PAPER

A congruently melting and deep UV nonlinear optical material: Li₃Cs₂B₅O₁₀†

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Single crystals of $Li_3Cs_2B_5O_{10}$ have been synthesized and its structure determined by single-crystal X-ray diffraction. $Li_3Cs_2B_5O_{10}$ crystallizes in the non-centrosymmetric space group $C222_1$ (No. 20). The structure consists of isolated B_5O_{10} groups that are bridged by LiO_n ($n = 4$, 5) and CsO_n ($n = 8$, 10) polyhedra through their vertex oxygen atoms to form an infinite three-dimensional structure. $Li_3Cs_2B_5O_{10}$ melts congruently and exhibits a short-wavelength absorption onset at 175 nm. As-prepared $Li_3Cs_2B_5O_{10}$ is both non-centrosymmetric and phase matchable as supported by second harmonic generation measurements.

Introduction

In the past decades much research interest has been focused on the synthesis and characterization of inorganic compounds for the exploration of nonlinear optical (NLO) materials.[1–17] Great efforts have been directed to new ultraviolet (UV) NLO materials because high-quality all-solid-state UV laser sources play an important role in many advanced technology areas such as ultraviolet lithography and high-resolution photoelectron spectroscopy.[18]

The high-performance crystals β-BaB₂O₄ (BBO),[9a] LiB₃O₅ (LBO),[10a] CsB₃O₅ (CBO)[11a] and CsLiB₆O₁₀ (CLBO)[12a] have extended frequency conversion from the visible to near-UV spectral regions and brought attention to borates for new NLO materials, especially for deep UV NLO materials.[15,16] The success of these materials can be attributed to the unique structural characteristics of boron–oxygen groups with planar BO₃ and tetrahedral BO₄ groups as the basic structures which can form NLO-active anionic groups.[9g] In borates, the B–O covalent bonds have no absorption in the UV region owing to their large covalent bond energy. The borates generally have high damage

thresholds since they are wide band-gap materials.[9f,19] In addition, the alkali metal–oxygen bond is ideal for the transmission of UV light because there are no d–d electron transitions in this range.[9f] Inspired by these principles, we expect that new phases combining borate groups with alkali metal ions will generate a whole new class of UV NLO materials.[20] To this end, a novel deep UV NLO material $Li_3Cs_2B_5O_{10}$ is developed for the first time.

Experimental

Synthesis and crystal growth

Reagents. Li₂CO₃ (98.0%, Tianjin Yaohua Chemical Reagent Co., Ltd), Cs₂CO₃ (99.5%, Institute of Xinjiang metal), and H₃BO₃ (99.5%, Tianjin Baishi Chemical Co., Ltd) as precursors from commercial sources were used as received.

Crystal growth. Small single crystals of $Li_3Cs_2B_5O_{10}$ were grown in air. A mixture of Li₂CO₃, Cs₂CO₃ and H₃BO₃ with a molar ratio of 2 : 1 : 6 was melted at 800 °C in a platinum crucible that was placed into a vertical, programmable temperature furnace and melted at exceptionally fast rates. It was held at that temperature for 24 h, then the furnace was slowly cooled down to 670 °C at a rate of 0.05 °C min⁻¹, and finally cooled to room temperature at a rate of 10 °C min⁻¹. Colorless block crystals were separated from the crucible for structural characterization. Crystals suitable for X-ray diffraction were selected under an optical microscope. A crystal of as-grown $Li_3Cs_2B_5O_{10}$ is shown in Fig. 1a.

Solid-state synthesis. Polycrystalline samples of $Li_3Cs_2B_5O_{10}$ were synthesized by solid-state reactions from mixtures of Li₂CO₃, Cs₂CO₃ and H₃BO₃ as the starting components in a molar ratio of 3 : 2 : 10. The mixture of Li₂CO₃, Cs₂CO₃ and H₃BO₃ was ground thoroughly. The sample was heated to 620 °C

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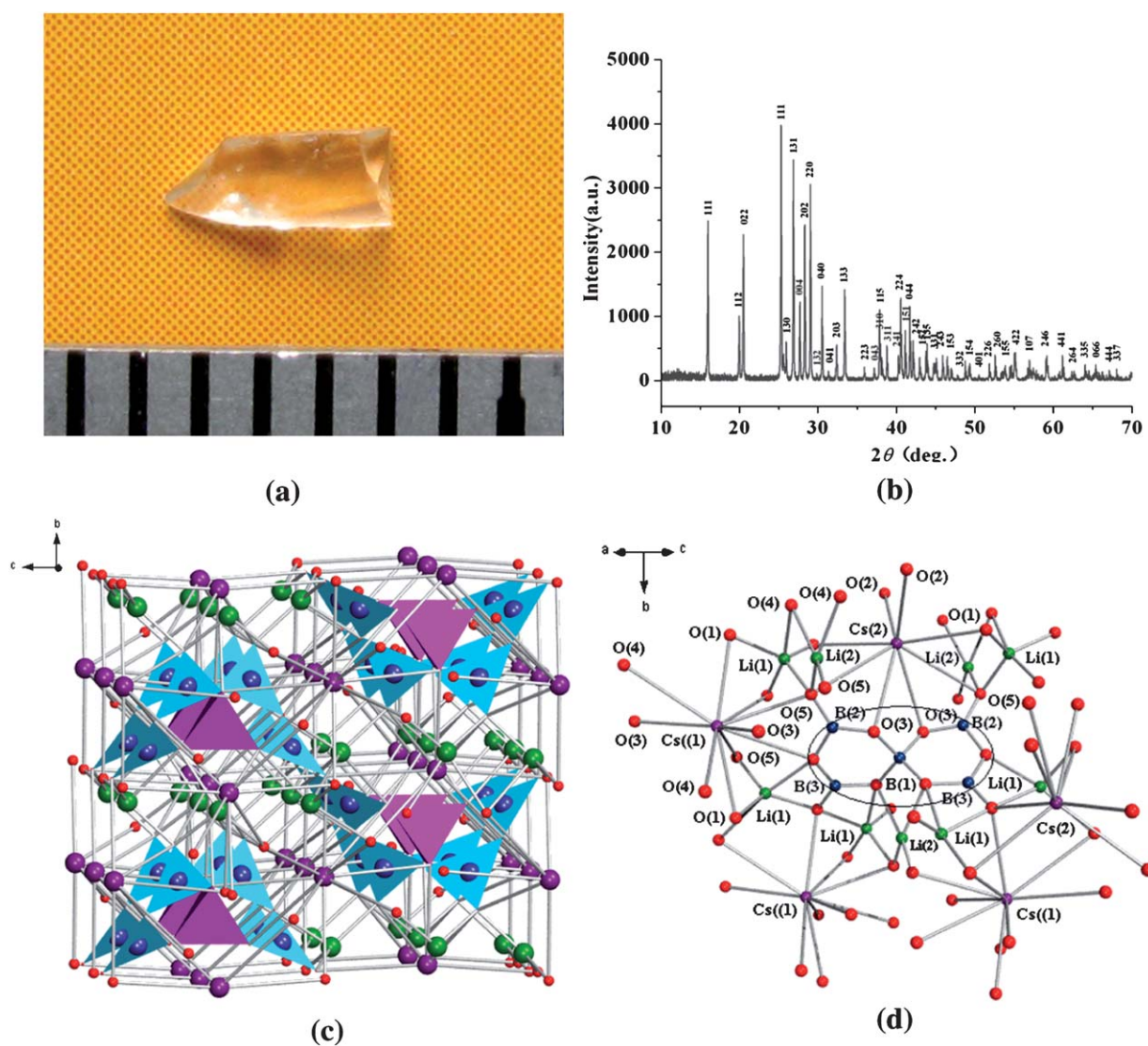**Fig. 1** (a) Photograph of $Li_3Cs_2B_5O_{10}$ crystal. (The minimum scale of the ruler is one millimetre.) (b) Powder XRD pattern of $Li_3Cs_2B_5O_{10}$. (c) The 3D framework of $Li_3Cs_2B_5O_{10}$ along the *a* axis (violet, Cs; green, Li; blue, B; red, O; pink, BO_4 group; blue, BO_3 group). (d) Cation-coordinated environments with the B_5O_{10} group in the ellipse.

slowly and held at this temperature for 48 h with several intermediate grindings. The purity of the sample was checked by powder XRD diffraction (Fig. 1b). The XRD measurements on $Li_3Cs_2B_5O_{10}$ were performed at room temperature on a Bruker D8 ADVANCE X-ray diffractometer with graphite monochromatized Cu-Kα (λ = 1.5418 Å) radiation. The diffraction patterns were taken from 10° to 70° (2θ). The measured XRD powder pattern matches the one simulated from single-crystal X-ray diffraction studies (Figure S1†).

X-Ray measurements

Powder XRD analysis of $Li_3Cs_2B_5O_{10}$ was performed on a Bruker D8 ADVANCE X-ray diffractometer equipped with a diffracted-beam monochromator set for Cu-Kα radiation (λ = 1.5418 Å). The crystal structure of $Li_3Cs_2B_5O_{10}$ was investigated by single-crystal X-ray diffraction on a Rigaku R-axis Spider diffractometer using monochromatic Mo-Kα radiation (λ =

0.71073 Å) at 293(2) K and integrated with a SAINT program.[21] All calculations were performed with programs from the SHELXTL crystallographic software package.[22] The structure was solved by direct methods using SHELXS-97.[23] Final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma (F_o^2)$. The structure was checked for missing symmetry elements with PLATON.[24] Crystal data and structure refinement information are summarized in Table 1. Final atomic coordinates and equivalent displacement parameters are given in Table S1.† Selected bond distances (Å) and angles (deg) for $Li_3Cs_2B_5O_{10}$ are listed in Table S2 in the ESI.†

Differential thermal analysis

Thermal analyses were carried out on a NETZSCH STA 449C instrument at a temperature range of 30–1100 °C with a heating rate of 10 °C min^{-1} in an atmosphere of flowing N_2.

Table 1 Crystal data and structure refinement for $Li_3Cs_2B_5O_{10}$

Empirical formula	$Li_3Cs_2B_5O_{10}$
Formula weight	500.69
Temperature	153(2) K
Crystal system	Orthorhombic
Space group	$C222_1$
Unit cell dimensions	$a = 7.2256(2)$ Å
	$b = 11.6583(4)$ Å
	$c = 12.7817(4)$ Å
Volume	1076.71(6) Å³
Z	4
Density (calculated)	3.0891 g cm⁻³
Absorption coefficient	6.808 mm⁻¹
F(000)	896
Crystal size	0.25 mm × 0.19 mm × 0.11 mm
Index ranges	$-9 \leq h \leq 8, -15 \leq k \leq 15, -16 \leq l \leq 16$
Completeness to theta = 27.49	97.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1184/0/94
Goodness-of-fit on F^2	1.040
Final R indices $[F_0^2 > 2\sigma(F_0^2)]^a$	$R_1 = 0.0246$, w$R_2 = 0.0585$
R indices (all data)^a	$R_1 = 0.0248$, w$R_2 = 0.0587$
Extinction coefficient	0.0037(4)

^{a} $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w\,F_0^4]^{1/2}$ for $F_0^2 > 2\sigma(F_0^2)$.

Elemental analysis

Elemental analysis of $Li_3Cs_2B_5O_{10}$ single crystals was measured by using a VISTA-PRO CCD Simultaneous ICP-OES. The crystal samples were dissolved in nitric acid at the boiling point for 1 h. Anal. calcd for the $Li_3Cs_2B_5O_{10}$: Li, 4.16; Cs, 53.09; B, 10.81; Found: Li, 3.93; Cs, 52.76; B, 10.46%.

Second-order NLO measurements

Powder second-harmonic generation (SHG) tests on $Li_3Cs_2B_5O_{10}$ were carried out by the Kurtz–Perry method.[25] A microcrystalline potassium dihydrogen phosphate (KDP) sample served as the standard. About 100 mg of powder was pressed into a pellet, which was then irradiated with a pulsed IR beam (10 ns and 10 kHz) produced by a Q-switched Nd:YAG laser of wavelength 1064 nm. A 532 nm filter was used to absorb the fundamental and pass the visible light onto a photomultiplier. A combination of a half-wave achromatic retarder and a polarizer was used to control the intensity of the incident power, which was measured with an identical photomultiplier connected to the same high-voltage source. This procedure was then repeated using a standard NLO material, microcrystalline KDP in this case, and the ratio of the second-harmonic intensity outputs was calculated. Because the SHG efficiency has been shown to depend strongly on the particle size,[25] polycrystalline $Li_3Cs_2B_5O_{10}$ was ground and sieved into distinct particle size ranges, <20, 20–38, 38–55, 55–88, 88–105, 105–150, and 150–200 μm. For comparisons, crystalline SiO_2 and KDP samples were also ground and sieved into the same particle size ranges.

UV-VIS-NIR diffuse-reflectance spectroscopy

UV-VIS-NIR diffuse-reflectance of $Li_3Cs_2B_5O_{10}$ crystalline samples was collected with a SolidSpec-3700DUV spectrophotometer using fluororesin as a standard in the wavelength range from 175 to 2600 nm under a N_2 atmosphere.

Results and discussion

Crystal structure

Crystallographic analysis reveals that the structure of the $Li_3Cs_2B_5O_{10}$ crystal belongs to the space group $C222_1$. Two unique lithium atoms, two unique caesium atoms, three unique boron atoms, and five unique oxygen atoms are in the asymmetric unit (Table S2†). The structure exhibits a three-dimensional (3D) network composed of LiO_n ($n = 4, 5$), CsO_n ($n = 8, 10$) distorted polyhedra, and isolated B_5O_{10} units (Fig. 1c). The basic structural unit is a double ring B_5O_{10} consisting of one BO_4 tetrahedron (□) and four BO_3 triangles (Δ) (Fig. 1d), which can be written as $4\Delta1\square{:}{<}2\Delta\square{>}{-}{<}2\Delta\square{>}$ according to the definition given by Burns et al.[6] Such a B_5O_{10} group can be found in a number of polyborates, e.g., $Na_3ZnB_5O_{10}$.[7a,26] The triangularly coordinated boron atoms have B–O distances in the range 1.319(6)–1.413(5) Å [av. = 1.399 Å] and the tetrahedral B atoms have longer B–O distances in the range 1.465(4)–1.474(4) Å [av. = 1.470 Å]. These values are in agreement with other borate compounds reported previously.[17b,17e] The angle between two hexagonal rings is 97.4°, which indicates that two hexagonal rings are almost perpendicular to each other in this unit.

$Cs(1)O_{10}$ and $Cs(2)O_8$ polyhedra are interconnected by shared oxygen atoms to form the 3D framework (Figure S3†) with Cs–O bond distances ranging from 3.047(3) to 3.554(4) Å. $Li(1)^+$ and $Li(2)^+$ cations are located between B_5O_{10} and CsO_n ($n = 8, 10$) groups to hold the groups through coordination with oxygen atoms (Fig. 1d). Each $Li(1)^+$ is surrounded by five O atoms forming trigonal bipyramids, and the plane is formed by three oxygen atoms O(1), O(1)′ and O(5). The mean deviation from the plane is 0.028 Å. The O(2), O(4) atoms are in axial positions with O(2)–Li(1)–O(4) = 166.1(4)°. $Li(2)^+$ is coordinated to four O atoms forming a distorted tetrahedron. $Li(1)O_5$ and $Li(2)O_4$ polyhedra are interconnected via sharing edges into a 2D sheet network (Figure S4†) with Li–O bond distances ranging from 1.842(6) to 2.306(8) Å.

The bond valence sums of each atom in $Li_3Cs_2B_5O_{10}$ were calculated[27,28] and are listed in Table S3 in the ESI.† These valence sums agree with expected oxidation states.

Thermal analysis

The DTA curve of $Li_3Cs_2B_5O_{10}$ in Fig. 2a shows one endothermic peak at 668 °C on the heating curve, which suggests that $Li_3Cs_2B_5O_{10}$ melts congruently at 668 °C. To verify the melting process, polycrystalline $Li_3Cs_2B_5O_{10}$ (5 g) was placed in a platinum crucible and heated to 800 °C, then slowly cooled to room temperature. The solidified melt exhibits a diffraction pattern identical to that of the initial $Li_3Cs_2B_5O_{10}$ powder, as is shown in Figure S2 in the ESI.† This unambiguously demonstrates that $Li_3Cs_2B_5O_{10}$ is a congruently melting compound, and crystals of $Li_3Cs_2B_5O_{10}$ can thus be grown from its stoichiometric melt.[17b]
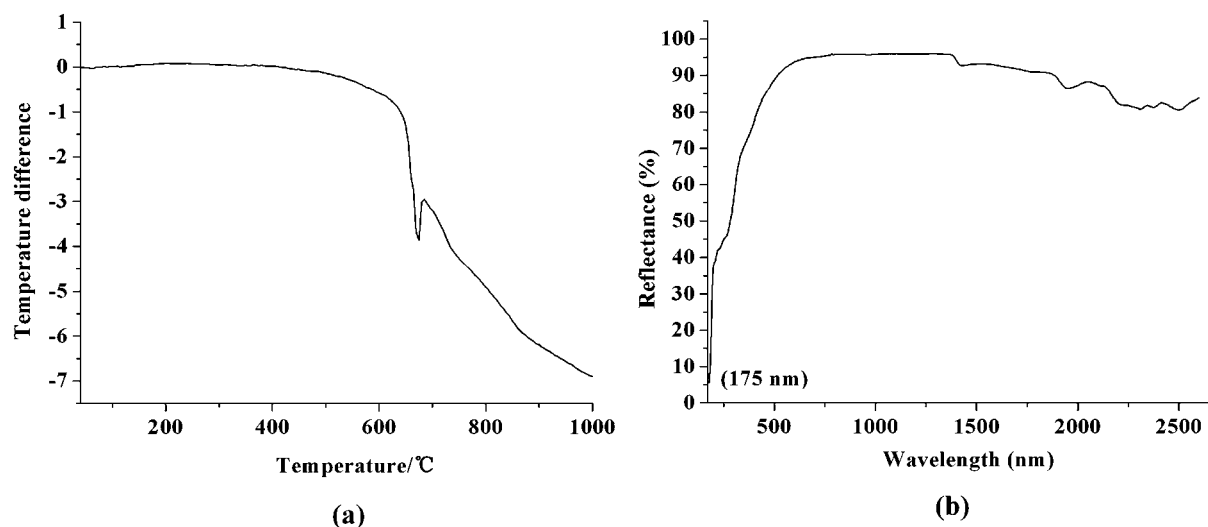
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Fig. 2 (a) DTA curve of $Li_3Cs_2B_5O_{10}$. (b) UV-VIS-NIR diffuse-reflectance spectrum of $Li_3Cs_2B_5O_{10}$.

UV-VIS-NIR diffuse-reflectance spectroscopy

The UV-VIS-NIR diffuse-reflectance spectrum of the $Li_3Cs_2B_5O_{10}$ crystalline sample is shown in Fig. 2b. Clearly, a wide transmission range is observed with a UV cut off edge at 175 nm. No obvious absorption peak in the range of 175–2600 nm was observed, indicating that the crystal may have potential use in UV NLO applications.

NLO measurements

Because of the non-centrosymmetric crystal structure of $Li_3Cs_2B_5O_{10}$, it is expected to possess NLO properties. According to anionic group theory of NLO activity in borates,[29] the BO_3 trigonal planes are responsible for the large SHG effects, and the BO_4 groups contribute less. The orientation of these groups also determines their total NLO contribution. Similar to KB5 ($KB_5O_8 \cdot 4H_2O$), the arrangement of B_5O_{10} groups are opposite and consequently the overall SHG efficiency of $Li_3Cs_2B_5O_{10}$ is about 50% KDP. The SHG measurements on sieved $Li_3Cs_2B_5O_{10}$ samples indicate that it is phase-matchable (Figure S5†).

Conclusions

A novel non-centrosymmetric borate crystal $Li_3Cs_2B_5O_{10}$ has been synthesized. Optical characterization of the $Li_3Cs_2B_5O_{10}$ crystal indicates that it possesses a UV cut off edge at 175 nm and is phase-matchable. Of particular merit, $Li_3Cs_2B_5O_{10}$ grows from its stoichiometric ratio and melts at exceptionally fast rates. The combined features of phase matching, congruently melting and a short wavelength UV cut off edge are important for advanced laser applications. Future efforts will be devoted to the growth of large crystals and relevant physical properties studies for this compound.

Acknowledgements

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