Structure of Ce doped $Na_{0.5}La_{0.5}MoO_4$ single crystals

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Résumé – Doping $NaLa(MoO_4)_2$ single crystals by Ce and Er impurities together with the proper growth conditions can provide new efficient materials that may be used as flashlamp-pumped laser hosts and scintillators. The main problem of the Ce doped material is the dual status of Ce ions as useful substitutors of La (Na) positions in the crystal and source for harmful CeO_2 precipitates. TEM/HRTEM/EDS/EELS study succeeded to get information on the nature and density of precipitates responsible of spurious Mie light scattering and as well as structure of the doped matrix.

1. Materials and Methods

$Na_{0.500}La_{0.495-x}Ce_xEr_{0.005}MoO_4$ (NLM:Er,Ce) crystals (x = 0.125, 0.15, and 0.25) were grown from extra-pure grade Na_2CO_3, La_2O_3, Er_2O_3, CeO_2, and MoO_3 by Czochralski method from iridium crucibles in a weakly oxidizing (99% N2 + 1% O2) atmosphere. Bar-shaped single crystal seeds oriented perpendicular to the fourfold axis of a tetragonal crystal were chosen to minimize the thermal stress. The pulling rate was 2 mm/h and the crystal rotation was varied from 15 to 20 rpm. The obtained single-crystal boules were transparent, optically homogeneous and did not contain macroscopic inclusions. They were subsequently subjected to short-term high-temperature (24 h, 1000°C) and/or long-term low-temperature (100 h, 700°C) air annealing which resulted in more or less severe sample opacity.

The aim of this study was to understand the origin of this opacification and to compare the microstructure of samples formed under different growth and annealing conditions.

Phase and structural analysis were done first by powder XRD (Cu$K\alpha$ radiation, diffracted-beam monochromator, $2\theta = 17°–100°$ with a step scan 0.02°/step and a counting time of 10 s per data point) and single-crystal diffraction (Mo$K\alpha$ radiation, graphite monochromator, ω scan mode and with the refinement of the lattice parameters among 25 reflections in the angular range $23° < \theta < 26°$).

Then carbon coated polished samples were characterized by SEM (backscattered electron mode) and EDS in a FEI XL30 Sirion/FEG. Finally the micro/nanostructure of ion milled thin foils were investigated by TEM, HRTEM, EDS, and EELS in a FEI CM300UT/FEG. The images were recorded on a Gatan 797 slow scan CCD camera and processed with the Gatan Digital Micrograph 3.11.0 software. The interpretation of the SAED patterns, HRTEM images and FT diffractograms were performed with the JEMS software package[2].

2. Results and Conclusions

The powder X-ray diffraction did not reveal the presence of second phase within the detection limit of 2 mass %. Rietveld profile fits of the XRD patterns showed that the lattice parameters changed with the Ce concentration and a reduction of the cell volume takes place at increasing concentrations [3].

However numerous CeO_2 precipitates were found in the SEM and TEM images of all annealed crystals and in most of the non-annealed crystals. Obviously two different mechanism of precipitation occurs. Part of the precipitates are found from SEM pictures to form long ribons of elongated platelets along distant lines close to [001] and [01-3] directions on [100] cuts although their habit can differ from these directions (Fig. 1a). BF and DF TEM shows that they are linked to matrix dislocations (Fig 1b). The remaining precipitates are more or less uniformely distributed in the matrix (Fig. 2a).

Two types of orientation relationships between the NLM crystal (tetragonal) and CeO_2 precipitates (cubic) were obtained from SAED and HRTEM observations: [100]NLM // [100]CeO_2 with (012)NLM // (011)CeO_2 or (001)NLM // (001)CeO_2 (Fig. 2b). The interface between (100)NLM//(100)CeO_2 as well as (010)NLM//(010)CeO_2 which have only 0.85% misfit are coherent while the 8.57 % lattice misfit between the (001) NLM//(001)CeO_2 lead to interfacial dislocations and incoherent interfaces.

EELS spectra exhibit an ELNES fine structure of the Ce edge [4]: the Ce^{4+} M_5 and M_4 edges consist in two main maxima at 884.0 and 901.6 eV and lower broader maxima at 889.2 and 906.7 eV. It was observed as expected in CeO_2 precipitates. The $M_{4,5}$ spectrum of Ce^{3+} differs in energy and shape from the Ce^{4+} one with the maxima at 882.0 and 899.7 eV, and with an inverse peak intensity ratio of the M_5 to M_4 edge. It was observed in the annealed matrix (Fig. 3) and corresponds to reduced Ce in substitutionnal position at the La/Na sites. The increase of number and size of CeO_2 precipitates after annealing is understood as precipitation of Ce in excess in the non-annealed matrix which status is still under investigation (interstitial Ce, oxide or reduced form?).

At contrary from XRD, electron microscopy has shown unambigously that CeO_2 precipitation occurred during the crystal growth and subsequent annealing. Faceting and coarsening of CeO_2 precipitates is observed after annealing, up to 200-300 nm in some samples. These precipitates are responsible of the degradation of optical properties (Mie light scattering). Optimization of growth and annealing conditions has allowed to significantly reduce the concentration and size of precipitates.

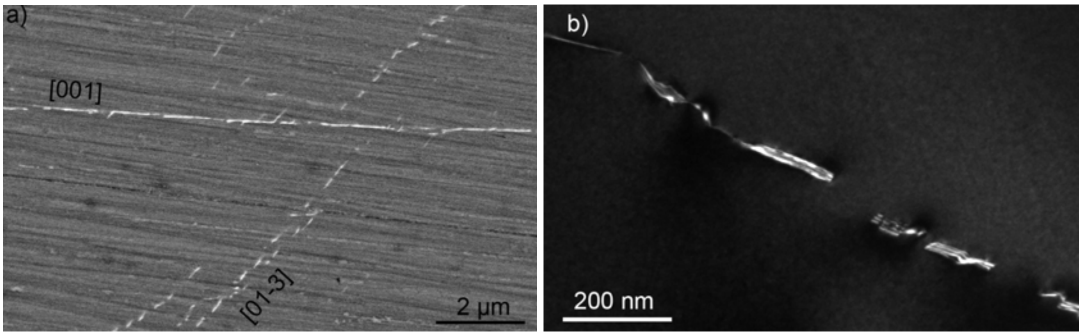

Figure 1: non-annealed sample. (a) SEM, 15kV, backscattered electron mode, thin CeO_2 precipitates aligned along the [001] and [01$\bar{3}$] direction; (b) TEM BF, decorated dislocations with thin precipitates

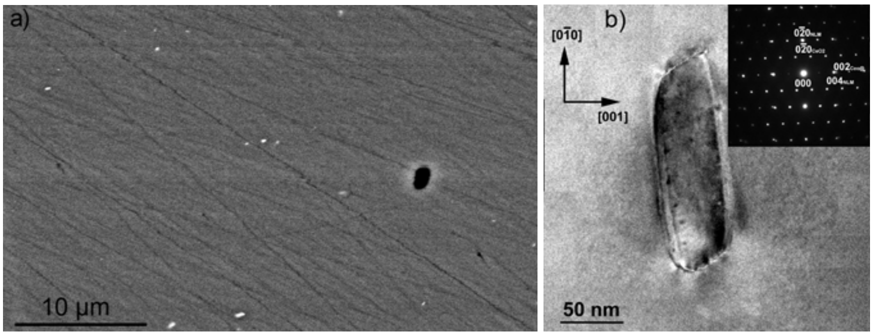

***Figure 2:** annealed sample. (a) SEM, 15kV, backscattered electron mode, CeO2 precipitates randomly dispersed in the matrix; (b) semi-coherent precipitate*

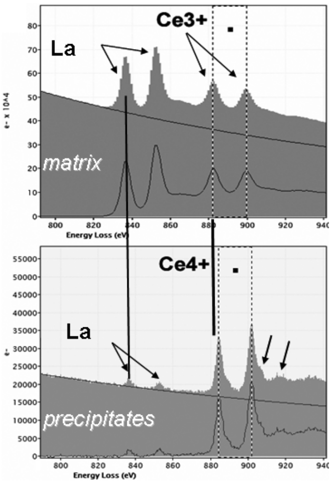

***Figure 3:** annealed sample, EELS spectra from Ce^{3+} (matrix) and Ce^{4+} (precipitate).*

3. Références

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