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Assembly of Disperse Red 1 Molecules in the Channels of AlPO₄-5 Single Crystals for Second-Harmonic GenerationF. Y. Jiang,^{†,‡,§} W. X. Lu,[†] J. P. Zhai,[†] J. T. Ye,[†] G. K. L. Wong,[†] J. R. Han,[‡] and Z. K. Tang^{*,†}

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Disperse red 1 (DR1) molecules have been successfully incorporated into the one-dimensional channels of AlPO₄-5 single crystals by means of vapor-phase diffusion. Polarizing microscope and SHG results indicate that the DR1 molecules are well aligned in a preferred direction along the crystal channels. The *p*-polarization (parallel to the *c*-axis of AlPO₄-5 crystal) SH intensity (I_{p-ex}), and *s*-polarization (perpendicular to the *c*-axis of AlPO₄-5 crystal) SH intensity (I_{s-ex}) of DR1-loaded AlPO₄-5 single crystals can be well fitted as a function of input polarization angle (α): $I_{p-ex} = 0.69 \cos^4 \alpha + 0.37 \sin^4 \alpha - 0.17$, $I_{s-ex} = 0.69 \cos^2 \alpha \sin^2 \alpha + 0.06$, respectively. This polarization angle dependence can be well explained by three different SHG processes of I_p (0°), I_p (90°), and I_s (45°), originated from different combinations of two polarized photons.

1. Introduction

Porous single crystals of the zeolite family, as the host materials for producing nanostructures, have attracted more and more attentions over the past decade. These novel guest–host composites are of many potential applications, such as for optical data storage,¹ laser-frequency conversion,^{2–4} and microcavity lasers.^{5,6} There are several reports on nonlinear optical properties of organic-molecule-loaded AlPO₄-5 crystals.^{2–4} An AlPO₄-5 crystal has a hexagonal structure with symmetry of *6mm* (AFI-type structure). Its framework consists of one-dimensional 12-ring channels (inner diameter: 0.73 nm), which are packed parallel to the *c*-axis. An AlPO₄-5 single crystal is electrically insulating, optically transparent from ultraviolet to infrared, and thermally stable up to 1173 K. These excellent physical properties, plus their unique opened pore structures, offer an excellent template to fabricate host–guest nanostructured composites.

Disperse red 1 (2-[[4-(4-nitrophenylazo)-phenyl]-ethyl-amino]-ethanol), hereafter referred to as DR1, is a push–pull chromophore which, together with its derivatives, has long been investigated as an optical nonlinear dopant in polymers,^{7–9} sol–gel silica matrixes,^{10–13} and organic–inorganic hybrid materials.^{14,15} Second-order nonlinearities can only be observed after poling in order to orient the DR1 molecules within the matrix. However, there are some shortcomings that restrict the application of those systems, such as the reorientation of the molecules,

low molecular concentration in the matrix, low matrix rigidity, and poor thermal stability.

We have reported the synthesis of optical-grade AlPO₄-5 single crystals with the size up to 0.72 mm × 0.35 mm.¹⁶ This achievement makes it easy to do some measurements on a single crystal. In this paper, we focus on assembly of DR1 molecules in the channels of AlPO₄-5 single crystals and study nonlinear optical properties of such host–guest nanostructured composites.

2. Experimental Section

Large AlPO₄-5 single crystals were synthesized hydrothermally by using tripropylamine (TPA) as an organic template.¹⁶ As-synthesized crystals were calcined to 673 K under a dynamic vacuum at a rate of 1 K/min, then calcined to 853 K under O₂ atmosphere at a rate of 1 K/min, and maintaining this temperature for 20 h to remove the organic templates TPA in the channels. Thus the channels were emptied. Then the calcined crystals were naturally cooled to room temperature.

DR1 (from Aldrich with a dye content ca. 95% and in powder form of a dark-brown color) was incorporated into the channels of AlPO₄-5 single crystals by the vapor-phase diffusion method. The scheme is shown in Figure 1. The calcined AlPO₄-5 crystals were loaded at one end of a glass tube; the DR1 was loaded in a small ampule and put in another end of the glass tube. The temperature of the AlPO₄-5 crystals was raised to 423 K at a rate of 1 K/min under dynamic vacuum and then kept at 423 K for 1 h; this procedure can remove the water that adsorbed in the channels of crystals (Figure 1a). When the product cooled to ca. 323 K, the small ampule that contained a sufficient amount of DR1 was sealed together with the empty AlPO₄-5 crystals (Figure 1b) at a vacuum of 10^{−1} Pa by acetylene–oxygen flame (Figure 1c). The sealed glass tube was put in an oven, raised

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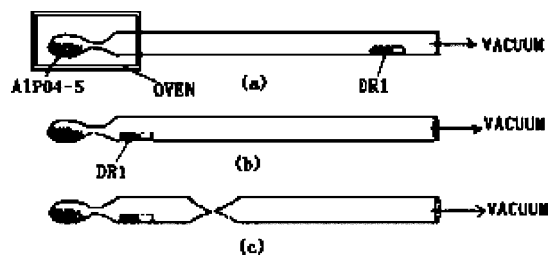


Figure 1. Schematic showing DR1 loading processes. (a) Removal of the water that adsorbed in the crystal channels. (b) Sliding the DR1 to the sealed side. (c) Sealing the DR1 together with $\text{AlPO}_4\text{-5}$ crystals.

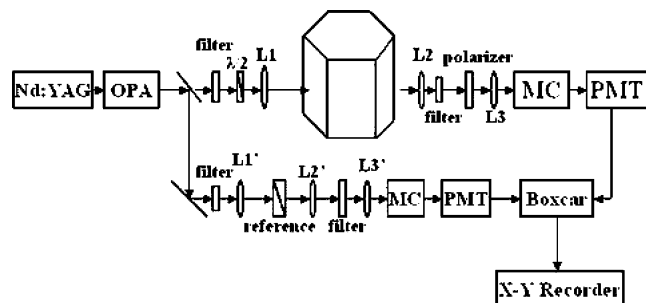


Figure 2. Experimental setup for second-harmonic generation measurement of the DR1-loaded $\text{AlPO}_4\text{-5}$ single crystals.

the temperature to 423 K at a rate of 0.5 K/min, and kept at 423 K for 20 h. The product was then cooled to room temperature, and red DR1-loaded $\text{AlPO}_4\text{-5}$ single crystals were obtained.

As-synthesized $\text{AlPO}_4\text{-5}$ crystals, calcined $\text{AlPO}_4\text{-5}$ crystals, and DR1-loaded $\text{AlPO}_4\text{-5}$ crystals were characterized by X-ray powder diffraction (XRD) by using a Philips PW1830 diffractometer.

The second-harmonic generation (SHG) experiment was carried out on an optical parametric amplifier (OPA) based measurement system.¹⁷ The SHG signal was measured in a transmission configuration. The experimental setup is shown schematically in Figure 2. The output wavelength of the OPA system is continuously tunable between 400 and 2000 nm with a peak power of 10 mW at short wavelengths (pulse duration 15 ps, repetition rate 10 Hz). The signal line width varies from <0.5 nm in the visible region to 2 nm at $2\ \mu\text{m}$. The laser beam is split to simultaneously generate the SHG from the sample and a reference material. To eliminate the coherence length effect and the walk-off effect, we used an *x*-cut quartz wedge and a *y*-cut quartz wedge with the wedge direction opposite to each other as reference material. By normalizing the sample SHG to the SHG from the reference material, the effects of pulse-to-pulse fluctuations and long-term drift in the laser power can be minimized, greatly improving the signal-to-noise quality of the data. A DR1-loaded $\text{AlPO}_4\text{-5}$ single crystal of size ca. $0.7\ \text{mm} \times 0.3\ \text{mm}$ was stuck on the top of a thin steel rod that was fixed on a 3D-tunable stage. The incident light was focused by a microscope lens, with a beam radius down to $30\ \mu\text{m}$. Glass filters were used to remove either the idler or the signal component of OPA output. Wide-band filters were placed after the sample to ensure that only the SHG signal was measured. The polarization dependence of the second harmonic was measured by using a fundamental wavelength of 1064 nm. The polarization of a fundamental beam can be changed by a half-wave plate placed in front of the sample. The polarization of the second-harmonic signal was checked by using a linear polarizer placed behind the filter. The intensities of SHG from the sample and that from the quartz wedge were detected by

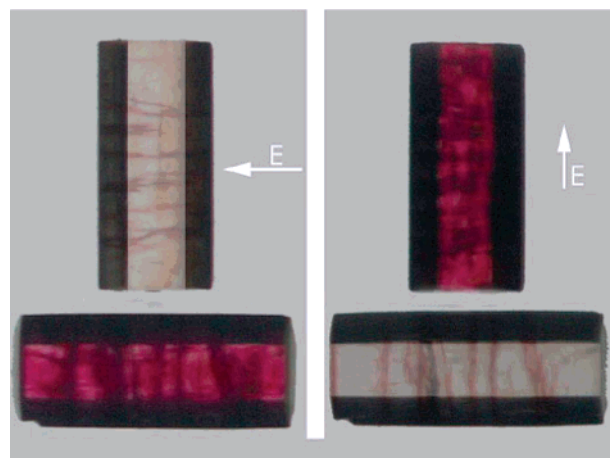


Figure 3. Optical image of the DR1-loaded $\text{AlPO}_4\text{-5}$ crystals under polarized light. Arrows indicate the direction of the electric field.

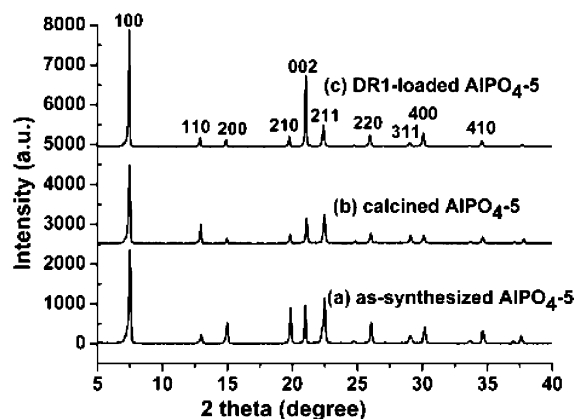


Figure 4. XRD patterns of (a) as-synthesized $\text{AlPO}_4\text{-5}$ crystals, (b) calcined $\text{AlPO}_4\text{-5}$ crystals, and (c) DR1-loaded $\text{AlPO}_4\text{-5}$ crystals

using two identical monochromators and photomultiplier tubes, averaged by a boxcar integrator, and then recorded by a computer. To ensure the uniform spectral response in the two detection arms, identical glass filters were used in each arm. More than five DR1-loaded $\text{AlPO}_4\text{-5}$ single crystals were detected in our experiment, and the same results were obtained.

3. Results and Discussion

The DR1-loaded $\text{AlPO}_4\text{-5}$ crystals were stable when exposed in air, even after being irradiated by a laser for a few to 10 h. However, the DR1 molecules can be gradually extracted from the channels when the crystals were washed in solvent acetone.

Figure 3 is a microscopic photograph of the DR1-loaded $\text{AlPO}_4\text{-5}$ single crystals under polarized light. The crystals behave as good polarizers with strong absorption of light polarized parallel to the *c*-axis, and nearly transparent for the light polarized perpendicular to the *c*-axis. This indicates that the DR1 molecules are well aligned by the one-dimensional channel system.

Figure 4 shows the XRD patterns of (a) as-synthesized $\text{AlPO}_4\text{-5}$ crystals, (b) calcined $\text{AlPO}_4\text{-5}$ crystals, and (c) DR1-loaded $\text{AlPO}_4\text{-5}$ crystals. The patterns are typical for the AFI structure and show that the structure is not affected by calcinations and loading of DR1 molecules, although the relative intensities of diffraction peaks change.

The light emission spectrum of the DR1-loaded $\text{AlPO}_4\text{-5}$ crystals irradiated by a laser of different wavelengths is shown in Figure 5. The wavelengths of the signal are well fitted with the incident light by a double-frequency relation, indicating the

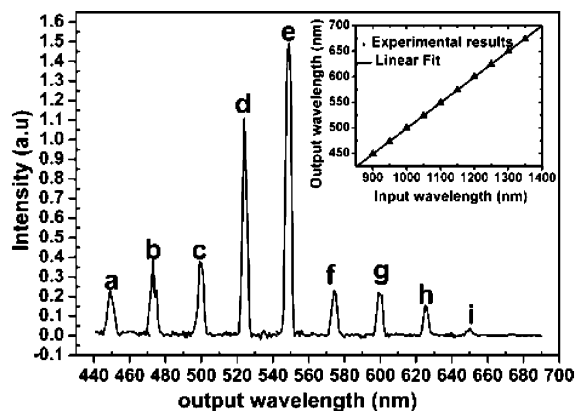


Figure 5. Spectrum of the DR1-loaded $\text{AlPO}_4\text{-5}$ crystals irradiated by laser of different wavelengths: (a) 900 nm, (b) 950 nm, (c) 1000 nm, (d) 1050 nm, (e) 1100 nm, (f) 1150 nm, (g) 1200 nm, (h) 1250 nm, (i) 1300 nm. Inset: the relationship between the input and output wavelength.

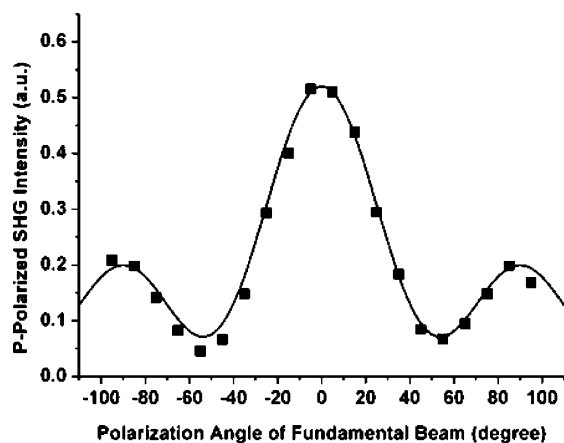


Figure 6. Plot of the p -polarization (parallel to the c -axis of $\text{AlPO}_4\text{-5}$ crystal) transmitted SH intensity ($I_{p\text{-ex}}$) of the DR1-loaded $\text{AlPO}_4\text{-5}$ single crystal vs the polarization angle (α) of the incident fundamental light. The solid squares represent the experimental results, and the solid curve is a fit to equation $I_{p\text{-ex}} = 0.69 \cos^4 \alpha + 0.37 \sin^4 \alpha - 0.17$.

SHG effect of the DR1-loaded $\text{AlPO}_4\text{-5}$ crystals. The occurrence of SHG implied that the DR1 molecules are well aligned in the channels of $\text{AlPO}_4\text{-5}$ crystals, and the molecules also have a preferred direction at least for domains of several light wavelengths in diameter. A pyroelectric effects study on p -nitroaniline-loaded $\text{AlPO}_4\text{-5}$ crystals^{18–20} indicated that the p -nitroaniline molecules formed unidirectionally aligned dipole chains in parallel molecular sieve channels and the polarization reverse in the center region of the crystals. This is due to the absorption mechanism that the molecules enter the channels with the negative nitro group in front. The DR1 molecule is also a polar molecule, so we can expect the same absorption mechanism and the formation of dipole chains in the channels of $\text{AlPO}_4\text{-5}$ crystals. Because the DR1 molecule is much longer than the p -nitroaniline molecule, one can expect that the deviation of the DR1 long molecule axis from the crystal c -axis is smaller than that of p -nitroaniline. For different incident laser wavelengths, the SHG intensity is different correspondingly, indicating that the DR1-loaded $\text{AlPO}_4\text{-5}$ crystal has a dispersion of SHG. The detailed analysis of the SHG dispersion will be reported elsewhere.

Figure 6 shows a plot of the p -polarization (parallel to the c -axis of $\text{AlPO}_4\text{-5}$ crystal) transmitted SH intensity ($I_{p\text{-ex}}$) of the DR1-loaded $\text{AlPO}_4\text{-5}$ single crystal versus the polarization angle (α) of the incident fundamental light, where the solid

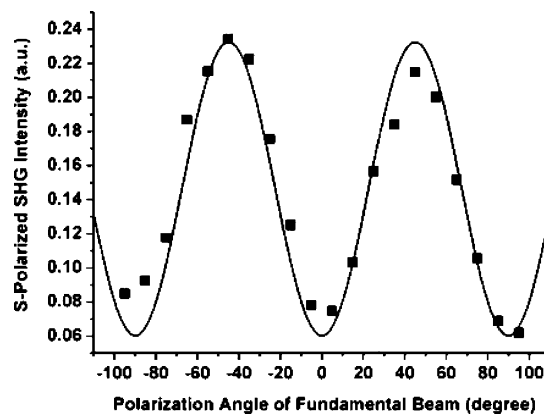


Figure 7. Plot of the s -polarization (perpendicular to the c -axis of $\text{AlPO}_4\text{-5}$ crystal) transmitted SH intensity ($I_{s\text{-ex}}$) of DR1-loaded $\text{AlPO}_4\text{-5}$ single crystal vs the polarization angle (α) of the incident fundamental light. The solid squares represent the experimental results, and the solid curve is a fit to equation $I_{s\text{-ex}} = 0.69 \cos^2 \alpha \sin^2 \alpha + 0.06$.

squares represent the experimental results, and the solid curve is a fit to equation $I_{p\text{-ex}} = 0.69 \cos^4 \alpha + 0.37 \sin^4 \alpha - 0.17$, α is the angle between the input polarization direction and c -axis of the $\text{AlPO}_4\text{-5}$ crystal. It shows that $I_{p\text{-ex}}$ reaches its first maximum when the input polarization is parallel to the c -axis ($\alpha = 0^\circ$) and reaches its second maximum when the input polarization is perpendicular to the c -axis ($\alpha = 90^\circ$). The α -dependence of the s -polarization (perpendicular to the c -axis of $\text{AlPO}_4\text{-5}$ crystal) transmitted SH intensity ($I_{s\text{-ex}}$) is shown in Figure 7. The $I_{s\text{-ex}}$ reaches its maximum when $\alpha = 45^\circ$, and the experimental data is well fitted to equation $I_{s\text{-ex}} = 0.69 \cos^2 \alpha \sin^2 \alpha + 0.06$. $\text{AlPO}_4\text{-5}$ crystals have symmetry of $6mm$; the DR1-loaded $\text{AlPO}_4\text{-5}$ crystals also have the same symmetry, as indicated by XRD patterns. For materials with $6mm$ symmetry, the intensity of p -polarized SHG ($I_{p\text{-th}}$) and s -polarized SHG ($I_{s\text{-th}}$) at the different polarization angle (α) of a fundamental wave can be given by²¹

$$I_{p\text{-th}}(\alpha) = A[d_{31} \sin^2 \alpha + (2d_{15} \sin \theta \cos \theta + d_{31} \cos^2 \theta + d_{33} \sin^2 \theta) \cos^2 \alpha]^2$$

$$I_{s\text{-th}}(\alpha) = B d_{15}^2 \sin^2 \theta \sin^2 \alpha \cos^2 \alpha$$

where d_{33} , d_{31} , d_{15} are the second-order nonlinear susceptibilities, and θ is the incidence angle. As a certain material with a certain incidence angle θ , the equations can be simplified as

$$I_{p\text{-th}}(\alpha) = (a \sin^2 \alpha + b \cos^2 \alpha)^2$$

$$I_{s\text{-th}}(\alpha) = c \sin^2 \alpha \cos^2 \alpha$$

Although our experimental data of the SHG intensity of s -polarization can be fitted well by $I_{s\text{-th}}$, the data of the p -polarization is very different from $I_{p\text{-th}}$, indicating that the SHG process of the DR1 molecules aligned in the AFI channels is different from the bulk material. The polarization dependences of the SHG signals shown in Figures 6 and 7 are different from that reported for p -nitroaniline-loaded $\text{AlPO}_4\text{-5}$ single crystal,²² in which only one maximum was observed for $I_{p\text{-ex}}$ at $\alpha = 0^\circ$, but very similar to that reported for DMABN-loaded $\text{AlPO}_4\text{-5}$ single crystal³. In ref 3, the three peaks of SHG signals of $I_{p\text{-ex}}(0^\circ)$, $I_{p\text{-ex}}(90^\circ)$, and $I_{s\text{-ex}}(45^\circ)$ were attributed to three different SHG processes of different polarization combinations of photons. We believe that the same mechanism of SHG processes is applicable to our observation. Being excited by the

laser photons, the DR1 molecule undergoes a transition from the ground state to the excited state. During such a transition, the electronic cloud is deformed. The movement of the electronic cloud may have two components: one along the molecular long axis and the other perpendicular to the molecular long axis. These two perpendicular components can mix waves of different polarizations to generate *p*-polarization and *s*-polarization SH signals.

4. Conclusions

DR1 molecules have been successfully incorporated into the channels of AlPO₄-5 crystals by means of vapor-phase diffusion. The loaded DR1 molecules are well aligned by the channels, as indicated by polarized microscope and SHG results. Polarization-dependent experiments reveal that the SHG processes that occurred in the DR1-loaded AlPO₄-5 crystals are quantitatively different from the bulk materials that have 6mm symmetry.

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