Measurement of second-order nonlinear optical coefficients of $BaMgF_4$

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The three independent second-order nonlinear optical coefficients of $BaMgF_4$ are determined by the Maker fringe method with a nanosecond pulsed Nd:YAG laser at 1064 nm wavelength. All the results are relative to the reference crystal congruent $LiNbO_3$. The largest element in a second-order nonlinear optical matrix of $BaMgF_4$ is d_{32}, with the value of 0.36 pm/V.

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At present, there is a strong demand for all-solid-state lasers (ASSLs) working at the vacuum ultraviolet (VUV) region for applications in optical lithography, high-resolution spectroscopy, and medical uses. Compared to the currently used excimer lasers, ASSLs have a large number of advantages, such as compact setup, high beam quality, and narrow bandwidth. To fabricate ASSLs, the traditional nonlinear materials (e.g., $KTiOPO_4$, β-BaB_2O_4, and LiB_3O_5) can not be utilized because they are nontransparent in VUV and have a short wave limit resulting from the origin of birefringent phase matching. Several years ago, $KBe_2BO_3F_2$ (KBBF) was found to possess some good properties, such as short cut-off wavelength at 155 nm and large birefringence [1], so it was applied to create 177.3 [2] and 156 nm [3] VUV radiation. Nevertheless, KBBF is too fragile because of its strong layer tendency along the Z axis, so it is hard to grow thicker than even 2 mm [1,4]. Furthermore, due to the restriction of cut-off wavelength and short wave limit, it is almost impossible to generate harmonics with higher power and even shorter wavelength in KBBF.

At the beginning of this century, $BaMgF_4$ was found to be another promising candidate for a VUV creator owing to its short cut-off wavelength of about 125 nm [5,6] and good ferroelectric properties (e.g., low coercive field) [7,8]. Besides, the periodically reversed ferroelectric domains of $BaMgF_4$ have been demonstrated [5–7], so it is theoretically possible to produce 125 nm VUV radiation in $BaMgF_4$ through the quasi-phase-matching (QPM) method [9] which may eliminate the restriction of the short wave limit. Some nonlinear optical characterizations of $BaMgF_4$ have already been performed. For example, the study of third-order nonlinear refractive indices as well as self-phase modulation has been reported recently by our group [10]. In addition, the second-order nonlinear optical (NLO) coefficients that determine the conversion efficiency of second-harmonic generation (SHG) were measured in the 1970s [11,12]. However, to the best of our knowledge, these are the only reports of the measurement of NLO coefficients of $BaMgF_4$. Besides, according to a recent theoretical simulation, the values did not agree well with the experimental results and remeasurement was suggested [13].

In this paper, we report our latest experimental results on NLO coefficients of $BaMgF_4$ through the standard Maker fringe method [14–16] with $LiNbO_3$ as a reference. It can help to correct our knowledge on the NLO coefficients of $BaMgF_4$ and provide more references for its future SHG experiments.

The $BaMgF_4$ crystal was grown by the Bridgman method. First, to create the starting materials, highly pure powders (99.99%) of BaF_2 and MgF_2 were mixed in stoichiometric composition. The charges were put in a Pt crucible and sintered in a muffle furnace under vacuum at 700 °C for 16 h. Then, $BaMgF_4$ single crystal was chosen as a seed and put into the seed well to induce $BaMgF_4$ crystal growth along the c axis. After the crucible was loaded with the raw materials, it was sealed to prevent the entering of the water and oxygen and mounted in a self-made vacuum vertical Bridgman furnace with temperature ranging from 1000–1020 °C to melt the $BaMgF_4$ polycrystal. Finally, the crystal was cooled down to room temperature at the rate of 30–80 °C/h. The temperature gradient and the growth rate were set at 50–80 °C/cm and 0.2–0.6 mm/h, respectively [10].

It is known that the point group of $BaMgF_4$ crystal is mm2 [17]. According to the group symmetry and Kleinman approximation, there are solely three nonvanishing NLO coefficients (i.e., d_{31}, d_{32}, and d_{33}). Thus, the NLO coefficient tensor of $BaMgF_4$ crystal can be written in the form

$$\begin{pmatrix} 0 & 0 & 0 & 0 & -d_{31} & 0 \\ 0 & 0 & 0 & -d_{32} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}. \quad (1)$$

To measure the corresponding coefficients, the grown $BaMgF_4$ crystal was precisely cut into two square plates oriented along the x axis and the y axis, as shown in

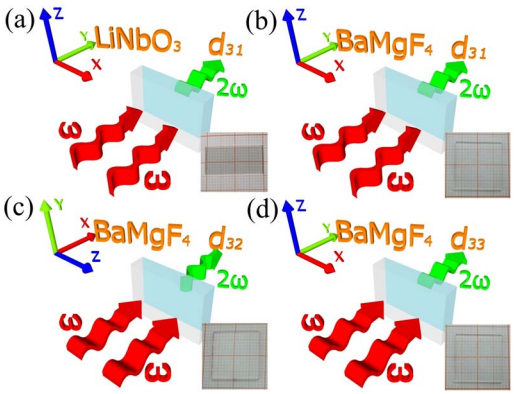

Fig. 1. (Color online) Sample cut with the corresponding polarizing direction of the fundamental and harmonic waves for determining (a) $d_{31}^{LiNbO_3}$, (b) $d_{31}^{BaMgF_4}$, (c) $d_{32}^{BaMgF_4}$, and (d) $d_{33}^{BaMgF_4}$.

Figs. 1(b)–(d). Note that the equivalence between the crystallographic and optical axes is $abc \equiv xyz$ in accordance with [11,12]. The two adjacent sides of every plate were also along the other two crystallographic axes. Thus, the three NLO coefficients could be determined by choosing the polarization direction of fundamental and harmonic beams along the corresponding axes. The sizes of the $BaMgF_4$ plates are 15 mm × 15 mm × 1 mm. The y-cut $LiNbO_3$ crystal plate was used as a reference [See Fig. 1(a)], so all the measured NLO coefficients of $BaMgF_4$ were relative to d_{31} of $LiNbO_3$. The size of the $LiNbO_3$ plate was 20 mm × 10 mm × 1 mm.

The standard Maker fringe experiment was performed to measure the NLO coefficients of $BaMgF_4$ crystal. The schematic diagram of experimental setup is illustrated in Fig. 2. The fundamental light source used in the experiment was a Q-switched Nb:YAG laser (Continuum Surelite SSP) with pulse duration of 30 nm and repetition frequency of 10 Hz at 1064 nm wavelength. The single pulse energy was 60 mJ and the peak power reached 2 MW. The laser beam was divided by a beam splitter into two parts. The reflected part was detected by the photodiode as a trigger signal of boxcar integrator and the transmitted part was polarized by the Glan–Thompson polarizer in the chosen polarization direction of the fundamental wave. Across the collimating lens systems, the beam was illuminated onto the sample, which was mounted on the angle maker driven by a step motor. The rotation speed that controlled by the computer was 4°/min. Through the second Glan–Thompson polarizer, the beam was polarized along the selected polarization direction of the harmonic wave. After passing the filter system, which was combined with the $CuSO_4$ solution, and the bandpass filter with a wavelength of 532 nm, the harmonic signal was extracted from the beam and detected by the highly sensitive photodiode multiplier tube. The amplified signal was integrated by the boxcar (Stanford Research System, Inc.) and recorded by the computer. All the devices and instruments were calibrated previously. In the same experimental environment, the reference crystal $LiNbO_3$ was measured first and then the $BaMgF_4$ samples were measured one by one.

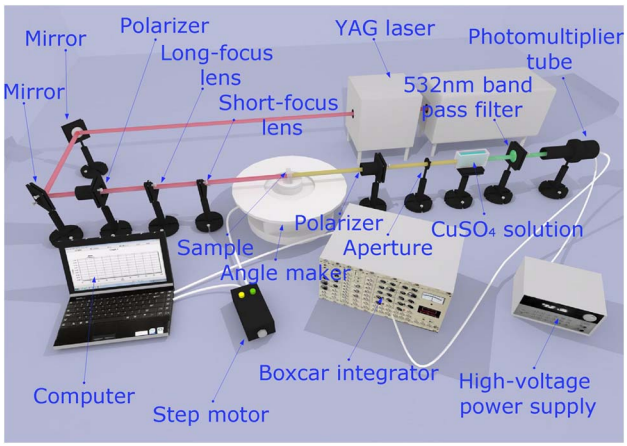

Fig. 2. (Color online) Schematic diagram of the Maker fringe experiment using a nanosecond pulsed Nd:YAG laser at a wavelength of 1064 nm.

The typical Maker fringes of $LiNbO_3$ and $BaMgF_4$ are acquired and shown in Fig. 3. As we can see, the curves are all Type I Maker fringes with excellent symmetry. The NLO coefficient d is determined by the following equation [15]:

$$d^2 = A\frac{I_M^{(0)}}{l_c^2}\frac{(n_\omega+1)^3(n_{2\omega}+1)^3(n_\omega+n_{2\omega})}{n_{2\omega}}\exp\left(\alpha_\omega+\frac{1}{2}\alpha_{2\omega}\right)L, \tag{2}$$

where $I_M^{(0)}$ represents the peak point of the envelope, l_c denotes the coherent length versus normal incidence, n_ω and $n_{2\omega}$ indicate the refractive indices of crystal with regard to the fundamental and harmonic waves, α_ω and $\alpha_{2\omega}$ are the absorption coefficients, and L is the propagating distance of the laser beam in the crystal. $I_M^{(0)}$ can be derived by fitting the maxima of the curve with the least square method. l_c can be calculated with angular positions of the minima of the curve. n_ω and $n_{2\omega}$ of $LiNbO_3$ and $BaMgF_4$ are obtained from the Sellmeier equations reported in [18] and [6], respectively. The depletion term $\exp(\alpha_\omega+\frac{1}{2}\alpha_{2\omega})L$ can be eliminated because $LiNbO_3$ and $BaMgF_4$ are both transparent at wavelengths of 1064 and 532 nm. All the measured NLO coefficients of $BaMgF_4$ are the relative values compared with d_{31} of $LiNbO_3$, which has the value 4.35 pm/V.

The results are summarized in Table 1. It can be seen that all the coefficients determined in this experiment are about 1 order of magnitude larger than the previous values (i.e., $d_{31}=0.022$ pm/V, $d_{32}=0.033$ pm/V, and $d_{33}=0.009$ pm/V) reported by Bechthold and Haussuhl [11]. Our experiment has been verified several times, so the reliability of our results can be guaranteed. The d_{33} of $BaMgF_4$ with the value of 0.12 pm/V reported by us is closer to the theoretical calculation (i.e., 0.19 pm/V) [13] than Bechthold's result (i.e., 0.009 pm/V) [11]. The deviation of Bechthold's work may be come from the inaccuracy in complicated determination of the optical axes in biaxial $BaMgF_4$ crystal [13]. For our experiment, the samples are oriented by the x-ray diffraction method and cut in a strict way to guarantee precision better than 30′. The largest NLO coefficient of $BaMgF_4$ is d_{32} with the value of 0.36 pm/V, which approaches that of KBBF [19]. Therefore, theoretically, harmonics with the same power can be generated in $BaMgF_4$ and KBBF if they are in identical experimental environments. Considering the other advantages of $BaMgF_4$ (e.g., QPM application, easier to grow, shorter cut-off wavelength), it can be envisaged that $BaMgF_4$ is a more promising nonlinear crystal to use to create VUV radiation.

In conclusion, the NLO coefficients of $BaMgF_4$ have been measured using the standard Maker fringe method. All the

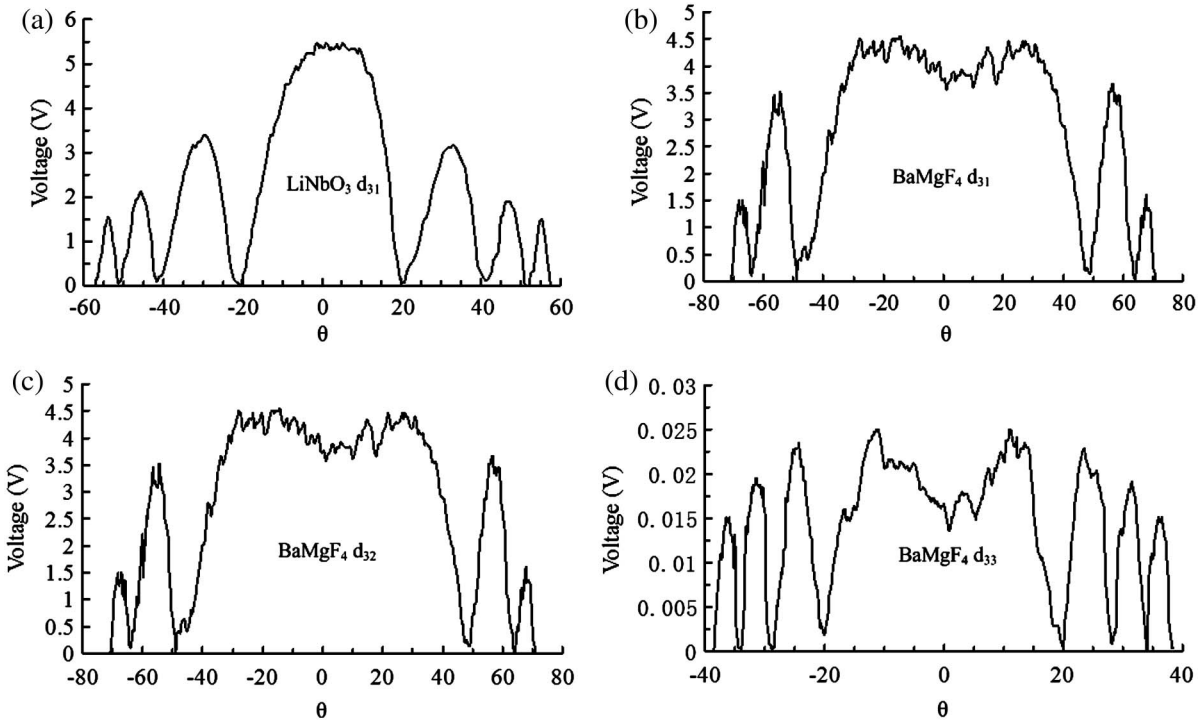

Fig. 3. (Color online) Maker fringes for (a) d_{31} of $LiNbO_3$, (b) d_{31} of $BaMgF_4$, (c) d_{32} of $BaMgF_4$, and (d) d_{33} of $BaMgF_4$. The thickness of all crystals is 1 mm.

Table 1. Relative and Absolute Values of NLO Coefficients of $BaMgF_4$ with the Corresponding Coherent Lengths[a]

Crystal	Coefficient	$d_{ij}/d_{31}^{LiNbO_3}$	d_{ij} (pm/V)	$l_c(\theta = 0)$ [μm]
$BaMgF_4$	d_{31}	0.035	0.15	380
	d_{32}	0.082	0.36	11
	d_{33}	0.028	0.12	35

[a]The d_{31} of $LiNbO_3$ is 4.35 pm/V

values are relative to the reference crystal $LiNbO_3$. The coefficients determined in this paper are about 1 order of magnitude larger than the previously reported results and consistent with the recent theoretical calculation. This work has great significance in modifying the parameters of the nonlinear characteristics of $BaMgF_4$.

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