Synthesis and Optical Properties of Sm\(^{3+}\) and Ho\(^{3+}\) Activated Li\(_3\)Ba\(_2\)La\(_3\)(MoO\(_4\))\(_8\)

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Department Chemical Engineering (~ 600 Students)

Laboratory for Material Sciences (Prof. T. Jüstel, Prof. M. Bredol, Prof. U. Kynast)

Research Group „Tailored Optical Materials“ (~ 10 Ph.D. Students + 20 undergraduates)
Research Areas

LED + FL Phosphors
Development of novel matrices and particle coatings, spectroscopic characterisation (garnets, silicates, (oxy)nitrides, carbodiimides)

Afterglow pigments
Revealing the electronic structure of Eu\(^{2+}/\)RE\(^{3+}\) codoped aluminates
Governing the defect density and depth

Particle coatings of nano- or microscale luminescent pigments
Enhancement of efficiency and stability of materials by coatings due to refractive index matching and diffusion barriers

NIR Phosphors
Biocompatible luminescent materials within the optical window of biomatter, i.e. in the NIR range (diagnostics, photodynamic therapy)

VUV Phosphors
Development of optimized phosphors for noble gas excimer discharges to enable high performance UV radiation sources

Scintillators
Reduction of afterglow of materials for Computed Tomography (CT)
Ultrafast scintillator crystals for Positron Emission Tomography (PET)

Laser materials
Novel Pr\(^{3+}\) and Nd\(^{3+}\) doped fluorides as gain media
Transparent garnet ceramics
Li$_3$Ba$_2$Ln$_3$(MoO$_4$)$_8$

- Li$_3$Ba$_2$Ln$_3$(MoO$_4$)$_8$ is derived from Scheelite:
  (Ca$_{8/8}$)WO$_4$ $\leftrightarrow$ (Li$_{3/8}$Ba$_{2/8}$Ln$_{3/8}$)MoO$_4$

- Various research activities regarding its potential as laser material:
  - Li$_3$Ba$_2$Y$_3$(MoO$_4$)$_8$:Nd$^{3+}$ - J Cryst Growth 308 (2007) 208
  - Li$_3$Ba$_2$Y$_3$(MoO$_4$)$_8$:Eu$^{3+}$,Tb$^{3+}$,Dy$^{3+}$ - J Electrochem Soc 158 (2011) H565
  - Li$_3$Ba$_2$Y$_3$(MoO$_4$)$_8$:Er$^{3+}$ - Mater Sci Eng B 176 (2011) 810
  - Li$_3$Ba$_2$Y$_3$(MoO$_4$)$_8$:Tm$^{3+}$ - CrystEngComm 15 (2013) 168
  - Li$_3$Ba$_2$Y$_3$(MoO$_4$)$_8$:Yb$^{3+}$ - J Alloys Compd 478 (2009) 423
  - Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$:Eu$^{3+}$ - J Mater Chem 22 (2012) 22126
  - Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$:Sm$^{3+}$ - Z Naturforsch B 69 (2014) 183
  - Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$:Dy$^{3+}$ - J Alloy Compd 607 (2014) 110
  - Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$:Er$^{3+}$ - Opt Mater 33 (2012) 1558
  - Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$:Eu$^{3+}$ - J Cryst Growth Design 12 (2012) 3878
  - Li$_3$Ba$_2$(La,Gd)$_3$(MoO$_4$)$_8$:Eu$^{3+}$ - J Alloy Compd 479 (2009) 607
  - Li$_3$Ba$_2$(La,Gd)$_3$(MoO$_4$)$_8$:Nd$^{3+}$ - J Alloy Compd 480 (2009) 839
  - Li$_3$Ba$_2$(La-Lu,Y)$_3$(MoO$_4$)$_8$ - Russ J Appl Chem 84 (2011) 384
  - Li$_3$Ba$_2$(Gd,Tm)$_3$(MoO$_4$)$_8$ - Zh Strukt Khim 33 (1992) 126
  - Li$_3$Ba$_2$Y$_3$(WO$_4$)$_8$:Yb$^{3+}$ - J Lumin 132 (2012) 1507
  - Li$_3$Ba$_2$La$_3$(WO$_4$)$_8$:Dy$^{3+}$ - Opt Mater 36 (2014) 1255
  - Li$_3$Ba$_2$La$_3$(WO$_4$)$_8$:Er$^{3+}$,Yb$^{3+}$ - PLoS ONE 7 (2012) e40631
  - Li$_3$Ba$_2$La$_3$(WO$_4$)$_8$:Tm$^{3+}$ - CrystEngComm 14 (2012) 3930
  - Li$_3$Ba$_2$Sr(La-Lu,Y)$_3$(MoO$_4$)$_8$ - Russ J Appl Chem 84 (2011) 1498

Eu$^{3+}$:LBLM Ceramics and Powders

Sm$^{3+}$:LBLM Powder
Baur, Jüstel et al., Z Naturforsch B 69 (2014) 183

No reports yet on Ho$^{3+}$:LBLM
Li$_3$Ba$_2$Ln$_3$(MoO$_4$)$_8$

- Structure derived from Scheelite CaWO$_4$ $\rightarrow$ (Li$_{3/8}$Ba$_{2/8}$Ln$_{3/8}$)MoO$_4$
- Two potential Ln$^{3+}$ doping sites:
  - $[\text{LnO}_{10}]$ bi-capped square prism
  - $[\text{LnO}_8]$ square antiprism

$\text{Ba 85\%}$  
$\text{Ln 67.5\%}$  
$\text{Li 25\%}$  
$\text{MoO}_4$

$\text{Ba 7.5\%}$  
$\text{Ln 15\%}$

- monoclinic
- $C12/c1$ (15)
- $5.31 \text{ Mg/m}^3$ (for Gd-compound)

**XRD/Synthesis**

Conventional solid state synthesis

**Educts:** Li$_2$CO$_3$, BaCO$_3$, La$_2$O$_3$, Sm$_2$O$_3$, Ho$_2$O$_3$, MoO$_3$

**Temperature:** 800 °C

**Duration:** 10 hours

→ Li$_3$Ba$_2$(La$_{1-x}$Ln$_x$)$_3$(MoO$_4$)$_8$

A complete solid solution series exists with good crystallinity and phase formation for all lanthanoid ratios.
Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$

SEM

- Sharp, regular formed primary particles: ~5 µm diameter + some „dust“

- Agglomerates: ~20-30 µm diameter

- The particle morphology and low melting point of molybdates are favorable for laser ceramics preparation
Sm$^{3+}$:Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$

- Optical band gap: ~320 nm; 3.65 eV
- Broadening of the absorption band in the doped samples likely stems from O$^2$-/Sm$^{3+}$ charge transfer
- The 4f-4f transitions of Sm$^{3+}$ exhibit unusually strong absorption in LBLM
- Reflectance is close to 100% in the orange to red spectral region which is important for high efficiency

- Pumping is possible via one of the multiplets between 360 and 550 nm
Sm$^{3+}$:Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$

**Emission & Excitation**

- **CT band** consists of two components (282 nm/4.40 eV & 310 nm/4.01 eV): Sm$^{3+}$ and Mo$^{6+}$ CT bands

- **Branching ratio** $^4G_{5/2} \rightarrow ^6H_{9/2}$: 59%

- **Highest emission intensities** can be found for the 5% Sm$^{3+}$ sample!

- **Shape and relative emission intensities** do not change with Sm$^{3+}$ concentration
**Sm\(^{3+}\):Li\(_3\)Ba\(_2\)La\(_3\)(MoO\(_4\))\(_8\)**

- With decreasing temperature lines sharpen due to lowered vibronic interactions

- A small blue-shift can be observed, presumably caused by lattice constriction (cf. red-shift caused by high-pressure: Rad Eff Defect Solid 169 (2014) 48)

- A bi-sigmoidal behaviour was observed, likely resulting from competitive absorption of host material and Sm\(^{3+}\)
  - \(T_{1/2,a} = 280\) K \((E_A = 0.2\) eV\)
  - \(T_{1/2,b} = 515\) K \((E_A = 0.6\) eV\)
Sm$^{3+}$:Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$

**Decay**

- Decay behaviour strongly depends on Sm$^{3+}$ concentration
- Fast non-radiative processes (cross-relaxation $^4G_{5/2} \rightarrow ^6F_{5/2}$ / $^6H_{5/2} \rightarrow ^6F_{11/2}$) shorten the decay time at higher Sm$^{3+}$ concentrations
- Bi-exponential decay curve at concentrations larger than 2% is assumedly linked to second doping site
- $IQE = \frac{W_r}{W_r + W_{nr}}$ – begins to decrease at concentration larger than 0.25%
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Sm$^{3+}$:Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$

- Decay times remain constant up to 500 K
- IQE remains constant up to 500 K, contrary to emission intensity $\rightarrow$ photon escape efficiency decreases
- This observation might be explained by temperature-driven reversible formation of Mo$^{5+}$ defects
- Lower decay time at 100 K might be an outlier or start of a trend
- He-cryostat measurements necessary for further investigation

Graphs showing decay time versus temperature and counts versus time.
A relatively high QE of 44% could be realized, this is rare in crystalline materials where high phonon frequencies quench Sm\(^{3+}\) NIR transitions.

Decay constants (i.e. IQE) decrease with increasing Sm\(^{3+}\) concentration, probably caused by cross-relaxation processes.
Ho\(^{3+}\):Li\(_3\)Ba\(_2\)La\(_3\)(MoO\(_4\))\(_8\)

**Reflection**

- The 4\(f\)-4\(f\) transitions of Ho\(^{3+}\) exhibit unusually strong absorption in LBLM

- 1\% Ho\(^{3+}\) exhibits only 60\% reflection around 450 nm, which is useful for pumping with blue laser diodes

- Reflectance approaches 100\%, indicating high sample quality

- Host absorption band is broader than in the undoped material
**Ho$^{3+}$:Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8**

**Emission & Excitation**

- Most efficient excitation via $^5$I$_8 \rightarrow ^5$G$_6$ peaking at 452 nm
- Excitation via CT bands results in very low QE, which is commonly observed in molybdates
- Highest emission intensity was observed for the 1% doped sample
- Decay times are unusually fast, measurement with µs-flashlamp was not possible
- This is likely a result of concentration quenching and samples with even lower activator concentration will be prepared
$\text{Ho}^{3+}:\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$

**Emission $f(T)$**

- Relative intensities of the high energy lines of the multiplet increases.
- This might be related to the emission originating from two separate levels: $^5F_4$ & $^5S_2$.
- The position of the lines does not shift with temperature.

- Broadening of the lines with increasing temperature is less pronounced than usually observed.
**Ho$^{3+}$:Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8**

- **Emission f(T)**

- Bi-sigmoidal behaviour similar to that of the Sm$^{3+}$ doped sample

- This seems to be a characteristic property of LBLM host material and molybdates in general, see F. Baur & T. Jüstel, Aust J Chem 68 (2015) 1727

- $T_{1/2,a} = 260$ K (assigned to CT excitation)

- $T_{1/2,b} = 455$ K (assigned to Ho$^{3+}$ 4f-4f excitation)

- $\lambda_{ex} = 452$ nm

```latex
\text{Emission integral LBLM:Ho}^{3+} \ (1\%)

\text{Double Fermi-Dirac Fit}
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- $T_{1/2,1} = 261$ K

- $T_{1/2,2} = 454$ K

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Er$^{3+}$:Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$

**Emission & Excitation**

- First experiments with LBLM:Er$^{3+}$ powder samples
- Single-phase material was synthesized
- Strong absorption of 4$^f$-4$^f$ transitions was observed

- Potential upconversion in Ho$^{3+}$/Er$^{3+}$ co-doped LBLM will be investigated
Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$ Conclusions

- High-quality, single-phase powder samples of Li$_3$Ba$_2$La$_3$(MoO$_4$)$_8$ doped with Sm$^{3+}$, Ho$^{3+}$ or Er$^{3+}$ were synthesized employing conventional solid state synthesis

- SEM images revealed particles (diameter ~ 5 µm) with a relatively uniform morphology, suitable for sintering towards transparent ceramics

- Strong absorption from the forbidden 4f-4f transition could be observed even in low-doped samples

- 44% EQE was found in the LBLM:Sm$^{3+}$ (2%) sample

- Temperature-dependence of IQE and EQE differ, indicating a decrease in photon escape efficiency at elevated temperatures

- LBLM:Ho$^{3+}$ exhibits very fast decay (low figure µs-range), very low dopant concentrations will be required to increase decay times

- LBLM:Er$^{3+}$ powder samples were successfully prepared and first measurements of the optical properties conducted
THANK YOU FOR YOUR ATTENTION