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Ab initio structure determination of novel borate $NaSrBO_3$

L. Wu[a,b,*], X.L. Chen[b,**], Y. Zhang[b], Y.F. Kong[a], J.J. Xu[a], Y.P. Xu[b]

[a]*The Key Laboratory of Advanced Technique and Fabrication for Weak-Light Nonlinear Photonics Materials, Ministry of Education, Nankai University, Tianjin 300457, PR China*

[b]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China*

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Abstract

A novel orthoborate, $NaSrBO_3$, has been successfully synthesized by standard solid-state reaction, and the crystal structure has been determined from powder X-ray diffraction data. It crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters: $a = 5.32446(7)$ Å, $b = 9.2684(1)$ Å, $c = 6.06683(8)$ Å, $\beta = 100.589(1)^\circ$. The fundamental building units are isolated BO_3 groups, which are parallelly distributed along two different directions. Because of the anisotropic polarizations of planar BO_3 groups, a considerable birefringence can be expected in it. The Na atoms are six-coordinated with O atoms to form octahedra, and the Sr atoms are nine-coordinated, forming tri-capped trigonal prisms. Those polyhedra connect with each other by bridging-oxygen atoms, forming infinite three-dimensional network, which indicates that the cleaving problem is expected to be overcome during the course of single-crystal growth. The infrared spectrum has been measured, and the result is consistent with the crystallographic study. Moreover, a comparison of the new structure type with the other known orthoborates is presented here.

Keywords: Borates; Structure determination; X-ray diffraction

1. Introduction

Inorganic borates have long been a focus of research for their variety of structure type, transparency to a wide range of wavelengths, high laser damage tolerance, and high optical quality. Studies of alkali-metal and alkaline-earth-metal borates have produced a large family of compounds with outstanding physical properties [1,2], such as β-BaB_2O_4 [3], LiB_3O_5 [4], $Sr_2Be_2B_2O_7$ [5] and $K_2Al_2B_2O_7$ [6]. Recently, with the development of optical communications and the semiconductor large-scale integrated circuit; the demand for birefringent crystals and the nonlinear optical (NLO) crystals in the deep UV band is soaring. A variety of BO atomic groups are considered to be a dominant factor for their physical properties, in particular the optical properties of borates. Among the various anionic groups, the planar $[BO_3]^{3-}$ groups attract our attention, because highly localized valence electrons, low absorption (173 nm) [5], and anisotropy polarizability indicate that some borates are likely to be good candidates for future deep-UV NLO and birefringent materials. With this in mind, we have investigated the systems M_2O–$M'O$–B_2O_3 (M is alkali metal; M' is alkaline-earth metal) to search for new useful optical materials. Several new compounds [7–10] were synthesized successfully, and the powder X-ray diffraction (XRD) patterns of them have been submitted for publication in the Powder Diffraction File (International Centre for Diffraction Data) in 2003 and 2004. Recently, another novel borate in the systems was found: $NaSrBO_3$. Although it has the same formula type $ABCX_3$ with $LiMgBO_3$ [11], $LiCaBO_3$ [7], $LiSrBO_3$ [12], $LiBaBO_3$ [12], $NaCaBO_3$ [10], and $NaBaBO_3$ [13], different structures are found in those orthoborates. The crystal structure of $NaSrBO_3$ has been determined by powder XRD by direct method. Isolated planar $[BO_3]^{3-}$ anionic groups were found in the new compound as

*Corresponding author. The Key Laboratory of Advanced Technique and Fabrication for Weak-Light Nonlinear Photonics Materials, Ministry of Education, Nankai University, Tianjin 300457, PR China.
**Also to be corresponded to.
E-mail addresses: lwu@nankai.edu.cn (L. Wu), xlchen@aphy.iphy.ac.cn (X.L. Chen).

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desired, just as in other orthoborates. The comparison of those structure types was discussed here, and the infrared spectrum of the new compound was analyzed to confirm the anionic groups.

2. Experimental

2.1. Solid-state syntheses

Polycrystalline samples $NaSrBO_3$ was prepared by sintering at high temperature through solid-state reactions. Stoichiometric mixtures of high-purity Na_2CO_3, $SrCO_3$, and H_3BO_3 were heated at 650 °C to decompose the carbonate and eliminate the water, and then elevated to sintering temperature of 850 °C for 72 h. In between sintering steps, the sample was cooled and then ground. Pure powder sample was characterized by powder XRD.

2.2. Ab initio structure determination

The data for $NaSrBO_3$ used for structure determination and Rietveld refinement was collected over a 2θ range of 10–135° in the step scan mode with a step size of 0.02° and a measurement time of 1 s per step at room temperature. Additional technical details are given in Table 1. The diffraction pattern ($2\theta \leqslant 65°$) of the compound was indexed using DICVOL91 [14] by successive dichotomy method. This gave out a monoclinic unit cell with $a = 5.3233(9)$ Å, $b = 9.273(2)$ Å, $c = 6.0681(8)$ Å, $\beta = 100.58(1)°$. Systematic absence of $h\,0\,l$ with $l = 2n + 1$, $0\,k\,0$ with $k = 2n + 1$, and $0\,0\,l$ with $l = 2n + 1$ suggests that the possible space group is $P2_1/c$.

The whole pattern of $NaSrBO_3$ was fit using the Fullprof program [15] based on the Le Bail method, [16] and a total of 406 independent $|F_{obs}|$ values were extracted. The final agreement factors converged to $R_B = 1.55\%$, $R_p = 5.97\%$, $R_{wp} = 9.09\%$, and $R_{exp} = 2.89\%$. Lattice parameters were refined to be $a = 5.32484(5)$ Å, $b = 9.26917(9)$ Å, and $c = 6.06630(6)$ Å, $\beta = 100.581(1)°$. The density of the samples was measured to be 3.80 g/cm^{-3}. According to this result and the symmetry information, it is determined that there are four $NaSrBO_3$ molecules in one unit cell. Direct methods were applied with *SHELXL97* program package [17] to the extracted $|F_{obs}|$. According to the atom distances, three peaks listed in the E-map were likely to correspond to the correct positions of atoms, one was assigned to the Sr atoms, another was Na, and the third one was assigned to one of the O atom. The other atoms were located by using difference Fourier synthesis. In this course, once an atom was located, it would be used for the next run of difference Fourier synthesis. At last, a satisfactory rough structure was obtained, and then it was refined using the Rietveld method [18,19] within the Fullprof program. In the final cycles of refinement a total of 43 parameters were refined (24 structural parameters and 19 profile parameters, including 5 background parameters and 5 peak shape parameters, the pseudo-Voigt function was used as peak shape function) and the finally agreement factors converged to $R_B = 6.86\%$, $R_p = 7.75\%$, $R_{wp} = 11.0\%$, and $R_{exp} = 2.88\%$. Lattice parameters were refined to be $a = 5.32446(7)$ Å, $b = 9.2684(1)$ Å, and $c = 6.06683(8)$ Å, $\beta = 100.589(1)°$. The final refinement pattern is given in Fig. 1. The crystallographic data, fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Tables 1 and 2; significant bond lengths and angles are listed in Table 3.

Table 1
Crystallographic data, experimental details of X-ray powder diffraction, and Rietveld refinement data for $NaSrBO_3$

Chemical formula	$NaSrBO_3$
Formula weight	169.42
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	5.32446 (7)
b (Å)	9.2684 (1)
c (Å)	6.06683 (8)
β (°)	100.589 (1)
Volume (Å^3)	294.30 (8)
Z	4
d_c (g cm^{-3})	3.824
Diffractometer	Rigaku D/Max-2400
Radiation type	Cu$K\alpha$
Wavelength (Å)	1.5418
Profile range (°2θ)	10–135
Step size (°2θ)	0.02
Number of observation (N)	6251
Number of contributing reflections	1095 ($K\alpha1 + K\alpha2$)
Number of structure parameters (P_1)	24
Number of profile parameters (P_2)	19
R_{Bragg} (%)	6.86
R_p (%)	7.75
R_{wp} (%)	11.0
R_{exp} (%)	2.88

Note: $R_p = \sum |y_{io} - y_{ic}| / \sum |y_{io}|$, $R_{wp} = [\sum w_i(y_{io} - y_{ic})^2 / \sum w_i y_{io}^2]^{1/2}$, $R_{exp} = [(N - P_1 - P_2) / \sum w_i y_{io}^2]^{1/2}$, $S = \sum [w_i(y_{io} - y_{ic})^2 / (N - P_1 - P_2)]^{1/2}$.

2.3. IR spectra measurement

Infrared spectra were recorded with a Perkin-Elmer 983 infrared spectrophotometer in the 300–1500-cm^{-1} wavenumber range using KBr pellets.

3. Results and discussion

3.1. Description of crystal structures

The $NaSrBO_3$ compound crystallizes in the space group $P2_1/c$. As illustrated in Figs. 2a and b, the foundational building units of $NaSrBO_3$ are isolated planar $[BO_3]^{3-}$ groups, which are parallelly distributed along two directions. The B–O bond lengths vary from 1.288(4) to 1.431(3) Å with an average value of 1.354 Å, and the O–B–O angles are between 104.35(3) and 128.07(4)°. These values are normal in a BO_3 plane triangle. The Na atoms

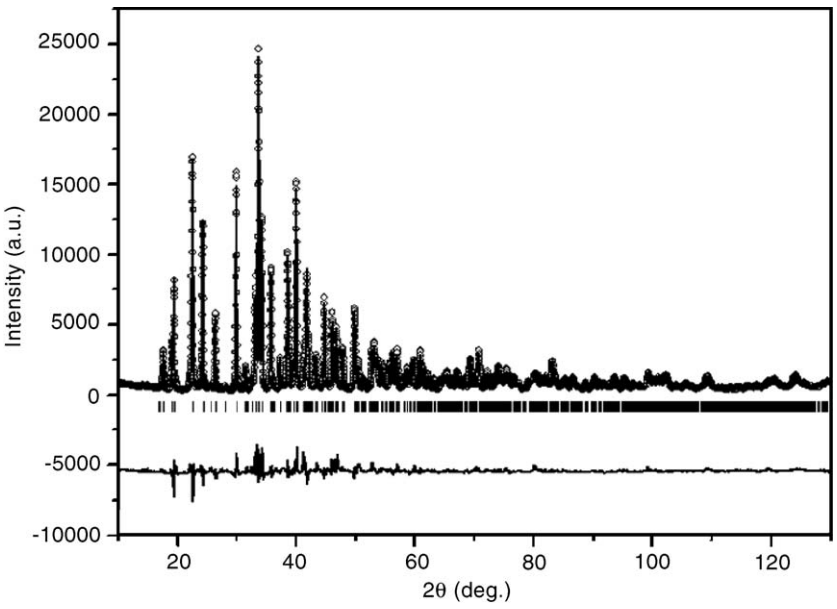

Fig. 1. Final Rietveld refinement plot of $NaSrBO_3$. Small circles (○) correspond to experimental values, and the continuous lines are the calculated pattern; vertical bars (|) indicate the positions of Bragg peaks. The bottom trace depicts the difference between the experimental and the calculated intensity values.

Table 2
Positional, atomic displacement, and occupancy parameters for $NaSrBO_3$

Atom	Site	x	y	z	U_{eq}(Å^2)	Occ.
Sr	4*e*	0.2422(1)	0.4136(1)	0.2186(1)	0.0033(1)	1.0
Na	4*e*	0.2554(7)	0.7573(3)	0.0309(4)	0.0109(2)	1.0
O(1)	4*e*	−0.0390(5)	0.6395(3)	0.2263(3)	0.0142(5)	1.0
O(2)	4*e*	−0.4274(5)	0.6484(3)	0.3631(3)	0.0086(5)	1.0
O(3)	4*e*	0.2677(5)	0.9413(2)	0.3177(3)	0.0097(4)	1.0
B	4*e*	−0.2615(7)	0.5861(3)	0.2652(4)	0.0076(6)	1.0

Table 3
Selected interatomic distances (Å) and angles (°)

Na–O1	2.396(4)	Sr–O2^{ii}	2.612(2)
Na–O1^{iii}	2.392(4)	Sr–O3	2.695(3)
Na–O2	2.585(4)	Sr–O3^{i}	2.671(3)
Na–O2^{iii}	2.299(4)	Sr–O3^{ii}	2.804(2)
Na–O3	2.428(3)		
Na–O3^{iii}	2.258(3)		
		B–O1	1.344(5)
Sr–O1	2.579(3)	B–O2	1.288(4)
Sr–O1^{i}	2.805(3)	B–O3^{i}	1.431(3)
Sr–O1^{ii}	2.762(2)	O1–B–O2	128.07(4)
Sr–O2	2.834(2)	O1–B–O3^{i}	104.35(3)
Sr–O2^{i}	2.728(2)	O2–B–O3^{i}	127.52(3)

Note: Symmetry codes: (i) $-x$, $y+1/2$, $-z+1/2$; (ii) $-x$, $-y$, $-z$; (iii) x, $-y+1/2$, $z+1/2$.

are coordinated with six O atoms to form octahedra, as illustrated in Fig. 3a. Those octahedra are face-sharing with each other to form infinite long chains along the *c*-axis, and are corner-sharing with the adjacent BO_3 triangles. The coordination surroundings of Sr atoms are shown in Fig. 3b. The Sr atoms are surrounded by nine O atoms, and form tri-capped trigonal prisms. The SrO_9 polyhedra are connected with each other by corners along the directions parallel to the *ab* plane, by edges and faces on the perpendicular directions, and share edges with the adjacent planar BO_3 triangles. The NaO_6 and SrO_9 polyhedra share bridging-oxygen atoms with each other, forming infinite three-dimensional network. The overall structure of $NaSrBO_3$ is similar to that of K_2CO_3 [20], which also contain chains of face-sharing octahedra, KO_6, linked by nine-coordinate K atoms and triangular CO_3 groups.

3.2. Comparison of the structures of all the known orthoborates

There are many known orthoborates in alkali metal and alkaline-earth metal borates, including $LiMgBO_3$ [11], $LiCaBO_3$ [7], $LiSrBO_3$ [12], $LiBaBO_3$ [12], $NaCaBO_3$ [10], and $NaBaBO_3$ [13]. The novel monoclinic compound has the same formula type ($ABCX_3$) with the others, but the crystal structures are remarkablely different. $LiCaBO_3$ and

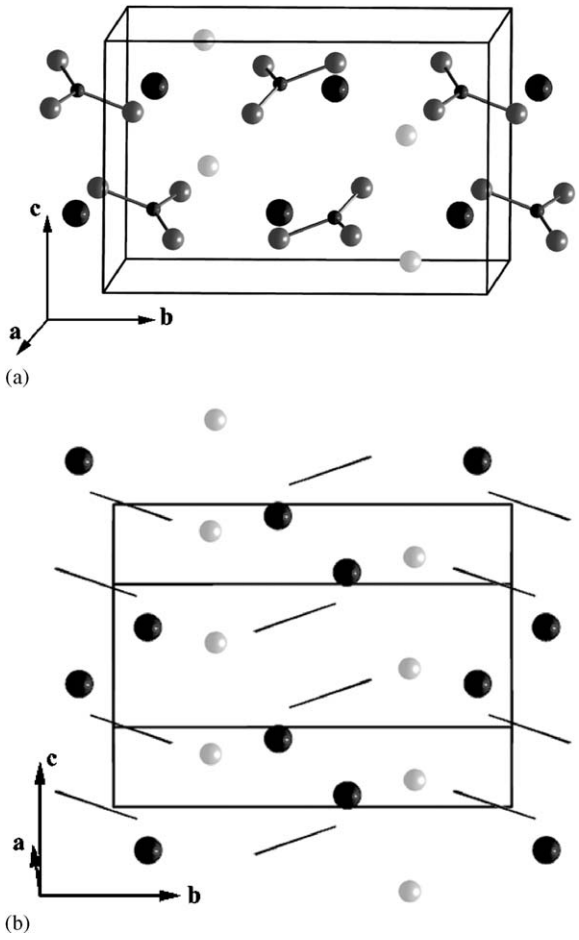

Fig. 2. (a) Structure projection of $NaSrBO_3$ viewed along [100]. Big black balls stand for Sr atoms, and small ones B atoms. White balls represent Na atoms, and gray ones O atoms. (b) Structure projection of $NaSrBO_3$ viewed along [102]. Black balls stand for Sr atoms, and white balls represent Na atoms. Black short lines are the side faces of BO_3 triangles. The B and O atoms are omitted for clarity.

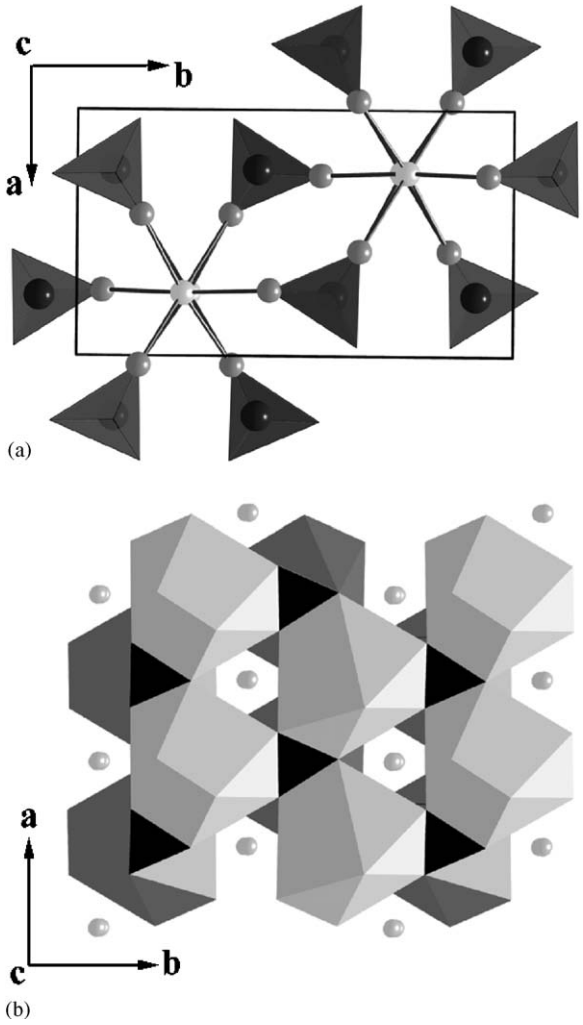

Fig. 3. (a) Coordination environments of Na with O atoms. Big black balls stand for Sr atoms. Gray balls depict O atoms, and white ones are Na atoms. The black triangles are BO_3 groups. (b) Coordination environments of Sr with O atoms. White balls depict Na atoms. The black triangles are BO_3 groups. Deep and grayish polyhedra are the SrO_9 tricapped trigonal prisms in the lower and upper layers.

$NaCaBO_3$ belong to orthorhombic system, while the other five are all monoclinic. The planar BO_3 groups distribute differently in those compounds. They are almost parallel to each other in $LiMgBO_3$, and perpendicular in $LiCaBO_3$, while parallelly distributed along different directions in the other compounds. The coordination manners of alkali metal and alkaline-earth metal are diverse. The Li atoms are five-coordinated in the four lithium borates, forming different distorted trigonal bipyramid. The Na atoms have different coordination manners in sodium borates: they appear in two crystallographically different environments with six- and eight-coordinated by O atoms, and mixed occupancy with Ca atoms in $NaCaBO_3$; in $NaSrBO_3$ and $NaBaBO_3$, it has only one coordination manner, forming octahedra. An interesting case is that no matter what coordination manners the Na atoms take, the Na-centered polyhedra will form chains along the *c*-axis by edges and faces in those orthoborates. The Mg atoms are five-coordinated in $LiMgBO_3$ to form trigonal bipyramids. The Ca atoms are surrounded by seven O atoms, forming mono-capped distorted triangle prisms in $LiCaBO_3$. In $NaCaBO_3$, they have two kinds of coordination manners: six and seven, and partially mixed occupied with Na atoms. The Sr atoms are seven-coordinated in $LiSrBO_3$, which is similar to that of Ca in $LiCaBO_3$, while nine-coordinated in $NaSrBO_3$, which is similar to the case of Ba in $LiBaBO_3$ and $NaBaBO_3$. As discussed above, alkali metal and alkaline-earth metal are very active, and are easy to form various crystal structures with boric acid, which bring us a large field to find new functional materials.

3.3. Infrared spectra analysis

To further confirm the coordination surroundings of B–O in the $NaSrBO_3$ structure, the IR spectrum of it was measured at room temperature and shown in Fig. 4a. The IR absorption at wavenumbers smaller than 500 cm^{-1}

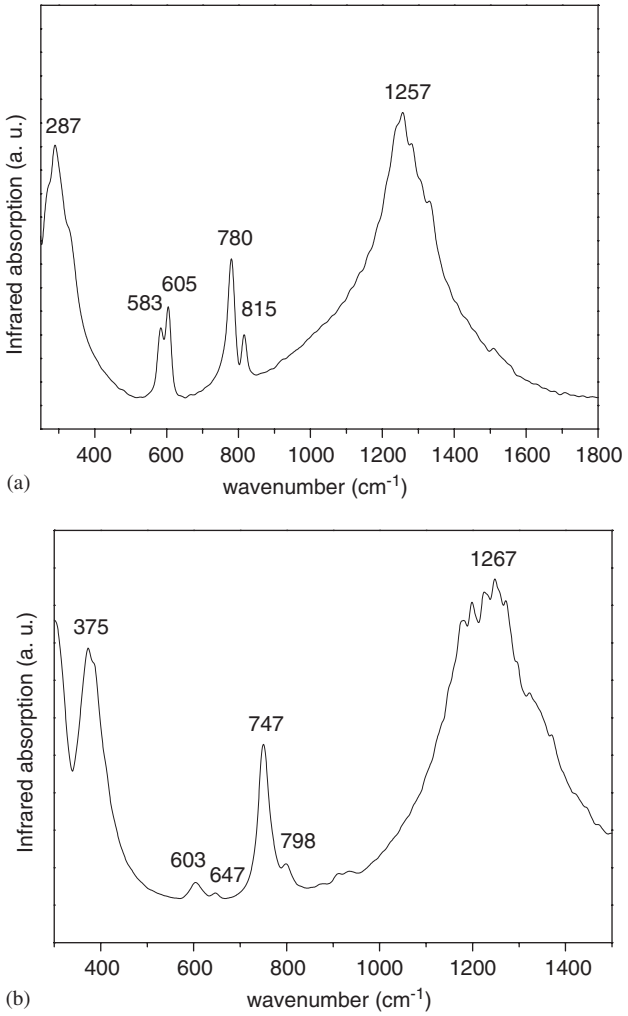

Fig. 4. (a) Infrared spectrum of $NaSrBO_3$. (b) Infrared spectrum of $NaCaBO_3$.

mainly originates from the lattice dynamic modes. The strong band observed above 1100 cm^{-1} should be assigned to the B–O stretching mode of triangular $[BO_3]^{3-}$ groups, while the bands with maxima at about 700–850 cm^{-1} should be attributed to the B–O out of plane bending, which confirm the existence of the $[BO_3]^{3-}$ groups [21]. A similar IR spectrum can be found from another sodium orthoborate $NaCaBO_3$ [10] (Fig. 4b), in which the fundamental building units are also isolated planar BO_3 groups.

4. Conclusion

In this work, a new compound, $NaSrBO_3$, has been synthesized by solid-state reactions. The crystal structure has been solved from powder X-ray diffraction data, and was further refined by the Rietveld method. It is composed of three coordinated boron atoms, six-fold coordinated sodium atoms, nine-fold coordinated strontium atoms. The isolated BO_3 triangles are parallelly distributed along two different directions. Because of the anisotropic polarizations of planar BO_3 groups, a considerable birefringence can be expected in it. The NaO_6 octahedra and SrO_9 polyhedra connect with each other by bridging-oxygen atoms, forming infinitely three-dimensional network, which indicates that the single crystal may not be too difficult to grow for possibly avoiding cleaving. The similarities and differences among the structure types of the new borate and the other known orthoborates are discussed, and the infrared spectrum is also reported here, which is in good agreement with the crystallographic study.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.01.003.

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