Experimental report

21/05/2024

Proposal: 5-22-811 **Council:** 10/2022

Title: Structural investigations in the La2O3-MoO3-CaO system

Research area: Chemistry

This proposal is a new proposal

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Samples: Ca1.5La10Mo3.5O27
La4CaMo3O16
Ca3La2Mo2O12

Instrument	Requested days	Allocated days	From	To
D2B	2	2	26/06/2023	28/06/2023

Abstract:

The first compound present a global composition of Ca3La2Mo2O12 but it could also present some cationic vacancies Ca3-xLa2+xMo2O12 with a rhombohedric cell a~9.7 Å and c~55.0 Å. This last compound is isostructural with Ca2.06La2.61Vac0.33W2O12 [4] which has been recently published. The second compound of formula La4CaMo3O16 is also an isostructural coumpound with La5Mo2NbO16 series. Nevertheless on the contrary of the strontium serie the calcium coumpond present a small distortion of the cubic cell Pn-3n (n°222) a~11.2 Å. For the third compound with a nominal composition La2O3 (~50%)-MoO3(~35%)-CaO(~15%) a big cell has been found from x-ray powder diffraction and PED orthorhombic unit cell (a~11.4 Å , b ~24.2 Å and c~16.2 Å , v~ 4469Å3). This compound is the first compound find in this ternary diagram. A fine investigation from electron and x-ray diffraction leads to a partial structure resolution (Fig.1). As the previous compound, this structure is closely related to the Scheelite structure (CaWO4). The cell parameters could be deduced :(anew ~ cScheelite , bnew ~ 3SQR2.a Scheelite and cnew~

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Structural investigations in the La2O3-MoO3-CaO system

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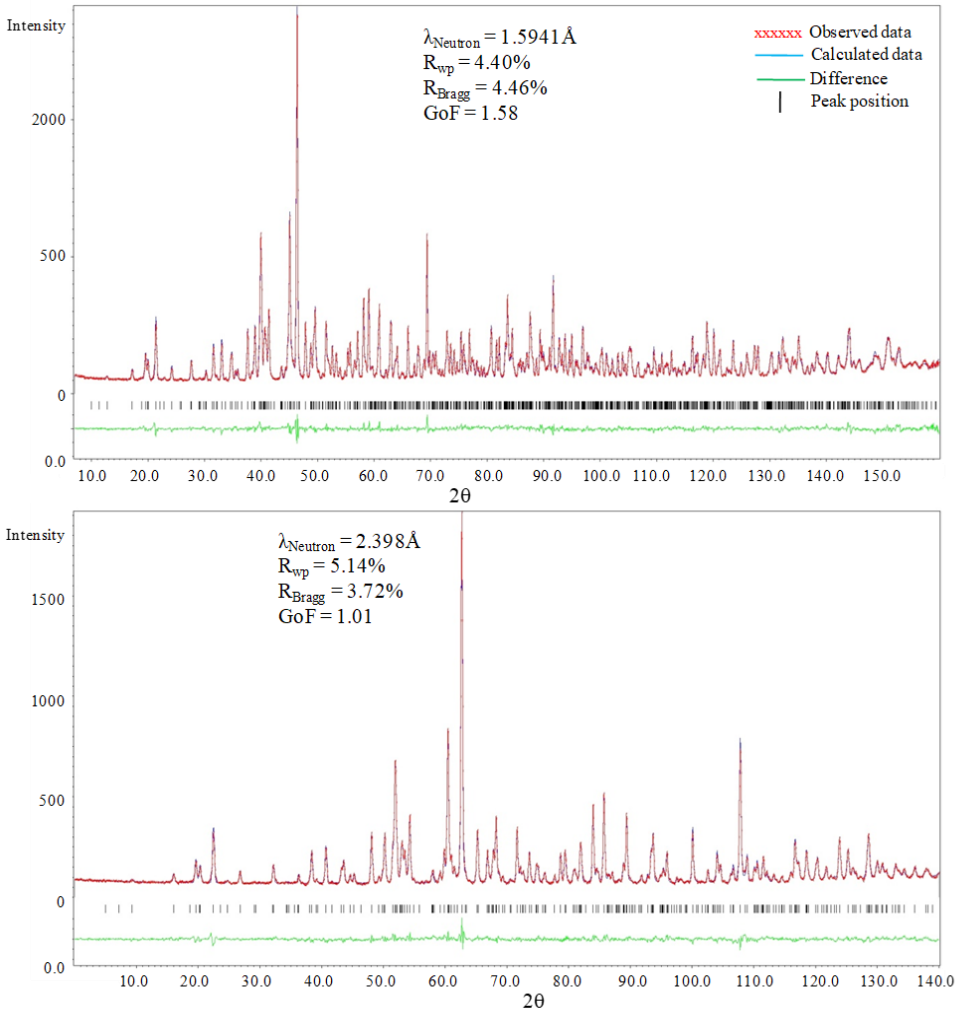
For the first compound $Ca_3La_2Mo_2O_{12}$, two sets of data have been collected at 1.6 and 2.4 Ang. An attentive examination of the data leads to a very different structure compare with the tungsten equivalent. For the tungsten the formula is $Ca_{2.06}La_{2.61}Vac_{0.33}W_2O_{12}$ with some vacancies of the Ca4 Wyckoff(6a) crystallographic site. On the contrary for the molybdenum compound the formula is $Ca_{4.04}La_{1.33}Mo_2O_{12}$ (Z=18), the Ca4 is fully occupied and an extra-occupation is observed on the Ca5 Wyckoff(12c). This structure is then closer to the $Na_3Pr_{14}Ru_6O_{36}$ (Z=6). The publication is under redaction.



For the final compound two set of data have been measured at 1.6 and 2.4 Ang. From these data a new structural model have been proposed by A. LeBail. The final structural model is formed by 9 lanthanum positions and 3 molybdenum positions and 24 oxygen positions. All these 36 atomic positions are in the 8f Wyckoff general position leading to 288 (x,y,z) refined parameters only for the structural model. This is of course a tough structure to be solved by powder diffraction. We are currently working on it.