MS36 Crystallography in solid state reactions and catalysis

Chairs: Fernando Lahoz, Krešo Bučar

MS36-P1 Solvent-free solid-state synthesis of lanthanide complexes monitored by in-situ XRPD

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Lanthanide complexes with organic ligands are good candidates for applications in different technologies, especially for their tunable luminescence properties. However, the presence of solvent (water) molecules in the coordination sphere of the metal may dramatically affect the photophysical properties (luminescence) of the target complex. Moreover, the presence of solvate molecules may change the crystal packing and the crystal structure of the solid, which can in turn modify the physical properties in the solid state. In this context, the usual synthetic reaction performed in solution may found some limitations such as low stability constant, competition with solvent molecules depending of the chemical affinity (especially when water is present), and solubility problems. Solvent-free solid state synthesis can be a welcome alternative to overcome these limitations. Well-known in solid state chemistry for the preparation of inorganic materials, this procedure recently received a renewal of interest for the synthesis of polymeric metal organic frameworks, and for the complexation of lanthanide salts with N heterocycles amines [1]. We present here some solvent-free solid state syntheses (using grinding and thermal treatment) of non-polymeric lanthanide complexes with tridentate terpyridine or bis-benzimidazole-pyridine based ligands. In-situ XRPD experiment is exploited to follow the reaction and to monitor the formation of the resulting complex (figure 1). Comparison with analogous compounds combined with crystal structures solved ab-initio using the Fox program [2] are applied for extracting the pertinent molecular structures. Our ultimate goal is the synthesis of new solvent free complexes, which are not yet accessible in solution.

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[2] Favre-Nicolin V., R. Cerny *J. Appl. Cryst.,* 2002, 35, 734-743.

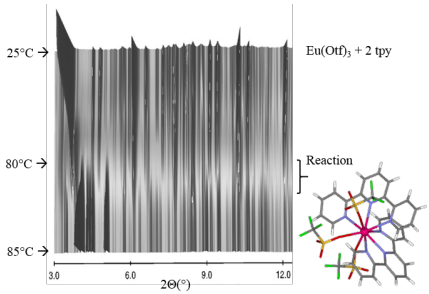

Figure 1. In-situ XRPD pattern (heating) and crystal structure of the complex [$EuTpy_2Otf_3$] formed.

Keywords: lanthanide complexes, in-situ XRPD, solid state synthesis