Discovering hidden order in disordered crystals

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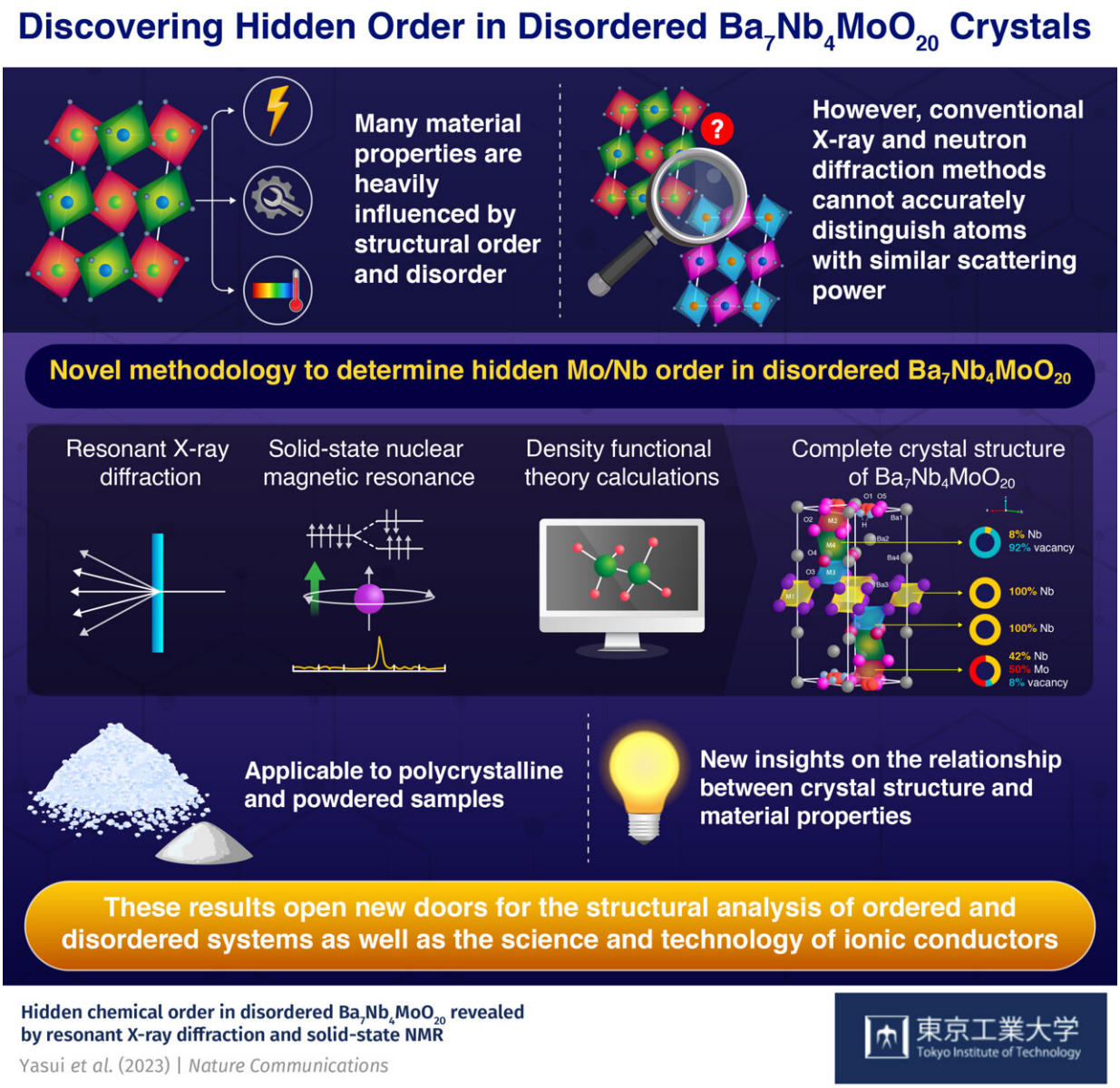

Credit: Professor Masatomo Yashima of Tokyo Institute of Technology

Researchers at Tokyo Tech have discovered hidden chemical order of the Mo and Nb atoms in disordered $Ba_7Nb_4MoO_{20}$, by combining state-of-the-art techniques, including resonant X-ray diffraction and solid-state nuclear magnetic resonance. This study provides valuable insights into how a material's properties, such as ionic conduction, can be heavily influenced by its hidden chemical order. These results would stimulate significant advances in materials science and engineering.

Determining the precise structure of a crystalline solid is a challenging endeavor. Materials properties such as ion conduction and chemical stability, are heavily influenced by the chemical (occupational) order and disorder. However, the techniques that scientists typically use to elucidate unknown crystal structures suffer from serious limitations.

For instance, X-ray and neutron diffraction methods are powerful techniques to reveal the atomic positions and arrangement in the crystal lattice. However, they may not be adequate for distinguishing different atomic species with similar X-ray scattering factors and similar neutron scattering lengths.

To tackle this issue, a research team led by Professor Masatomo Yashima of Tokyo Institute of Technology (Tokyo Tech) in Japan sought to develop a novel and more powerful approach to analyze the order and disorder in crystals. They combined four different techniques to analyze the crystal structure of an important ionic conductor, $Ba_7Nb_4MoO_{20}$.

"We chose $Ba_7Nb_4MoO_{20}$ as $Ba_7Nb_4MoO_{20}$-based oxides and related compounds are a class of emerging materials with interesting properties such as high ionic conduction and high chemical stability," explains

Prof. Yashima. "However, given that both the Mo^{6+} and Nb^{5+} cations have similar scattering powers, all structural analyses of $Ba_7Nb_4MoO_{20}$ until now have been performed assuming complete Mo/Nb disorder."

As described in their recent paper published in *Nature Communications*, the researchers used an approach that combined two experimental techniques, resonant X-ray diffraction (RXRD) and solid-state nuclear magnetic resonance (NMR) aided by computational calculations based on density functional theory (DFT). The NMR provided direct experimental evidence that the Mo atoms occupy only the crystallographic *M2* site in $Ba_7Nb_4MoO_{20}$, indicating the chemical order of Mo atoms.

Next, the researchers used RXRD to quantify the occupancy factors of Mo and Nb atoms. They found that the occupancy factor of Mo atoms was 0.5 at the *M2* site but zero at all other sites. Interestingly, the *M2* site is close to the oxide-ion conducting, oxygen-deficient layer of $Ba_7Nb_4MoO_{20}$. This suggests that the Mo atoms at the *M2* site have key role in the high ion conduction of $Ba_7Nb_4MoO_{20}$. Furthermore, DFT calculations indicated that the Mo ordering stabilizes Mo excess composition exhibiting high ionic conductivity. Positions, occupancy, and atomic displacements of protons and oxide ions were also determined by neutron diffraction.

"Our results demonstrate that the Mo order affects the material properties of $Ba_7Nb_4MoO_{20}$," says Prof. Yashima. "In this regard, our work represents a major advance in our understanding of the correlation between the crystal structure and the material properties of ionic conductors." Further, in contrast to single-crystal X-ray and neutron diffraction, the proposed approach can even be extended to other polycrystalline and powdered samples.

Overall, the methodology presented in this study can open up new

avenues for an in-depth analysis of chemical order/disorder in materials. In turn, this could lead to the development of physics, chemistry, and materials science and technology.

More information: Yuta Yasui et al, Hidden chemical order in disordered Ba7Nb4MoO20 revealed by resonant X-ray diffraction and solid-state NMR, *Nature Communications* (2023). DOI: 10.1038/s41467-023-37802-4

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