Local Structural Distortion as a New Design Strategy for High-Performance Nonlinear Optical Materials

A new tungsten bronze compound synthesized with a new molecular design strategy exhibits a strong SHG response, 39 times that of KDP.

Nonlinear optical (NLO) materials play a crucial role in modern laser technology by effectively expanding the spectral range of a laser; they have many important applications in photolithography, spectral analysis, tissue imaging, environmental monitoring, *etc*. Up to now, the strategies for molecular design of NLO materials have focused on the introduction of NLO-active molecular units with a large polarization, *e.g*., second-order Jahn-Teller distorted octahedra (Ti^{4+}, Nb^{5+}, Ta^{5+}, Te^{6+}, W^{6+}, Mo^{6+}, *etc*.), stereochemically active lone-pair cations (Pb^{2+}, Bi^{3+}, I^{5+}, Te^{4+}, *etc*.), π-orbital anionic groups (BO_3, B_3O_6, CO_3, NO_3, *etc*.), and d^{10} metal cations with a polar displacement, into non-centrosymmetric crystal structures.[1] Kun Lin (University of Science and Technology Beijing, China) and his coworkers recently proposed that a local structural distortion induced with vacancies, apart from the NLO-active units, can also be employed to improve the NLO effect in solids. Accordingly, a new tungsten bronze (TB) oxide, $Pb_2(Pb_{0.15}Li_{0.7}\square_{0.15})Nb_5O_{15}$, PLN (□ representing vacancies), has been successfully designed and prepared, which exhibits a strong second-harmonic generation (SHG) response, 39 times that of KH_2PO_4 (KDP)(**Figs. 1(a) and 1(b)**).

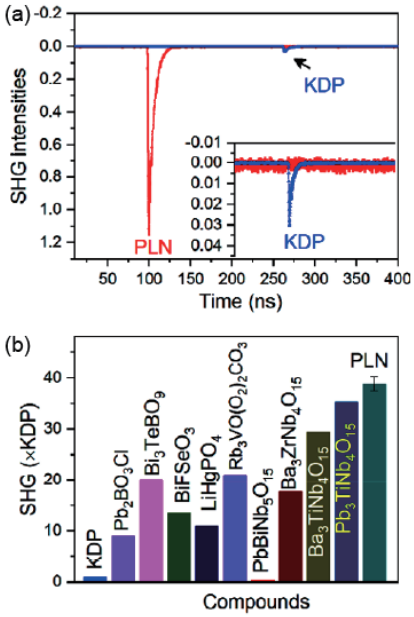

Fig. 1: (a) Experimental oscilloscope traces of SHG signals using the method of Kurtz and Perry with a 1064-nm Q-switched laser. (b) Comparison of powder SHG response. [Reproduced from Ref. 1]

Multiple experimental probes were employed to study both average and local structures of PLN. To study the local structural distortion in PLN, Lin and his coworkers applied an atomic-level scanning transmission electron microscope (STEM) and neutron total scattering (Spallation Neutron Source, Oak Ridge National Laboratory). The obtained local structural information was compared with the averaged structure deduced from single-crystal X-ray diffraction, synchrotron radiation X-ray powder diffraction (BL44B2, SPring-8) and high-resolution neutron powder diffraction (BT-1, National Institute of Standards, and **ECHIDNA** at Australian Nuclear Science and Technology Organisation (ANSTO)). The structural model of PLN, obtained from NPD and XRD, exhibits a strong site preference of the vacancy. The vacancies are distributed in quadrangular A1 tunnels surrounded by four columns of corner-sharing NbO_6 octahedra, of which the Pb sites in A2 tunnels are fully occupied. A semi-quantitative analysis of the TEM data led to the same conclusion. Lin and coworkers also observed that, in the nPDF, the signal associated with the Nb–O bond length inside the NbO_6 octahedra in PLN is significantly broadened. This effect indicates that the second-order Jahn-Teller-distorted NbO_6 octahedra have a larger distortion on a local scale, confirming the observations from the STEM.

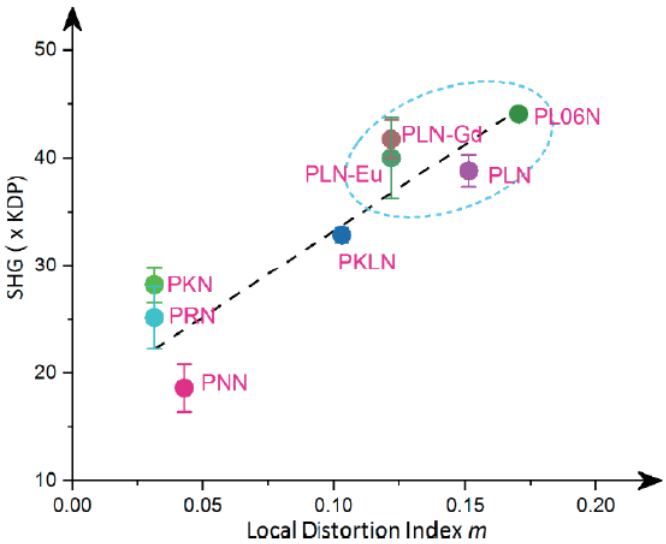

Fig. 2: SHG response versus geometric local distortion index *m* for a series of lead-niobate-based TB oxides. PL06N: $Pb_{2.15}Li_{0.6}Nb_5O_{15}$, PLN-Re: $Pb2Li_{0.94}Re_{0.02}Nb_5O_{15}$ (Re = Eu, Gd), PKLN: $Pb_2K_{0.5}Li_{0.5}Nb_5O_{15}$, PKN: $Pb_2KNb_5O_{15}$, PNN: $Pb_2NaNb_5O_{15}$, PRN: $Pb_2RbNb_5O_{15}$. The dashed line serves for visual guidance; the dashed circle indicates the A-site with vacancies. [Reproduced from Ref. 1]

To demonstrate further the feasibility of the proposed design strategy, Lin and his coworkers introduced the local structural distortions on cross-substituting the A-site atoms in the TB structure and discovered a series of new compounds

with nominal composition $Pb_2(Pb,Li,Na,K,Rb,Re)_{1-x}Nb_5O_{15}$ ($0 \leq x \leq 0.15$, Re = rare earth). Interestingly, many of these compounds also exhibit a large SHG response. These workers proposed a new parameter, called local distortion index *m*, to evaluate the degree of local distortion of these compounds. Please refer to the Supporting Information of Ref. 1 for the definition of local distortion index *m*. **Figure 2** shows the distribution of the SHG response and local distortion index *m* of several NLO materials. The SHG response evidently tends to be strengthened with the enhancement of local distortions.

In summary, the analysis of the local structure unveiled that the structural vacancies at the A1-site strengthen the local distortion and local dipole moments of nearby NbO_6 octahedra and significantly improve the NLO effect. Lin's work is a perspective for the search and design of new materials with an effective NLO performance. (Reported by Chin-Wei Wang)

This report features the work of Kun Lin and his collaborators published in J. Am. Chem. Soc. ***142****, 7480 (2020).*

ANSTO ECHIDNA – High-resolution Powder Diffractometer

- NPD, XRD, Total Scattering
- Materials Science, Chemistry

Reference

1. K. Lin, P. Gong, S. Chu, Q. Li, Z. Lin, H. Wu, Q. Wang, J. Wang, M. J. Kim, K. Kato, C.-W. Wang, X. Liu, Q. Huang, J. Chen, H. Zhu, J. Deng, X. Xing, J. Am. Chem. Soc. **142**, 7480 (2020).

Magnetic Frustration Induces Liquid-Like Short-Range Ordering in Cubic $Mn_{1.5}Cr_{1.5}O_4$

Short-range magnetic correlation manifested by the liquid-like structure factor is observed at temperatures well above T_N in the title compound.

Neutron diffraction is a powerful tool to study magnetic phenomena. It is the best method to determine the magnetic structure and can detect the short-range magnetic correlation between magnetic spins. It is known that competing antiferromagnetic interactions among the magnetic spins on a regular lattice could lead to geometrically magnetic frustration, resulting in the absence of long-range magnetic order or extremely low ordering temperatures. In such systems, the diffuse scattering and unconventional spin dynamics could be observed in a neutron-scattering experiment. Spinel compounds of formula AB_2O_4 have been studied for a long time. The B-site (16*b* of space group *F d* -3 *m*) cations form a regular corner-sharing tetrahedral network, which is potentially geometrically frustrated. Hsiung Chou (National Sun Yat-sen University) and his coworkers maintain a great interest in spinel compounds and recently conducted the powder neutron experiments on $Mn_{1.5}Cr_{1.5}O_4$, employing both high-resolution diffractometer **ECHIDNA** and high-intensity diffractometer **WOMBAT** of ANSTO.

This work determined the cation distribution and magnetic structure of $Mn_{1.5}Cr_{1.5}O_4$, using the high-resolution NPD data (**Fig. 1(a) and 1(b)**). The magnetic structure is collinear ferrimagnetic; the uncompensated A- and B-site sublattice produces a net magnetization. The magnetic order parameter obtained from neutron diffraction (**Fig. 1(a)**) matches satisfactorily with the spontaneous magnetization for the transition temperature and the critical exponent (**Fig. 1(a)**), but the deviation from the Curie-Weiss behavior occurs at a much higher temperature, $T' \sim 170$ K, indicating that diffuse scattering might be detectable in neutron-diffraction experiments. Detailed temperature-dependent measurements were hence conducted employing HIPD WOMBAT (**Fig. 2(a)**). **Figure 2(a)** shows that modulation of the background intensities develops below T' before it eventually collapses onto the magnetic Bragg reflections at T_N. The diffuse magnetic scattering weakens but continues to co-exist with the ferrimagnetic phase below T_N. The difference between the diffraction patterns collected at 163 K and 63 K clearly reveals the modulation (**Fig. 2(b)**). Because of the *Q* dependence of the instrument resolution, the oscillation at higher *q* is smeared out and becomes shallower, but the oscillation persists. Chou suggested that the liquid-like short-range order develops because of the presence of magnetic frustration in the system.

This observation of diffuse scattering above the magnetic-ordering temperature is neither the first time reported nor a rare case. For example, magnetic diffuse scattering of the textbook example, MnO, was reported in the 1940s.[2] The broad diffuse