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# X-Ray Absorption Fine Structure of Ti Coordination Changes in $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ Glass System

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The $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ glass was prepared by adding 8 wt % $TiO_2$ into the basic glass $10Na_2O$-$50B_2O_3$-$40SiO_2$ (mol %). Application Ti K-edge X-ray absorption fine structure (XAFS), the change of Ti structure during the glass phase separation process was mainly investigated. Glass phase separation and $TiO_2$ crystallization of the samples were characterized by X-ray diffraction, scanning electron microscope and transmission electron microscope. The results indicated that $Ti^{4+}$ formed $[TiO_4]$ tetrahedral structure in high-temperature homogeneous glass of $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ system. At low temperature heat treatment (500 °C) $Ti^{4+}$ entirely transformed from $[TiO_4]$ to $[TiO_6]$ and then formed nucleus pre-group and anatase crystal nucleus, which were advantageous to crystallize $TiO_2$. With the increasing of heat-treatment temperature, Ti-ion structure is closed to that of anatase and $TiO_2$ began to crystallize at heat-treatment 550 °C.

**Keywords: Glass phase separation, X-ray absorption fine structure, Ti coordination, $TiO_2$ crystallization.**

## INTRODUCTION

Glass phase separation phenomenon refers to two immiscible glass phases co-existence in homogeneous multi-system glasses. The study of phase separation in $Na_2O$-$B_2O_3$-$SiO_2$ glass system had attracted widespread attention[1-3]. A large number of new materials were developed by utilizing the glass phase phenomenon. Glass phase separation is closely related to glass composition and heat treatment conditions, which has great influence on the crystallization of glass system. We had succeeded in preparing $TiO_2$ nano-assembled material, which was directly loaded on $Na_2O$-$B_2O_3$-$SiO_2$ porous glass by selecting optimal glass composition and heat treatment condition and this new material has better catalysis and photocatalytic property.

The structure of alkali borate and borosilicate glasses has been extensively studied by infra-red, Raman and NMR spectroscopy *e.g.*[4]. Most of them were focused on B's structure changes and the other oxides' structure changes of multi-components borosilicate glasses have been seldom reported. The subject of the present paper is to study the change of Ti structures' by X-ray absorption fine structure[4]. X-ray absorption fine structure is a mature and comprehensive useful experiment technique with the development of synchrotron radiation facility, which is one of very important method of studying material structure. By studying on Ti K-edge X-ray absorption fine structure during the phase separation process in $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ glass, the glass phase separation structure influencing on $TiO_2$ crystallization could be attained[5,6].

## EXPERIMENTAL

Glass in the system $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ (with 10, 50 and 40 mol % $SiO_2$) was prepared from commercial grade borax, boric acid, quartz and then added 8 wt % titanium dioxide into this system. The glass batches were blended thoroughly. They were melted at 1100 °C for 2 h. The melt were quenched in water and then heated treatment at different temperatures (500, 530, 550 and 580 °C) for 12 h.

The crystalline phase of the samples was identified by XRD (D/MAX2500PC, $CuK_\alpha$ Japan). The particle size and morphology of samples were examined by TEM (JEM-2010, Japan) and SEM (KYKY-2800B, China).

Ti K-edge XAFS spectra were recorded by EXAFS experiment station of 4W1B beam line in Beijing synchrotron radiation facility (BSRF) National Laboratory. Double crystal Si(III) Monochromator, store circle energy 2.2 GeV, electric current 50-100 mA and transmission method collection Ti K-edge XAFS data, the experiment data were dealt with by using FEFF 6 program. The absorption spectrum curves of Ti K-edge XAFS were fit according to the standard sample of anatase $TiO_2$. The test samples were prepared by grinding into powder and the powder passed through 400 mesh sieve. The samples were formed thickness about 5-6 μm and fixed in adhesive tape.

## RESULTS AND DISCUSSION

The heat treatment lead to glass phase separation and cause $TiO_2$ crystallization in the $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ glass system.

The SEM micrographs of the samples at different heat treatment temperature are shown in Fig. 1. The photograph (a) and (b) indicated that the samples did not separate phase at 500 and 530 °C. The phase separation structure (Fig. 1c and d) became clear when the heat treatment of the sample were at 550 and 580 °C and the size of phase separation was about 100 nm.

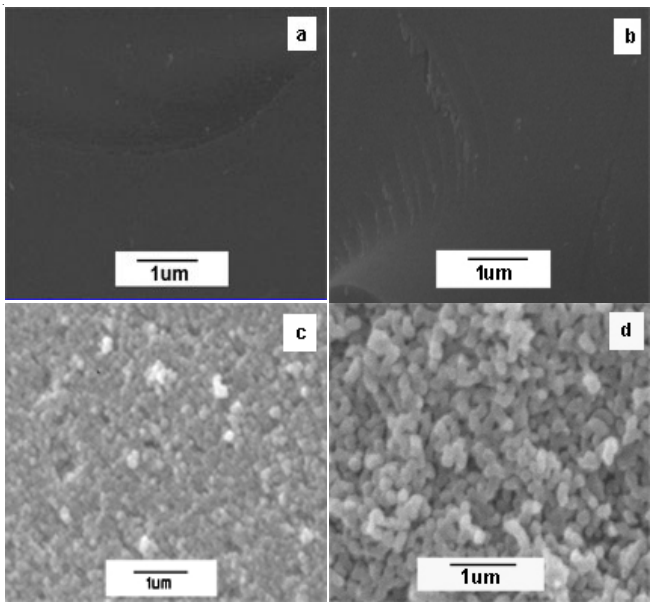


Fig. 1. SEM micrographs of the samples at different heat treatment temperature (a) 500 °C, (b) 530 °C, (c) 550 °C, (d) 580 °C

The X-ray results of the samples (Fig. 2) revealed that $TiO_2$ crystallization of the samples heated treatment from 550 to 580 °C. When the heat treatment temperature was under 530 °C, there was no $TiO_2$ crystallization. With the temperature varies from 550 to 580 °C, the intensity of $TiO_2$ peaks increased, that it to say, the crystal grain size of the samples grew up gradually.

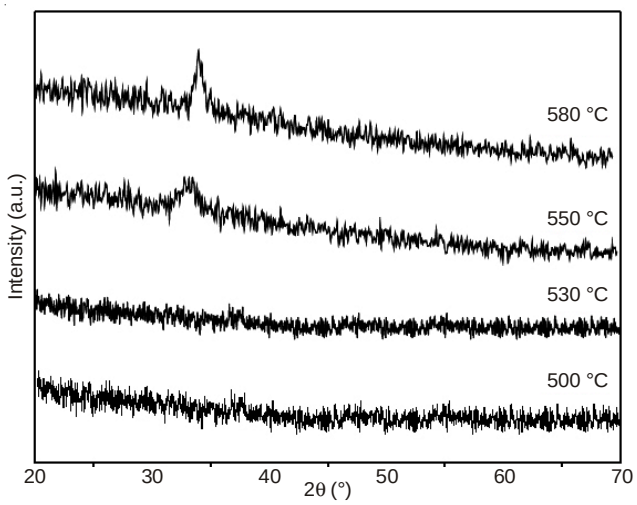


Fig. 2. X-ray of the samples

Fig. 3 shows the TEM of the sample heated treatment at 580 °C. The result indicated that $TiO_2$ crystal was octahedral positive pyramid euhedral crystal and the crystal size was about 30 nm.

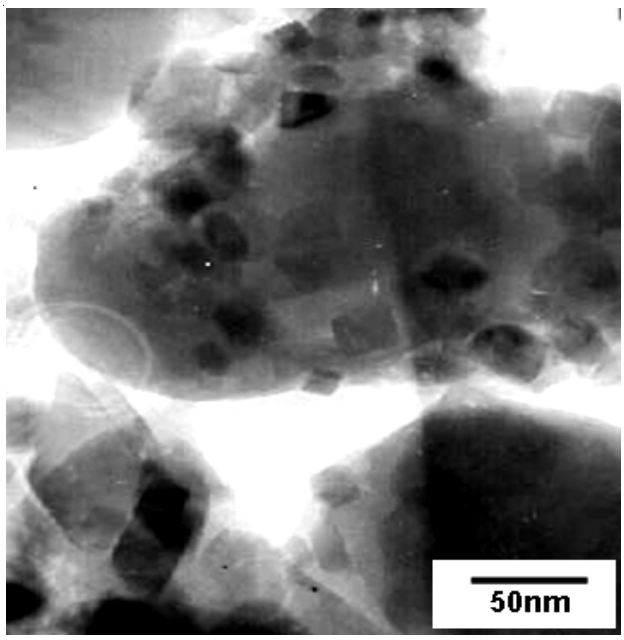


Fig. 3. TEM result of the sample heated at 580 °C

**Ti-ion coordination state:** Ti K-edge XANES is shown in Fig. 4. The Ti K-edge fore-edge structure of unheated treatment original glass sample1 shows intense single peak, which is the fore-edge characteristic of $Ti^{4+}$ tetrahedral structure [$TiO_4$]. This indicated that tetrahedron [$TiO_4$] as well as [$SiO_4$], [$BO_3$], [$BO_4$] formed glass network together at high temperature in $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ glass system. The K-edge shape of heated treatment samples 2, 3 and 4 is similar to the anatase standard sample's, which characteristic peak is dominated by three features, labeled A1, A2 and A3 in Fig. 4, so the Ti structure of heated treatment samples is octahedral$TiO_6$. It can be concluded from the Fig. 4 that the [$TiO_4$] of the samples entirely changed into [$TiO_6$] when the samples were heated over (> =) 500 °C. It could be explained that the glass former $B_2O_3$ adjusted structure from [$BO_3$] to [$BO_4$] during the heating treatment, so promoted the change of $Ti^{4+}$ from [$TiO_4$] to [$TiO_6$]. But at this time due to lower temperature, mass migration difficulties, have not been able to form sub-phase structure.

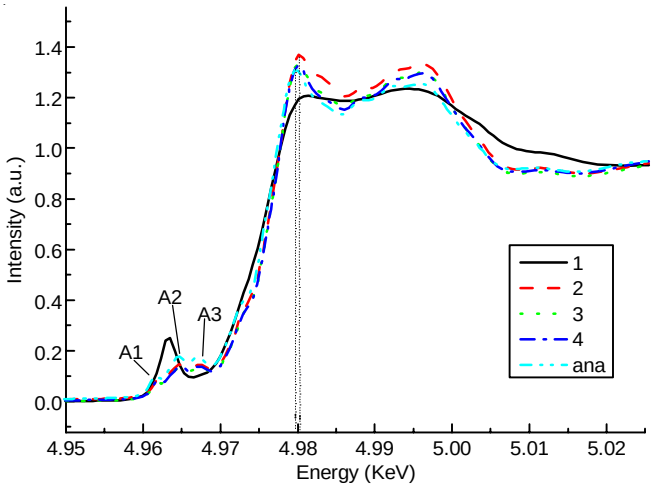


Fig. 4. Ti K-edge XANES of unheat ed and heated treatment samples: ana. = anatase, 1 = unheated, 2 = 500 °C, 3 = 530 °C, 4 = 580 °C

Ti K-edge fore-edge structure is formed by 1*s*-3*d* electronic transition. Theoretically, 1*s*-3*d* electronic transition should be prohibited. However, non-centro-symmetric structures, such as deformed octahedron and tetrahedron, owing to the final state *d*-*p* orbital hybridization, partial d orbital have characteristics with *p*-orbital. Therefore, the Ti pre-edge peak can be observed in X-ray absorb spectrum. Furthermore the higher orbital hybridization is, the more intensive of pre-edge peak is. The highest *d*-*p* hybridization degree is tetrahedron structure, higher in five-coordinate and high in abnormal octahedron. Tetrahedron structure showed the strongest pre-edge peak in XANES, the sample 1 in Fig. 4 showed the features of the former structure. In anatase, the closest Ti coordinate number is 6, which is the octahedron structure. In Fig. 4, the anatase three feature peaks corresponding to transition are: A2 and A3 belong to 1*s*→3*d* in octahedral field, that is to say, they belong to $1s \rightarrow 2t_{2g}$ and $1s \rightarrow 3e_g$ electro-transition separately. however A1 belongs to $1s \rightarrow 1t_{1g}$ electro-transition. The Ti K-edge energy of anatase standard sample is 4979.5 eV. The Ti K-edge energy of heat treatment samples drift to high energy direction, which indicates that Ti structure environment of boron silicate glass changes. With the increasing of heat treatment, the peak intensity is lower and the signal nears the standard and the structure environment is similar to anatase.

Fourier transformation curves of Ti K-edge EXAFS of samples are shown in Fig. 5. The Fourier curve is also named radial structure function (RSF) curve and the distance between neighboring particles can be directly attained from the curve. Owing to the stronger Ti-O interaction force in tetrahedron [$TiO_4$], Ti-O particles spacing R(Ti-O) of [$TiO_4$] is less than that of octahedron [$TiO_6$]. In fig. 5, the sample 1 only existed [$TiO_4$] whereas the rest samples and the anatase standard sample existed merely [$TiO_6$] without [$TiO_4$]. Although $TiO_2$ crystallization of the samples at 500 °C and at 530 °C did not observed in XRD (Fig. 2), the Ti of samples transferred into [$TiO_6$] entirely (Fig. 4) and formed nucleus pre-group and then formed anatase crystal nucleus. The former research had shown that it was observed phase separation at 550 °C in $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ system, so the $TiO_2$ nucleus forming of the sample heat treatment at 500 °C was earlier than that of phase separation of the glass system. That is to say, $TiO_2$ crystallization did not depend on the forming of phase separation interface. The R (Ti-O) peaks heights of the samples 2, 3, 4 increased with the increasing of heat treatment temperature, which were due to the anatase crystal growth and the normal bond length particles increase.

In Fig. 5, R (Ti-O) of the samples 2, 3, 4 were lower than that of anatase standard sample. It could be explained that the standard sample formed bigger lattice distortion during grinding of the preparation sample. However, the rest samples, because the glass body were forced and broken firstly during the preparing samples, the anatase $TiO_2$ particles of embedded in glass (Fig. 3) were not destroyed.

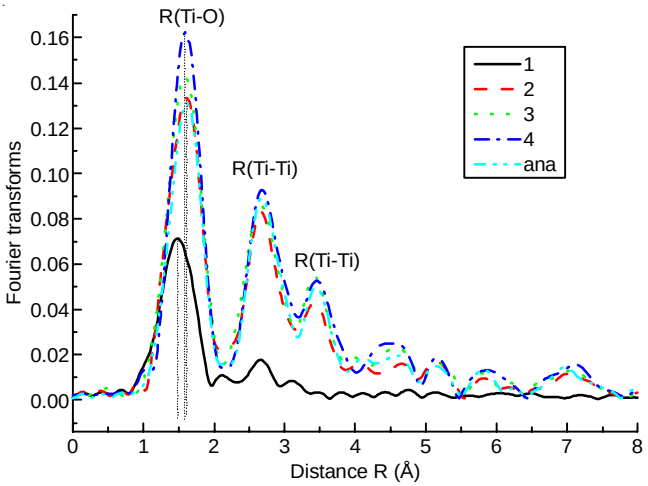


Fig. 5. Fourier transformation curves of Ti K-edge EXAFS of samples: ana. = anatase, 1 = unheated, 2 = 500 °C, 3 = 530 °C, 4 = 580 °C

## Conclusion

In high-temperature homogeneous glass of the $Na_2O$-$B_2O_3$-$SiO_2$-$TiO_2$ system, [$TiO_4$] with [$SiO_4$], [$BO_3$] and [$BO_4$] constituted the glass network and participated in network structure. At a lower temperature (500 °C) heat treatment, due to structures adjusting of B-ion from [$BO_3$] to [$BO_4$], $Ti^{4+}$ changed [$TiO_4$] into [$TiO_6$] and turned network formed ion into network adjusting ion. [$TiO_6$] concentrated nucleus pre-group and then formed anatase crystal nucleus, which was beneficial to $TiO_2$ crystallization. With the heat treatment temperature increasing, the structure environment of Ti ion closed to anatase's. At 550 °C, anatase $TiO_2$ began to crystallize, for being a pyramid-type self-octahedral crystal. The results indicated that $TiO_2$ crystal nucleus formed easily in the selected composition phase separation glass, but the formation of nucleus does not depend on favorable nucleation sites of phase separation interface provided.

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