

Structure of Ce doped Na_{0.5}La_{0.5}MoO₄ single crystals

Elena I. Suvorova^{a,b}, Galina M. Kuz'micheva^c, Kirill A. Subbotin^d, Evgeniy V. Zharikov^d, Marco Cantoni^a and Philippe A. Buffat^a

^a Centre Interdisciplinaire de Microscopie Electronique, Ecole Polytechnique Fédérale de Lausanne, CH-1015, Switzerland

^b Institute of Crystallography, Russian Academy of Sciences, pr. Leninsky 59, Moscow, 119333, Russia

^c Lomonosov State Academy of Fine Chemical Technology, pr. Vernadskogo 86, Moscow, 119571, Russia

^d Prokhorov Institute of General Physics, Russian Academy of Sciences, ul. Vavilova 38, Moscow, 119991, Russia

Résumé – Doping NaLa(MoO₄)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 substituents of La (Na) positions in the crystal and source for harmful CeO₂ 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}MoO₄ (NLM:Er,Ce) crystals ($x = 0.125, 0.15, \text{ and } 0.25$) were grown from extra-pure grade Na₂CO₃, La₂O₃, Er₂O₃, CeO₂, and MoO₃ 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 (CuK α radiation, diffracted-beam monochromator, $2\theta = 17^\circ\text{--}100^\circ$ with a step scan 0.02°/step and a counting time of 10 s per data point) and single-crystal diffraction (MoK α radiation, graphite monochromator, ω scan mode and with the refinement of the lattice parameters among 25 reflections in the angular range $23^\circ < \theta < 26^\circ$).

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 CeO₂ 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 ribbons 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 uniformly distributed in the matrix (Fig. 2a).

Two types of orientation relationships between the NLM crystal (tetragonal) and CeO₂ precipitates (cubic) were obtained from SAED and HRTEM observations: [100]NLM // [100]CeO₂ with (012)NLM // (011)CeO₂ or (001)NLM // (001)CeO₂ (Fig. 2b). The interface between (100)NLM// (100)CeO₂ as well as (010)NLM// (010)CeO₂ which have only 0.85% misfit are coherent while the 8.57 % lattice misfit between the (001)NLM// (001)CeO₂ lead to interfacial dislocations and incoherent interfaces.

EELS spectra exhibit an ELNES fine structure of the Ce edge [4]: the Ce⁴⁺ M₅ and M₄ 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 CeO₂ precipitates. The M_{4,5} spectrum of Ce³⁺ differs in energy and shape from the Ce⁴⁺ one with the maxima at 882.0 and 899.7 eV, and with an inverse peak intensity ratio of the M₅ to M₄ edge. It was observed in the annealed matrix (Fig. 3) and corresponds to reduced Ce in substitutional position at the La/Na sites. The increase of number and size of CeO₂ 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 unambiguously that CeO₂ precipitation occurred during the crystal growth and subsequent annealing. Faceting and coarsening of CeO₂ 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.

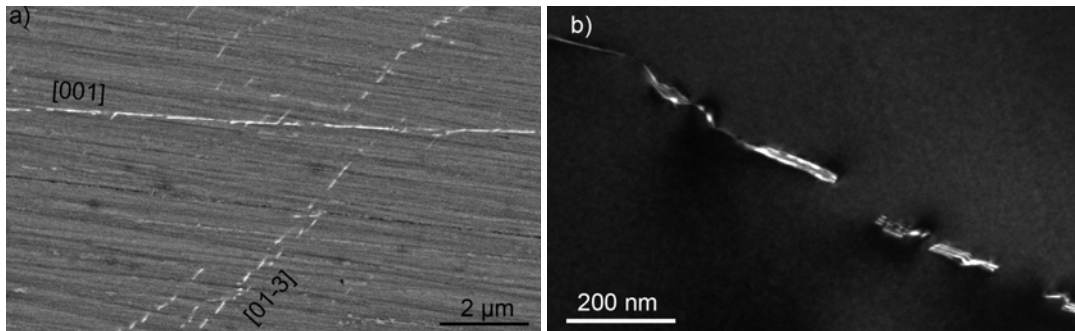


Figure 1: non-annealed sample. (a) SEM, 15kV, backscattered electron mode, thin CeO₂ precipitates aligned along the [001] and [013] direction; (b) TEM BF, decorated dislocations with thin precipitates

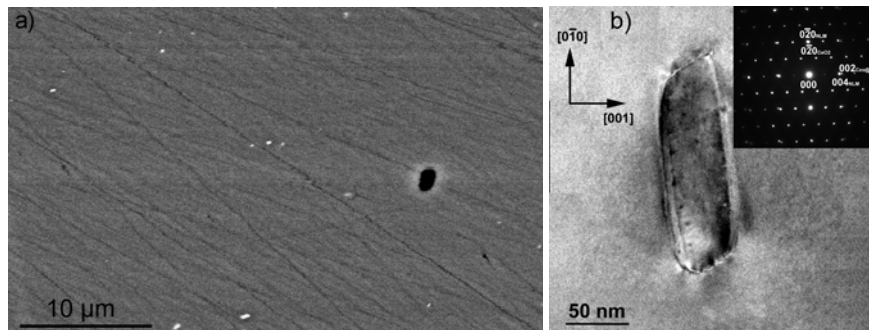


Figure 2: annealed sample. (a) SEM, 15kV, backscattered electron mode, CeO₂ precipitates randomly dispersed in the matrix; (b) semi-coherent precipitate

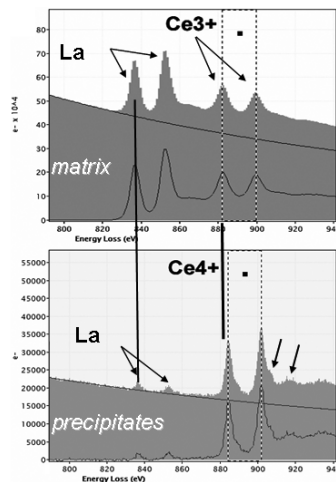


Figure 3: annealed sample, EELS spectra from Ce³⁺ (matrix) and Ce⁴⁺ (precipitate).

3. Références

- [1] E. I. Suvorova, G. M. Kuz'micheva, A. V. Morozkin, E. V. Zharikov, D. A. Lis and K. A. Subbotin, *Microstructure of (Na_{0.5}La_{0.5})MoO₄ Crystals Coactivated with Cerium and Erbium Ions*, *Inorganic Materials*, **43** (2007) 287-291.
- [2] P.A. Stadelmann, JEMS, <http://cimewww.epfl.ch/people/Stadelmann/jemsWebSite/jems.html>
- [3] G. M. Kuz'micheva, V. B. Rybakov, E. V. Zharikov, D. A. Lis and K. A. Subbotin, *Unusual Structural Properties of (Na_{0.5}La_{0.5})MoO₄:Er,Ce Crystals.*, *Inorganic Materials*, **42** (2006) 303-309
- [4] L.A. Garvie and P.R. Busek, *Determination of Ce⁴⁺/Ce³⁺ in electron-beam-damaged CeO₂ by electron energy-loss spectroscopy*, *J. Phys. Chem. Sol.* **60** (1999) 1943-1947