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Crystal growth, structure and optical properties of a new acentric crystal $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ with short UV absorption edge

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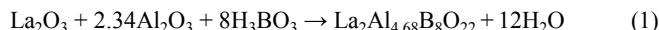
A new acentric borate $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ was synthesized by the solid state reaction and the single crystals were successfully grown with B_2O_3 -LiF flux by the top-seeded solution growth method. The structure of title crystal features two-dimensional layered structure composed of $[\text{BO}_4]$ and $[\text{AlO}_5]$ groups that are bridged by skeletal structure of $[\text{LaO}_6]$ polyhedron along the c axis. Optical properties including the transmittance spectrum, IR spectroscopy and refractive indices have been systematically evaluated for the first time.

Rare earth aluminium borates was firstly discovered by Ballman in 1962 and have been focused on for decades as prospective laser and nonlinear optical (NLO) materials due to their excellent properties including wide transparency, high chemical, thermal and mechanical stability, and large laser damage threshold.^{2,3} Usually the anhydrous rare earth aluminium borates can be divided into two large families: $\text{ReAl}_3(\text{BO}_3)_4$ ($\text{Re}=\text{Nd-Lu}$)⁴⁻⁹ with triangular BO_3 units and $\text{ReAl}_{1.67+0.67x}(\text{B}_4\text{O}_{10})\text{O}_x$ ($x \leq 1$, $\text{Re}=\text{La, Ce, Nd, Pr}$) with BO_4 tetrahedral groups.¹⁰⁻¹⁴ Among these rare earth ions, Y or La containing compounds have short absorption edges down to the UV or deep-UV region which is favourable as NLO crystals. For example, the cutoff wavelength of $\text{YAl}_3(\text{BO}_3)_4$ is located at 170nm if the extrinsic absorption is overcome.⁸

In the La_2O_3 - Al_2O_3 - B_2O_3 system $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$ was first reported by P. Yang et al in 1998.¹³ Its structure is determined by single crystal X-ray diffraction in the hexagonal space group $P\bar{6}2m$ with cell parameters $a = 4.606(1) \text{ \AA}$, $c = 9.348(2) \text{ \AA}$ and $V = 171.75 \text{ \AA}^3$. Then Capitelli, F. reported a detailed crystal chemical study of this compound by means of single crystal X-Ray diffractometer and revised its formula to be $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ with cell parameters $a = 4.61700(10) \text{ \AA}$, $c = 9.3640(3) \text{ \AA}$ and $V = 172.86 \text{ \AA}^3$.¹² We believe that $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$ and $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ are actually the same compound. The crystal structure is noncentrosymmetry and may be used as a new NLO crystal, but no work has focused on the crystal growth and its optical properties have not been understood yet. To realize some of these applications, high quality single crystals are indispensable. It inspired us to further investigate the crystal growth and related optical properties. In this work, we are

intended to grow bulk $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ crystals for optical characterization. During the crystal growth of $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$, a new phase was found and the structure was analysed to be $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$. Its crystal growth, structure and thermal behaviour as well as the linear and nonlinear optical properties are presented for the first time.

Polycrystalline $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ was synthesized by conventional solid state methods with a stoichiometric mixture of La_2O_3 , Al_2O_3 and H_3BO_3 from commercial sources. The chemical equation can be expressed as follows:



$\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ powder has been synthesized which was proved to be pure phase by Powder X-ray diffraction as shown in Fig. 1. At first glance, the diffraction pattern is close to that of $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ except for a small additional peak locating at 52.5° . By carefully checking the PXRD pattern, a large amount of peaks split into two sub-peaks in a range of 35° to 80° for the new phase as shown in Fig. 1.

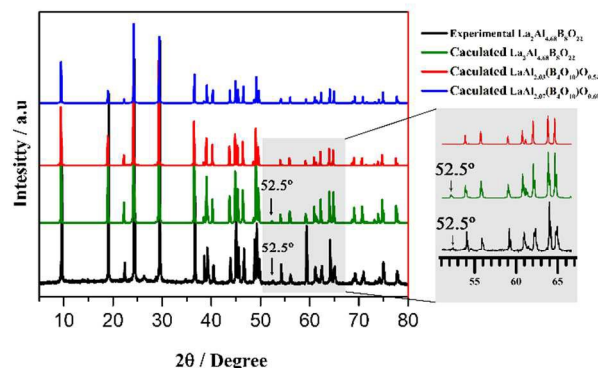


Fig. 1 Comparison powder X-ray diffraction patterns of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ with simulated $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$, $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$, and $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$.

Differential scanning calorimetric (DSC) measurements were carried out with crystal powders. The DSC curve shows a sharp

endothermic peak at about 1150 °C in the heating curve, but no exothermic peak was observed in the cooling curve (Fig.2). The TGA curve demonstrates that the compound remains stable until 1124.4 °C without weight loss. After melting, the remains were characterized by powder XRD which shows different to that of the original compound powders (see Fig.S1). The result demonstrates that $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ is an incongruent melting compound. Therefore, large crystals of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ should be grown using flux method below the decomposition temperature.

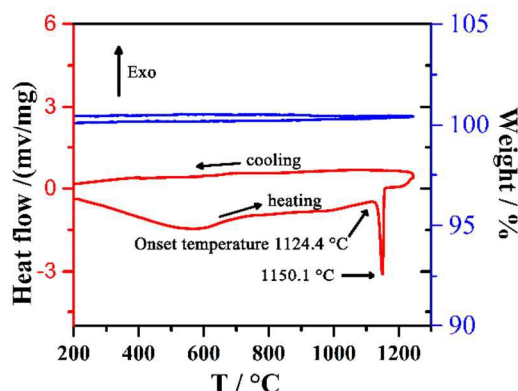


Fig. 2 DSC curves for $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$.

According to our knowledge, there are two flux systems that can grow $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ crystals, the $\text{K}_2\text{Mo}_3\text{O}_{10}$ flux system and the $\text{PbF}_2\text{-PbO}$ flux system.^{12, 13} Nevertheless, our earlier study of YAB revealed that the incorporation of Mo or Pb ions into the crystal lattice will cause an extrinsic absorption in the UV region.⁸ In order to circumvent this problem, Mo or Pb ions-free flux systems are desired. We have developed several flux systems including $\text{Li}_2\text{CO}_3\text{-B}_2\text{O}_3$, and $\text{LiF-B}_2\text{O}_3$. By using the former flux, the solution shows a serious volatilization and the as-grown crystal exhibits a serious layering tendency along the c-axis (Fig.3a). These problems have been overcome by changing Li_2CO_3 with LiF.

Finally, centimeter-grade crystal of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ up to $55 \times 25 \times 13 \text{ mm}^3$ with a weight of 49.74 g was obtained by utilizing the $\text{LiF-B}_2\text{O}_3$ flux by the TSSG method, as shown in Fig.3b. The crystals were stable in air for months and not soluble in hot hydrochloric acid or nitric acid, indicating that $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ is nonhygroscopic and high chemical stability.

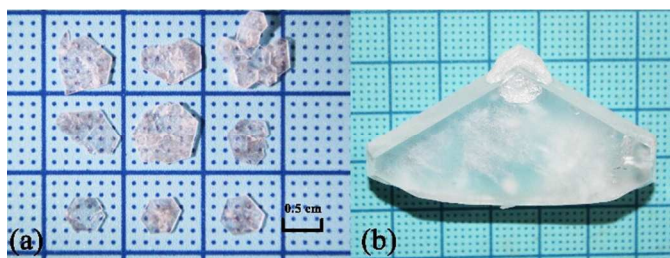


Fig.3 Plate-like $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ crystal (a); Bulk $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ crystal with the dimensions of $55 \times 25 \times 13 \text{ mm}^3$ (b)

$\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ crystallizes in the hexagonal space group $P\bar{6}2m$ with units cell parameters of $a = 4.6149(7) \text{ \AA}$, $c = 18.720(4) \text{ \AA}$ and $z=1$. During the structure refinement, all atoms are well resolved except for Al1 atoms with the occupancy of 0.78. In the structure,

both B1 and B2 atoms are surrounded by four O atoms to form distorted tetrahedra. The B–O bond lengths at B(1) site vary from 1.442(9) to 1.490(3) Å and O–B(1)–O bond angles from 114.7(2)° to 129.31(12)°, while the B–O bond lengths at B(2) site vary from 1.410(9) to 1.491(3) Å and O–B(2)–O bond angles from 114.29(19)° to 129.58(12)°. The Al atom are in distorted square pyramidal coordination environments with bond distances of 1.799(5) to 1.851(3) Å. The La(1) and La(2) atoms coordinated to six O atoms to form trigonal prismatic configurations, respectively. $[\text{BO}_4]$ groups share corners to form a net parallel to the ab plane, and the $[\text{AlO}_5]$ and $[\text{LaO}_6]$ polyhedral share corners and edges. The corner-sharing $[\text{BO}_4]$ tetrahedral groups pile up with each other in the alignment toward the c-axis that characterizes a feature of layer stacking (Fig.4a). In a general manner the crystal structure of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ can be described as a layer-type structure, since there is alternate stacking along the c-axis of: B_1O_4 ($z = 0.11$); AlO_5 ($z = 0.25$); B_2O_4 ($z = 0.39$); LaO_6 and La_2O_6 on the mirror plane at $z = 0$ and $1/2$ (Fig. 4a). Within this description, the $[\text{BO}_4]$ tetrahedra are arranged in rows running along the c-axis and they could be projected on the C positions of the compact packing (Fig. 4b). Relevant crystallographic data and details of the experimental conditions were summarized in Table S1. Selected bond distances, bond angles and atomic coordinates are listed in Tables S2-3.

The structures of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ and $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ viewed along the [001] and [210] directions are presented in Fig.4a, respectively. When we doubling cell $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ in the c, there is a slight difference between $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ and $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ structures by only rotating the $[\text{BO}_4]$ group in the a–b plane, thus it is difficult to separate these two structures from the images viewed along [210]. After a detailed examination, we directly observed two kinds of $[\text{BO}_4]$ groups in $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ along the [001] orientation, showing the torsion angle about 28.5°.

As shown in Fig.1, the PXRD pattern of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ is compared with the calculated one derived from the single-crystal data, which shows good agreement. For $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ and the theoretical simulation from the single-crystal crystallographic data, there appears a small peak locating at 52.5° that cannot be indexed by the $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ or $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$. Thus it is believed that the structure of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ is more convincing.

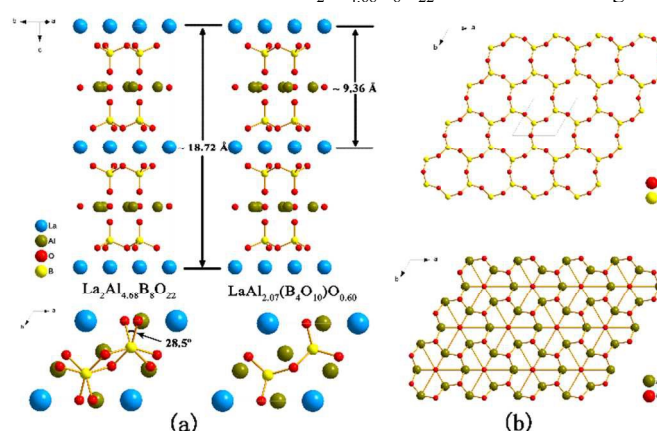


Fig.4 (a) Structures of the $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ (left) and the $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ (right) along [210] and [001]. (b) Repetition of B_6O_{18} rings within $[\text{BO}_4]$ and Al_6O_{16} rings within $[\text{AlO}_5]$ level down c of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$

X-ray rocking curve was measured to evaluate the quality of the as-grown crystal (Fig.S4). The peak is of good shape and the full-width at half-maximum (FWHM) is about 0.0083°, equaling to 29.9 arcsec, which indicates that the crystal is of good crystalline quality.

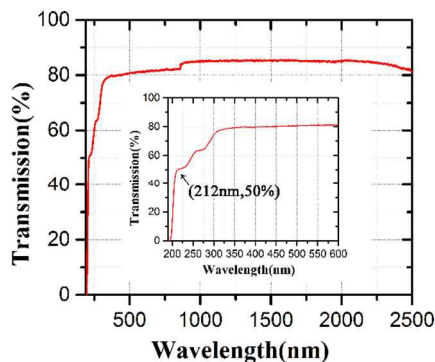


Fig.5 The transmission spectra of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$

Fig.5 shows the transmittance spectrum from 2500 to 193 nm. The transmittance was higher than 70% from 291 to 2500 nm. The UV cut-off wavelength is located at 193 nm indicating that the crystal has a short absorption edge. According to our previous research about YAB, the impurity of Fe^{3+} may be the reason for the absorption in the 212–300 nm region.

Fig.S3 displays the infrared spectrum of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ in a range from 400 to 1500 cm^{-1} . The peaks in the 439.8, 486 and 555.5 cm^{-1} correspond to tetrahedral B–O bending vibrations. The absorptions at about 1006.8 and 1041.6 cm^{-1} correspond to tetrahedral B–O asymmetric stretching vibrations.

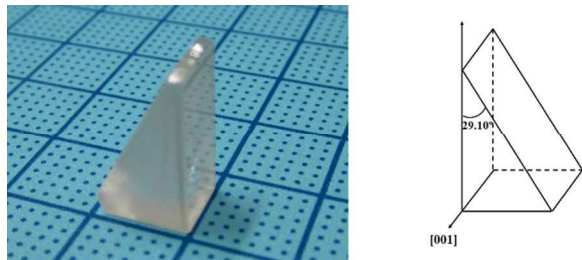


Fig.6 Right angle prism of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ for refractive measurement.

$\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ is a positive uniaxial crystal, which has two corresponding principal refractive indices, n_o and n_e . Thus, only one prism is needed for the measurement. The as-grown crystal was cut into a right-angle prism with the edge at the apex parallel to the crystallographic c-axis, as shown in Fig.6. The apex angle of the prism was 29.10° and the inaccuracy for apex angle was less than 5°. Both measuring faces were well polished with a flatness better than $\lambda/4$. During the measurement, the deviation angles of the extraordinary light at each wavelength were larger than those of the ordinary light. Considering the temperature will influence the refractive indices, the temperature on the crystal was strictly controlled at 24 °C with a fluctuation within 0.2 °C. The measured and calculated results are listed in Table S4.

From these data, the Sellmeier equations are fitted as follows (λ in μm):

$$n_o^2 = 2.94274 + \frac{0.0177226}{\lambda^2 - 0.0151055} - 0.0175182\lambda^2 \quad (2)$$

$$n_e^2 = 2.88469 + \frac{0.0170091}{\lambda^2 - 0.014203} - 0.0140833\lambda^2 \quad (3)$$

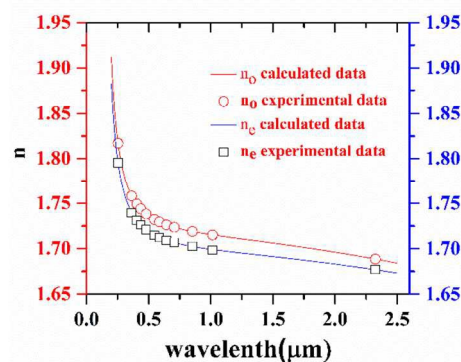


Fig.7 Measured and calculated refractive indices of $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$

Fig.7 shows the measured and calculated refractive indices, from which it can be seen that the theoretical values agree quite well with the experimental data. The birefringence is relatively small due to the $[\text{BO}_4]$ anionic groups and it is not phase-matchable for second harmonic generation.

Large $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ crystals were successfully grown from B_2O_3 -LiF flux by the top-seeded solution growth method for the first time. Its structure is revised compared with previously reported $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$, which is twice along the c-axis than the old one. According to the crystal structure, rare-earth ions can replace the site of La^{3+} in $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ without lattice distortion, owing to the similar ionic radius of the La^{3+} ions and the other rare-earth ions. Due to the specific structure, in which the neighbouring La-positions are separated with a large distance (9.360 Å) by the BO_4 groups, the interactions of the active ions was reduced even at high dopant concentrations. The $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ crystal exhibits a short absorption edge at 193 nm. Refractive indices were measured and the Sellmeier equations were fitted. $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ crystal is proposed to be a good host for doping for laser applications and more work is still carrying on.

Experimental

The $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ polycrystalline samples were obtained by traditional solid-state reaction with a stoichiometric mixture of La_2O_3 (AR, 3.26 g, 0.01 mol), Al_2O_3 (AR, 2.39 g, 0.0234 mol), H_3BO_3 (99.999%, 4.95 g, 0.080 mol), which are from commercial sources. The raw materials were ground thoroughly, packed tightly in platinum crucible, and gradually elevated to 500 °C to ensure the decomposition of H_3BO_3 . Then the mixture was ground adequately and heated gradually to the temperatures of 900, 1000, 1100 °C respectively and kept at this temperature in air for 24 h. To ensure sufficient reaction, the mixture was ground again every time after it was cooled down to room temperature. The powder samples were characterized by powder X-ray diffraction measurement.

The $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$ single crystals were grown by the top-seeded solution growth (TSSG) method using B_2O_3 -LiF as flux. This solution was prepared in a $\Phi 70 \times 70$ mm platinum crucible after melting of a mixture of La_2O_3 (107.52 g, 0.33 mol), H_3BO_3 (370.98 g, 6.00 mol), Al_2O_3 (79.53 g, 0.78 mol), and LiF (25.94 g, 1.00 mol). The mixture was heated in a temperature-programmable electric furnace at 1150 °C for 2 days until the solution became

homogeneous. A three-zone resistance-heated furnace was adopted in order to get an adjustable temperature distribution. The temperature field in the axis direction was shown in Fig.S2, which is 0.8 °C/cm in the solution. A tentative seed was used to test the saturation point. After that, the temperature was cooled to 5 °C above the saturation temperature, which is around 995 °C. Thereafter, the temperature was decreased at a rate of 0.5-1.0 °C/d. During the growth, the seed crystal was rotated at 25-30 rpm with the rotation direction inverted every 2min. The whole growth process took about 60 days with a cooling range of about 40°C. When the growth was completed, it was carefully drawn out of the solution and slowly cooled down to room temperature.

A colourless crystal with dimensions of 0.29 mm × 0.18 mm × 0.16 mm was selected for single-crystal X-ray diffraction. The diffraction data were collected on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromatic Mo K α radiation (λ = 0.71073 Å) at 153 K and a Saturn CCD detector. CrystalClear program was used to record the intensity data and to conduct cell refinement and data reduction. The structure was solved by the direct method with SHELXS-97¹⁵ and refined with SHELXL-97 by the full-matrix least-squares techniques.

The thermal property of La₂Al_{4.68}B₈O₂₂ was investigated by the differential scanning calorimetric (DSC) analysis together with the thermogravimetric analysis (TGA) using a NETZSCH STA 409C/CD thermal analyzer (the DSC was calibrated with Al₂O₃). 28.8 mg powder sample was placed in a platinum crucible and heated from room temperature to 1244 °C at a rate of 10 °C/min in nitrogen atmosphere. The melted residues were examined and analysed by X-ray powder diffraction after the experiments.

The infrared (IR) spectrum was obtained at room temperature on a Bio-Rad FTS-60 FTIR spectrometer from 400 to 4000 cm⁻¹ with a resolution of 1 cm⁻¹. The sample was mixed thoroughly with dried KBr.

The transmittance spectrum was recorded by a Lambda 900 UV-vis-NIR spectrophotometer at room temperature. The X-ray rocking curve was measured using a PANalytical X'Pert PRO MRD X-ray diffractometer. The refractive indices were measured with a Trioptics SpectroMaster UV-VIS-IR refractometer with a high accuracy of 1×10⁻⁵ from TRIOPTICS of Germany. In the experiment, mercury lamp at wavelengths of 0.2537, 0.363, 0.4047, 0.4358, 0.5461, 1.014, and 2.325 μm, Chromium lamp at wavelengths of 0.480 and 0.6438 μm, and Helium lamp at wavelengths of 0.5875 and 0.7065 μm were used.

Notes and references

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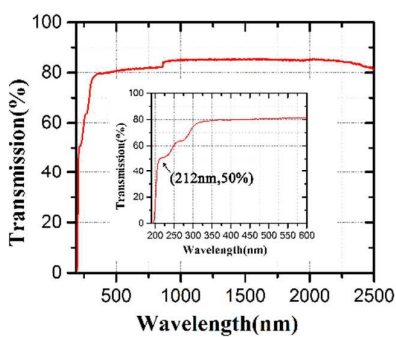
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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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Graphical Abstract



A new acentric borate $\text{La}_2\text{Al}_{4.68}\text{B}_8\text{O}_{22}$, grown by the top seeded solution growth method, shows a short absorption edge at 193 nm.