ESRF	**Experiment title:** Powder diffraction studies of new precursors of ceramics	**Experiment number: HC323**
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Names and affiliations of applicants (* indicates experimentalists):

F. Favier*[†], J.L. Pascal*[†], F. Cunin[†], A. Fitch*[‡] and G. Vaughan*[‡]

[†] LAMMI, UPRESA 5072, Université Montpellier II, Place E. Bataillon, C.C.015, F-34095 Montpellier cedex 5

[‡] ESRF, BP 220, F-38043 Grenoble Cedex.

Report:

In the development of new preparative methods for ceramics as dispersed powders, the thermolysis at moderate temperature of a fully inorganic precursor with weak oxy-ligands such as nitrates or perhallogenates, is an alternative way of synthesis which can promote attractive properties. Perchlorates generally decompose bellow 250-350°C giving fine powders of oxides in which the metal is in its highest oxidation state. However, when we recently tried to prepare oxides of lanthanides by this method, we found that, with the exception of Ce(ClO,),, the resulting powders were oxychlorides rather than oxides. In order to control the structure and morphology of the resulting material, it nethertheless remains of importance to know the structure of the precursor as well as those of the successive intermediate solids. Recording data on the Dl6-BL15 line has allowed us to determine, in a first step, the crystalline and molecular structures for $Ln(ClO_4)_3$ compounds with Ln = Tm., Yb and Lu, and subsequently with La, Ce, Pr, Sm, Eu, Ho and Er.

X-ray patterns recorded in-house showed that $Ln(ClO_4)_3$ complexes can be separated into two different groups of isostructural compounds. The first group includes complexes of La, Ce, Pr, Sm, Eu, Ho, Er and the low temperature form (LT) of Tm and Yb (LT), and the second involves the high temperature forms (HT) of Tm and Yb, and Lu perchlorates. High resolution X-ray diffraction patterns of europium, ytterbium (HT and LT), thulium (HT) and

lutetium complexes were collected at the ESRF. The indexing of the powder patterns was carried out using the TREOR90 program. Rietveld refinements and profile matchings were performed using the FULLPROF program on a PC computer.As an example, plots, for $Yb(ClO_4)_3$ LT and HT forrns, of the experimental and calculated X-ray diffraction patterns, and difference data after the final Rietveld refinements are depicted in Figure 1. The profile matching option of FULLPROF allows us to calculate the refined lattice parameters for other synthezised $Ln(ClO_4)_3$ compounds.

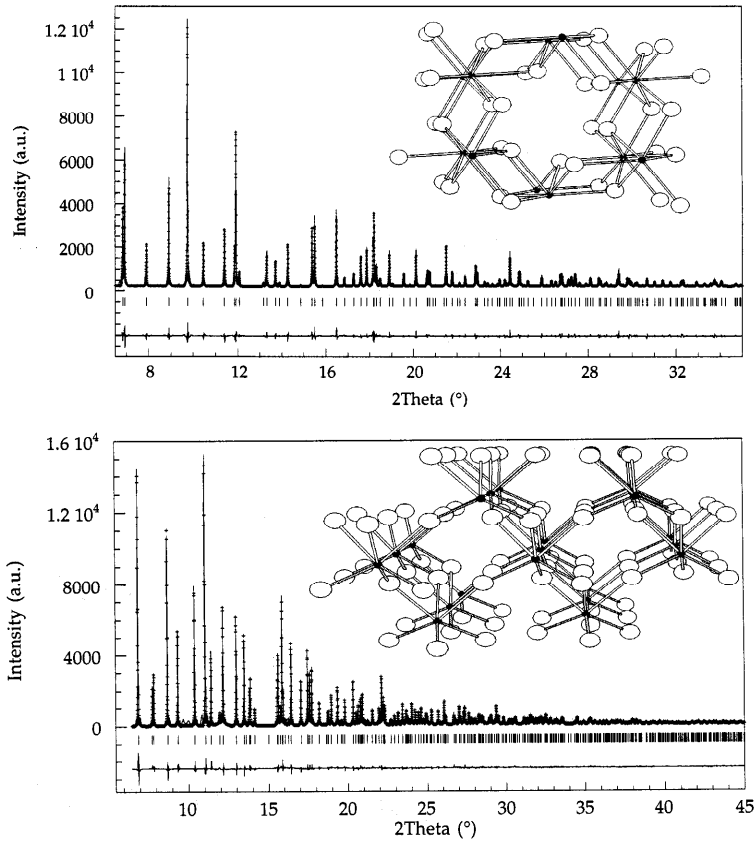

Figure 1 : Observed (line), calculated (crosses) and difference plots for $Yb(ClO_4)_3$ LT (top) and HT (bottom). Corresponding schematic packings are also depicted; black circles for Yb atoms and large open circles represent $[ClO_4]$ groups.

This work was presented at ESRF users'meeting 96 (poster) and at the XVII Conference on Applied Crystallography at Wisla (Poland, September 97) (oral communication). Three publications were submitted (special issue of the Journal of Applied Crystallography, Dalton Transactions and Inorganic Chemistry).