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# Structure Determination and Relative Properties of Novel Noncentrosymmetric Borates $MM'_4(BO_3)_3$ ($M = Na$, $M' = Ca$ and $M = K$, $M' = Ca, Sr$)

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A series of novel noncentrosymmetric borates, $MM'_4(BO_3)_3$ ($M = Na$, $M' = Ca$; $M = K$, $M' = Ca, Sr$), have been successfully synthesized via a standard solid-state reaction. The crystal structures have been determined by the SDPD (structure determination from powder diffraction) method. They crystallize in the noncentrosymmetric space group *Ama*2 with the following lattice parameters: $a = 10.68004(11)$ Å, $b = 11.28574(11)$ Å, $c = 6.48521(6)$ Å for $NaCa_4(BO_3)_3$; $a = 10.63455(10)$ Å, $b = 11.51705(11)$ Å, $c = 6.51942(6)$ Å for $KCa_4(BO_3)_3$; and $a = 11.03843(8)$ Å, $b = 11.98974(9)$ Å, $c = 6.88446(5)$ Å for $KSr_4(BO_3)_3$. The fundamental building units are isolated $BO_3$ anionic groups. Their second harmonic generation (SHG) coefficients were one-half ($NaCa_4(BO_3)_3$), one-third ($KCa_4(BO_3)_3$), and two-thirds ($KSr_4(BO_3)_3$) as large as that of $KH_2PO_4$ (KDP). The infrared and UV–vis spectra of the three compounds are discussed. Moreover, a comparison of the structures of these novel compounds and three other novel cubic compounds with the same formula, $MM'_4(BO_3)_3$ ($M = Li$, $M' = Sr$; $M = Na$, $M' = Sr, Ba$), is presented here.

## Introduction

Inorganic borates have long been a focus of research for their variety of structure types, 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 $\beta$-$BaB_2O_4$[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 nonlinear optical crystals in the deep UV band is soaring. A variety of BO atomic groups are considered to be a dominant factor in 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 the 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 nonlinear optical (NLO) and birefringent materials. With this in mind, we have investigated the $M_2O-M'O-B_2O_3$ ($M = Li, Na, K$; $M' = Ca, Sr, Ba$) systems to search for new useful optical materials. Twelve new compounds, $LiCaBO_3$,[7] $Li_4CaB_2O_6$,[8] $LiSr_4(BO_3)_3$,[9] $NaCaBO_3$,[10] $NaCa_4(BO_3)_3$, $NaSrBO_3$, $NaSr_4(BO_3)_3$,[9] $Na_3SrB_5O_{10}$, $NaSrB_5O_9$, $NaBa_4(BO_3)_3$,[9] $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$ were synthesized successfully. The powder XRD patterns of them have been submitted for publication in the Powder Diffraction File (International Centre for Diffraction Data) in 2003 and 2004. Three of the twelve new borates, $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$, are isostructural and have been structurally deter-

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**Table 1.** Crystallographic Data, Experimental Details of X-ray Powder Diffraction, and Rietveld Refinement Data for $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$

| | | | |
|---|---|---|---|
| chemical formula | $NaCa_4(BO_3)_3$ | $KCa_4(BO_3)_3$ | $KSr_4(BO_3)_3$ |
| fw | 359.73 | 375.84 | 566.01 |
| cryst syst | orthorhombic | orthorhombic | orthorhombic |
| space group | *Ama*2 | *Ama*2 | *Ama*2 |
| *a* (Å) | 10.68004(11) | 10.63455(10) | 11.03843(8) |
| *b* (Å) | 11.28574(11) | 11.51705(11) | 11.98974(9) |
| *c* (Å) | 6.48521(6) | 6.51942(6) | 6.88446(5) |
| vol ($Å^3$) | 781.68(2) | 798.49(2) | 911.14(2) |
| *Z* | 4 | 4 | 4 |
| $d_c$ ($g\ cm^{-3}$) | 3.056 | 3.161 | 4.125 |
| diffractometer | MXP21VAHF/M21X MAC Science | MXP21VAHF/M21X MAC Science | MXP21VAHF/M21X MAC Science |
| radiation type | Cu Kα | Cu Kα | Cu Kα |
| wavelength (Å) | 1.5418 | 1.5418 | 1.5418 |
| profile range (deg, $2\theta$) | 10−120 | 10−120 | 10−120 |
| step size (deg, $2\theta$) | 0.02 | 0.02 | 0.02 |
| no. of observations (*N*) | 5500 | 5500 | 5500 |
| no. of contributing reflns | 696(Kα1 + Kα2) | 712(Kα1 + Kα2) | 809(Kα1 + Kα2) |
| no. of structural params ($P_1$) | 39 | 39 | 39 |
| no. of profile params ($P_2$) | 18 | 18 | 18 |
| $R_{Bragg}$ (%) | 6.64 | 6.93 | 5.70 |
| $R_p{}^a$ (%) | 9.10 | 8.78 | 7.12 |
| $R_{wp}{}^a$ (%) | 12.9 | 13.6 | 9.59 |
| $R_{exp}{}^a$ (%) | 5.28 | 5.18 | 2.57 |

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

mined from powder X-ray diffraction data. They crystallize in the noncentrosymmetric space group *Ama*2. Three other cubic borates, $LiSr_4(BO_3)_3$, $NaSr_4(BO_3)_3$, and $NaBa_4(BO_3)_3$, which crystallize in the cubic space group *Ia-3d*,[9] are remarkable in that they have the same novel formula type, $AB_4C_3X_9$, but they have different structures. A comparison of the two structure types is discussed here.

Isolated planar $[BO_3]^{3-}$ anionic groups were found to be the fundamental building units in the title compounds. Because of the noncentrosymmetric space group, nonlinear optical properties were expected in the new compounds. The second harmonic generation coefficients of $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$ were detected and were one-half, one-third, and two-thirds, respectively, as large as that of $KH_2PO_4$ (KDP). The UV−vis reflection spectra indicated that the absorption cutoff was about 280−300 nm.

## Experimental Section

**Solid-State Syntheses.** Polycrystalline samples of $MM'_4(BO_3)_3$ (M = Na, M′ = Ca; M = K, M′ = Ca, Sr) were prepared by sintering at high temperatures via solid-state reactions. Stoichiometric mixtures of high-purity $Na_2CO_3$ (AR), $CaCO_3$ (AR), and $H_3BO_3$ (>99.99%) (NaCa); $K_2CO_3$ (AR), $CaCO_3$ (AR), and $H_3BO_3$ (>99.99%) (KCa); and $K_2CO_3$ (AR), $SrCO_3$ (AR), and $H_3BO_3$ (>99.99%) (KSr) were heated at 600 °C in platinum crucibles to decompose the carbonate and eliminate the water; then the reaction mixtures were elevated to sintering temperatures of 880, 900, and 800 °C, respectively, for 72 h. Between sintering steps, the samples were cooled and then ground. The powder samples were characterized by powder X-ray diffraction. Pure $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$ were obtained, and they were found to be isostructural.

**Ab Initio Structure Determination.** The data for $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$ used for structure determination and Rietveld refinement were collected over a $2\theta$ range of 10−120° in the step scan mode with a step size of 0.02° and a measurement time of 1 s/step at room temperature. Additional technical details are given in Table 1. The diffraction patterns of the three compounds were indexed using DICVOL91,[11] giving an orthorhombic unit cell with $a = 10.685(4)$ Å, $b = 11.275(2)$ Å, $c = 6.482(1)$ Å for $NaCa_4(BO_3)_3$; $a = 10.652(2)$ Å, $b = 11.542(2)$ Å, $c = 6.529(1)$ Å for $KCa_4(BO_3)_3$; and $a = 11.040(1)$ Å, $b = 11.983(1)$ Å, $c = 6.8853(5)$ Å for $KSr_4(BO_3)_3$. The systematic absence of *hkl* with $k + l = 2n + 1$, $0kl$ with $k + l = 2n + 1$, $h0l$ with $h, l = 2n + 1$, $hk0$ with $k = 2n + 1$, $h00$ with $h = 2n + 1$, $0k0$ with $k = 2n + 1$, and $00l$ with $l = 2n + 1$ suggests that the possible space groups are $Cmc2_1$, *Ama*2, and *Cmcm*. All three compounds are isostructural.

The whole pattern of $KSr_4(BO_3)_3$ was fit using the Fullprof program,[12] based on the Le Bail method,[13] with the three possible space groups. The final agreement factors converged to $R_B = 1.81\%$, $R_p = 5.95\%$, $R_{wp} = 8.65\%$, and $R_{exp} = 2.58\%$ for $Cmc2_1$; $R_B = 1.80\%$, $R_p = 5.37\%$, $R_{wp} = 7.63\%$, and $R_{exp} = 2.58\%$ for *Ama*2; and $R_B = 1.81\%$, $R_p = 5.95\%$, $R_{wp} = 8.65\%$, and $R_{exp} = 2.58\%$ for *Cmcm*. The result of the space group *Ama*2 was better than the other two, so it was tested first. A total of 360 independent $|F_{obs}|$ values were extracted. Lattice parameters were refined to $a = 11.03578(13)$ Å, $b = 11.98681(13)$ Å, and $c = 6.88236(8)$ Å. Patterson methods were applied with SHELXL97 program package[14] to the extracted $|F_{obs}|$. According to the atom distances, four peaks listed in the E map were likely to correspond to the correct positions of atoms; three were assigned to the Sr atoms, and the other was assigned to the K atom. The other atoms were located using difference Fourier synthesis. 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[15,16] within the Fullprof program. In the final cycles of refinement, a total of 57 parameters were refined (39 structural parameters and 18 profile parameters), and

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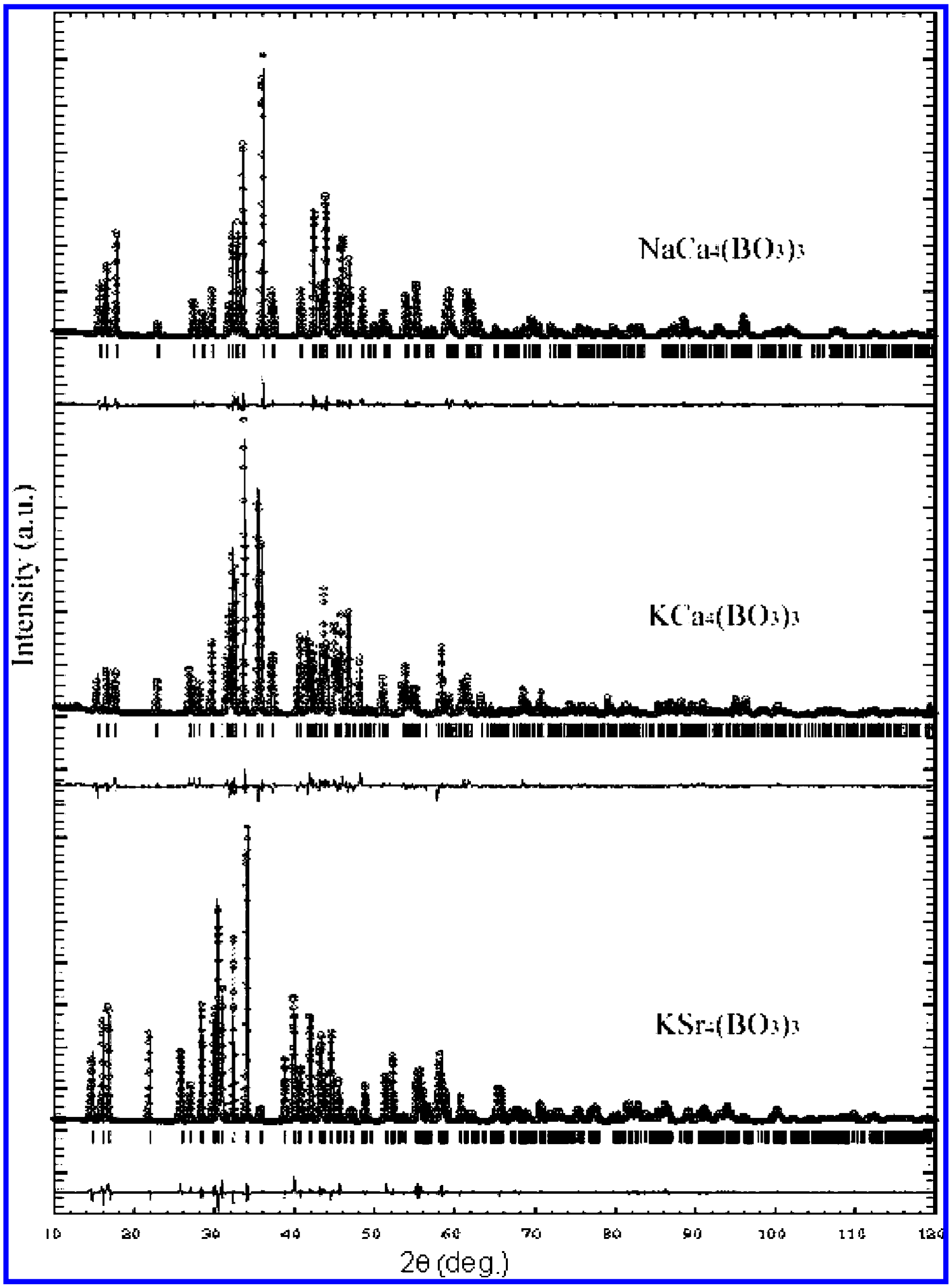

**Figure 1.** Final Rietveld refinement plots of the $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$. Small circles (○) correspond to the experimental values and the continuous lines represent the the calculated pattern; the vertical bars (|) indicate the positions of the Bragg peaks. The bottom trace depicts the difference between the experimental and the calculated intensity values.

the final agreement factors converged to $R_B = 5.70\%$, $R_p = 7.12\%$, $R_{wp} = 9.59\%$, and $R_{exp} = 2.57\%$. Lattice parameters were refined to be $a = 11.03843(8)$ Å, $b = 11.98974(9)$ Å, and $c = 6.88446(5)$ Å. Structure determination was also attempted with the other two possible space groups, but no satisfactory results were obtained. The final result was put into the PLATON program package,[17] and no additional symmetry was found. The final space group was determined to be *Ama*2. The structures of $NaCa_4(BO_3)_3$ and $KCa_4(BO_3)_3$ were determined by the Rietveld method on the basis of the structural model of $KSr_4(BO_3)_3$. In the final cycle of refinement, a total of 57 parameters were refined (39 structural parameters and 18 profile parameters), and the final agreement factors converged to $R_B = 6.64\%$, $R_p = 9.10\%$, $R_{wp} = 12.9\%$, and $R_{exp} = 5.28\%$ for $NaCa_4(BO_3)_3$ and $R_B = 6.93\%$, $R_p = 8.78\%$, $R_{wp} = 13.6\%$, and $R_{exp} = 5.18\%$ for $KCa_4(BO_3)_3$. Lattice parameters were refined to be $a = 10.68004(11)$ Å, $b = 11.28574(11)$ Å, $c = 6.48521(6)$ Å for $NaCa_4(BO_3)_3$ and $a = 10.63455(10)$ Å, $b = 11.51705(11)$ Å, $c = 6.51942(6)$ Å for $KCa_4(BO_3)_3$. The final refinement patterns are given in Figure 1. The crystallographic data, fractional atomic coordinates, and equivalent isotropic displacement parameters are reported in Tables 1 and Table S1; significant bond lengths and angles are listed in Table S2.

**IR Spectra Measurement.** Infrared spectra were recorded with a Perkin-Elmer 983 infrared spectrophotometer in the 300 to 1500 $cm^{-1}$ wavenumber range using KBr pellets.

**SHG, UV−vis, and PL spectra measurement.** The SHG of the samples were measured using the Kurtz powder technique[18]

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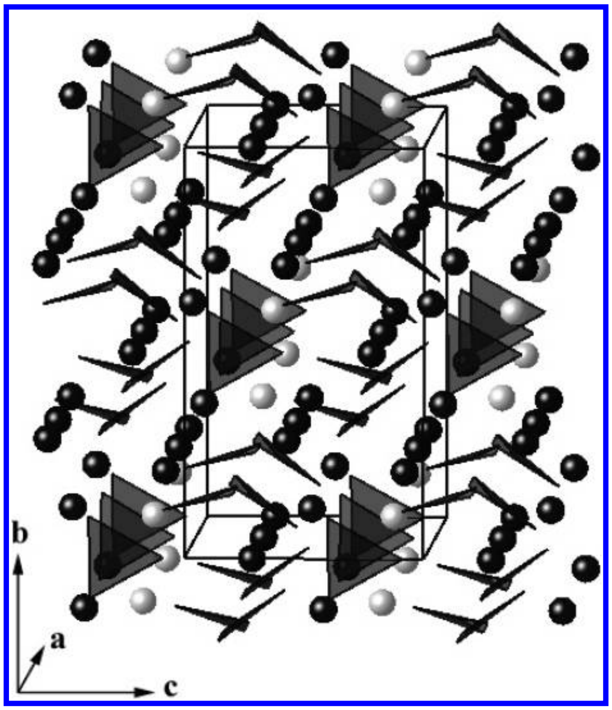

**Figure 2.** Structure projection of MM′$_4$(BO$_3$)$_3$ viewed along [100]. The big black spheres are the M′ atoms, and white ones represent the M atoms. The black triangles are the planar BO$_3$ triangles (M = Na, M′ = Ca and M = K, M′ = Ca, Sr).

with a Nd:YAG laser (1064 nm) as the incident light source. The UV−vis optical reflections of the samples were examined by a Tu-1901 reflection spectrometer with BaSO$_4$ as the standard, which has a cutoff point at about 240 nm. The photoluminescence (PL) spectrum of KCa$_4$(BO$_3$)$_3$ was taken on a PTI-C-700 fluorescence spectrometer with a He−Cd laser line (325 nm) used as the excitation source.

## Results and Discussion

**Description of Crystal Structures.** The MM′$_4$(BO$_3$)$_3$ (M = Na, M′ = Ca; M = K, M′ = Ca, Sr) compounds crystallize in the noncentrosymmetric space group *Ama*2. As expected, the volume evolution follows the values of the ionic radii of the various M and M′ ions ($Na^+ < K^+$ and $Ca^{2+} < Sr^{2+}$): $V_{NaCa} < V_{KCa} < V_{KSr}$ (Table 1). They show a novel structure type, and no other member of this structural family has been found previously in borates. As illustrated in Figure 2, the foundational building units of MM′$_4$(BO$_3$)$_3$ (M = Na, M′ = Ca; M = K, M′ = Ca, Sr) are isolated planar $[BO_3]^{3-}$ groups, which are distributed parallelly along six directions. The B−O bond lengths vary from 1.30(2) to 1.44(2) Å with an average value of 1.39 Å, and the O−B−O angles are between 111.8(1) and 123.9(2)°. These values are normal in a BO$_3$ plane triangle. The coordination environment of M (M = Na or K in the following text) atoms is shown in Figure 3a. The M atoms are surrounded by eight oxygen atoms, and the MO$_8$ polyhedron is a distorted bicapped trigonal prism. The MO$_8$ polyhedra are connected via a bridging oxygen atom to form infinite long chains along the *a* axis, and they share four edges and two corners with the BO$_3$ triangles. The M′ (M′ = Ca or Sr) atoms appear in three crystallographically different environments, as shown in Figure 3b. The M′(1) atoms (in the 4*b* position) are coordinated with eight oxygen atoms, forming distorted bicapped trigonal prisms, while the M′(2) atoms (in the 8*c* position) are eight-coordinated to oxygen atoms, forming distorted trigonal dodecahedra. The M′(2)O$_8$ polyhedra share faces with the adjacent one along the *c* axis and share corners with the next one along the *a* and *b* axes. The M′(1)O$_8$ polyhedra share faces with the four surrounding M′(2)O$_8$ polyhedra. The M′(3) atoms (in the 4*a* position) are nine-coordinated by oxygen atoms, forming distorted tricapped trigonal prisms, and they are connected via their corners along the *a* axis. The M′(3)O$_9$ polyhedra share faces with one adjacent M′(1)O$_8$ and four M′(2)O$_8$ units, and they share corners with another two surrounding M′(2)O$_8$ polyhedra,

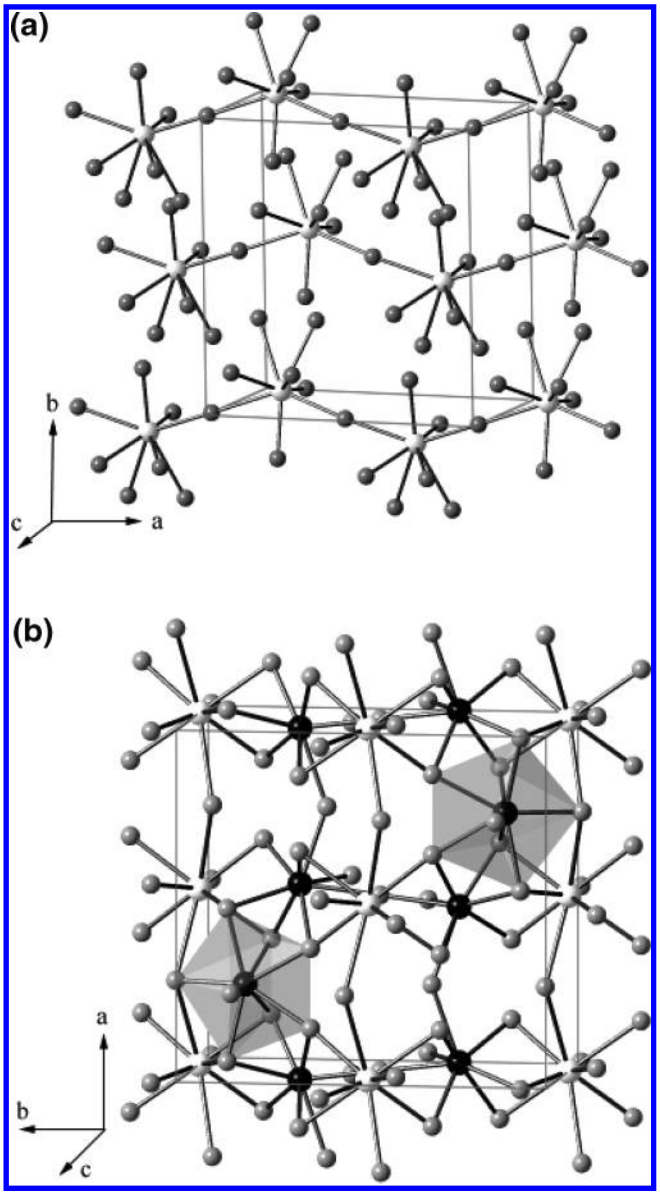

**Figure 3.** Coordination environments of (a) M (M = Na or K) with O atoms and (b) M′ (M′ = Ca or Sr) with O atoms. Black spheres represent the M′(1) and M′(2) atoms, M′(1)O$_8$ bicapped trigonal prisms are shown as gray polyhedra to distinguish them from M′(2). The white spheres represent the M atoms in a and the M′(3) atoms in b. The gray spheres depict the O atoms; the BO$_3$ triangles, M (in a), and M′ (in b) are omitted for clarity.

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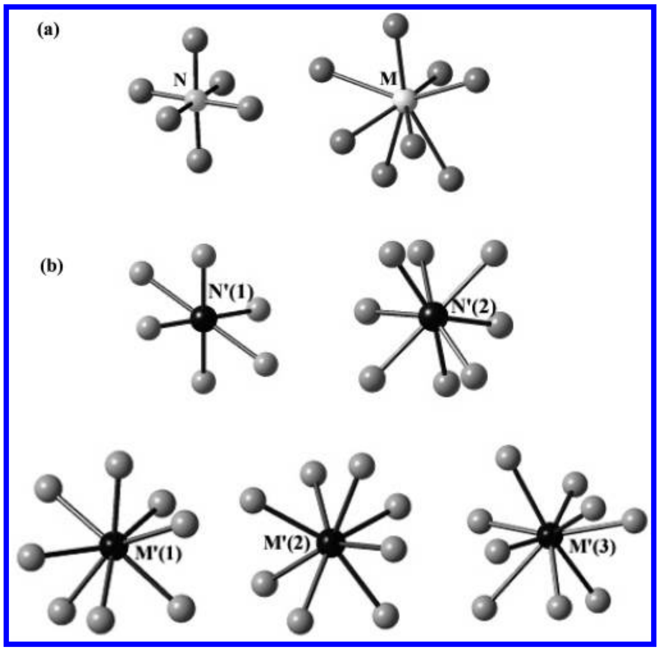

**Figure 4.** Coordination environment of the (a) alkali metal atoms and (b) alkaline earth metal atoms in $NN'_4(BO_3)_3$ and $MM'_4(BO_3)_3$. The white spheres represent the alkali metal atoms; the black ones are the alkaline earth metal atoms, and the gray ones depict the O atoms (N = Li, N′ = Sr and N = Na, N′ = Sr, Ba; M = Na, M′ = Ca and M = K, M′ = Ca, Sr).

forming a complex three-dimensional network. The $MO_8$ polyhedra in the M′O network, share faces, edges, and corners with the surrounding two $M'(1)O_8$, four $M'(2)O_8$, and four $M'(3)O_9$ units.

**Comparison of the Structures of Two Types of Borates.** The novel orthorhombic compounds have the same formula type ($AB_4C_3X_9$) as three other borates, $LiSr_4(BO_3)_3$, $NaSr_4(BO_3)_3$, and $NaBa_4(BO_3)_3$, which crystallize in the cubic space group *Ia-3d*.[9] To make the structure comparison concise, the orthorhombic compounds will be noted as $MM'_4(BO_3)_3$ (M = Na, M′ = Ca; M = K, M′ = Ca, Sr) and the cubic compounds will be written as $NN'_4(BO_3)_3$ (N = Li, N′ = Sr; N = Na, N′ = Sr, Ba) in the following text. The $NN'_4(BO_3)_3$ compounds were synthesized first, and the radii of the alkali metal cations were found to be small, while those of the alkaline earth metal cations are comparatively large. The N′ atoms separate the unit cell into sixty-four cubic grids, and the comparatively large N′ atoms make enough interspace for the cubic grids to place the $MO_6$ cubic octahedra and isolated $BO_3$ triangles. When a larger alkali metal cation was introduced to replace the lithium and sodium or a smaller alkaline earth metal cation was introduced to replace the strontium and barium, no isostructural cubic compound can be synthesized, and at the same time, three new compounds with a different type of structure were found. The radii of the cations in $MM'_4(BO_3)_3$ were found to be similar. It is believed that the substitution of larger alkali metal cations for N or the substitution of smaller alkaline earth metal cations for N′ make the centrosymmetric cubic structure unstable and then change it into the noncentrosymmetric orthorhombic structure. In both types of crystal, the fundamental building units are isolated $BO_3$ triangles distributed in different directions. Large differences exist in the coordination environments of the other cations. As illustrated in Figure 4a, the alkali metal atoms are six-coordinate in $NN'_4(BO_3)_3$ and eight-coordinate in $MM'_4(BO_3)_3$. The different coordination environments of alkaline earth metal atoms in the two structures are shown in Figure 4b. They are six-coordinate and eight-coordinate in $NN'_4(BO_3)_3$, and they form three different coordinated polyhedra in $MM'_4(BO_3)_3$.

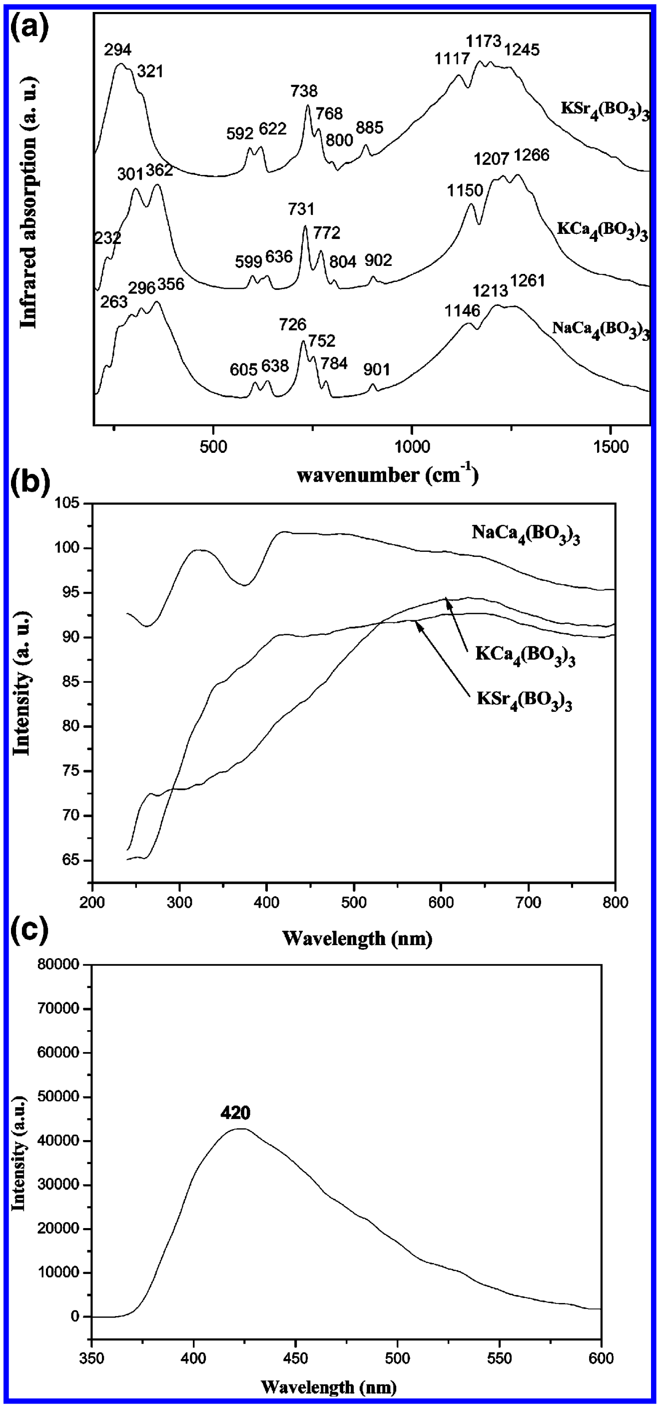

**Figure 5.** (a) Infrared spectra of $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$. (b) Reflection spectra of $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$ from the visible to the ultraviolet. (c) Photoluminescence spectrum of $KCa_4(BO_3)_3$ ($\lambda_{exc}$ = 325 nm).

**Infrared Spectra Analysis.** To further confirm the coordination environment of B−O in the $MM'_4(BO_3)_3$

structure, the IR spectra of $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$ were measured at room temperature; they are given in Figure 5a. The IR absorption at wavenumbers smaller than 500 cm$^{-1}$ mainly originates from the lattice dynamic modes. The strong bands observed above 1100 cm$^{-1}$ should be assigned to the B−O stretching mode of the triangular $[BO_3]^{3-}$ groups, while the bands with maxima at about 700−800 cm$^{-1}$ should be attributed to the B−O out-of-plane bending, which confirms the existence of the $[BO_3]^{3-}$ groups.[19] It is found that there are many closely spaced peaks above 1100 cm$^{-1}$, which are believed to come from the different bond lengths of B−O.

**SHG, Ultraviolet Reflection, and Photoluminescence.** The SHG coefficients were detected on powder samples with KDP ($KH_2PO_4$) as the standard. The $NaCa_4(BO_3)_3$ exhibited a SHG effect half as large as of that of KDP, and that of $KCa_4(BO_3)_3$ was one-third as large as that of KDP, while that $KSr_4(BO_3)_3$ was two-thirds as large as the SHG value of KDP. The reflection spectra of $MM'_4(BO_3)_3$ (M = Na, M′ = Ca; M = K, M′ = Ca, Sr) from visible to ultraviolet were measured, and the patterns are given in Figure 5b. The data were collected from compacted powder samples, and the absorption cutoff can be seen at approximately 280−300 nm. In the UV−vis spectrum of $KCa_4(BO_3)_3$, an absorption occurred at about 350−550 nm, which indicated a self-trapped exciton emission from the laser experiment. The luminescence spectrum was illustrated in Figure 5c and showed a broad emission band with maximum near 420 nm. This result was consistent with the absorption in UV−vis spectrum.

## Conclusions

Three novel NLO borates, $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$, were synthesized by solid-state reaction, and their structures were solved using powder X-ray diffraction data. Isolated planar $[BO_3]^{3-}$ anionic groups were found tobe the fundamental building units. Because they were distributed in a parallel manner along six different lattice planes, most of the anisotropic polarizations were counteracted, and then the resulting SHG coefficients were not very large. The M and M′ atoms were coordinated with O atoms, forming various polyhedra, and those polyhedra were connected to form a complex three-dimensional network. The structure is very different from that of three other cubic borates: $LiSr_4(BO_3)_3$, $NaSr_4(BO_3)_3$, and $NaBa_4(BO_3)_3$. The differences may come from the ratios of the radii of alkali metal and alkaline earth metal cations. The infrared, UV−vis reflection, and photoluminescence spectra were investigated, and the results were in good agreement with those of the crystallographic study.

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**Supporting Information Available:** Tables S1 and S2 and a CIF file for $NaCa_4(BO_3)_3$, $KCa_4(BO_3)_3$, and $KSr_4(BO_3)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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