

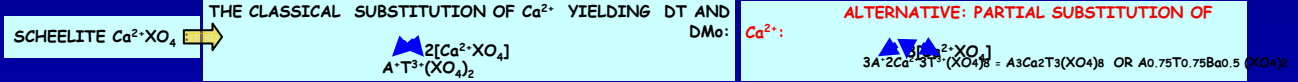


Growth, structural and spectroscopic properties of disordered Yb³⁺-doped Li_{0.75}Gd_{0.75}Ba_{0.5}(MoO₄)₂ crystals

A. García-Cortés, C. Cascales* and C. Zaldo*
 Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas. c/ Sor Juana Inés de la Cruz, 3. Cantoblanco. 28049 Madrid. Spain. *ccascales@icmm.csic.es; cezaldo@icmm.csic.es

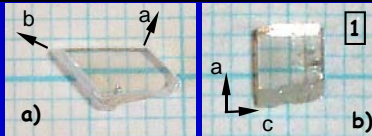
In the last years there has been a significant advance of the knowledge on certain families of scheelite-related tungstate and molybdate crystals as rare-earth (RE) hosts for solid-state lasers. Recently tetragonal/double tungstate (DT) and double molybdate (DMo) AT(XO₄)₂ (shortly ATX) crystals, A²⁺ = Li, Na, T³⁺ = Y, La, Gd and Lu, have emerged as interesting laser crystals, particularly in the tunable and ultrashort (fs) laser pulse domains. Tetragonal DT and DMo are structurally disordered crystalline materials, yielding a range of differentiated Yb³⁺ crystal fields, and thus spectral inhomogeneous broadening and broader stimulated gain bandwidth. Efficient diode-pumping, wide wavelength tunability, up to 65 nm for Yb-doped NaGdW,¹ and the generation of ultrashort pulses from mode-locked lasers, 53 fs achieved with Yb-NYW,² are their specific characteristics.

Searching for new RE³⁺-based large bandwidth laser materials, and within the framework of the scheelite-related systems, we have undertaken the crystal growth, crystallographic characterization and study of the spectroscopic properties of RE³⁺-doped ternary Li⁺-T³⁺-Ba²⁺ molybdate hosts. We present the first results for Yb-Li_{0.75}Gd_{0.75}Ba_{0.5}(MoO₄)₂ crystals.



CRYSTAL GROWTH

Li_{0.75}Gd_{0.75}Yb_{0.06}Ba_{0.5}(MoO₄)₂ (LiGdBaMo) [Yb] = 4.0685×10²⁰ at/cm³ crystals have been grown in air by the Top Seeded Solution Growth slow cooling method in a Li₂Mo₂O₇ flux. The prepared polycrystalline precursor was used in a (1:6) mixture with the flux, and melted at 610°C in a Pt crucible. The rotation of the Pt wire seed was 12 rpm and the cooling rate 0.08 °C/h. Figure 1a shows the transparent colourless platelets, with pseudo-diamond shape.



(a) (001) oriented plate showing the spontaneously growth face. (b) (010)-cut sample.

CRYSTAL STRUCTURE

Monoclinic space group C2/c (No. 15), with a = 5.2355(3) Å, b = 12.7396(8) Å, c = 19.1626(11) Å, β = 91.170(1)°, V = 1277.84(13) Å³. Our structure determination (R₁ = 0.044) indicated the following main features:

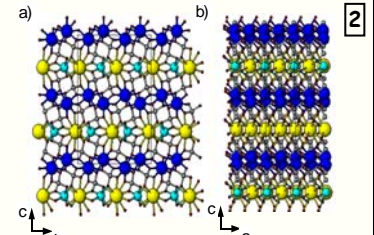
A) 0.725 Gd³⁺: 0.06 Yb³⁺: 0.215 Li⁽¹⁾ IN A SINGLE 8f SITE

B) QUASI-ORTHORHOMBIC CRYSTAL SYMMETRY:

C) CLEAVAGE IN THE (001) PLANE

A) Due to the mixed Gd(Yb)/Li 8f site occupancy the structure presents some local disorder around Yb³⁺ centers, and thus spectral broadening.

B) Three polarization configurations along the three crystal axes, and some anisotropy in spectroscopic measurements is expected.



(a) bc plane view of square antiprisms Gd(Yb)O₆/LiO₆ (blue), distorted octahedra LiO₆ (cyan) and BaO₁₀ polyhedra (yellow). (b) ac plane, with alternate corrugated layers with rings of Gd(Yb)O₆/LiO₆ polyhedra and planar layers with rings of BaO₁₀ polyhedra and LiO₆ octahedra, both kind of layers perpendicular to the c axis.

Yb³⁺ SPECTROSCOPY

From 6 K optical absorption and photoluminescence measurements the Yb³⁺ sequence of energy levels results:

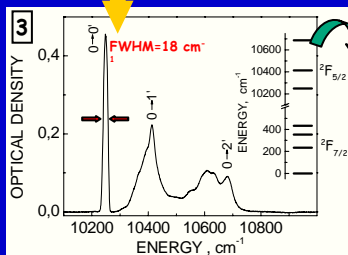
²F_{7/2}: 0, 223, 353, 433 cm⁻¹
²F_{5/2}: 10248, 10413 and 10687 cm⁻¹, see Fig. 3.
 The absorption cross section σ_{ABS} is calculated from OA coefficients α/[Yb]³⁺, σ_{ABS} show the expected anisotropy.

σ_{ABS} is higher for E//b polarization, with a peak value of 2.38×10⁻²⁰ cm².

calculated for the three polarizations using the reciprocity principle see the Fig. 4.

The expected oscillation wavelength can be predicted calculating the gain cross section σ_{GAIN}(λ) = βσ_{EMI}(λ) - (1-β)σ_{GSA}(λ). The Fig 5 shows the calculated σ_{GAIN}(λ) for different β values in the three polarization configurations.

The Table shows the optical parameters for the Yb-LiGdBaMo crystal and the comparison with other ordered and disordered DT and DMo laser crystal hosts.

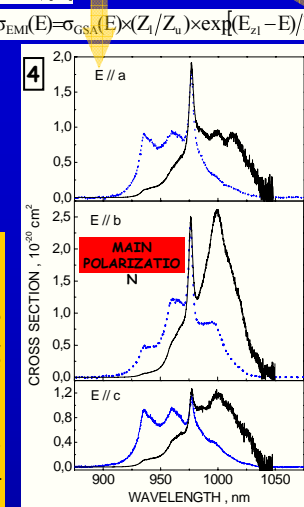


6 K unpolarized optical absorption. The inset shows the Yb³⁺ sequence of energy levels

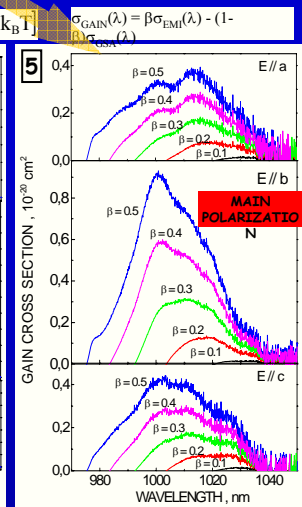
CONCLUSIONS

With regards to tetragonal DT and DMo laser hosts the biaxial characteristics of LiGdBaMo confer higher anisotropy to its OA and PL polarized spectra: σ_{ABS} and σ_{EMI} values are more dependent on the crystal orientation.

Perspectives for laser emission are favourable. Structural disorder - although lesser than in tetragonal DT and DMo-, and Yb³⁺ electron-phonon coupling are yielding the observed tunability of the laser oscillation in this Yb³⁺-LiGdBaMo crystal.



300 K polarized absorption (blue dots) and emission (solid black line) spectra



Calculated gain cross sections for the three polarizations and different inversion ratios

TAILORING THE SPECTROSCOPIC PROPERTIES THROUGH THE STRUCTURAL DISORDER

Yb-doped:	KGW	GdBaMo	LiGdBaMo	NaLuW	NaGdW
Symmetry ^a	M, o	M, o	M, d	T, d	T, d
σ _{ABS} [10 ⁻²⁰ cm ²]	12 (N _m)	1.8 (Y) 2.5 (Z) 1.1 (X)	1.77 (a) 2.38 (b) 1.15 (c)	1.65 (σ) 2.22 (π)	1.36 (σ) 1.78 (π)
λ [nm]	981	977	976	973.8	975
σ _{EMI} [10 ⁻²⁰ cm ²]	3.0 (N _m)	3.2 (Z)	0.93 (a) 2.60 (b) 1.20 (c)	1.4 (σ) 2.1 (π)	0.75 (σ) 1.89 (π)
λ [nm]	1026 (N _m)	1007	999	1000	1000
FWHM of σ _{GAIN} [nm] for β=0.5	42 (X)	34 (Z)	45 (a) 31 (b) 41 (c)	26 (σ) 25 (π)	48 (σ) 40 (π)
Reference	3	4	This work	5	1

M = monoclinic; T = tetragonal; o = ordered; d = disordered

IMPROVEMENT OF THE LASER TUNABILITY WITH THE STRUCTURAL DISORDER

LiGdBaMo: DISORDER OVER 1 SITE NaLuW: DISORDER OVER 2 SITES NaGdW: ENHANCED DISORDER OVER 2 SITES

- C. Cascales et al., Phys. Rev. B, 17 (2006) 174114.
- A. García-Cortés et al., IEEE J. Quantum Electr., submitted.
- N. V. Kuleshov et al., Opt. Lett. 22 (1997) 1317.
- Haomiao Zhu et al., J. Appl. Phys. 101 (2007) 063109.
- A. García Cortés et al., J. Appl. Phys. 101 (2007) 063110.