Vol 13 No 6, June 2004
1009-1963/2004/13(06)/0968-06

Chinese Physics

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Study of the microstructural transformations of borate glass and barium metaborate crystals induced by femtosecond laser*

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(Received 10 July 2003; revised manuscript received 18 November 2003)

This paper describes the microstructural transformations of borate glass and barium metaborate crystals induced by femtosecond laser. Such structural transformations were verified by Raman spectroscopy. The borate glass is transformed into low temperature (LT) phase of barium metaborate (BaB_2O_4) crystals after being irradiated for 10 min by a femtosecond laser. In addition, after 20 min of irradiation, high temperature (HT) phase of BaB_2O_4 crystals is also produced. Further studies demonstrate that LT phase BaB_2O_4 crystals are formed in the HT phase BaB_2O_4 crystals after femtosecond laser irradiation for 10 s.

Keywords: femtosecond laser, borate glass, barium metaborate crystal, Raman spectra
PACC: 8240J, 4270C, 7830

1. Introduction

It is well known that glass is in a metastable state with an inherent tendency to change into a more stable state. Therefore it is possible to rearrange glass structures with the influence of strong field (such as electric field, magnetic field etc).[1,2]

Barium metaborate (BaB_2O_4) crystal, with a melting point of 1095±5 °C, possesses a phase transition temperature at 925±5 °C. The high temperature (HT) phase of barium metaborate (α-BaB_2O_4, α-BBO) and low temperature (LT) phase of barium metaborate (β-BaB_2O_4, β-BBO) are two structurally distinct types of the BaB_2O_4 crystal, while sharing the common unit of the $(B_3O_6)^{3-}$ ring. α-BaB_2O_4, which possesses a space group of D_{3d}^6–$R\bar{3}c$, is centrosymmetric and is characterized by fine birefraction and well transmissibility in the ultraviolet band. β-BaB_2O_4, with a space group of $C_3^4 - R3c$, is an excellent nonlinear optical material for SHG (second-harmonic generation), OPA (optical parametric amplifier), and OPO (optical parametric oscillator). Since β-BaB_2O_4 was discovered by Chen *et al*,[3] many interesting studies have focused on analysing the phase transitions between the HT and LT phases of BaB_2O_4 crystal.[4–7]

Recently, more and more interest has been focused on the study of the interaction between femtosecond laser and transparent optical materials (such as glass). This is mainly due to the ability of the femtosecond laser to induce optical and structural changes in these transparent materials.[8]

In this paper, we report on the ability of femtosecond laser irradiation to induce the microstructure transformations in borate glass and in barium metaborate crystals. Raman spectroscopy demonstrates the formation of α-BaB_2O_4 and β-BaB_2O_4 crystals in focal areas on the borate glass samples as well as the generation of β-BaB_2O_4 crystals in focal areas of α-BaB_2O_4 crystal samples, respectively. Therefore, in principle, it is possible to apply femtosecond laser technology in the fabrication of integrated optical devices such as three-dimensional (3D) waveguide, optical coupling and other devices in the future.

*Project supported by the National Natural Science Foundation of China (Grant Nos 60377017 and 59832080), and 'Hundred Talents Programme' of the Chinese Academy of Sciences.

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2. Experiment

The composition of the borate glass studied was $47.5BaO–47.5B_2O_3–5Al_2O_3$ (mol.%). Reagent grade $BaCO_3$, B_2O_3 and $Al(OH)_3$ powders were used as starting materials. A mixed batch was melted in a Pt crucible at 1250 °C for about 2 h, which was then quenched into cold water in order to prevent crystallization of the glass. The glass obtained was cut and polished into a cuboid of $X \times Y \times Z = 5\,\text{mm} \times 5\,\text{mm} \times 2\,\text{mm}$.

The femtosecond laser system consists of three main parts, including the femtosecond laser source, the beam focusing system, and a 3D movable platform (see Fig.1). The irradiation source employed was a regenerative amplified 800 nm Ti:sapphire laser that emits mode-locked light with a pulse duration of 120 fs and a repetition rate of 200 kHz. The beam focusing system is a microscope with a 5× objective lens and a numerical aperture of 0.8. The laser beam with a spot size about 10 μm was focused on a plane 100 μm below the surface of the sample. It is essential to control the laser intensity to avoid damage to the glass where the laser is focused. In this experiment, we set the fluence of the laser irradiation at $4.0\times10^{12}\,\text{W/cm}^2$.

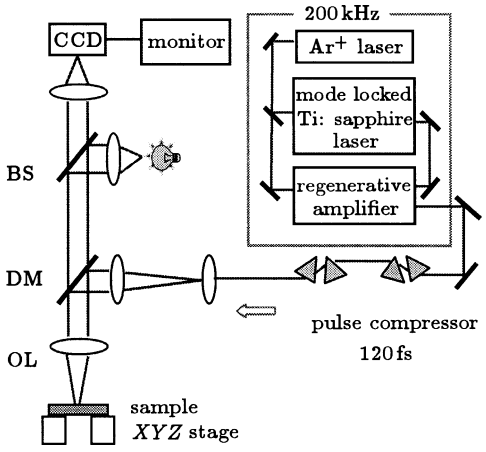


Fig.1. Femtosecond laser system.

The Raman scattering experiment was performed with a Dilor laser confocal Raman spectrometer. The excitation light source was a He–Ne laser with a wavelength of 632.8 nm and the output power of 2 mW. The grating was 1800 lines/mm. A 50× objective lens was used to focus the beam onto the sample. The spectrum centre line was $644.95\,\text{cm}^{-1}$ with a scattering detection region ranging from 130 to $1400\,\text{cm}^{-1}$ and with a 300 s exposure time. The scattered radiation was measured at an angle of 180° from the incident laser beam. All experiments were carried out at room temperature of 25 °C.

3. The borate glass irradiated by femtosecond laser

The femtosecond laser beam was focused on a plane 100 μm below the surface of the glass sample. After the femtosecond laser irradiation for different duration of time, a spherical area around the focal plane was analysed under a microscope with a 20× objective lens (see Fig.2).

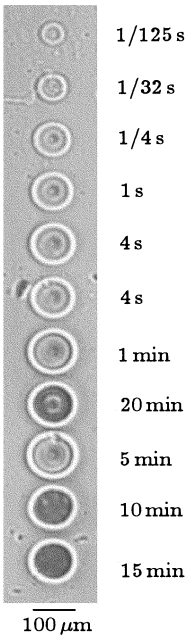


Fig.2. Microscope photograph of the borate glass on the focal plane. after being irradiated for different time duration by a femtosecond laser.

The Raman spectra of different sites in the focal area of the borate glass which have been irradiated by the femtosecond laser for different time duration are shown in Fig.3.

In Fig.3, curve *a* shows the Raman spectra of borate glass in the unirradiated area. The broad bands represent the vibrations of borate groups in the network of borate glass. The peak at $214\,\text{cm}^{-1}$ originates from the translation vibration of Ba^{2+} and Al^{3+} ions in the glass. The peak at $498\,\text{cm}^{-1}$ can be assigned to the asymmetrical transforming vibration of the BO_4 units. The weak band at $630\,\text{cm}^{-1}$ is from the breathing vibration of $(B_3O_6)^{3-}$ rings. The strong peak at $755\,\text{cm}^{-1}$ can be attributed to the vibration of borate units within the BO_4 tetrahedron, and the peak at $940\,\text{cm}^{-1}$ is assigned to the symmetrical stretching vibration of B–O bond in orthoborate units BO_3.[9]

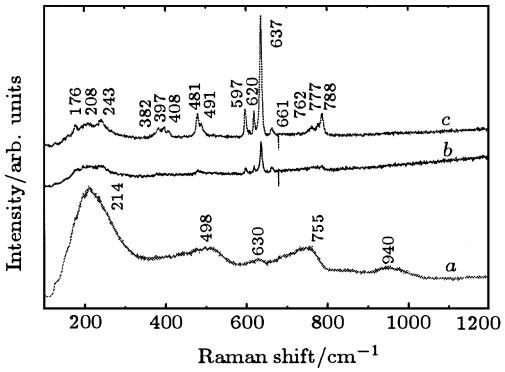


Fig.3. Raman spectra of borate glass obtained at two irradiation times. Curve *a*: unirradiated; curves *b* and *c*: irradiated 10 and 15 min respectively.

The Raman spectra of the focal area irradiated for 10 min are shown by curve *b* in Fig.3. The emergence of some narrow peaks indicates the formation of β-BaB_2O_4 crystals in the focal area. In the low-frequency region, the intensity increases at 176, 208 and 243 cm^{-1}. The peak at 176 cm^{-1} is assigned to the 'A' symmetry vibrational mode of metaborate ring $(B_3O_6)^{3-}$, while the peaks at 208 and 243 cm^{-1} are the translational modes of $(B_3O_6)^{3-}$ ring. The peak at 481 cm^{-1} is due to $(B_3O_6)^{3-}$ ring vibration of 'E' symmetry. The peaks at 597 and 620 cm^{-1} of 'A' symmetry are ascribed to the vibration of $(B_3O_6)^{3-}$ in the LT phase of BaB_2O_4 crystals. The Raman spectra also indicate the presence of a strong peak at approximately 637 cm^{-1}, which arises from the breathing vibration of the $(B_3O_6)^{3-}$ ring and is the fingerprint peak of BaB_2O_4 crystals.[6,10]

Since the ratio of ^{10}B to ^{11}B is 19:81, there are four isotopic structures for each class of $(B_3O_6)^{3-}$: $(^{10}B_3O_6)^{3-}$, $(^{10}B_2^{11}BO_6)^{3-}$, $(^{10}B^{11}B_2O_6)^{3-}$ and $(^{11}B_3O_6)^{3-}$ in Nature. The abundance ratio of these classes is 0.8, 9.4, 38.2 and 51.6, respectively. Many shoulder structures due to isotopes are shown in the Raman spectra, such as those at 382, 397, 481 and 491 cm^{-1}. Furthermore, the shoulder structures around 176, 208, 243 cm^{-1} could be ascribed not only to the isotope effect, but also to the coupling between the translation of Ba^{2+} ion and the vibrational mode of the $(B_3O_6)^{3-}$ (see Ref.[4]).

The Raman spectra of the focal area irradiated for 15 min are shown by curve *c* in Fig.3. The intensity of the peaks is obviously increased, which may lead to the conclusion that the degree of crystallization of the LT phase BaB_2O_4 crystal is more perfect in the focal area after 15 min than 10 min of irradiation.

After the borate glass was irradiated for 10 min by the femtosecond laser, blue light could be observed at the focused point which presumably is due to the microstructural change of the glass, which is even more intense when the glass is irradiated for 15 min. It is suggested that the blue light is related to the SHG effect of the 800 nm femtosecond laser (Fig.4).

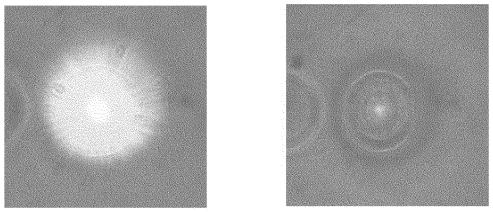


Fig.4. SHG effect at the focal point of the laser beam.

In the glass, which possesses a low diffusion coefficient, the structural rearrangement is confined to a small region at the peak of the Gaussian irradiance distribution of the femtosecond laser. When the peak intensity of the laser exceeds the damage threshold of the glass, a dramatic rise of temperature ($T \approx 10^6$ K) occurs in the focused area of the femtosecond laser beam. At such a HT, a strong shock wave and a high internal pressure field (200 GPa) are produced at the focal area inside the glass.[11] It is well known that glass is in a metastable state with an inherent tendency to change into a more stable state. The glass-transition temperature and the crystallization temperature are approximately 510 and 560°C, respectively, which are relatively low. Consequently, the HT and the strong internal pressure fields driven by the femtosecond laser pulse should be sufficient to rearrange the structure and produce β-BaB_2O_4 crystals in the focal area of the glass. Before irradiation, the Raman scattering measurements show various groups of constituents such as the triborate groups, the di-triborate groups, the orthoborate groups and the boroxol rings, which give rise to a disordered network in the glass. During irradiation, the rearrangement of the glass structure occurs by converting these groups into the $(B_3O_6)^{3-}$ rings.

In Fig.5, curves *a*, *b* and *c* show the Raman spectra from different sites in the same focal plane in the borate glass irradiated for 10, 15 and 20 min, respectively. In the spectrum from the site irradiated for 10 min, the bands are all very weak except for the fingerprint peak at 637 cm^{-1}. These peaks, however, are shown in much higher intensity in the spectrum from the site irradiated for 15 min. Since these peaks are assigned to the vibration of the groups in the β-BaB_2O_4 crystals, it can be concluded that all the

structures in the focal area of the borate glass have been transformed completely into β-BaB_2O_4 crystals after 15 min irradiation. However, additional changes have also taken place in the spectrum from the area after being irradiated for 20 min by the femtosecond laser, which are to be discussed in the following paragraph.

In the Raman spectra of the barium metaborate crystals, low-frequency groups emerge by the translation of the $(B_3O_6)^{3-}$ ring and the Ba^{2+} ion, and the high-frequency ones by the internal vibration of $(B_3O_6)^{3-}$ ring. The emergence of the peak at 609 cm^{-1} is the most apparent, which is the Raman peak of α-BaB_2O_4 (see Fig.6) and is not the characteristic band of β-BaB_2O_4 crystals. This peak can be attributed to the vibrational mode of the $(B_3O_6)^{3-}$ ring in α-BaB_2O_4 crystals. The intensity of the band at 220 cm^{-1} is increased distinctly. At the same time, new peaks also emerge at 409 and 762 cm^{-1}, which are all clearly characteristic peaks of α-BaB_2O_4 crystals.[4,10] Therefore, it can be concluded that some α-BaB_2O_4 crystals are also generated despite the fact that the majority of the crystals are β-BaB_2O_4.

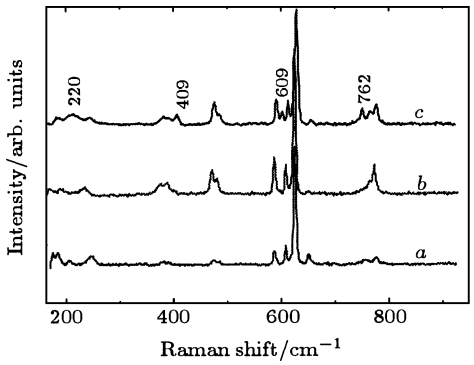


Fig.5. Comparison of Raman spectra from different points in the same focal plane in the borate glass after being irradiated for 10 min (curve *a*), 15 min (curve *b*) and 20 min (curve *c*).

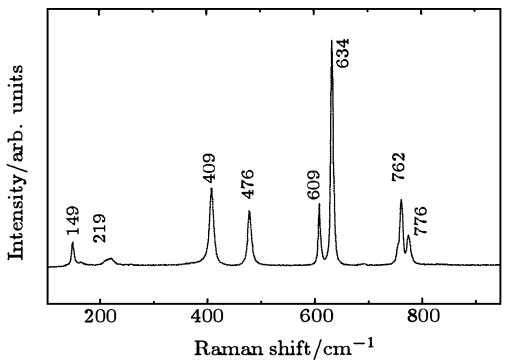


Fig.6. Raman spectra of α-BaB_2O_4 crystals.

Femtosecond laser irradiation can also change the refractive index in the focal area due to heat stress created by the femtosecond laser. In Fig.7, the emergence of the extinction of the black cross under crossed polarized light indicates that the microstructure of the borate glass has not changed. After 10, 15 or 20 min of irradiation, β-BaB_2O_4 crystals are formed and interference colours show up at these irradiated sites.

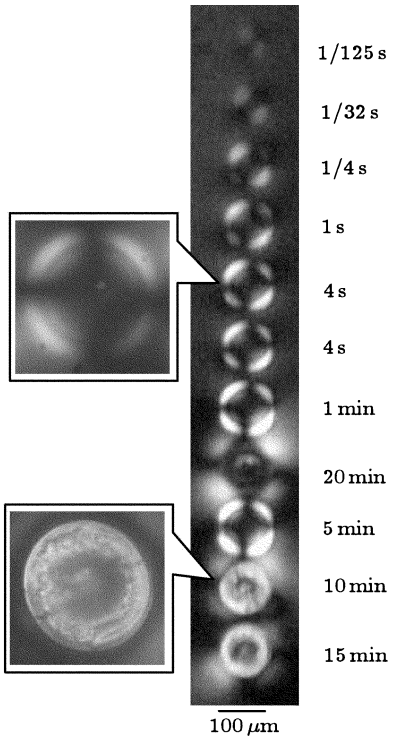


Fig.7. Micrograph of the microstructures for different durations of irradiation, taken under cross polarized light.

4. The α-BaB_2O_4 crystals irradiated by femtosecond laser

Figure 6 shows the Raman spectra of α-BaB_2O_4 crystal which have main Raman peaks at 149, 219, 409, 476, 609, 634, 762 and 776 cm^{-1} (see Ref.[10]). Figure 8 shows the Raman spectra of α-BaB_2O_4 irradiated for 10 s. For convenience, the comparison between α-BaB_2O_4 crystal and the one irradiated for 10 s is shown in the frequency bands of 100–400 cm^{-1} and 550–800 cm^{-1} in Fig.9.

In Fig.9, three new peaks emerge between 100 and 400 cm^{-1}. The peak at 178 cm^{-1} can be assigned to the 'A' symmetry vibrational mode of $(B_3O_6)^{3-}$ ring. The peak at 244 cm^{-1} is the translational modes of $(B_3O_6)^{3-}$ ring, and the peak at 382 cm^{-1}

is the 'E' symmetry vibrational mode of $(B_3O_6)^{3-}$ ring. They are all characteristic peaks of β-BaB_2O_4 crystals.[4,6,10] At the same time, the bands at 161 and 219 cm^{-1} become stronger.

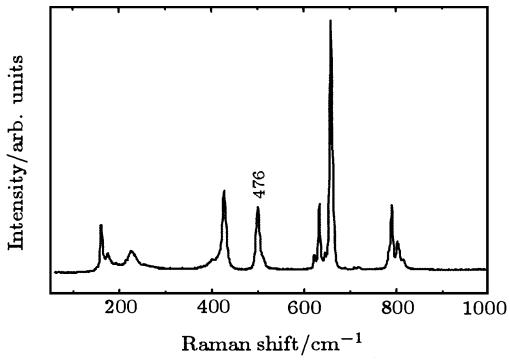


Fig.8. Raman spectra of α-BaB_2O_4 crystals after being irradiated for 10 s by the femtosecond laser.

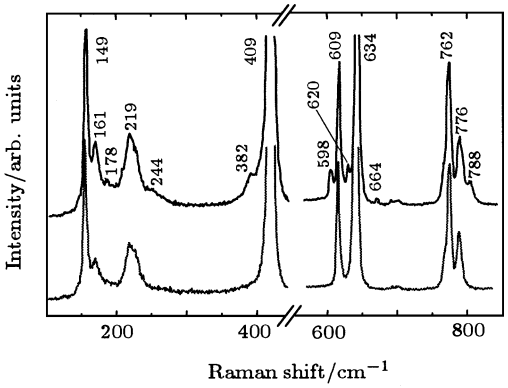


Fig.9. Comparison of Raman spectra of α-BaB_2O_4 before (below) and after (above) femtosecond laser irradiation.

The assigned peaks of Raman spectra of α-BaB_2O_4 and of the irradiated α-BaB_2O_4 are summarized in Table 1. From these data we conclude that there is a structural transformation of the α-BaB_2O_4 crystals, and the β-BaB_2O_4 crystals are formed.

Table 1. Peak assignment of the Raman spectra of α-BaB_2O_4 before and after irradiation.

Mode	Frequencies/cm^{-1}		Symmetry[a]	Attribution
	α-BaB_2O_4	irradiated		
1	149	149	A,E	translation of Ba^{2+} ion
2	161	161[b]	E	translation of Ba^{2+} ion
3		178	A	vibration of $(B_3O_6)^{3-}$ ring
4	219	219[b]	A,E	translation of $(B_3O_6)^{3-}$ ring
5		244	A,E	translation of $(B_3O_6)^{3-}$ ring
6		382	E(op)	vibration of $(B_3O_6)^{3-}$ ring
7	409	409	E(op)	vibration of $(B_3O_6)^{3-}$ ring
8	476	476	E(op)	vibration of $(B_3O_6)^{3-}$ ring
9		598	E	vibration of $(B_3O_6)^{3-}$ ring
10	609	609	A	vibration of $(B_3O_6)^{3-}$ ring
11		620	A(rab)	vibration of $(B_3O_6)^{3-}$ ring
12	634	634	A(rs)	vibration of $(B_3O_6)^{3-}$ ring
13		664	E(rab)	vibration of $(B_3O_6)^{3-}$ ring
14	762[c]	762		
15	776	776	E	vibration of $(B_3O_6)^{3-}$ ring
16		788	A(rs)	vibration of $(B_3O_6)^{3-}$ ring

[a] op, out-of-plane mode; rs, in-plane ring-stretching mode; rab, in-plane ring-angle-bending mode.
[b] This Raman band becomes stronger.
[c] Result of the isotope effect.

Four peaks also emerge between 550 and 800 cm^{-1}. The presence of the shoulder peaks at 598, 620, 664 and 788 cm^{-1}, which can be attributed to the vibration of the $(B_3O_6)^{3-}$ ring, clearly indicates the formation of β-BaB_2O_4 crystals.

Previous studies have confirmed that phase transition of the crystal may occur under the conditions of high temperature and high pressure. Many experiments have been conducted to investigate the phase transition between α-BaB_2O_4 and β-BaB_2O_4. The transition triggered by the femtosecond laser irradiation may be related to many factors, such as the

wavelength, the output power, the pulse width and the repetition rate of the laser. However, when the parameters related to the femtosecond laser are all defined, the irradiation duration may become the paramount factor. During the course of the rearrangement of the BaB_2O_4 crystals, the energy needed must exceed the potential structural energy barrier in order to form a new phase. Consequently, a certain reaction time would be needed for a successful transition. In our experiments, 10 s irradiation duration is not sufficient for every unit to react. After irradiation, the temperature and pressure in the focal area return to normal, which cannot provide the transition conditions for the crystal. Therefore, most of the α-BaB_2O_4 crystals in the focal area are still unchanged. When the glass is irradiated by the femtosecond laser for a longer duration, all the peaks of Raman spectra of β-BaB_2O_4 crystals start to emerge. And by 15 min of irradiation, perfect β-BaB_2O_4 crystals are formed. So it can be concluded that sufficient irradiation time is required for the formation of an entirely new structure. Such an irradiation time requirement varies among different structural transformations.

5. Conclusions

After the borate glass was irradiated by a femtosecond laser for 10 min, blue light emission was observed from the focal area, and after 15 min, on the other hand, results were much more intense emission. Under HT and high pressure created by the femtosecond laser, the borate glass may change from its metastable state to a stable state after 10 min of irradiation. In this case, β-BaB_2O_4 crystals are formed in borate glass, which was confirmed by Raman spectroscopy. The structure of the crystal can be seen under crossed polarized light. When 15 min irradiation is employed, the structure of β-BaB_2O_4 is more perfect. However, after 20 min of irradiation, some α-BaB_2O_4 crystals are also produced in the glass sample. As shown above, although 10 s of irradiation is not long enough for the complete transition from the initial α-BaB_2O_4 crystals, the emergence of Raman characteristic peak of β-BaB_2O_4 crystals implies that phase transition from α-BaB_2O_4 to β-BaB_2O_4 has taken place. We therefore conclude that sufficient duration of irradiation is required for the formation of β-BaB_2O_4 crystals from α-BaB_2O_4 crystals.

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