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# Femtosecond laser induced space-selective precipitation of a deep-ultraviolet nonlinear $BaAlBO_3F_2$ crystal in glass

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ABSTRACT

A deep-ultraviolet (UV) nonlinear optical $BaAlBO_3F_2$ crystal was space-selective precipitated in stoichiometric $50BaF_2$–$25Al_2O_3$–$25B_2O_3$ glass by using a 500 kHz femtosecond pulse laser, which was confirmed by X-ray diffraction analysis (XRD). The distribution of $BaAlBO_3F_2$ crystals in glass was analyzed by Raman spectra and Raman mapping. The second-harmonic generation (SHG) intensity of $BaAlBO_3F_2$ crystals in glass could be tuned by changing the laser average power and exposure time. Absorption spectra were used to investigate the transmittance of the glass sample before and after the femtosecond laser irradiation.



## 1. Introduction

Femtosecond (fs) laser has been proven to be a powerful tool for the fabrication of three-dimensional (3D) functional microstructures in transparent materials owing to their ultrashort pulse and ultrahigh peak power [1–3]. During the interaction of the fs laser and transparent materials, nonlinear optical effects play important roles in energy transference and structural modification, which facilitate the findings of many novel phenomena and applications [4–6]. Recently, high repetition rate fs laser induced crystallization in glasses has attracted considerable attention for its potential applications in fabrication of functional optical components due to their ability to rapidly and precisely deposit energy through nonlinear excitation and absorption. When a high repetition rate fs laser is focused into glass, an increasing amount of energy will continuously accumulate in the modified region where a high temperature elevation occurs [7,8]. Localized crystallization will be formed in the modified region when the local temperature reaches a certain temperature range for nucleation and crystal growth. So far, a series of functional nonlinear crystals such as $\beta$-$BaB_2O_4$ [9], $Ba_2TiSi_2O_8$ [10], $LaBGeO_5$ [11] and $LiNbO_3$ [12] have been space-selectively precipitated in glass using fs laser irradiation.

Based on many important and attractive applications in laser micromachining and material processing, the generation of deep-UV coherent light has caused widely attentions and studies [13–15]. The generation of deep-UV coherent light is mainly from the SHG of specific nonlinear optical crystals, such as $BaAlBO_3F_2$ [13], $Cs_2B_4SiO_9$ [14] and $Ba_4B_{11}O_{20}F$ crystals [15]. However, these nonlinear optical crystals are hardly prepared due to the strict conditions of single crystal growth, let alone realization of optical components. Komatsu et al. have prepared the oxyfluoride glass containing $BaAlBO_3F_2$ crystals by heat-treatment or continuous laser irradiation [16]. However, $BaAlBO_3F_2$ crystals are precipitated inside glass randomly or on the glass surface.

Herein, space-selective precipitation of deep-UV $BaAlBO_3F_2$ crystals inside a transparent glass induced by high repetition rate femtosecond laser pulses has been successfully achieved, which may be used as arrayed wavelength converter. The crystalline distribution in the modified region is examined by Raman spectra and Raman mapping. We also investigate the influence of laser average power and exposure time on the SHG intensity of $BaAlBO_3F_2$ crystals. The transmittance of the glass sample before and after the femtosecond laser irradiation is analyzed by absorption spectra.

## 2. Experimental

A glass sample with the composition of stoichiometric $50BaF_2$–$25Al_2O_3$–$25B_2O_3$ (mol%) was prepared by conventional melt-quenching technique using analytical pure $BaF_2$ and $Al_2O_3$ and $B_2O_3$ reagents as raw materials. A mixed batch about 20 g in weight was mixed homogenously in an agate mortar, and then melted at 1100 °C for 20 min in air. Melts were poured onto a stainless steel and pressed into a thickness of about 1 mm using another stainless steel plate. The

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sample was cut and then well polished for laser modification and optical measurements.

A fiber laser chirped pulse amplified fs laser (FLCPA-02USCT11, Calmar Laser, Inc.) was used to generate 1030 nm, 370 fs, and 500 kHz laser beam. The laser beam was tightly focused by a microscope objective (50×, NA = 0.8) into the glass sample which is 100 μm beneath the glass surface. The glass sample was fixed on a computer controlled three dimensions XYZ stage. The precipitated crystalline phase induced by fs laser was identified by XRD (PANalytical B.V. X'Pert Pro MPD, The Netherlands) using $CuK_\alpha$ ($\lambda = 1.5418$ Å) radiation. Microstructure of the glass was recorded with a 200 kV FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscopy (HRTEM) instrument. Emission spectra during the fs laser irradiation were recorded by a spectrometer (Ocean Optics HR4000). Raman spectra were measured using a Raman spectrometer (Renishaw inVia, Gloucestershire, UK) with a laser excitation source of 532 nm. The spatial resolution of micro-Raman spectrum in horizontal direction and vertical direction is 0.5 μm and 2 μm, respectively. The optical absorption spectra of the glass sample before and after the fs laser irradiation were recorded on a Perkin-Elmer Lambda-900 UV/vis/NIR spectrophotometer (Perkin Elmer, Waltham, MA). All the measurements were performed at ambient atmosphere.

## 3. Results and discussion

### 3.1. The precipitation of $BaAlBO_3F_2$ crystals in glass

Fig. 1(a) shows the XRD patterns of the fs laser irradiated and unirradiated glasses. The fs laser irradiated parallel grating structure with the size of 3 mm × 3 mm (in which 300 lines spaced 10 μm with length 3 mm are inscribed) is achieved. The writing speed is 5 μm/s and the pulse energy is 1.8 μJ. The broad bands are observed, which indicates the amorphous nature of the unirradiated glass. However, four sharp and weak diffraction peaks in irradiated glass are observed, which can be assigned to the $BaAlBO_3F_2$ crystal (ICDD: 01-071-2773). Therefore, precipitation of $BaAlBO_3F_2$ crystals in glass was confirmed. Fig. 1(b) shows the TEM image of fs laser irradiated glass. $BaAlBO_3F_2$ nanocrystals with diameter less than 10 nm are observed.

### 3.2. The distribution of $BaAlBO_3F_2$ crystals in glass

Micro-Raman spectra of the glass sample with four different position in modified region are shown in Fig. 2(a). The static exposure time was 5 s and the laser average power was 900 mW. The Raman spectrum of a glass sample heat-treated at 550 °C for 3 h (black curve in Fig. 2(a)) is added in Fig. 2 for comparison in which $BaAlBO_3F_2$ crystals were precipitated and confirmed by XRD analysis [16]. The Raman spectrum of the heat-treated glass sample exhibits three sharp bands at 353 $cm^{-1}$, 469 $cm^{-1}$ and 978 $cm^{-1}$, which can be assigned to the bending or stretching modes of $BO_3$ units in $BaAlBO_3F_2$ crystal [16]. Three characteristic Raman bands at 353 $cm^{-1}$, 469 $cm^{-1}$ and 978 $cm^{-1}$ of $BaAlBO_3F_2$ crystals are also observed in both the center (point A) and at the surroundings (point B) of the laser modified region. However, no apparent characteristic Raman bands due to $BaAlBO_3F_2$ crystals are observed at point C and point D of the laser modified region. The Raman spectrum of the point D also means the Raman spectrum of the unirradiated precursor glass. In addition, the intensities of characteristic Raman

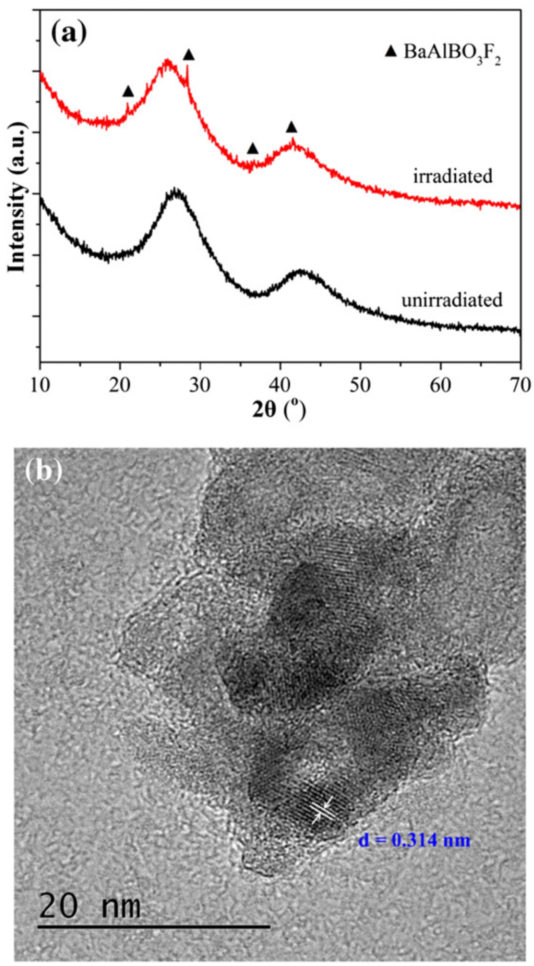


**Fig. 1.** (a) XRD patterns of fs laser irradiated and unirradiated glasses. (b) TEM image of fs laser irradiated glass.

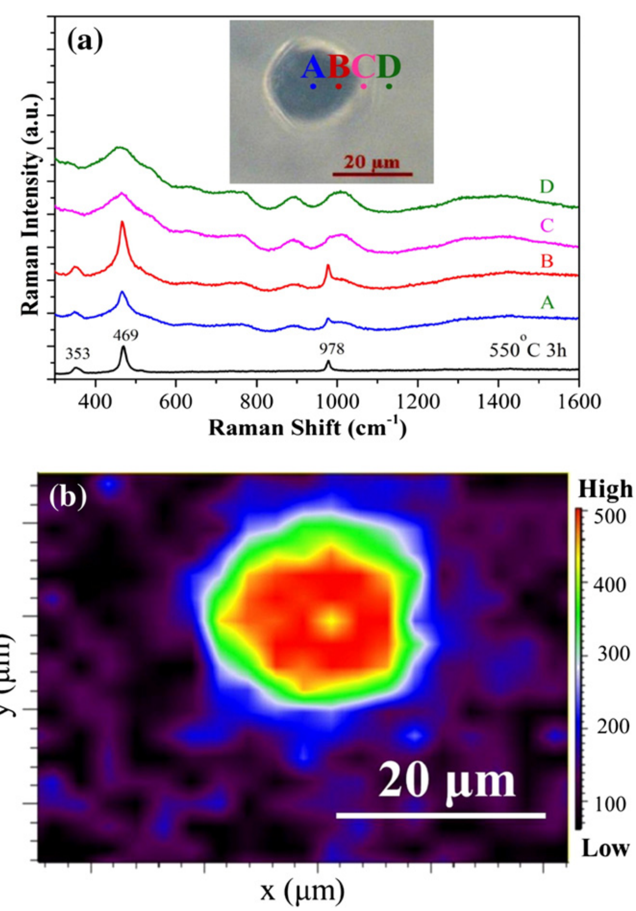


**Fig. 2.** (a) Micro-Raman spectra of the femtosecond laser-irradiated region with different position, Raman spectrum of the heat-treated glass sample is added for comparison. (b) Micro-Raman mapping at the 469 $cm^{-1}$ peak relative to the baseline in the modified region.