solid-Solutions: From Modulation of the Plastic Transition to the Development of Novel Solid-State Electrolytes

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Plastic Crystals are materials in which the molecules or ions occupy the exact center of mass as in regular crystal lattice but have freedom of rotation. They show typical disorder-order transitions that lead to realizing various sorts of functional materials. Especially organic ionic plastic crystals (OIPCS) have gained much attention over the past years thanks to their potential usage as solid-state electrolytes [1].

Solid solutions are non-stoichiometric multi-component crystals in which two or more components combine homogeneously in a single crystalline phase [2]. To attain the formation of a solid-solution, the miscibility of the components is a critical condition, which in turn depends on the components' similarity in size and shape.

This topic deals with the realization of binary and ternary solid solutions in a series of supramolecular salts and compounds made up of globular species and studying temperature-dependent phase transitions associated with the onset of plastic phases. Examples will be given about both ideal cases [3,4], i.e. when all the components display a high degree of similarity, and non-ideal ones, in which the size and shape criteria are not fulfilled [5]. As it will be shown, this will have a profound impact on the transition temperature and type, spanning from a non-linear modulation to the suppression of the transition, which makes, de facto, these solids dynamically disordered in their plastic phases permanently. Solid solutions were prepared using either solution or mechanochemical methods. A combination of variable temperature XRD and spectroscopic techniques (SS-NMR and Raman) were used to study the range of the components' miscibility and how the resulting composition affected the order-disorder transition. Additionally, Electrochemical Impedance Spectroscopy was successfully applied to study anhydrous ions showing how in such materials, the conductivity increases almost linearly before the plastic phase transition and non-linearly soon after, which is attributed to a marked acceleration of motion associated with temperature variations and the plastic phase transition, and indicating that these materials are indeed promising to the development of novel solid-state electrolytes.

References

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