

In situ study on the structural transition in YBO₃ through Raman spectroscopy

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ABSTRACT

Raman spectroscopy is a powerful tool to judge the fundamental building units contained in crystal structure. In this work, it was used to investigate the basic structural groups involved in the low temperature (LT) and high temperature (HT) phase YBO₃. The characteristic Raman vibrational bands of the LT and HT phases YBO₃ were identified respectively. The characteristic vibrational peaks of the LT phase YBO₃ locate around 410 cm⁻¹ and 500 cm⁻¹, both of them are attributed to the ring bending modes of B₃O₉ group. The strong characteristic vibrational band of the HT phase YBO₃, arising from the symmetric stretching mode of BO₃ group, locates around 940 cm⁻¹. A structural phase transition with a large thermal hysteresis was found. During the phase transition process, the B–O bonds of the BO₄ groups break and the B₃O₉ rings cleave into the BO₃ plane conjugated groups.

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1. Introduction

YBO₃ is one of the best hosts of red phosphors applied in the plasma display panels and the mercury-free fluorescence lamps because of its vacuum ultraviolet transparency, high quantum efficiency, strong luminescence intensity, chemical stability and low toxicity [1,2]. There are two known phases for YBO₃. The structure of the low temperature (LT) phase has caused considerable controversies in the past decades [3–16]. The first determination was done by Bartram and Felten [6]. They proposed that the LT phase YBO₃ crystallizes in a hexagonal cell with the P6₃/mmc space symmetry, and the fundamental building units are isolated BO₃ groups. Another possible structure was proposed by Bradley et al. [7] who suggested that YBO₃ also crystallizes in a hexagonal cell but with the space group P6̄c2; the boron atoms in the structure are all tetrahedrally coordinated and form the B₃O₉ six-membered rings. The difficulty of precisely determining the LT-phase YBO₃ crystal structure originates mainly from the weak scattering power of boron and oxygen atoms for X-rays which is usually used to study crystal structures. NMR [8], IR [9–11] and Raman spectroscopy [16] studies all supported that the fundamental building units in the LT phase YBO₃ are the B₃O₉ groups. However, these techniques cannot determinate the crystal space group. Recently, Lin et al. solved and refined the structure of the LT phase YBO₃ from neutron powder diffraction data [8]. Their results indicated that it crystallizes in a

monoclinic cell with the C2/c space symmetry, and confirmed that the B₃O₉ six-membered rings are the only borate species contained in the structure. The structure was further supported by the calculated results of ligand-to-metal CT (charge transfer) energies based on the dielectric theory of complex crystal [17]. High-temperature (HT) phase YBO₃ was initially solved by the neutron diffraction method as well [8]. The HT phase YBO₃ also crystallizes in a monoclinic cell with the C2/c space symmetry; the borate groups in the structure are all isolated plane BO₃ groups.

Raman spectroscopy is a technique that provides chemical and structural information of almost all materials at different temperatures. Compared to other analysis techniques, it combines the advantages of *in situ* measurement and microscale analysis [18]. Recently, we applied Raman spectroscopy to investigate *in situ* the phase transition at the liquid–solid interface in order to understand the micro crystal growth mechanism of some important borate crystals [19,20]. However, the high temperature thermal radiation made it difficult to collect Raman signals clear enough to obtain unambiguous structural information. Generally, the Raman signals of crystalline materials are stronger than those of melts at high temperature. Therefore, we expect to find a similar phase transition process in crystalline state to obtain clearer Raman signals and then more accurate structural information. As pointed out by Lin et al. [8], when YBO₃ undergoes a structural phase transition on heating or cooling, the boron atoms transform from fourfold coordinated at low temperature into threefold coordinated at high temperature or reverse. Such a conversion of boron atoms between threefold and fourfold coordinated exists widely in borate glasses and melts, and plays an extremely crucial role in the borate crystal growth processes [18,21]. In this paper, we applied Raman spectroscopy to study the phase transition process of YBO₃ in order to collect the

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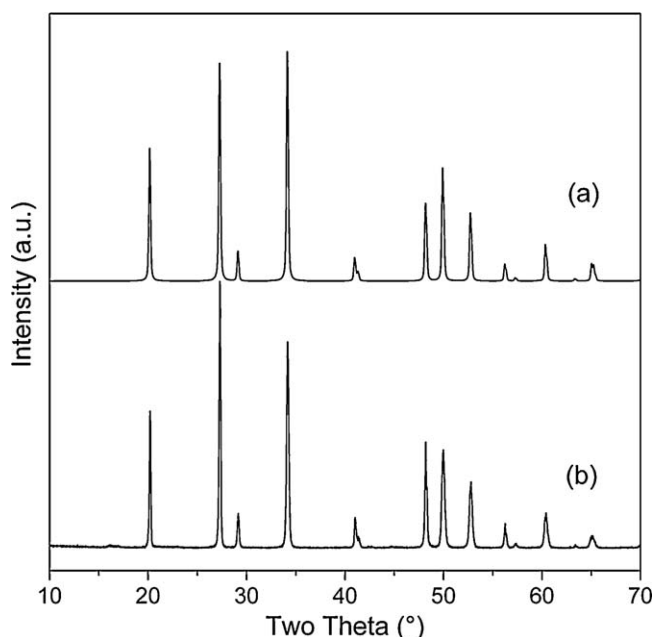


Fig. 1. (a) Standard XRD pattern (JCPDS no. 88-0356) of YBO_3 powder and (b) XRD pattern of the as-synthesized YBO_3 powder.

clear HT Raman signals of the borate groups involved in the LT and HT phase YBO_3 , and further to judge correctly the borate groups contained in the HT phase YBO_3 .

2. Experimental

YBO_3 powder was prepared by conventional solid-state reaction starting from analytical pure Y_2O_3 and H_3BO_3 . A stoichiometric mixture of the starting reagent (5 mol% excess of H_3BO_3 was added on account of the volatility of B_2O_3) was ground and placed in a corundum crucible. After heated at 500°C for 24 h, the materials were finely ground and heated again at 1100°C for 24 h. Finally, a white polycrystalline powder was obtained.

Powder X-ray diffraction (XRD) analysis of the product was carried out on a Rigaku X-ray diffractometer with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The XRD pattern was collected in the range of $10\text{--}70^\circ$, $0.01^\circ/\text{step}$. Raman spectra were recorded on a Horiba Jobin Yvon LabRam high temperature Raman spectrometer with a backscattering geometry. The light source was a Q-switched pulsed THG-Nd:YAG laser (355 nm) with a typical output of 0.80 W. The spectrometer was equipped with an intensive charge-coupled device (ICCD) detector and an integrated Olympus BX41 optical microscope. The sample was placed in a platinum crucible of 7 mm diameter and 4 mm height, and heated by a platinum wire winding in a Leitz Microscopy Heating Stage system. Raman spectra were collected in the range of $100\text{--}1300 \text{ cm}^{-1}$ at a spectral resolution of about 2 cm^{-1} . A standard silicon wafer was used to calibrate the spectrometer.

3. Results and discussions

The XRD pattern of the polycrystalline product is shown in Fig. 1. The reflections are all in agreement with the reported data of the LT phase YBO_3 (JCPDS no. 88-0356). The strong peaks indicate that the product has good crystallization.

A typical Raman spectrum recorded at room temperature is shown in Fig. 2. About 16 peaks were detected; all of them are in the range of $100\text{--}1100 \text{ cm}^{-1}$. The spectrum is in agreement with the previous data reported by Denning et al. [16]. They suggested that the coupling between the B_3O_9 rings and the rest of the YBO_3 lattice is weak, it is thus a good approximation to divide the vibrational modes into external modes and internal modes. The vibrational peaks of the LT phase YBO_3 can be assigned based on the B_3O_9 group. The B_3O_9 ring has D_{3h} symmetry with twelve atoms, which leads to 30 vibrational modes represented as:

$$\Gamma = 4A'_1 + A'_1 + 2A'_2 + 3A'_2 + 6E' + 4E''$$

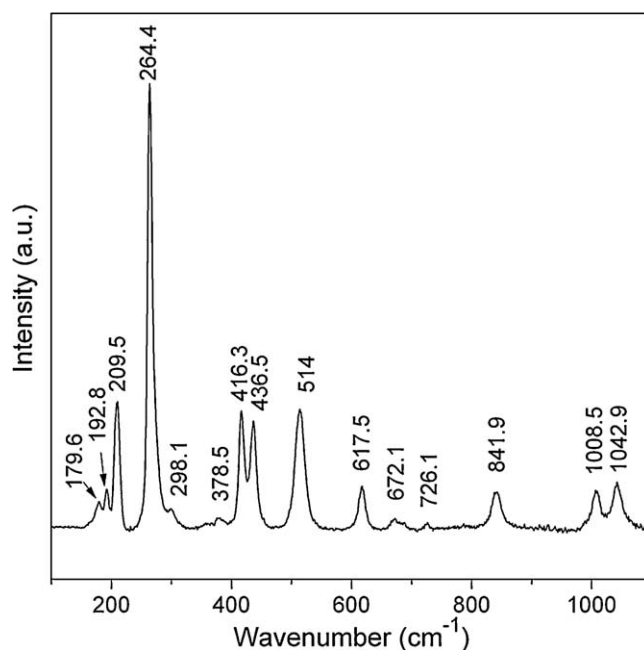


Fig. 2. Raman spectrum of the YBO_3 powder at room temperature.

Among which $4A'_1 + 6E' + 4E''$ are Raman active. Therefore, at least 14 Raman peaks are expected in the Raman spectrum of the LT phase YBO_3 . Indeed, the coupling between the Y^{3+} cations and B_3O_9 groups should be considered because of their strong interaction. The Raman peaks in the low wavenumber region, such as those located at 180 cm^{-1} , 193 cm^{-1} and 210 cm^{-1} , should be related to the translations of the Y^{3+} cations and the B_3O_9 groups, and the librational modes of the B_3O_9 groups. The other bands in the $250\text{--}1200 \text{ cm}^{-1}$ region are related to the internal modes of the B_3O_9 groups. Some splits of the internal vibrational bands should be attributed to the crystal field effect which may reduce the site symmetry of the B_3O_9 groups.

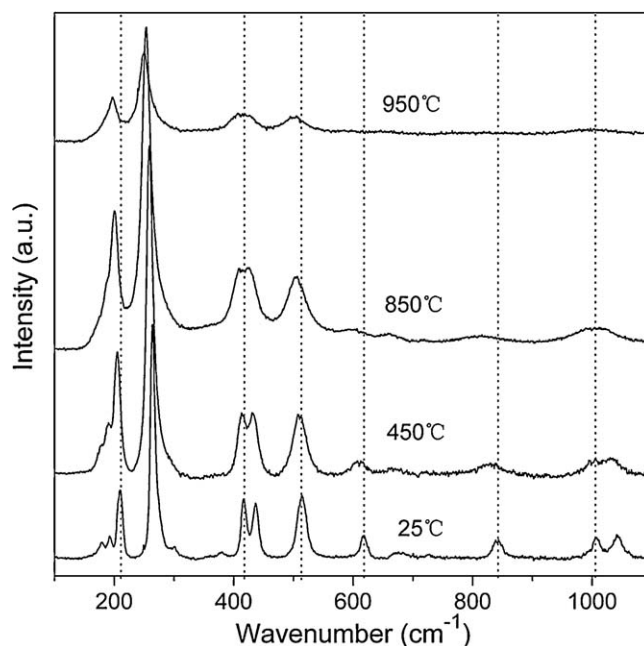


Fig. 3. Raman spectra of the YBO_3 powder at different temperatures when heating.

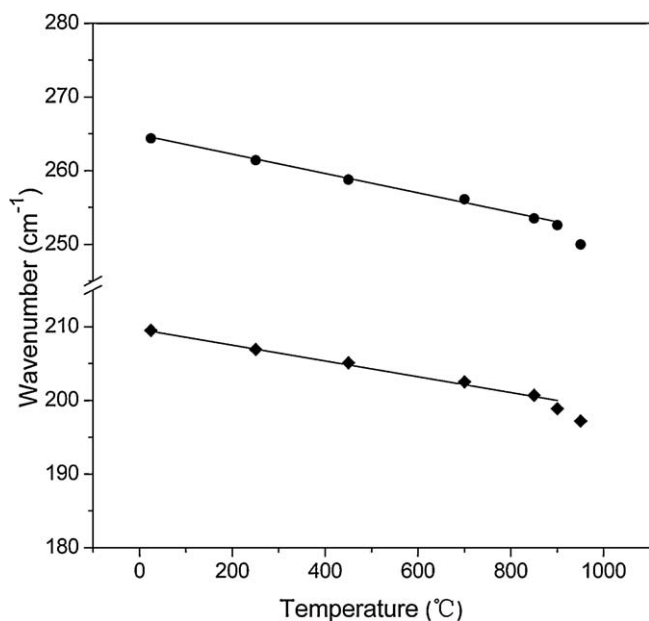


Fig. 4. Temperature dependence of the Raman shifts of the peaks respectively located around 260 cm^{-1} and 210 cm^{-1} .

Fig. 3 presents the Raman spectra of the LT phase YBO_3 at various temperatures when heating. All the peaks systematically reduce in intensity and shift to lower wavenumber, accompanied by peak broadening in different extent. These are mainly attributed to the wider bond angle distribution and larger range interatomic distances in the YBO_3 crystal due to the increasing temperature, reflecting an increase of distortions of the crystal structure owing to the thermal effect [22].

The temperature dependence of Raman shifts of the peaks respectively located around 210 cm^{-1} and 260 cm^{-1} is shown in Fig. 4. The wavenumbers of the two peaks decrease near linearly with the increasing temperature below 800°C . However, a non-linear variation of the wavenumbers vs. temperature was found within $800\text{--}950^\circ\text{C}$, which implies that a possible phase transition would happen above 950°C . When the sample was heated up to 1050°C , the Raman peaks of the LT phase YBO_3 vanished, and a series of new peaks appeared (see Fig. 5(a)), confirming that the sample underwent a conformational transition around the temperature and transformed into the HT phase YBO_3 . Furthermore, we cooled the HT phase YBO_3 to room temperature, and collected the Raman spectra during the cooling process. The results showed that the HT phase returned to the LT phase in the range of $650\text{--}550^\circ\text{C}$. The transition from the HT to LT phase occurred at much lower temperature than that from the LT to HT phase, exhibiting that the phase transition has a larger thermal hysteresis (see Fig. 5(b)). The similar phenomena were also found in the DTA measurements of some rare earth orthoborates [14,23]. The relatively large thermal hysteresis suggests that the phase transition process has a large potential barrier.

At high temperatures, the two bands respectively located around 410 cm^{-1} and 500 cm^{-1} should be the unambiguous indicative of the presence of the B_3O_9 rings. Interestingly, both of the bands are attributed to the ring bending modes (A'_1 and E') [16], the only two in-plane bending modes of the B_3O_9 groups, as shown in Fig. 6. Both of the modes are related to the bridge oxygen atoms of the B_3O_9 groups, but not related to the terminal oxygen atoms. Thus we infer that the bridge oxygen atoms are more insensitive to the temperature compared to the terminal oxygen atoms.

As described by Lin et al. [8], the HT phase YBO_3 crystallizes in the monoclinic C2/c space group, and the borate groups in the

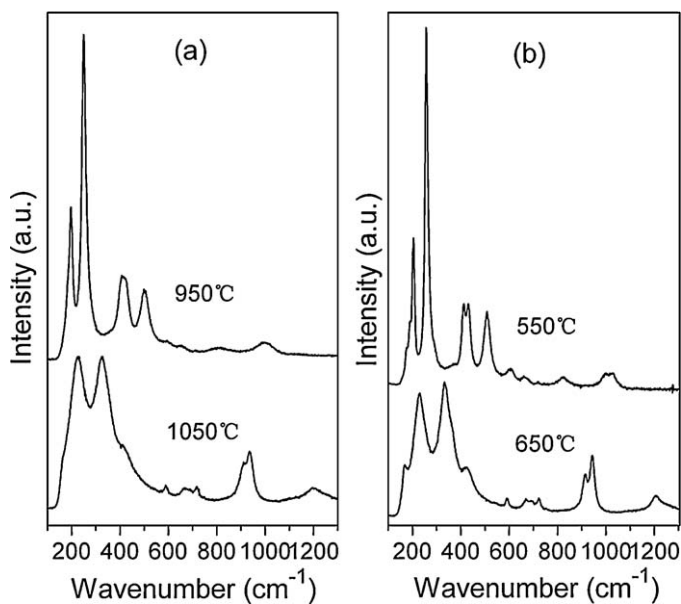


Fig. 5. Raman spectra of the YBO_3 sample near the phase transition temperature when: (a) heating and (b) cooling.

structure are all isolated BO_3 triangles. The point group symmetry of the isolated BO_3 group is D_{3h} and the corresponding irreducible representations of the normal modes are given by $\Gamma = A'_1 + A'_2 + 2E'$, of which $A'_1 + 2E'$ are Raman active: (1) $A'_1 (\nu_1)$, the symmetric stretching mode can be observed near 940 cm^{-1} which is the characteristic vibrational wavenumber of the BO_3 group. In Fig. 5, the band splits into two strong Raman peaks since the occupation site of the BO_3 group is less than threefold symmetry in the HT phase YBO_3 . (2) $E' (\nu_3)$, the asymmetric stretching mode was found near

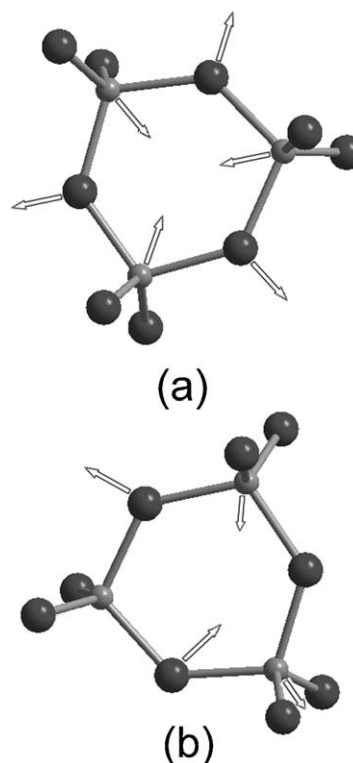


Fig. 6. Wavenumber and related atomic displacements for (a) A' and (b) E' modes of the B_3O_9 ring.

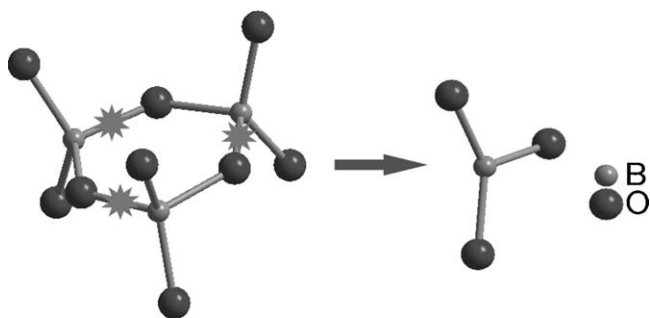


Fig. 7. The conformational transition occurring in the YBO_3 sample from the LT to HT phase transition.

1200 cm^{-1} . $(3) E' (\nu_4)$, the in-plane bending mode locates at around 590 cm^{-1} . It is worth noting that the infrared active $A'_2 (\nu_2)$ mode (out-plane bending mode) also becomes Raman active in the HT phase YBO_3 ; its vibrational bands are in the range of $660\text{--}740\text{ cm}^{-1}$. The observed wavenumbers are consistent with the reported values of other orthoborates [24–27]. Under high temperature condition, the presence of the BO_3 group is marked by the strong Raman band at about 940 cm^{-1} , as well as the characteristic bands at around 590 and 1200 cm^{-1} . Our experimental results further prove the BO_3 group existing in the HT phase YBO_3 .

The different borate groups in the LT and HT phase YBO_3 demonstrate that the YBO_3 sample underwent a structural phase transition during the heating and cooling cycle. From the LT to HT phase, the B_3O_9 rings are cleaved to isolated BO_3 triangles with the breaking of B–O bonds of the BO_4 groups in the B_3O_9 ring, as shown in Fig. 7. The structural phase transition has a large potential barrier which leads to a large thermal hysteresis.

4. Conclusions

A series of Raman spectra of YBO_3 at different temperatures during the heating and cooling cycle were recorded. Under high temperature conditions, the characteristic vibrational bands of LT phase YBO_3 locate around 410 cm^{-1} and 500 cm^{-1} , both of them arise from the ring bending modes of the B_3O_9 group. Trigonal planar BO_3 group was identified in HT phase YBO_3 ; its characteristic vibrational bands attributed to the symmetric stretching mode locate near 940 cm^{-1} . Temperature-induced phase transition from the LT to HT phase YBO_3 occurred between 950 and $1050\text{ }^\circ\text{C}$, accompanying the breaking of B–O bonds of BO_4 in B_3O_9 rings and the formation of the isolated BO_3 triangles. The reverse phase transition process, from the HT to LT phase, occurs at $650\text{--}550\text{ }^\circ\text{C}$, indicating that the phase transition of YBO_3 has a large thermal hysteresis. These results will provide us the precise spectroscopic information

of the B_3O_9 and the BO_3 groups at high temperatures, and help us understand the similar phase transition occurring either in crystalline state or in crystal growth process. Our experiment indicates that Raman spectroscopy is a powerful tool both to judge the fundamental structural units contained in HT crystal structure and to study the structural phase transition.

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