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# Crystal Growth, Structure, and Properties of New Nonlinear Optical Materials: $K_2Ln(NO_3)_5 \cdot 2H_2O$ ($Ln = $ La, Ce, Pr, Nd, Sm)

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**Single crystals of $K_2Ln(NO_3)_5 \cdot 2H_2O$ ($Ln = $ La, Ce, Pr, Nd, Sm) (K*Ln*N) were grown by evaporation in aqueous solution under constant temperature conditions. The structure of KPrN was determined from the single-crystal X-ray diffraction data. The KPrN crystallizes in the orthorhombic space group *Fdd*2 with parameters $a = 21.411(3)$ Å, $b = 11.2210(10)$ Å, $c = 12.208(2)$ Å, $Z = 6$, $V = 2933.0(7)$ Å$^3$, $R = 0.0240$, $R_w = 0.0603$. The powder second harmonic generation (SHG) intensities of *KLn*N ($Ln = $ La, Ce, Pr, Nd, Sm) are also studied. The results demonstrate that their SHG intensities are 4–9 times larger than that of KDP, in which the KPrN shows the highest SHG coefficient.** © 1999 Academic Press

***Key Words:*** **rare earth; potassium lanthanide nitrate hydrate; crystal growth.**

## INTRODUCTION

Recently there has been an increasing interest in the investigation of obtaining perfect SHG (second harmonic generation) materials under mild experimental conditions in which crystals can be easily grown with large size and high quality. Such kinds of nonlinear optical materials of K*Ln*N (*Ln* = La, Ce) were reported in 1993 (1) for the first time. The properties of a series of double nitrates of praseodymium with alkali metals including $Li_2Pr(NO_3)_5 \cdot 4H_2O$, $Na_2Pr(NO_3)_5 \cdot H_2O$, and $Cs_2Pr(NO_3)_5 \cdot H_2O$ were studied by Molodkin (2). However, the crystal of $K_2Pr(NO_3)_5 \cdot 2H_2O$ was not obtained in the same experimental conditions. In order to study the nonlinear optical properties of this series of double nitrates, we changed experimental conditions in (2) and got K*Ln*N (*Ln* = Pr, Nd, Sm). Their structure and nonlinear optical properties were studied by FCD (four-circle diffractometer) and powder SHG measurements, respectively.

## EXPERIMENTAL

### Crystal Growth

The complexes of K*Ln*N (*Ln* = La, Ce, Pr, Nd, Sm) are water soluble crystals and can be easily grown by evaporation under constant temperature conditions or by slow cooling. In this paper, evaporation under constant temperatures between 40–65°C has been successfully used to obtain K*Ln*N crystals. For example, for KPrN's crystal growth, 260 ml aqueous solution containing $KNO_3$ (concentration: 5.5 M) and $Pr(NO_3)_3$ (concentration: 2.65 M) was evaporated at 55°C. Molodkin did not obtain the crystal of KPrN in aqueous solution with $[H^+] \approx 6$ N. The pH value was adjusted to 1–2 when the volume of the solution was reduced to about 170 ml. Later the single crystal of KPrN grew slowly from the solution and it took three days to grow to the dimensions 18 × 18 × 10 mm, shown in Fig. 1. The single crystal of K*Ln*N (*Ln* = La, Ce, Pr, Nd) was grown from a solution containing K and *Ln* in a molar ratio 2:1 in a similar way and kept in the normal desiccator while a single crystal of KSmN whose crystal shape is the same as K*Ln*N (*Ln* = La, Ce, Pr, Nd) should be kept in a vacuum container because the transparent light-yellow single crystal of KSmN became opaque as soon as it was pulled out of the solution of $KNO_3$ and $Sm(NO_3)_3$. The chemical analysis demonstrated that the molecular formula of these crystals is $K_2Ln(NO_3)_5 \cdot 2H_2O$ (*Ln* = La, Ce, Pr, Nd). The picture of a single crystal of $K_2Pr(NO_3)_5 \cdot 2H_2O$ with dimensions of 18 × 18 × 10 mm is shown in Fig. 1.

### Characterization

The structure of KPrN was solved on Siemens P4 four-circle diffractometer which used graphite monochromatic Mo*K*α radiation ($\lambda_{MoK\alpha} = 0.71073$ Å). The SHG intensity was measured by powder SHG measurement with the experimental conditions of 1.06 μm (YAG:Nd) laser wavelength, ~3.14 kw/cm$^2$ peak power density, 3 mJ single

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**FIG. 1.** Single crystal of $K_2Pr(NO_3)_5 \cdot 2H_2O$.

pulse energy, 700 V photoelectricity multiplication tube, and a M118 difference preamplifier. All reagents used in our experiments are analytical reagents.

## RESULTS AND DISCUSSION

### *Structure of KPrN*

The crystal structures of KLaN, KCeN, and KNdN have been described in (3, 1, 4). We have determined the crystal structure of KPrN, which proved to be isostructural to KLaN, KCeN, and KNdN. The X-ray diffraction data of a light-green single crystal of KPrN with dimensions approximately $0.50 \times 0.40 \times 0.36$ mm were collected on the Siemens P4 four-circle diffractometer with graphite monochromater and Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 1468 reflections were measured, of which 1204 ($R_{int} = 0.0200$) were unique and considered significant with $I_{net} > 2d(I_{net})$ in the range $5 < 2\theta < 60$ by the $\omega$-$2\theta$ scan technique at room temperature. All data were corrected for Lorentz factors and empirical absorption. The structure was solved by direct method and all nonhydrogen and hydrogen atoms were found in difference electron density maps. The atomic coordinates and anisotropic temperature factors for nonhydrogen atoms were refined by a full-matrix least-squares method using the SHELXTL-PLUS program package. The final unweighted and weighted agreement factors of $R = \sum||F_o - F_c||/\sum|F_o| = 0.0240$ and $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2} = 0.0603$ were obtained. The largest peaks on the final difference Fourier map had a height of 2.181eÅ$^{-3}$. A summary of the crystal and intensity measurements data are given in Table 1 and atomic coordinates are given in Table 2. Table 3 shows the anisotropic displacement parameters [Å$^2 \times 10^3$] for KPrN.

Figure 2 shows a portion of the structure of KPrN. It illustrates that the Pr atom is coordinated by twelve oxygen atoms, ten of them belong to five bidentate nitrate groups and two are water molecules. The K atom is nine-coordinated, including two bidentate nitrate groups, four

**TABLE 1**
**Crystal Data and Structure Refinement for KPrN**

| | |
|---|---|
| Crystal data | |
| Empirical formula | $K_2Pr(NO_3)_5 \cdot 2H_2O$ |
| Formula weight | 565.19 |
| Crystal system | Orthorhombic |
| Space group | *Fdd*2 |
| Unit cell dimensions | $a = 21.411(3)$ Å, $b = 11.2210(10)$ Å,<br>$c = 12.208(2)$ Å, |
| Volume, $Z$ | 2933.0(7) Å$^3$, 6 |
| Density (calculated) | 1.920 Mg/m$^3$ |
| Absorption coefficient | 2.998 mm$^{-1}$ |
| $F(000)$ | 1632 |
| Crystal size | $0.50 \times 0.40 \times 0.36$ mm |
| Intensity measurements | |
| Temperature | 293(2) K |
| Radiation wavelength | 0.71073 Å |
| $\theta$ range for data collection | $2.64 < \theta < 29.96°$ |
| Limiting indices | $-1 \le h \le 30$, $-1 \le k \le 15$,<br>$-1 \le l \le 17$ |
| Reflections collected | 1468 |
| Independent reflections | 1204 ($R_{int} = 0.0200$) |
| Max. and min. transmission | 0.30753 and 0.21446 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| data/restraints/parameters | 1204/1/116 |
| Goodness-of-fit on $F^2$ | 1.147 |
| Final $R$ indices [$I > 2\theta(I)$] | $R = 0.0240$, $R_w = 0.0603$ |
| $R$ indices (all data) | $R = 0.0244$, $R_w = 0.0606$ |
| Absolute structure parameter | $-0.04(2)$ |
| Extinction coefficient | 0.0154(5) |
| Largest diff. peak and hole | 2.181 and $-1.031$ eÅ$^{-3}$ |

**TABLE 2**
**Atomic Coordinates [Å×10$^4$] and Equivalent Isotropic Displacement Parameters [Å$^2$×10$^3$] for KPrN**

| | $x$ | $y$ | $z$ | $U$(eq)$^a$ |
|---|---|---|---|---|
| Pr | 0 | 10000 | 5000(1) | 16(1) |
| K | 1042(1) | 5583(1) | 4799(1) | 30(1) |
| O(1) | 609(2) | 9518(3) | 3208(3) | 24(1) |
| O(2) | 397(2) | 7797(4) | 5124(4) | 28(1) |
| O(3) | − 586(2) | 8596(3) | 3544(4) | 30(1) |
| O(4) | − 1487(2) | 3269(4) | 4543(3) | 35(1) |
| O(5) | − 483(1) | 8155(3) | 5914(3) | 27(1) |
| O(6) | − 165(2) | 6320(3) | 5727(5) | 38(1) |
| O(7) | 0 | 5000 | 3567(4) | 57(3) |
| O(8) | 459(2) | 9614(5) | 7024(4) | 34(1) |
| N(1) | − 741(2) | 9430(4) | 2910(4) | 22(1) |
| N(2) | − 86(2) | 7385(4) | 5595(5) | 22(1) |
| N(3) | 0 | 5000 | 2565(6) | 30(2) |
| OW | 1225(2) | 9868(4) | 5250(3) | 27(1) |

$^a U_{(eq)}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

**TABLE 3**
**Anisotropic Displacement Parameters [Å$^2$×10$^3$] for KPrN**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Pr | 17(1) | 16(1) | 15(1) | 0 | 0 | 2(1) |
| K | 29(1) | 27(1) | 35(1) | − 6(1) | − 1(1) | 3(1) |
| O(1) | 23(2) | 20(2) | 28(2) | − 1(1) | 4(1) | 0(1) |
| O(2) | 22(2) | 23(1) | 40(2) | 3(2) | 11(2) | 6(1) |
| O(3) | 39(2) | 22(2) | 28(2) | 6(2) | − 5(2) | − 4(1) |
| O(4) | 41(2) | 40(2) | 23(2) | 2(2) | − 9(2) | 7(2) |
| O(5) | 25(2) | 24(1) | 31(2) | 4(1) | 9(2) | 5(1) |
| O(6) | 41(2) | 17(2) | 54(3) | 7(2) | 3(2) | 0(2) |
| O(7) | 51(5) | 109(9) | 12(3) | 0 | 0 | − 22(4) |
| O(8) | 27(2) | 45(2) | 31(2) | 9(2) | 4(2) | 12(2) |
| N(1) | 20(2) | 26(2) | 21(2) | − 2(2) | 1(2) | − 4(2) |
| N(2) | 25(2) | 20(2) | 22(2) | 5(2) | 0(2) | 1(1) |
| N(3) | 22(4) | 50(5) | 17(3) | 0 | 0 | − 6(2) |
| OW | 24(2) | 32(2) | 24(3) | − 6(2) | 4(1) | − 1(1) |

*Note.* The anisotropic displacement factor exponent takes the form $-2\pi^2[(ha^*)^2U_{11} + \cdots + 2hka^*b^*U_{12}]$.

nomodentate nitrate groups, and one water molecule. The Pr and K atoms are connected through $NO_3^-$ or $NO_3^-$ and $H_2O$, while K and K atoms are connected through $NO_3^-$. The $[Pr(NO_3^-)_5 \cdot 2H_2O]^{2-}$ complex has no direct contact with adjacent Pr-complexes, but the three-dimensional framework is formed by potassium ions, nitrate groups, and hydrogen bonds.

Table 4 lists the selected bond distances and angles concerning a portion of the structure of KPrN. The Pr–O bond lengths, including the coordinated nitrate and water oxygens, vary in a narrow range (2.570–2.693 Å) and the average bond length of Pr–O ($NO_3^-$) is 2.634 Å and of Pr–O($H_2O$) is 2.646 Å, indicating that the coordination icosahedron around Pr is slightly distorted.

It is well known that the free nitrate group is a plane anion with a threefold symmetry axis. Its symmetry is slightly distorted when it coordinates an atom of metal. It can be seen that the O–N–O interbond angles of N1 and N2 nitrate groups in KPrN show a small deviation from 120° and the N–O distances are all unequal. However, the N3 nitrate group shows a twofold symmetry, as can be seen from Fig. 3. Usually in rare-earth nitrates of alkali cations the $Ln^{3+}$ ion locates in the same plane as nitrate groups (5). It is found that the N–O distances vibrate within the limits 1.217–1.228 Å for the O atoms not coordinated by Pr atoms while within 1.260–1.273 Å for those coordinated. Therefore the presence of the Pr–O bond elongates the corresponding distance O–N and the oxygen atoms uncoordinated by Pr are closer to the nitrogen atom than those coordinated. We also found that the O–N–O interbond angle involving the two coordinated oxygen atoms is smaller than 120° (average value is 116.6°) and the other two angles are slightly larger than 120° (average value 121.7°).

### *Powder SHG Measurement*

A powder technique for the evaluation of nonlinear optical materials (6) was used to measure the SHG intensity of K*Ln*N (*Ln* = La, Ce, Pr, Nd, Sm). The results were listed in Table 5.

The SHG powder data of K*Ln*N demonstrates that their SHG intensities are at the same order of magnitude. Ebbers *et al.* have reported SHG nonlinear coefficients for KLaN (1):

$$d_{31} = -1.13 \pm 0.15 \text{ pm/v}$$

$$d_{32} = +1.10 \pm 0.10 \text{ pm/v}$$

$$d_{33} = +0.13 \pm 0.10 \text{ pm/v}.$$

As we know, the SHG intensity ($I_i^{2\omega}$) has direct relations to non-phase-matching SHG coefficients ($d_{NPM}$), refractive indexes ($n$), average values of the particle size ($r$), and the thickness of the plate ($l_c$):

$$I^{2\omega} \propto \frac{\langle d_{ijk}^2 \rangle}{(n+1)^6} * \frac{l_c^2}{2r}.$$

It can yield

$$\frac{d_{NPM}^2(i)}{d_{NPM}^2(\text{KDP})} = \frac{I_i^{2\omega}}{I_{KDP}^{2\omega}} * \frac{(n_i+1)^6}{(n_{KDP}+1)^6},$$

where $n_{KDP} = 1.49$ ($\lambda = 0.53$ μm) and $n_i \approx n_{KLnN} = 1.5382$ ($\lambda = 0.5461$ μm). It can be seen that the average values of $d_i$ of K*Ln*N in Table 5 coincide with those of KLaN, reported by Ebbers *et al.* Since KPrN itself reflects green light ($\lambda = 530$ nm) which is received by the SHG measurements, the value of $d_{KPrN}$ is much larger than that of K*Ln*N (*Ln* = La, Ce, Nd, Sm).

From the point of crystal structure, it is well known that only 16 of the 32 kinds of point groups have the nonzero SHG coefficient; they are 1, 2, *m*, *mm*2, 222, 4, $\bar{4}$, 4*mm*, $\bar{4}$2*m*, 3, 3*m*, 32, 6, $\bar{6}$, $\bar{6}$2*m*, 6*mm*. The point group of KPrN is *mm*2, which is among the 16 kinds. At the same time, some theoretical models have been established to explain and predict the nonlinear optical properties of the crystals; the anharmonic vibronic oscillator model (7), the charge transfer process (8, 9), the ionic group theory (10) and so on (11–13). Among them, the ionic group theory, set up by Chen in 1977, is very helpful to explain the nonlinear optical properties of the crystals of type *AB*, in which *A* is a cation and *B* is an anion. Its main idea is that the nonlinear optical property of the crystal *AB* is a local effect and it is the anionic group (not a simple anion) that accounts for this property. The anionic group should be a planar noncentrosymmetric units with $\pi$–$\pi^*$ character and lone pair electrons. According to this theory, if the investigated *KLn*N is regarded as a type $A_1A_2B$ crystal, in which $A_1$ and $A_2$ are

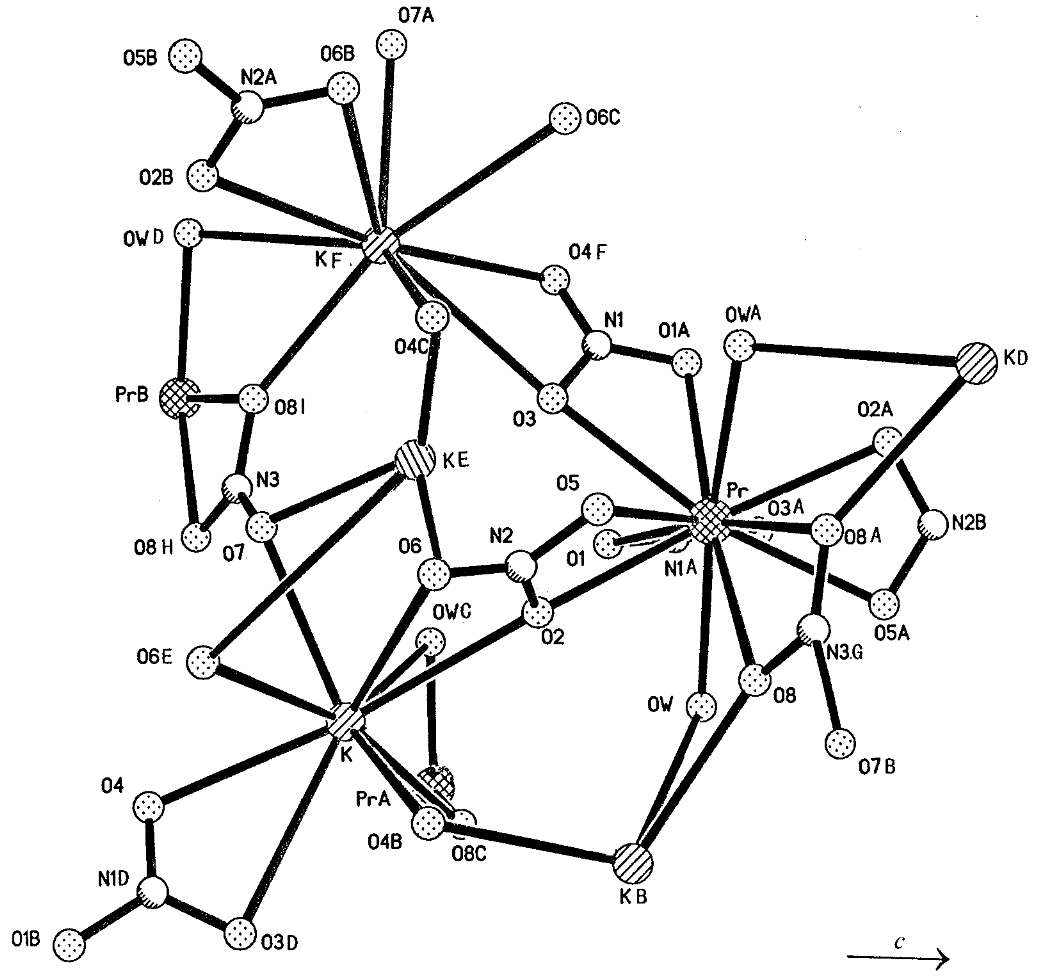

**FIG. 2.** Portion of the structure of KPrN. (A–I corresponding to a–i in Table 4.)

two metal cations, then the anionic group $NO_3^-$ ($\pi_4^6$, four atoms with six electrons) must be one of the main origins of the nonlinear optical properties because it has the above characters which can be seen from the structural analysis of KPrN. We also guess that the anionic group $[Ln(NO_3^-)_5 \cdot 2H_2O]^{2-}$ may be responsible for another main origin of the properties since it is a slightly distorted icosahedron.

The K*Ln*N crystals have two main obvious merits: first, their SHG coefficients are 2–3 times larger than that of KDP($KH_2PO_4$), comparing very favorably to those of KTP($KTiOPO_4$) and $KNbO_3$; second, they can be easily grown from water solution with a larger size and higher damage threshold than those of the higher temperature crystals. Ebbers *et al.* (1) have also pointed out that the isostructural crystals of KLaN and KCeN possess a rather rare attribute: they are nearly noncritically phase matched at room temperature for Type I frequency doubling of 1.064 μm light and for type II doubling of light near 0.95 μm. Therefore, the phase-matching properties of KLaN compare very favorably to those of LBO($LiB_3O_5$). However, their disadvantage is also obvious: their stability is not very good because of their water solubility, but it can be overcome by coating them with hydrophobic film. For the above reasons, the series of K*Ln*N (*Ln* = La, Ce, Pr, Nd, Sm) may be very useful for generating blue-green light by frequency doubling high power near infrared lasers.

## CONCLUSIONS

The single crystals of $K_2Ln(NO_3)_5 \cdot 2H_2O$ ($Ln$ = La, Ce, Pr, Nd, Sm) (K*Ln*N) are water-soluble crystals and can be easily grown in water solution by evaporation under constant temperature between 40–65°C. The structure of KPrN was solved by direct method and proved to be isostructural to KLaN, KCeN, and KNdN. The space group of KPrN is *Fdd*2 with crystal parameters $a = 21.411(3)$ Å, $b = 11.2210(10)$ Å, $c = 12.208(2)$ Å, $Z = 6$. $V = 2933.0(7)$ Å$^3$,

**TABLE 4**
**Selected Bond Length (Å) and Angles (°) for KPrN**

| | | | | | |
|---|---|---|---|---|---|
| Pr–O(1) | 2.604(4) (Å) | Pr–O(2) | 2.618(4) (Å) | Pr–O(3) | 2.686(4) (Å) |
| Pr–O(1)$^{a}$ | 2.604(4) (Å) | Pr–O(2)$^{a}$ | 2.618(4) (Å) | Pr–O(3)$^{a}$ | 2.686(4) (Å) |
| Pr–O(5) | 2.570(4) (Å) | Pr–O(8) | 2.693(5) (Å) | Pr–OW | 2.646(4) (Å) |
| Pr–O(5)$^{a}$ | 2.570(4) (Å) | Pr–O(8)$^{a}$ | 2.693(5) (Å) | Pr–OW$^{a}$ | 2.646(4) (Å) |

| | | | |
|---|---|---|---|
| O(5)–Pr–O(5)$^{a}$ | 128.5(2) (°) | | |
| –O(1) | O5$^{a}$–Pr–O(1)$^{a}$ | 113.54(12) (°) | |
| –O(1)$^{a}$ | –O(1) | 109.30(12) (°) | |
| –O(2) | –O(2)$^{a}$ | 49.08(1) (°) | |
| –O(2)$^{a}$ | –O(2) | 127.22(12) (°) | |
| –OW | –OW$^{a}$ | 107.71(11) (°) | |
| –OW$^{a}$ | –OW | 66.13(11) (°) | |
| –O(3) | –O(3)$^{a}$ | 68.08(13) (°) | |
| –O(3)$^{a}$ | –O(3) | 161.45(12) (°) | |
| –O(8) | –O(8)$^{a}$ | 67.61(14) (°) | |
| –O(8)$^{a}$ | –O(8) | 65.4(2) (°) | |
| O(1)–Pr–O(1)$^{a}$ | 65.6(2) (°) | | |
| –O(2) | O(1)$^{a}$–Pr–O(1)$^{a}$ | 71.94(13) (°) | |
| –O(2)$^{a}$ | –O(2) | 114.02(14) (°) | |
| –OW | –OW$^{a}$ | 65.73(12) (°) | |
| –OW$^{a}$ | –OW | 127.24(12) (°) | |
| –O(3) | –O(3)$^{a}$ | 63.63(12) (°) | |
| –O(3)$^{a}$ | –O(3) | 48.07(12) (°) | |
| –O(8) | –O(8)$^{a}$ | 123.71(12) (°) | |
| –O(8)$^{a}$ | –O(8) | 170.64(11) (°) | |
| O(2)–Pr–O(2)$^{a}$ | 173.4(2) (°) | | |
| –OW | O(2)$^{a}$–Pr–OW$^{a}$ | 67.59(12) (°) | |
| –OW$^{a}$ | –OW | 111.59(12) (°) | |
| –O(3) | –O(3)$^{a}$ | 68.65(13) (°) | |
| –O(3)$^{a}$ | –O(3) | 116.13(12) (°) | |
| –O(8) | –O(8)$^{a}$ | 71.2(2) (°) | |
| –O(8)$^{a}$ | –O(8) | 102.5(2) (°) | |
| OW–Pr–OW$^{a}$ | 166.7(2) (°) | | |
| –O(3) | OW$^{a}$–Pr–O(3)$^{a}$ | 120.45(12) (°) | |
| –O(3)$^{a}$ | –O(3) | 69.28(12) (°) | |
| –O(8) | –O(8)$^{a}$ | 61.55(12) (°) | |
| –O(8)$^{a}$ | –O(8) | 105.34(12) (°) | |
| O(3)–Pr–O(3)$^{a}$ | 97.1(2) (°) | | |
| –O(8) | O3$^{a}$–Pr–O(8)$^{a}$ | 122.07(14) (°) | |
| –O(8)$^{a}$ | –O(8) | 133.08(14) (°) | |
| O(8)–Pr–O(8)$^{a}$ | 47.0(2) (°) | | |

| | | | | | |
|---|---|---|---|---|---|
| K–O(4) | 2.783(4) (Å) | K–O(8)$^{c}$ | 2.765(4) (Å) | K–O(6) | 2.938(5) (Å) |
| K–O(4)$^{b}$ | 2.748(4) (Å) | K–O(7) | 2.769(5) (Å) | K–O(6)$^{e}$ | 3.059(5) (Å) |
| K–O(2) | 2.870(4) (Å) | K–O(3)$^{d}$ | 3.058(4) (Å) | K–OW$^{c}$ | 3.243(4) (Å) |

| | | | |
|---|---|---|---|
| O(4)$^{b}$–K–O(8)$^{c}$ | 95.23(14) (°) | O(8)–K–O(7) | 134.8(2) (°) |
| –O(7) | 122.8(2) (°) | –O(4) | 107.54(14) (°) |
| –O(4) | 100.98(14) (°) | –O(2) | 81.44(14) (°) |
| –O(2) | 77.63(14) (°) | –O(6) | 123.52(13) (°) |
| –O(6) | 64.9(2) (°) | –O(3)$^{d}$ | 88.32(14) (°) |
| –O(3)$^{d}$ | 64.21(13) (°) | –O(6)$^{e}$ | 162.50(14) (°) |
| –O(6)$^{e}$ | 70.85(14) (°) | –OW$^{e}$ | 53.37(12) (°) |
| –OW$^{c}$ | 136.48(12) (°) | | |
| O(7)–K–O(4) | 89.68(9) (°) | O(4)–K–O(2) | 171.02(13) (°) |
| –O(2) | 83.79(10) (°) | –O(2) | 127.35(13) (°) |
| –O(6) | 64.3(2) (°) | –O(2) | 43.27(11) (°) |
| –O(3)$^{d}$ | 128.07(9) (°) | –O(2) | 66.44(13) (°) |
| –O(6)$^{e}$ | 62.7(2) (°) | –OW$^{c}$ | 115.92(12) (°) |
| –OW$^{c}$ | 81.41(14) (°) | | |

**TABLE 4**—*Continued*

| | | | |
|---|---|---|---|
| O(2)–K–O(6) | 43.95(11) (°) | O(6)–K–O(3)$^{d}$ | 121.32(14) (°) |
| –O(3)$^{d}$ | 139.35(13) (°) | –O(6)$^{e}$ | 61.00(14) (°) |
| –O(6)$^{e}$ | 104.95(12) (°) | –OW$^{c}$ | 104.91(12) (°) |
| –OW$^{c}$ | 69.25(11) (°) | | |
| O(3)$^{d}$–K–O(6)$^{e}$ | 76.21(12) (°) | O(6)$^{e}$–K–OW$^{c}$ | 144.09(13) (°) |
| –OW$^{c}$ | 132.08(11) (°) | | |

| | | | | | |
|---|---|---|---|---|---|
| N(1)–O(1)$^{a}$ | 1.267(6) (Å) | N(2)–O(2) | 1.271(6) (Å) | N(3)–O(7) | 1.224(10) (Å) |
| N(1)–O(4)$^{f}$ | 1.228(6) (Å) | N(2)–O(5) | 1.273(6) (Å) | N(3)–O(8)$^{h}$ | 1.260(6) (Å) |
| N(1)–O(3) | 1.260(6) (Å) | N(2)–O(6) | 1.217(6) (Å) | N(3)–O(8)$^{i}$ | 1.260(6) (Å) |

| | | | |
|---|---|---|---|
| O(4)$^{f}$–N(1)–O(3) | 121.3(5) (°) | O(6)–N(2)–O(2) | 121.9(5) (°) |
| O(4)$^{f}$–N(1)–O(1)$^{a}$ | 121.6(5) (°) | O(6)–N(2)–O(5) | 122.3(5) (°) |
| O(3)–N(1)–O(1)$^{a}$ | 117.1(5) (°) | O(2)–N(2)–O(5) | 115.8(4) (°) |
| O(7)–N(3)–O(8)$^{h}$ | 121.6(4) (°) | Pr–OW–K$^{b}$ | 106.02(12) (°) |
| O(7)–N(3)–O(1)$^{i}$ | 121.6(4) (°) | | |
| O(8)$^{h}$–N(3)–O(8)$^{i}$ | 116.8(7) (°) | | |

*Note.* Symmetry transformations used to generate equivalent atoms: a, $-x$, $-y+2$, $z$; b, $-x+1/4$, $y+1/4$, $z+1/4$; c, $-x+1/4$, $y-1/4$, $z-1/4$; d, $x+1/4$, $y+5/4$, $z+1/4$; e, $-x$, $-y+1$, $z$; f, $x+1/4$, $-y+5/4$, $z-1/4$; g, $x$, $y+1/2$, $z+1/2$; h, $x$, $y-1/2$, $z-1/2$; i, $-x$, $-y+3/2$, $z-1/2$.

$dc = 1.920\ \mathrm{kgm}^{-3}$, $\mu = 2.998\ \mathrm{mm}^{-1}$, $R = 0.0240$, $R_w = 0.0603$. The powder SHG intensities of K*Ln*N (*Ln* = La, Ce, Pr, Nd, Sm) are 4–9 times larger than that of KDP. The average SHG coefficient of KPrN is a little higher than that of K*Ln*N (*Ln* = La, Ce, Nd, Sm). Their nonlinear optical properties can be explained by the ionic group theory. The $NO_3^-$ must be one of the main origins of the nonlinear optical properties because it is a planar noncentrosymmetric units with $\pi$–$\pi^*$ character and lone pair electrons. Their SHG coefficients are 2–3 times larger than that of KDP($KH_2PO_4$) and can be easily grown from a water solution with a larger size and higher damage threshold than those of the higher temperature crystals. These series of K*Ln*N (*Ln* = La, Ce, Pr, Nd, Sm) are prospective crystals for generating blue-green light by frequency doubling high power near infrared lasers.

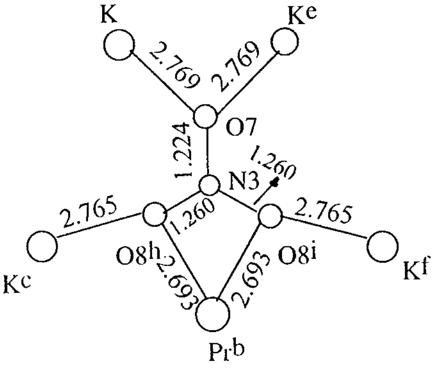

**FIG. 3.** The surrounding of N3 nitrate groups. The distances are given in Å units.

**TABLE 5**
**Powder SHG Data for K*Ln*N (*Ln* = La, Ce, Pr, Nd, Sm)**

| Material | Particle size (μm) | Color | $I_i^{2w}/I_{KDP}^{2w}$ | $d_i$ (pm/v) |
|---|---|---|---|---|
| KLN | 252–500 | white | 7 | 1.14 |
| KCN | 252–500 | white | 7 | 1.14 |
| KPrN | 252–500 | light green | 9 | 1.30 |
| KNdN | 252–500 | violet | 5 | 0.97 |
| KSmN | ungraded | light yellow | $4^a$ | 0.86 |
| KDP | 252–500 | white | 1 | 0.43 |

[a] This value can only be referenced because the complex of KSmN changed its structure when placed in air.

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