Synthesis, Structure, and Frequency-Doubling Effect of Calcium Cyanurate**

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Abstract: *Calcium cyanurate is synthesized by reacting calcium chloride with potassium cyanate following a solid-state reaction. The formation of the new compound Ca_3-$(O_3C_3N_3)_2$ (CCY), which occurs by the cyclotrimerization of cyanate ions, was examined thermoanalytically and the crystal structure was determined by single-crystal structure analysis. The structure of CCY is closely related to the structure of the well-known oxoborate β-BaB_2O_4 (BBO). Second harmonic generation (SHG) measurements on crystal powders show a higher SHG efficiency for CCY than for BBO by about one order of magnitude.*

Nonlinear optical (NLO) materials with frequency-doubling (second harmonic generation, SHG) properties are interesting for wide areas of optics, for example, the generating laser beams in the visible range, in laser medicine, optical signal transfer and processing or optical data storage. NLO materials are key components of future photonic technologies, which can transfer and process data at the speed of light.

Metal borates represent one of the largest groups of materials with NLO properties.[1] This observation possibly also results from the fact that borates crystallize particularly often in non-centrosymmetric structures.[2] After the discovery of the first metal borate $KB_5O_8\cdot4H_2O$ in 1975 numerous other borates were discovered. LiB_3O_5 (LBO), β-BaB_2O_4 (β-BBO), and BiB_3O_6 (BIBO) are among the most prominent representatives. Crystals of these compounds belong to the mostly frequently used NLO materials, along with several other important compounds, such as $KTiOPO_4$ (KTP). As a result of intensive research on borates, further new compounds have been discovered recently that show or are expected to show NLO properties.[3] Amongst these are $Li_3Cs_2B_5O_{10}$,[4] $Li_6CuB_4O_{10}$,[5] and a high-pressure modifica-

tion of BiB_3O_6.[6] The crystal structures of many of these borates include units of anionic BO_3, B_3O_6, B_3O_7, B_3O_8, B_5O_{12}, and B_5O_{13} building blocks, which are considered to be responsible for the nonlinear optical behavior.[7] Thus it is reasonable to search for new SHG materials in specific substance groups such as borates.

From a crystallographic viewpoint, potential SHG materials must meet various requirements. These include the absence of an inversion center, birefringent properties, an assembly with high polarizability that contains covalent bonds, optical transparency up to the far-UV range, thermal stability, stability against water and humidity, as well as congruent melting (crystal growth).

One of the most important SHG materials is based on the compound BaB_2O_4 (BBO), which contains ring-shaped $(B_3O_6)^{3-}$ ions. BBO is found to crystallize in two modifications. The high-temperature modification α-BBO crystallizes centrosymmetrically ($R\bar{3}c$) and is stable above 925°C. Upon cooling, α-BBO transitions into the non-centrosymmetric ($R3c$) low-temperature modification β-BBO.[8] Large β-BBO single crystals for SHG applications can be produced in flux media which create a melt below the phase-transition temperature ($T = 925$°C), from which moderately moisture-sensitive crystals can be grown.

The cyanurate ion $(O_3C_3N_3)^{3-}$ displays close structural analogy to the $(O_3B_3O_3)^{3-}$ ion (Figure 1).
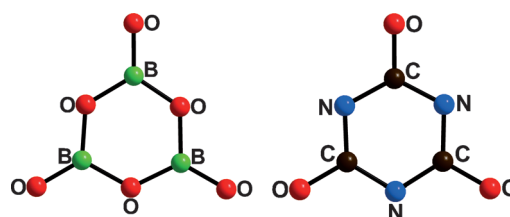
Figure 1. Comparison of $(B_3O_3O_3)^{3-}$ (left) and $(O_3C_3N_3)^{3-}$ (right). The bond lengths in β-BBO are $d_{(B-O)} = 1.3916–1.4114$ Å, $d_{(B-O)exocyclic} = 1.3079–1.3170$ Å, and in CCY $d_{(C-N)} = 1.3301–1.3510$ Å, $d_{(C-O)exocyclic} = 1.2274–1.2956$ Å.

Until shortly crystal structures of inorganic metal cyanurates were unknown, although the existence of individual compounds has been postulated. An exception is the compound $(SbCl_4NCO)_3$, which was crystallized from liquid SO_2 and structurally characterized.[9]

Following a new preparative route, metal cyanurates are produced in good crystalline form via solid-state metathesis reactions. For this purpose, a metal halide is reacted with lithium cyanate under controlled conditions (the reaction is

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monitored by differential scanning calorimetry (DSC) or differential thermoanalysis (DTA)). The resulting cyclotrimerization from cyanate to cyanurate, which is well known in organic chemistry, was observed for the first time in the synthesis of the metal cyanurates $LiSr(O_3C_3N_3)$ and $Li_3Sr_2F(O_3C_3N_3)_2$ in a flux-controlled solid-state reaction.[10]

The compound $Ca_3(O_3C_3N_3)_2$ (CCY) was prepared according to the same reaction principle as the synthesis of the previously mentioned cyanurates.[11] However, instead of Li(OCN), the more thermally stable K(OCN) was used. The synthesis of calcium cyanurate takes place at 400 °C according to Equation (1).

$$3\,CaCl_2 + 6\,K(OCN) \rightarrow Ca_3(O_3C_3N_3)_2 + 6\,KCl \qquad (1)$$

Upon heating the reaction mixture consisting of $CaCl_2$ and K(OCN), K(OCN) melts at roughly 300 °C, followed by the cyclotrimerization of the cyanate ions. When heating the mixture to 400 °C a melt of lower viscosity emergs, from which upon cooling colorless, rodlike hexagonal crystals form. Pure samples of CCY are isolated by washing with water or ethanol To remove the metathesis salt.

The course of the reaction generating CCY was investigated by heating a mixture of $CaCl_2$ and K(OCN) in a 1:3 molar ratio in a differential scanning calorimeter (in gold-plated stainless steel containers) (Figure 2). These investiga-
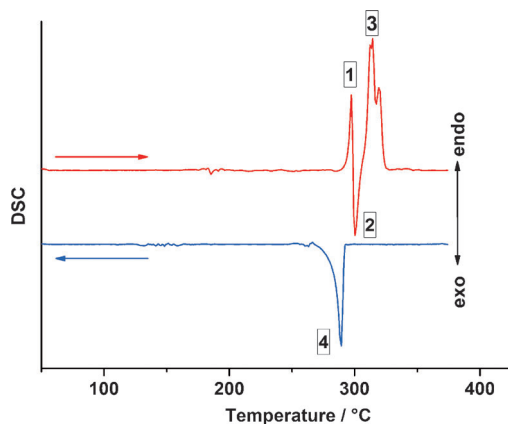

Figure 2. DSC measurement of the reaction of $CaCl_2$ with an excess of K(OCN) between 50 °C and 375 °C.

tions revealed that the formation of CCY (2, centered at 300 °C) is initiated by the melting of the starting materials (1, onset at 288 °C).[12] Upon further heating, the reaction mixture consisting of CCY, KCl, and excess K(OCN) melts (3, centered at 314 °C) and upon cooling crystallizes (4, onset at 292 °C). When cooling a melt, colorless columnar single crystals with a hexagonal prismatic shape are obtained.

The crystal structure of CCY can be described as isotypic to that of β-BBO.[13] Both compounds contain cyclic $[C_3N_3]$ and $[B_3O_3]$ units, each with three additional exocyclic oxygen atoms. For BBO, the notation $Ba_3(B_3O_6)_2$ can be chosen to take into account the presence of $(B_3O_6)^{3-}$ ions.

As expected, the average bond lengths in the cyanurate ion are somewhat shorter than the corresponding distances in the isostructural oxoborate ion (Figure 1).

The presence of isotypic crystal structures for β-BBO and CCY is plausible, considering that the structure of CCY, in comparison that of to BBO, represents the combination of the smaller cation (Ca^{2+}) with the smaller anion (cyanurate). The homologous compound $Ba_3(O_3C_3N_3)_2$ (BCY)[12] crystallizes isotypically to the structure of the high-temperature modification of BBO (α-BBO).

The crystal structure of CCY contains two crystallographically distinguishable cyanurate ions in the trigonal unit cell, which are arranged according to the principle of hexagonal packing of sticks along the threefold axis (Figure 3). Along these colums, the cyanurate rings are rotated by about 9.91° and 22.07° relative to the glide plane (in $R3c$). A similar rotation con be found in the structure of β-BBO (ca. 9° and 20°).[2] In the *ab* plane, the almost planar cyanurate units are assembled as layers.
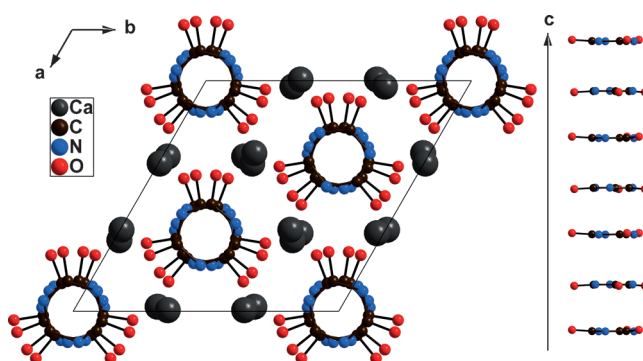

Figure 3. Projection of the unit cellof $Ca_3(O_3C_3N_3)_2$ on the *ab* plane (left) and a sequence of the cyanurate ions stacked along the *c* direction (right).

As expected, the average distances between the centers of gravity of neighboring rings stacked along the *c*-axis in CCY (3.1424(8) Å and 2.9421(7) Å) are shorter than those in β-BBO (2.9999(2) Å and 3.3643(2) Å).[14] The calcium ions occupy distorted trigonal-prismatic voids between the layers formed by the cyanurate ions, with Ca–O bond lengths of 2.393(3)–2.938(3) Å (Figure 4). Three Ca–N distances
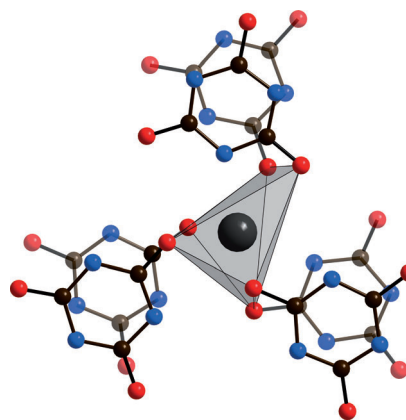

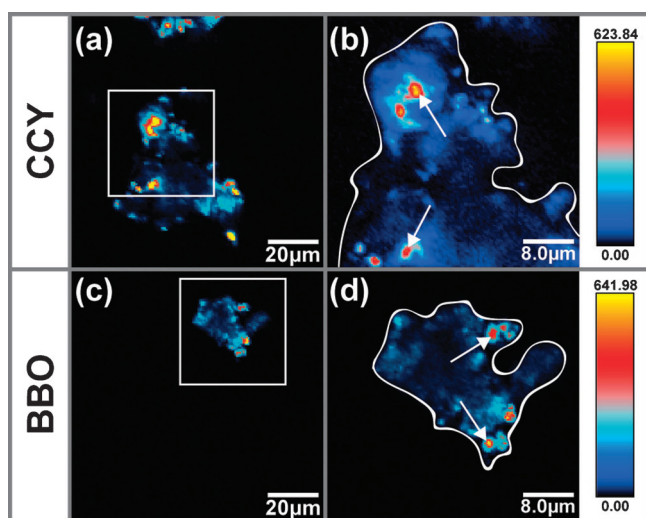***Figure 4.*** Distorted trigonal-prismatic environment of Ca^{2+} in the structure of CCY.

Figure 5. a,b) Images of CCY crystals; c,d) corresponding images of BBO crystals. The scan size in (a) and (c) is 100×100 μm, and (b) and (d) are enlargements of the sections marked by the white rectangles. In both samples an inhomogenous distribution of the signal intensity can be observed, and the white arrows mark the positions on which the spectra shown in Figure 6 were recorded.

(2.459(4)–2.472(3) Å) in the range of typical Ca−N bond lengths are also present.[15]

A crystalline powder of CCY was used to investigate the nonlinear optical properties. β-BBO was synthesized for comparison.[16] The crystal powders were both ground in agate mortars before recording NLO-spectra. SHG measurements were carried out with an inverted confocal microscope[17]. A detailed description can be found in Refs. [18,19]. Figure 5a,b displays the nonlinear signals recorded for CCY, while in Figure 5c,d corresponding measurements for β-BBO are presented. The image size is 100×100 μm in (a) and (c) and 40×40 μm in (b) and (d).

In this case the complete nonlinear spectrum is integrated on the detector. Furthermore, the spectroscopic investigations in Figure 6a and b show that no two-photon luminescence can be observed. SHG is thus the only detectable signal and hence responsible for the optical contrast in Figure 5.

In principle both CCY and β-BBO exhibit an inhomogenous intensity distribution, and large regions show only weak SHG-signals. Nevertheless, certain positions demonstrate a very efficient SHG and the arrows in Figure 5 mark such positions. These positions were used for the spectroscopic investigations presented in Figure 6. Figure 6 displays the nonlinear spectra of CCY for three different excitation powers over a wide spectral range, as well as an enlarged section around the SHG peak for a wider range of exitation powers (12–243 μW). The different excitation powers are shown on the right side of Figure 6b. The corresponding spectra of β-BBO are not illustrated here, as they exhibit exactly the same spectral profile. In Figure 6c, the dependence of the SHG signal intensity on the excitation power is depicted in a double logarithmic representation. SHG is a nonlinear second-order process and thus both linear-fit lines have a slope of approximately 2 (2.04 for CCY and 2.21 for β-
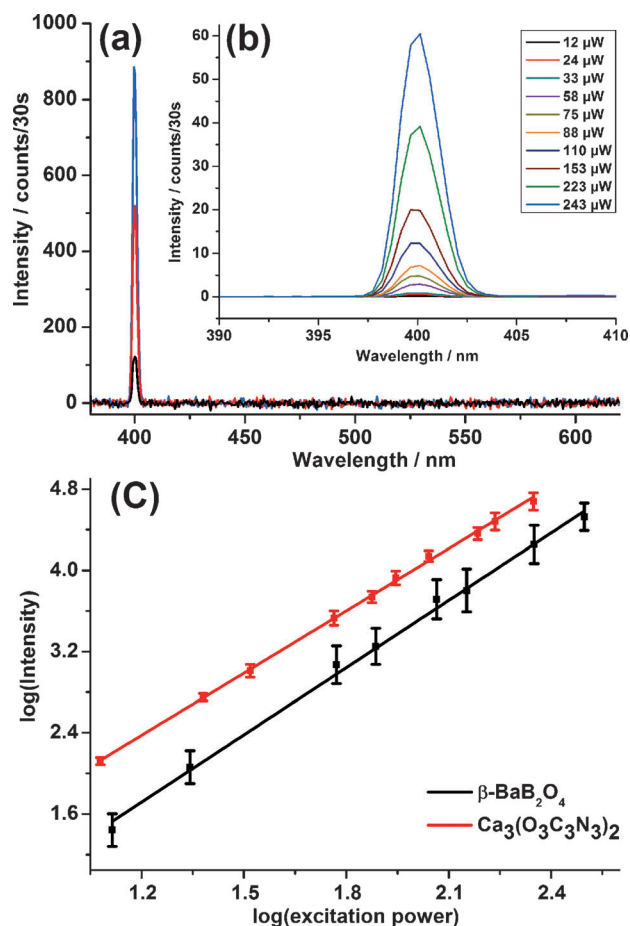

Figure 6. a) Spectra of the nonlinear effects of CCY for three different excitation intensities; exclusively SHG is observed. b) Enlarged section around the SHG signal for a larger range of excitation intensities. The logarithmic representation of the dependence of the excitation intensity in (c) show that the SHG signal intensity is a function of the excitation intensity's square and that CCY is more efficient than BBO.

BBO). The slope of the linear-fit lines and the spectral position confirm that the observed nonlinear signal is based on SHG. In this representation it is apparent that CCY has, in comparison to β-BBO, a higher SHG efficiency of about one order of magnitude and hence CCY could be a promising candidate for applications such as the frequency doubling of laser radiation.

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[11] $Ca_3(O_3C_3N_3)_2$ was produced from (dried) calcium chloride and potassium cyanate in an hermetically sealed quartz glass ampoule (300 mg starting compounds, 6 cm³ ampoule volume). The mixture was heated to 550°C for one hour, held at this temperature for 30 minutes, and then annealed at 525°C for 6 hours. After this it was cooled to room temperature at a cooling rate of 0.1 K min⁻¹. The ampoules were opened to air and the product washed with water and rinsed with ethanol.

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[13] Crystal structure data of $Ca_3(O_3C_3N_3)_2$: $M_r = 372.36$, trigonal, space group $R3c$ (No. 161), $a = 11.519(2)$ Å, $c = 12.175(3)$ Å, $Z = 6$, $F(000) = 1116$, $\rho_{ber.} = 2.652$ g cm⁻³, $\mu = 1.823$ mm⁻¹, crystal dimensions $0.9 \times 0.03 \times 0.02$ mm³, $\theta = 3.54–24.45°$, MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å), $T = 293$ K, 4262 measured reflections (STOE IPDS diffractometer), of which 532 were independent ($R_{int.} = 0.0496$). Lorentz, polarization, and absorption correction (software STOE IPDS I). Structure solution by direct methods (SHELXS). Refinement according to the least squares method with full matrix procedure for F^2 values, data/parameter ratio 532/65; final R values $R1 = 0.0245$, $wR2 = 0.0584$ for all data, GOF = 1.122, Flack parameter 0.37(6). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-428357.

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