Nonlinear Optics

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Promising Material for Infrared Nonlinear Optics: NaI_3O_8 Salt Containing an Octaoxotriiodate(V) Anion Formed from Condensation of $[IO_3]^-$ Ions**

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The crystal engineering of efficient materials for quadratic nonlinear optics (NLO) led us to take an interest in the coordination chemistry of metal iodates.[1–8] In the 1970s, metal iodates had been extensively studied at Bell Laboratories for their NLO properties but also for their ferroelectric, piezoelectric, and pyroelectric properties.[9–14] Interest for iodate compounds resumed in the beginning of the 2000s. The work of Albrecht-Schmitt and co-workers was mainly devoted to actinide iodates regarding their radiation stability.[15–17] However, some compounds such as $RbMoO_3(IO_3)$ and $CsMoO_3(IO_3)$ have been studied for NLO properties.[18] To obtain high nonlinear susceptibilities, the molecular or ionic arrangement of the crystal has to contain a periodic system of polarizable free electrons, in addition to the acentric crystal structure. Accordingly, the asymmetric $[IO_3]^-$ ion with the lone electron pair on iodine is an appropriate building block that favors the formation of acentric inorganic crystals[19] and promotes the formation of polar structures by coordination to metal ions through its oxygen atoms.[6,7,11,14,20]

Recently, we have shown that metallic iodates are particularly interesting for infrared applications as they possess a large domain of transparency from the visible region to the beginning of the far-IR region (12.5 μm), thus covering the three atmospheric transparency windows.[6–8] Furthermore, they present high nonlinear coefficients and high optical damage thresholds on powders. Their preparation is simple and reproducible; they are thermally stable at least up to 400 °C. These results are important since until now, only two classes of materials, the chalcopyrites and the halides, present such a transparency. Nevertheless, these materials are respectively difficult to prepare or are chemically unstable.[21,22] Thus, we believe that the iodate family could be an alternative to these materials for potential applications in the third atmospheric transparency window.[23]

During our explorations for obtaining new metallic iodates, we discovered a new NaI_3O_8 phase. The crystal structure reveals the octaoxotriiodate(V) $[I_3O_8]^-$ ion, which was only mentioned in 1941, in KI_3O_8 and RbI_3O_8 compounds.[24] It was named pyroiodate, but no structure was proposed, and the existence of the $[I_3O_8]^-$ ion has not been proved. The previously known compound HI_3O_8 should rather be referred to as a $HIO_3(I_2O_5)$ complex.[25–28] Until now, only polyiodate anions of heptavalent iodine are known, such as $[I_2O_9]^{4-}$, $[I_2O_{10}]^{6-}$, and $[I_3O_{14}]^{7-}$.[29] For pentavalent iodine there are only two iodate anions: the widely studied $[IO_3]^-$ ion and the recently characterized $[IO_4]^{3-}$ ion in $Ag_4(UO_2)(IO_3)(IO_4)_2O_2$ and $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$.[17,30] The $[I_3O_8]^-$ ion is therefore the first characterized polyiodate of pentavalent iodine. It contains three stereochemically active lone electron pairs and is the result of the condensation of three $[IO_3]^-$ ions. Herein, we present the crystal structure of NaI_3O_8, as well as its thermal analysis, IR spectroscopy, and optical damage threshold on the powder. These data show that NaI_3O_8 has remarkable properties as a potential NLO material.

NaI_3O_8 crystallizes in the acentric space group $P\bar{4}$.[31] The asymmetric unit consists of two sodium ions in special positions on the $\bar{4}$ axes and one half of the $[I_3O_8]^-$ ion (as $IO(IO_3)$), whose central iodine atom is located in a special position on the twofold axis. This $[I_3O_8]^-$ ion is made of two terminal iodate groups (I1 and $I1^I$) with tetrahedral geometry, whereas the central iodine atom (I2) is in a trigonal-bipyramidal environment, corresponding to an AX_3E and AX_4E configuration, respectively (Figure 1).

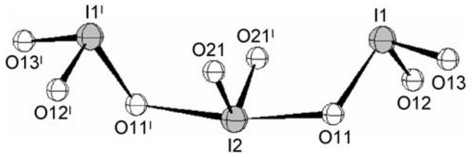

Figure 1. Representation of the $[I_3O_8]^-$ ion with C_{2v} symmetry. Selected bond lengths [Å] and angles [°]: I1-O11 1.919(3), I1-O12 1.785(4), I1-O13 1.780(4), I2-O21 1.806(4), I2-O11 2.046(3); O21-I2-O21^I 105.4(3), O21-I2-O11 89.6(2), O21^I-I2-O11 83.7(2), O11-I2-O11^I 168.9(2), I1-O11-I2 116.9(2). Equivalent positions: I superscript: (1−*x*, −*y*, *z*).

The I1 atom has two short I−O bonds with double-bond character (mean bond length 1.783(4) Å). The I1−O11 bond length is larger (1.919(3) Å), corresponding to the O11 atom bridging two iodine atoms. The I2 atom, which is located on a point of C_{2v} symmetry, has two short I2−O21 (1.806(4) Å) and two long I2−O11 bonds (2.046(3) Å). This geometry is very similar to the one observed for the $[IO_4]^{3-}$ ion, for which the

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axial bond lengths are in the range 1.97(2)–2.054(6) Å.[17,30] Furthermore, the O11-I2-O11^I angle (168.9(2)°) is intermediate between 153.9(7)° and 175.7(2)° found in the $[IO_4]^{3-}$ ion. In the structure of I_2O_5, the I–O bonds bridging the two iodine atoms are both shorter (1.92(2) and 1.95(3) Å).[32] Three additional I···O interactions (in the range 2.479(4) to 2.759(4) Å) and two others (2.910(4) Å) fill up the environment of I1 and I2, respectively, leading to a distorted octahedral sphere of coordination for each iodine atom (see the Supporting Information).[33] The geometry of the iodine atoms indicates without any doubt the presence of a lone electron pair on both of them, as confirmed by a bond valence sum calculation (BVS(I1) = 5.42, BVS(I2) = 5.32), corresponding to pentavalent iodine.[34,35] The difference between calculated BVS values and the corresponding classical valence is due to the distortion in the coordination polyhedron influenced by the presence of the lone electron pair.[36]

The $[I_3O_8]^-$ ion is coordinated to four sodium cations (Figure 2): Na1 is bound through O11 and O13 in a chelating fashion, leading to the formation of a four-membered ring, and Na2 is bound through O12 in a monodentate fashion. The Na2 coordination sphere is a slightly distorted tetrahedron: four Na2–O12 bonds of length 2.319(4) Å and O-Na2-O bond angles of 107.5(1)° and 113.5(2)°. The polyhedron of the Na1 atom, composed of eight oxygen atoms from four octaoxotriiodate groups, is distorted between a bicapped trigonal prism and an Archimedean antiprism. The Na1–O11 and Na1–O13 bond lengths are equal to 2.420(3) and 2.707(4) Å, respectively, and the O-Na1-O angles are between 60.5(1) and 146.2(1)°.

The crystal packing is made of layers parallel to the (001) plane (Figure 2). The Na1···Na1 and Na2···Na2 separations are equal to the *a* cell parameter (8.082(5) Å) although the sodium atoms are connected in a different fashion from the same $[I_3O_8]^-$ ion. The shortest intermetallic separation (5.715(5) Å) is between the Na1 and Na2 atoms through terminal iodate groups. The layers stack along the [001] direction, and the separation between the layers is equal to the *c* cell parameter (5.741(5) Å). The packing cohesion is assumed by two kinds of I···O interactions with separations equal to 2.479(4) Å (I1···O21) and 2.643(4) Å (I1···O13), leading to a three-dimensional network that ensures a good thermal stability of the compound up to 350 °C (see the Supporting Information).

The $[I_3O_8]^-$ ion is formed from the condensation of three iodate anions in concentrated nitric acid (HNO_3/H_2O azeotropic composition) without change in the valence of the iodine(V) atom. We can consider that in a first step a condensation by dehydration leads to the formation of iodic anhydride. Then, this species condenses with an iodate anion to form a dative bond. NaI_3O_8 is very soluble in aqueous solution (187 g L^{-1}, 25 °C), and the evaporation of the latter leads again to NaI_3O_8, thus demonstrating the stability of the anion.

Moreover, NaI_3O_8 is obtained as millimetric single crystals (Figure 3). This fact is a key point for the study of NLO properties on crystals and further for the development of device systems. Indeed, among metallic iodate compounds, α-$LiIO_3$ is until now the only one extensively studied, as the growth of large single crystals has allowed its NLO properties to be fully characterized.[37]

The IR spectrum of NaI_3O_8 shows a wide window of transparency from 2.5 μm to 12.5 μm (4000 to 800 cm^{-1}), corresponding to the beginning of the far-IR region (Figure 4). In contrast to α-$LiIO_3$, which shows an absorption band at 6.5 μm and two others around 3 μm and 6 μm attributable to H_2O, NaI_3O_8 is not hygroscopic and is transparent in both atmospheric transparency windows as all metallic iodates previously studied.[6–8]

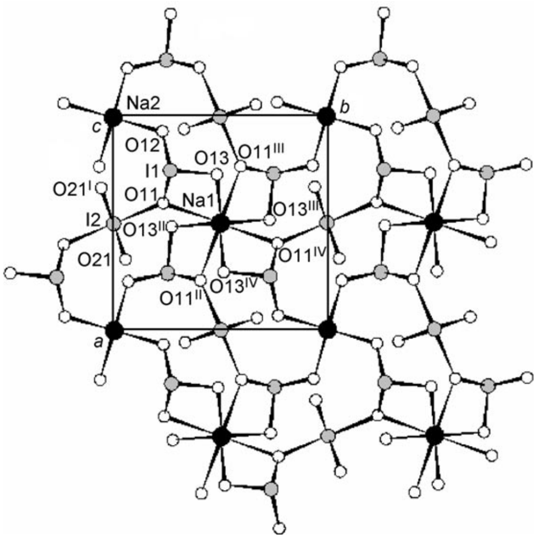

Figure 2. Projection of the NaI_3O_8 structure parallel to the (001) plane. Equivalent positions: I: (1−*x*, −*y*, *z*); II: (1−*y*, *x*, 1−*z*); III: (*y*, 1−*x*, 1−*z*); IV: (1−*x*, 1−*y*, *z*). In this projection, *c* is coming out of the page.

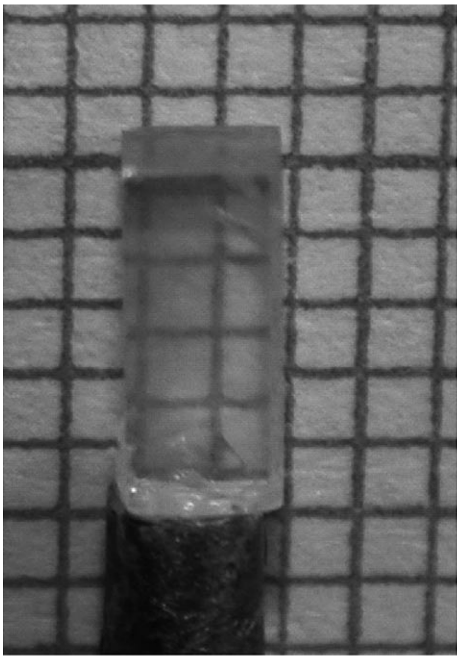

Figure 3. Photograph of a NaI_3O_8 single crystal (2×2×5 mm^3).

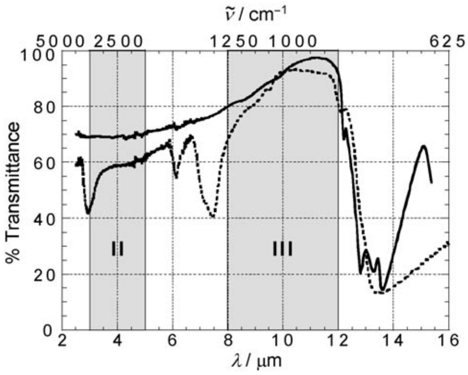

Figure 4. Transmittance curves of NaI_3O_8 (solid line) and $LiIO_3$ (dashed line) in the 2.5–15-µm region (gray bands correspond to the atmospheric transparency windows II and III).

NaI_3O_8 shows an intense second-harmonic-generation (SHG) powder activity which is qualitatively comparable to the signal generated by α-$LiIO_3$.[7] Moreover, it shows high optical damage thresholds on the powder: NaI_3O_8, 4.2 ± 0.3 GW cm^{-2}; α-$LiIO_3$, 3.0 ± 0.3 GW cm^{-2}. This value obtained on the powder is underestimated, and the value measured on a single crystal should be higher, as observed for α-$LiIO_3$ (8 GW cm^{-2}).[37] These damage thresholds are close to the ones measured at the same wavelength on commercial single crystals: 23 GW cm^{-2} for KDP with pulses of 200 ps and 10 GW cm^{-2} for BBO with pulses of 100 ps.[37]

In conclusion, this new compound is thermally stable, nonhygroscopic, and easy to synthesize. It crystallizes in an acentric space group and is obtained as millimetric single crystals. Moreover, it is transparent up to the beginning of the far-IR region, its SHG signal is intense, and its optical damage threshold is high. All these arguments lead us to conclude that this compound is a future candidate for a quadratic NLO material. As for iodate compounds, it is one of the first oxide materials which is transparent up to the far-IR region. In addition, this compound contains a novel anion that opens the way for new chemistry.

Experimental Section

NaI_3O_8 was obtained by evaporation at 60 °C of a solution containing $NaIO_3$ (1.781 g, 9 mmol) in nitric acid (30 mL, 7 M). After the water was evaporated, colorless prismatic crystals occurred in the azeotropic composition of the binary HNO_3/H_2O system. Yield: 90 %. Elemental analysis (%) calcd for NaI_3O_8: Na 4.32, I 71.60; found: Na 4.22, I 70.70. IR (Nicolet Magna 550 spectrometer using the ATR technique with a diamond crystal): $\tilde{\nu} = 820$ ($\nu_{I\text{-}O}$, w), 780 ($\nu_{I\text{-}O}$, s), 755 ($\nu_{I\text{-}O}$, s), 735 cm^{-1} ($\nu_{I\text{-}O}$, s). Optical damage threshold: the fundamental beam was emitted by a Q-switched mode-locked Nd^{3+}:YAG laser operating at 1.064 µm and generating pulses of 150-ps duration every 200 ms. The energy of the laser emission was gradually increased until the sample (grounded crystals placed between two glass sheets) became brown.

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[31] Crystal data of NaI_3O_8: $M_r = 531.69$ g mol^{-1}, colorless square-prismatic crystal ($0.2 \times 0.3 \times 0.3$ mm^3), tetragonal, space group $P\bar{4}$ (no. 81), $a = 8.082(1)$, $c = 5.741(1)$ Å, $V = 375.0(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 4.709$ g cm^{-3}, $\mu = 6.654$ mm^{-1}. NONIUS κ-CCD diffractometer, $Ag_{K\alpha}$ radiation ($\lambda = 0.56087$ Å), $T = 293$ K, $2\theta_{max} = 42.8°$, 5444 measured and 830 independent reflections, $R_{int} = 0.027$, $R1 = 0.017$ (821 data with $I > 2\sigma(I)$ and $wR2 = 0.039$ (all 5444 data) for 55 refined parameters, GOF = 1.241, max./min.

residual electron density 0.743/−0.828, Flack parameter 0.05(8). Corrections for Lorentz and polarization effects and empirical absorption correction (SADABS) were carried out. Structure was solved by direct methods with the SIR92 program and refined by full-matrix least squares, based on F^2, using the Shelxl software through the WinGX program suite. The refinement was performed with anisotropic thermal parameters for all atoms. 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-418336. A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343; G. M. Sheldrick, SHELXL-97, A program for crystal structure analysis, University of Göttingen, Germany, **1997**; L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

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