Poster

Second-harmonic generation effect enhanced by Li^+ substitution for Na^+ in $(Li_xNa_{6-x})Mo_9O_{30}$

S.-H. Park[1], V. Vuksan[1], Y. Cheng[1], A. Buyan Arivjikh[1], M. Kurashvili[2], K. Gméling[3], L. Szentmiklósi[3]

[1]Section Crystallography, Dept. Earth & Environmental Sciences, Ludwig-Maximilians-Universität München (LMU), 80333 Munich, Germany; [2]Chair for photonic & optoelectronics, Nano-Institut München und Fakultät für Physik, LMU, 80539 Munich, Germany; [3]HUN-REN, Centre for Energy Research, Budapest, 1121, Hungary

sohyun.park@lmu.de

This study case deals with structure-related linear and non-linear optical properties of a new solid solution series, $Li_1(Li_XNa_{5-X})Mo_9O_{30}$ [1]. Large single crystals grown using the Czochralski were oriented on a X-ray Laue camera and cut into plates parallel to the crystallographic main directions to determine non-linear optical (NLO) coefficients d_{ij} by means of the rotational Maker fringe technique (MF) [2]. The same plate samples were used to record the transmission in UV/Vis optical spectroscopy. A combined use of X-ray single crystal diffraction (XSD) with neutron activation analysis (NAA) [3] could deliver accurate structural and compositional contents of three solid-solution compounds with the Li substitution X = 0, 1.2, and 2.8. These new compounds crystallize in their common polar space group ***F***dd2, showing static disorder of Li over three independent Na sites (Fig. 1a). Structure refinements revealed a preference for the Li substitution within a less distorted octahedron, Na1O6. Overall, max. 76% Na could be replaced by Li. Direction-dependent transmission and reflective indices confirmed their reciprocally proportional values [4]. The crystal of a Li-rich member, $Li_1(Li_{2.8}Na_{2.2})Mo_9O_{30}$ exhibits a high transmission but with weak absorption of the second-harmonic generation (SHG) light (455-460 nm), as observed in UV/Vis spectra. This explains the suppressed SHG intensity for X = 2.8 compared to that for X= 1.2 (Fig. 1b). Relative magnitudes NLO values agree with d_{3j} for X=1.2 at largest, as well (Fig. 1c and d). This could be proved by the same order of NLO coefficients resulted from DFT calculations, i.e., d_{3j} (X=1.2) > d_{3j} (X=2.8) > d_{3j} (X=0) [1]. So far investigated, $Li_1(Li_{1.2}Na_{3.8})Mo_9O_{30}$ is the best SHG compound among the title solid-solution members, as meeting an optimal compromise for both high transmission and low absorption in the SHG wavelength region. At the meeting ECM 2024, we present details of structural and optical behaviors of this material system highly sensitive to Li^+ replacing Na^+.

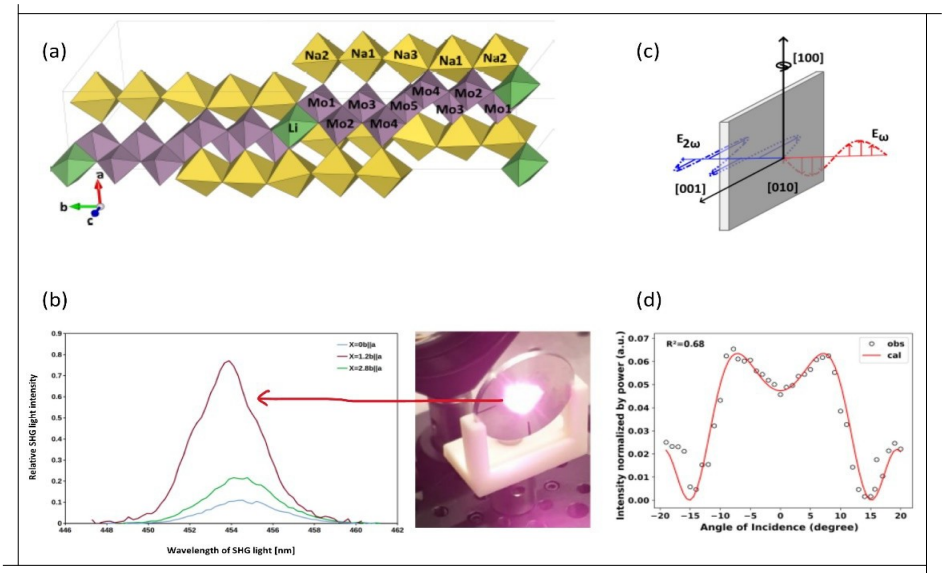

Figure 1. (a) A part of the structure of the endmember $Li_1Na_5Mo_9O_{30}$ shows slabs of 5er NaO_6 octahedra where Li can replace Na to make a solid solution series; (b) The SHG intensity increases when Na is substituted by Li but at largest with X = 1.2 rather than X=2.8; (c) A plate single crystal sample is oriented with respect to the polarization of both fundamental (E_ω) and the SHG beam ($E_{2\omega}$) to probe MF, e.g., X=0b‖a to determine a relative NLO coefficient, d_{31}. (d) The corresponding MF data and least-squares fit.

[1] V. Z. Vuksan, Y. Cheng, S.-H. Park, E. Sturm, M.Kurashvili, J. Feldmann, K. Gméling, L. Szentmiklósi, *Submitted.*

[2] I. Shoji, T. Kondo, A. Kitamoto, M. Shirane, R. Ito (1997). *J. Opt. Soc. Am.* **B14** (9), 2268.

[3] László Szentmiklósi, Dénes Párkányi, Ibolya Sziklai-László (2016). *J. Radioanal. Nucl. Chem.* **309**, 91.

[4] W. Zhang, H. Yu, J. Cantwell, H. Wu, K. Poeppelmeier, S. Ha-lasyamani (2016). Chem. Mater. **28** (12), 4483.