Nanocluster crystals of lacunary polyoxometalates as structure-design-flexible, inorganic nonlinear materials

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Lacunary polyoxometalates, large inorganic, structure-design-flexible, nanocluster crystals are found to have higher optical nonlinearity than KH_2PO_4 by the powder second-harmonic-generation method. Moreover, the capability of generating ultraviolet radiation down to around 300 nm is found. The basic criteria to design the high nonlinearity are also discovered by the reduction of the molecular symmetry. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1419230]

The development of optical nonlinear crystals for the frequency conversion of light is a field of great continuing interest as the best choice of the material strongly depends on the applications. Of the known nonlinear crystals, phosphate and borate crystals have been the most widely studied.[1–7] The design philosophy for these materials involves the selection of an anionic group which creates the largest possible nonlinearity with sufficient transmission for the designed wavelength and adequate birefringence for phase matching. This is demonstrated in crystals of β-BaB_2O_4,[1] LiB_3O_5,[2] $Li_2B_4O_7$,[3] $CsLiB_6O_{10}$,[4,5] $Gd_xY_{1-x}Ca_4O(BO_3)_3$[6] and $KBe_2BO_3F_2$.[7] To overcome the limitations of molecular variation inherent in such small molecules, research on organic compounds has been pursued. In spite of significant efforts, a practical nonlinear organic crystal has yet to be found. In this work we report a group of large inorganic, structure-design-flexible, nanocluster materials, lacunary polyoxometalates,[8,9] that were found to have greater optical nonlinearity than KH_2PO_4 (KDP), and are capable of generating ultraviolet radiation down to around 300 nm by the powder second-harmonic-generation (SHG) method.[10] We will also explain the basic criteria for designing higher nonlinearity into such nanocluster materials.

Historically, nanoclusters of polyoxometalate molecules have been intensively examined for application as potential catalysts. A subset of these nanoclusters was selected for testing of an extremely flexible design methodology for the creation of an optical nonlinear material. Owing to their extremely large molecular weight as inorganic material, the selected polyoxometalates are related to the $[XM_{12}O_{40}]^{n-}$ series (noted as XM_{12}), in which X=P, Si, or Ge and M=W or Mo. The structure of XM_{12} consists of an XO_4 tetrahedron sharing its oxygen atoms with four M_3O_{13} groups. These M_3O_{13} groups, made of three edge-sharing octahedra, are linked together at the corners. This is the well-known Keggin structure labeled D0 in Fig. 1(a). By removing one MO_6 octahedron from the XM_{12} skeleton the defect-Keggin structure XM_{11} is derived, labeled D1 in Fig. 1(b), while the removal of three MO_6 octahedra leads to the defect-Keggin structure XM_9, labeled D3 in Fig. 1(c). For example, $Na_{10}SiW_9O_{34}\cdot 18H_2O$[11] and $Na_{10}GeW_9O_{34}\cdot 18H_2O$[11] have the structure of XM_9, where X=W, as a result of the removal of three MO_6 units. $K_7PW_9Mo_2O_{39}\cdot xH_2O$[12] has the structure of XM_{11}, as a result of the removal of one MO_6 unit, and the substitution of two W atoms for two Mo atoms labeled S2.

To examine the optical nonlinearity of the nanocluster crystals, we used the conventional powder SHG method using a 1064 nm optical pulse from a *Q*-switched Nd:$Y_3Al_{15}O_{12}$ (YAG) laser. The green light at 532 nm was filtered and detected with an image sensor. As can be seen from Fig. 2, three of the nanocluster crystals were found to exhibit significant nonlinearity and $Na_{10}SiW_9O_{34}\cdot 18H_2O$ showing about ten times the efficiency of KDP powder under the same conditions was the most efficient. Interestingly, all the three compounds are of defect-Keggin structure with noncentrosymmetry. However, crystal structures of $Na_{10}GeW_9O_{34}\cdot 18H_2O$ and $K_7PW_9Mo_2O_{39}\cdot xH_2O$ could be analyzed by the centrosymmetric space groups of $P\bar{1}$ and C2/m, respectively. One may point out the discrepancy between their crystal lattices and observable SHG, since SHG should be observed for noncentrosymmetric lattices. After several cycles of refinement with anisotropic temperature factors, three W atoms for $Na_{10}GeW_9O_{34}\cdot 18H_2O$ were found to occupy two disordered positions of α and β forms and the occupancy factors for the two equivalent atoms were assumed to be 0.1 and 0.9. For $K_7PW_9Mo_2O_{39}\cdot xH_2O$, four PO_4–O atoms were also found to occupy two disordered positions at approximate cubic corners (in P–O distances of 1.50–1.55 Å) with an occupancy ratio of 1/1 for the two equivalent atoms. Such a disordered crystal structural feature for the two compounds indicates the disappearance of noncentrosymmetric center in the lattice, which supports the observation of SHG signal. Although the crystal structure of the most SHG-efficient $Na_{10}SiW_9O_{34}\cdot 18H_2O$ compound is not clear due to a failure of the preparation of its single crystal, we expect the similar disorder of α and β forms for

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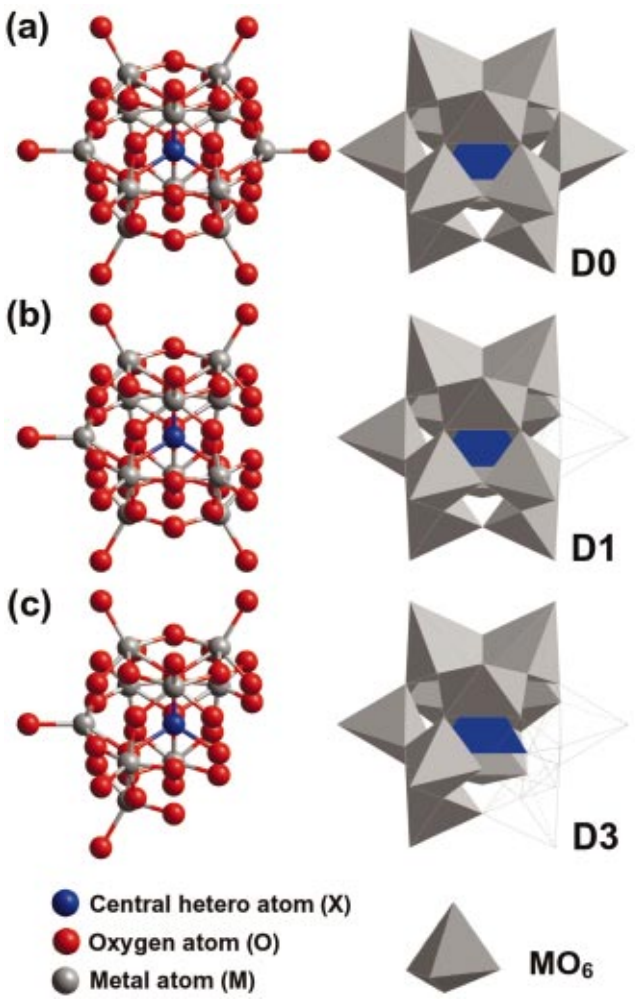

FIG. 1. (Color) Keggin structures of the polyoxometalate. (a) Defect-free Keggin structure, which is related to the $[XM_{12}O_{40}]^{n-}$ series (noted as XM_{12}). The structure of XM_{12} consists of an XO_4 tetrahedron sharing its oxygen atoms with four M_3O_{13} groups. These M_3O_{13} groups, consisting of three edge-sharing octahedra, are linked together at the corners, labeled D0. (b) Defect-Keggin structure derived from XM_{12} by the removal of one MO_6 octahedron, XM_{11}, labeled D1. (c) Defect-Keggin structure derived from XM_{12} by the removal of three MO_6 octahedra, XM_9, labeled D3.

$Na_{10}GeW_9O_{34}\cdot 18H_2O$ for the $P\bar{1}$ space group of β form.[13] The introduction of the disorder of isomers of compound in the lattice provides a new design for the SHG-sensitive crystals.

From these results, we have defined three design criteria that are expected to enhance the optical nonlinearity of this class of nanoclusters. The first criterion is that the cluster molecule should have a heavy center atom ($Ge \geqslant Si > P$) for larger nonlinearity. The second criterion is that a defect-Keggin structured molecule has greater nonlinearity than that of a defect-free molecule. The third criterion is that the metal atom of the molecule should be partially substituted. The second and third criteria illustrate the importance of reducing symmetry within the clusters to increase nonlinearity.

Of additional interest is knowledge of the shortest possible second-harmonic wavelength achieved by the three nonlinear nanocluster crystals determined using the linear transmission and phase-matching conditions. Before evaluation of nonlinear frequency conversion capabilities in the ultraviolet region, diffuse reflection was measured for the nanoclusters and KDP powders to determine the transmission

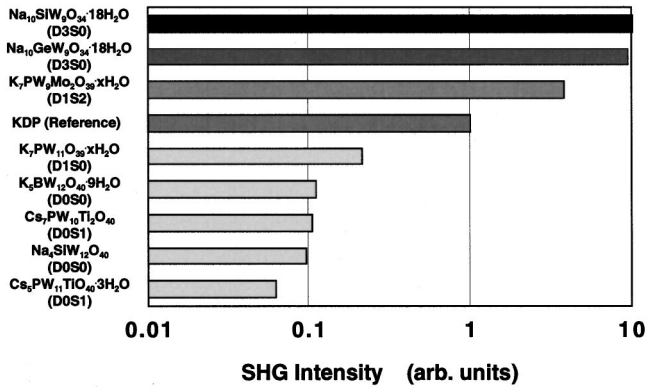

FIG. 2. Powder second-harmonic-generation method results using a 1064 nm optical pulse from a *Q*-switched Nd:YAG laser as the fundamental radiation. Label S denotes the substitution number of metal atom.

edge of the shortest wavelength as shown in Fig. 3. The cutoff wavelengths for these materials reached down to 300, 288, and 334 for $Na_{10}SiW_9O_{34}\cdot 18H_2O$, $Na_{10}GeW_9O_{34}\cdot 18H_2O$, and $K_7PW_9Mo_2O_{39}\cdot xH_2O$, respectively. Such superior transmission down to the ultraviolet region is the one major attractive feature of these inorganic complexes. This represents a significant advantage over flexible designed organic material with poor ultraviolet transmission.

The SHG capability dependence over different fundamental wavelengths was evaluated using the powder SHG method illustrated above. Differing from the prior use of infrared fundamental light, the fundamental visible optical pulse from 410 to 700 nm was provided by the output signal from an optical parametric oscillator pumped by the third harmonic of a *Q*-switched Nd:YAG laser in which the output pulse energy was regulated by a pair of polarizers. For the detection of the scattered second harmonic light, an interference filter was introduced for the ultraviolet-transparent imaging optics (UV Nikkor 105 mm) and ultraviolet-sensitive charge coupled device (CCD) camera (Hamamatsu photonics C-8000). As the fundamental wavelength was tuned a filter with appropriate transmission characteristics was selected. The intensity of the detected light was digitized from the integration of the radiation passed through the optics. The relative SHG efficiency was evaluated by considering this digitized signal, the spectral response of the CCD detector, and the transmission through the optics as shown in Fig. 4. The actual SHG cutoff wavelengths were found to be 305, 305, and 250 nm for $Na_{10}SiW_9O_{34}\cdot 18H_2O$,

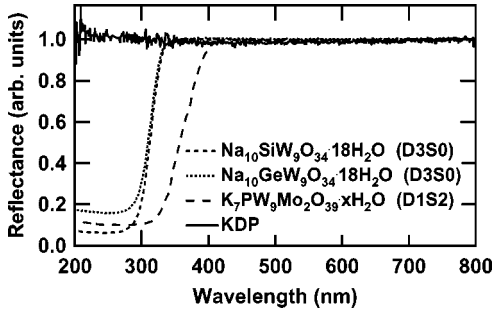

FIG. 3. Diffuse reflection spectra for $Na_{10}SiW_9O_{34}\cdot 18H_2O$, $Na_{10}GeW_9O_{34}\cdot 18H_2O$, $K_7PW_9Mo_2O_{39}\cdot xH_2O$, and KDP. The cutoff wavelengths for these materials are defined as the value at 20% reflectance.

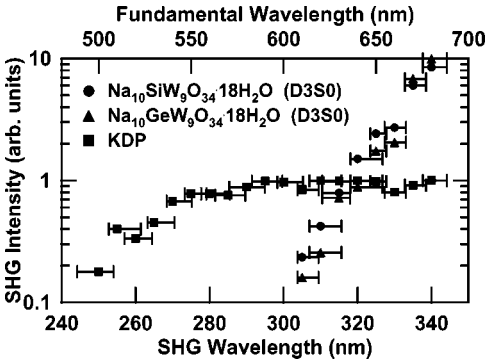

FIG. 4. SHG efficiency of $Na_{10}SiW_9O_{34}\cdot 18H_2O$, $Na_{10}GeW_9O_{34}\cdot 18H_2O$, and KDP for different fundamental wavelengths. All values are normalized by the maximum value of KDP and error bars represent the bandwidth of the interference filter.

$Na_{10}GeW_9O_{34}\cdot 18H_2O$ and KDP, respectively, within 10 nm accuracy considering the 10 nm bandwidth of the interference filter. This measurement agrees well with the shortest reported SHG wavelength of 258 nm for the KDP reference. All of these results using powder material are summarized in Table I including transmission cutoff wavelength, SHG cutoff wavelength, and SHG intensity. The application of a SHG device with high conversion efficiency or the determination of detailed optical properties such as the Sellmeier equation, birefringence, and the *d*-coefficient, require larger crystals with appropriate surface treatments. For this purpose, a number of millimeter-sized $K_7PW_9Mo_2O_{39}\cdot xH_2O$ crystals have been grown from solution as shown in Fig. 5. We hope to grow crystals with size larger than 1 cm that will satisfy all requirements after additional efforts toward enhancing crystal growth.

In conclusion, we found three inorganic, flexibly designed, nanocluster materials which exhibit greater optical nonlinearity than KDP. The potential SHG capability down to 300 nm promises further material development flexibility down to the deep ultraviolet region that had been obviously

TABLE I. Experimental results of nanocluster crystals.

	Transmission cutoff wavelength (nm)	SHG cutoff wavelength (nm)	SHG intensity (normalized)
$Na_{10}SiW_9O_{34}\cdot 18H_2O$	300	305 ± 10	10.2
$Na_{10}GeW_9O_{34}\cdot 18H_2O$	288	305 ± 10	9.4
$K_7PW_9Mo_2O_{39}\cdot xH_2O$	334	···	3.8
KDP	174[a]	250 ± 10 (258.5[a])	1

[a]Reference 14.

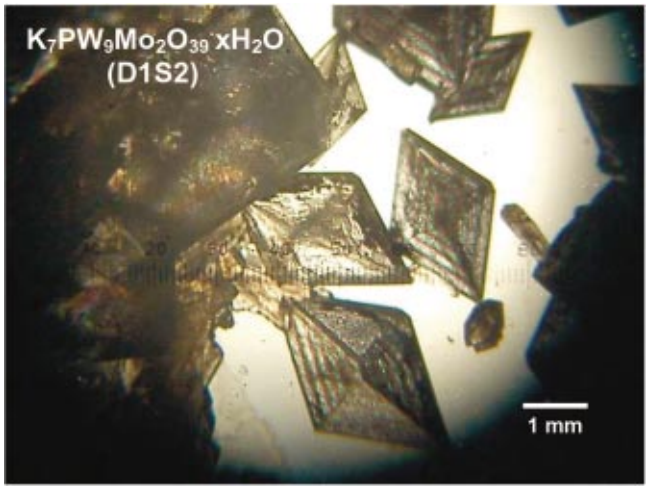

FIG. 5. (Color) Photograph of a few millimeter-sized $K_7PW_9Mo_2O_{39}\cdot xH_2O$ crystals grown from solution.

impossible to achieve with most organic nonlinear molecules. Moreover, we also show three basic design criteria for increasing nonlinearity that are more flexible than possible with most inorganic materials. This application of nanoclusters in nonlinear optics should open the door to a vast and hitherto unexplored region of material science.

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[1] H. Vanherzeele and C. Chen, Appl. Opt. **27**, 2634 (1988).
[2] C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li, and S. Lin, J. Opt. Soc. Am. B **6**, 616 (1989).
[3] R. Komatsu, T. Sugawara, K. Sassa, N. Sarukura, Z. Liu, S. Izumida, Y. Segawa, S. Uda, T. Fukuda, and K. Yamanouchi, Appl. Phys. Lett. **70**, 3492 (1997).
[4] Y. Mori, I. Kuroda, S. Nakajima, T. Sasaki, and S. Nakai, Jpn. J. Appl. Phys., Part 2 **34**, L296 (1995).
[5] Y. Mori, I. Kuroda, S. Nakajima, T. Sasaki, and S. Nakai, Appl. Phys. Lett. **67**, 1818 (1995).
[6] M. Iwai, T. Kobayashi, H. Furuya, Y. Mori, and T. Sasaki, Jpn. J. Appl. Phys., Part 2 **36**, L276 (1997).
[7] L. Mei, Y. Wang, C. Chen, and B. Wu, J. Appl. Phys. **74**, 7014 (1993).
[8] J. F. Keggin, Nature (London) **132**, 351 (1933).
[9] T. Yamase and M. Sugeta, J. Chem. Soc. Dalton Trans., 759 (1993).
[10] S. K. Kurtz and T. T. Perry, J. Appl. Phys. **39**, 3798 (1968).
[11] G. Hervé and A. Tézé, Inorg. Chem. **16**, 2115 (1977).
[12] R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, and M. Fournier, Inorg. Chem. **16**, 2916 (1977).
[13] F. Robert and A. Tézé, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **37**, 318 (1981).
[14] V. G. Dmitriev, G. G. Gurzadyan, and D. N. Nikogosyan, in *Handbook of Nonlinear Optical Crystals* (Springer, Berlin, 1999).