Identifying an Efficient, Thermally Robust Inorganic Phosphor *via* Machine Learning

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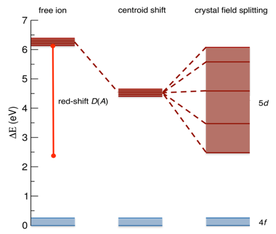
Introduction

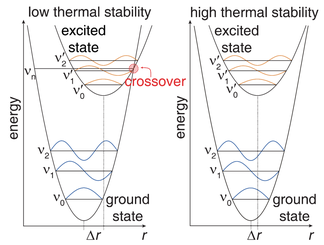
Inorganic phosphors are composed of a host crystal structure that are substituted with a rare-earth luminescent center, such as Ce^{3+} and Eu^{2+}.

When an rare-earth ion is placed in a host crystal, two major effects dictate the photoluminescent properties: the centroid shift and crystal field splitting. Overall these effects lead to a decrease in the energy difference between the 5*d* and 4*f* energy levels.

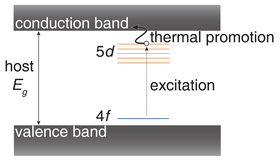


Two main non-radiative pathways to diminish the photoluminescent quantum yield (PLQY, Φ).

1. Phonon-assisted relaxation



2. Photoionization



The search for new phosphors has recently centered on identifying inorganic compounds that form rigid crystal structures, as probed by their Debye temperature (Θ_D). In addition to a high Θ_D, these crystal structures also require a wide electronic band gap (E_g) for the rare-earth ion to down-convert the absorbed photons to the visible light region.

Machine-learning Debye Temperature

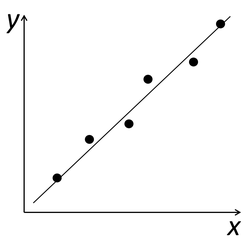
The machine-learning model was constructed based on a Support Vector Machine regression (SVR) analysis using PLS_Toolbox within the MATLAB® environment.

Training set is composed of 2610 compounds, whose Θ_D were calculated from its elastic constants.

$$v_L = \left(\frac{B + \frac{4G}{3}}{\rho}\right)^{\frac{1}{2}} \text{ and } v_T = \left(\frac{G}{\rho}\right)^{\frac{1}{2}}$$

$$v_m = \left[\frac{1}{3}\left(\frac{2}{{v_T}^3} + \frac{1}{{v_L}^3}\right)\right]^{-\frac{1}{3}}$$

$$\Theta_D = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A \rho}{M}\right)\right]^{\frac{1}{3}} v_m$$

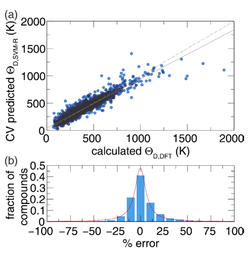


10-fold venetian blinds cross-validation

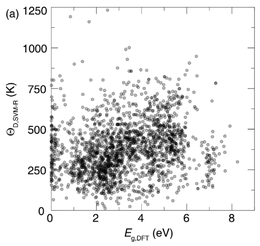
The model was validated with a 10-fold venetian blinds cross-validation.

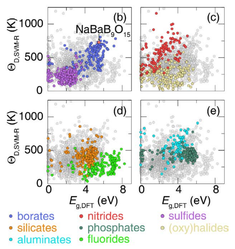
RMSECV = 60.0 K (within 4% of the ranges covered for each Θ_D)

75% of predictions are within ≈15% error.



Plotting Θ_D as a function of E_g





A sorting diagram helps to optimize Θ_D and E_g.

The Θ_D of 2071 compounds was predicted with the SVR model.

The E_g were calculated by DFT and exacted from the Material Project (MP).

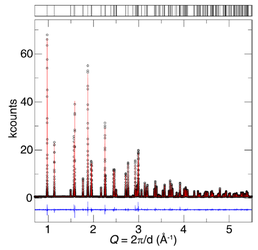
Compounds can be visualized by its compositional categories.

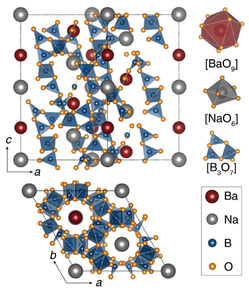
$NaBaB_9O_{15}$ shows outstanding predicted Θ_D (729K) and DFT calculated E_g (5.5 eV).

Synthesis and Structure

Polycrystalline samples of $NaBa_{1-x}Eu_xB_9O_{15}$ were made by grinding stoichiometric amounts of $NaHCO_3$, $BaCO_3$, H_3BO_3 and Eu_2O_3.

600°C for 2 h in air —grind→ 700°C for 15 h under flowing 5% H_2/95% N_2 gas —grind→ 750°C for 5 h under flowing 5% H_2/95% N_2 gas —grind→ Sieved (-325 mesh)





High resolution synchrotron X-ray powder diffraction was done using the 11-BM at the APS, Argonne National Laboratory. Rietveld refinements confirm phase purity and are refined to obtain the crystal structure.

$NaBaB_9O_{15}$ adopts the non-centrosymmetric trigonal space group $R3c$ (no. 161).

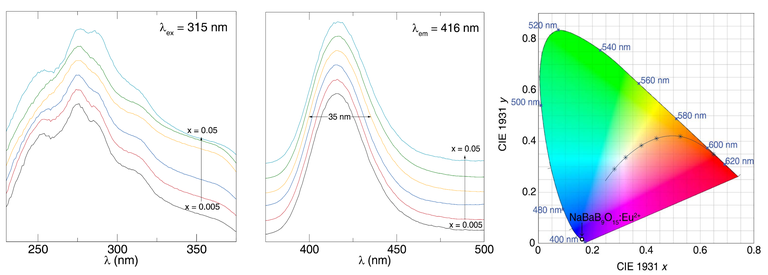
The arrangement of the $[B_3O_7]^{5-}$ units generates large tunnels along the [001] direction.

Optical Properties

When excited by 315 nm, $NaBa_{1-x}Eu_xB_9O_{15}$ has a peak emission at 416 nm.

The emission is a bright, deep-violet and has a very narrow full width at half maximum (*FWHM*) .

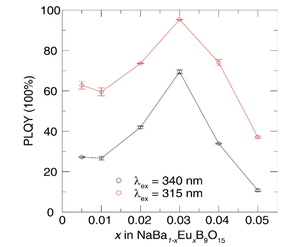
In fact, $NaBaB_9O_{15}$:Eu^{2+} is the narrowest blue-emitting phosphor identified to date.

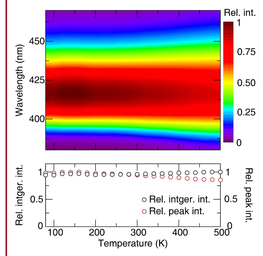


Measured Φ of $NaBaB_9O_{15}$ substituted with varying concentrations of the rare-earth Eu^{2+} shows that it has higher Φ when excited at 315 nm.

3 mol% Eu^{2+} concentration has the highest Φ = 95% when excited at 315 nm.

Increasing the Eu^{2+} concentration causes an abrupt drop in Φ due to quenching.



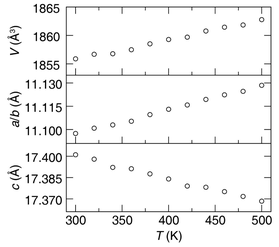


The emission spectrum broadness of $NaBaB_9O_{15}$:3%Eu increases slightly with increasing temperature.

The integrated area of the emission peak shows zero thermal quenching.

The loss of emission intensity is accompanied by a widening of the FWHM of the emission spectrum.

Thermal Expansion Properties



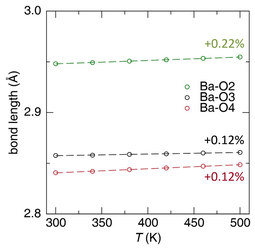
The unit cell parameters were obtained with Le Bail refinements on laboratory X-ray diffraction data.

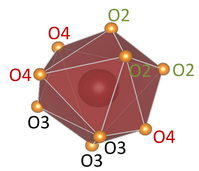
The unit cell volume, *a* and *b* length increase as temperature going higher.

However, *c* length shows negative thermal quenching phenomenon.

Three different crystallographic sites exist for oxygen in $[BaO_9]$ or $[EuO_9]$ polyhedra.

Bond lengths between Ba^{2+}/Eu^{2+} and oxygens show only tiny increasing, which could give rise to the excellent thermal behaviors.





Conclusions

Machine learning method is used to successfully predict Debye temperature.

The combination of machine learning and computation has the ability to discriminate potential high Φ inorganic phosphor hosts a priori .

Substituting Eu into $NaBaB_9O_{15}$ produced a viable near-UV excited deep violet phosphor.

$NaBaB_9O_{15}$:Eu^{2+} possesses a quantum yield of 95% and shows excellent thermal stability which could be attributed to its negative thermal expansion property.

References

1. N. C. George, K. A. Denault, and R. Seshadri, *Annu. Rev. Mater. Res.*, 43, 481-501 (2013).

2. J. Brgoch, S. P. DenBaars, and R. Seshadri, *J. Phys. Chem. C*, 117, 17955-17959 (2013).

3. S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma, and Q. Y. Zhang, *Mater. Sci. Eng.*, 71, 1-34 (2010).

4. Y. Zhuo, A. Mansouri Tehrani, A. O. Oliynyk, A. C. Duke and J. Brgoch, *Nat. Commun.*, 9, 4377 (2018).

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