

$\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ 溶胶-凝胶玻璃的制备及固体核磁共振结构解析

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摘 要: 针对铋掺杂玻璃发光机理不明确的问题, 以 $\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ 玻璃为研究对象, 对其开展结构研究。采用硝酸铋、乳酸铝、磷酸三乙酯和正硅酸四乙酯作为前驱体, 通过溶胶-凝胶法制备了 $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ ($0 \leq x \leq 0.15$) 的三元体系玻璃, 并使用固态核磁共振(NMR)技术及 X 射线光电子能谱系统解析了 $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ 玻璃的原子级结构。NMR 结果证明: 制备的玻璃由 AlPO_4 和 SiO_2 纳米团簇组成。XPS 结果表明该系列的玻璃中没有形成 Bi--O--Bi 键。通过 $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR、 $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR, ^{31}P CT-DRENAR-BABA-xy16, 及 ^{29}Si MAS 单共振实验证明: Bi_2O_3 的加入促进了 AlPO_4 团簇逐步增大, 直到最后形成明显的分相, Bi_2O_3 同时存在于 SiO_2 和 AlPO_4 两相中。

关键词: 铋; 玻璃; 结构; 固体核磁共振; 溶胶凝胶

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Structural Investigations of Sol-Gel Prepared $\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ Glasses by Solid State Nuclei Magnetic Resonance Spectroscopy

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Abstract: A series of $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses ($0 \leq x \leq 0.15$) were prepared by a sol-gel process. The local structures of glasses were investigated by magic angle spinning nuclei magnetic resonance (MAS NMR) and X-ray photoelectron spectroscopy (XPS). Based on the ^{27}Al MAS NMR spectra. The results show that there is Bi--O--Bi connectivity in all these glasses. In addition, the prepared glass is composed of AlPO_4 - and SiO_2 -nanodomains according to the results of $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR, $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR, ^{31}P CT-DRENAR-BABA-xy16, and ^{29}Si MAS NMR. The addition of Bi_2O_3 promotes the increase of AlPO_4 clusters, forming the final phase, and Bi_2O_3 exists both in SiO_2 and AlPO_4 nanodomains.

Keywords: bismuth; glass; structure; solid-state nuclei magnetic resonance; sol-gel

1 Introduction

As a promising gain material, Bi-doped glasses have attracted much attention for broadband fiber amplifier and tunable fiber laser due to the wideband near-infrared (NIR) luminescence^[1-6]. Some researchers doped bismuth with a variety of glass matrices (such as silicate, borosilicate, germanate, phosphate and borate) to investigate the luminescent properties of bismuth doped glass. Different mechanisms on the NIR luminescence of bismuth doped glass were proposed and the corresponding

extensive work was carried out. However, the mechanism of Bi-related NIR luminescence is still not clarified. The local structure of bismuth has a decisive influence on the optical properties of Bi-doped glasses, such as absorption and luminescence^[7-11]. It is thus important to explore the structural organization of these glasses.

$\text{AlPO}_4\text{--SiO}_2$ glasses containing two types of network formers, *i.e.*, P_2O_5 and SiO_2 , are of great fundamental interest in materials chemistry because SiO_2 is isoelectronic with AlPO_4 ^[12]. However, it is impossible to prepare glassy $\text{AlPO}_4\text{--SiO}_2$ glasses by conventional melt-quenching methods^[13-14]. As a quite

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attractive technique, sol-gel method is used for preparing of multi-component oxide glasses due to its advantages like the mixture of the starting materials on a molecular scale, lower temperature for processing, the flexible control of composition, purity, and homogeneity^[15–17]. Eckert *et al.* prepared aluminium phosphate and aluminophosphosilicate glasses including AlPO_4 , $\text{Na}_2\text{O}-\text{AlPO}_4$, $\text{AlPO}_4-\text{SiO}_2$, and $\text{Na}_2\text{O}-\text{AlPO}_4-\text{SiO}_2$ glasses *via* a sol-gel process^[12, 18–22]. For $\text{AlPO}_4-\text{SiO}_2$ system, the solid-state NMR results revealed that no $-\text{P}-\text{O}-\text{Si}-$ and $-\text{Al}-\text{O}-\text{Si}-$ connectivity existed in these glass, indicating the formation of AlPO_4 and SiO_2 sub-domains.

This work was to investigate the network structure of $\text{Bi}_2\text{O}_3-\text{AlPO}_4-\text{SiO}_2$ ternary system and the distribution of Bi^{3+} in glass. We prepared $x\text{Bi}_2\text{O}_3-\text{AlPO}_4-\text{SiO}_2$ glasses by a simple sol-gel route with bismuth nitrate, aluminum lactate, triethyl phosphate and tetraethyl orthosilicate as precursors. In addition, the structure of the glasses was also analyzed by a combined multinuclear nuclei magnetic resonance (NMR) and X-ray photoelectron (XPS) technique.

2 Experimental

2.1 Materials and methods

The samples of $x\text{Bi}_2\text{O}_3-\text{AlPO}_4-\text{SiO}_2$ ($x=0, 0.025, 0.050, 0.075, 0.100, 0.125, 0.150$) glasses were fabricated *via* a sol-gel method^[20] with bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) (99%, Sinopharm Chemical Reagent Co., Ltd, China), aluminium lactate (95%, Sigma Aldrich, USA), triethyl phosphate (TEP) (98%, Alfa Aesar, USA), tetraethyl orthosilicate (TEOS) (99%, Aladdin, China) as precursors. After gelling at 50 °C and annealing at 650 °C, we

obtained transparent and colorless $x\text{Bi}_2\text{O}_3-\text{AlPO}_4-\text{SiO}_2$ glasses. The XRD patterns of the samples were characterized on an X-ray diffractometer (PANalytical Empyrean, Netherlands). The X-ray photoelectron spectra (XPS) were determined a spectrometer (Thermo Fisher Scientific, USA).

2.2 Solid-state NMR

All the solid-state NMR experiments were performed on a model Bruker AVANCE III HD (500 MHz) spectrometer (11.7 T, Bruker, Germany). A 4 mm MAS NMR probe was used to approach the ^{27}Al , ^{31}P , ^{29}Si single-pulse experiments. To reduce the relaxation time of silicon for the ^{29}Si NMR spectra, the bismuth- aluminophosphosilicate glasses were doped with 0.1% (in mole fraction) manganese carbonate. Table 1 shows the experimental conditions. The signal deconvolutions was carried out by a software package named DMFIT^[23]. The $^{27}\text{Al}\{^{31}\text{P}\}$ compensated rotational echo double resonance (REDOR)^[24–26], and $^{31}\text{P}\{^{27}\text{Al}\}$ rotational echo adiabatic passage double resonance (REAPDOR)^[27–28] experiments were carried out on a 4 mm MAS NMR probe with a spinning rate of 12 kHz. In the $^{27}\text{Al}\{^{31}\text{P}\}$ compensated REDOR experiments, the relaxation delay was 0.5 s. The 180° pulses lengths were 8.2 μs and 8.6 μs for ^{27}Al and ^{31}P , respectively. The $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR were done with 90° pulses lengths of 4.3 μs for ^{31}P . The width of the adiabatic-passage pulse was 27.8 μs . The relaxation delay was 15 s. ^{31}P -CT-DRENAR-BABA-xy16 (constant-time based dipolar recoupling effects nuclear alignment reduction based on BABA-xy16 pulse blocks)^[29] experiments were performed on a 2.5 mm MAS NMR probe. The spinning rate was set as 25 kHz. The 90° pulse lengths were 3.6 μs . The recycle delay was 60 s.

Table 1 Experimental conditions of single-pulse experiments

Single-pulse	Resonance	Spinning rate/kHz	Relaxation delay/s	Pulse length/ μs	Chemical shift standards
^{27}Al	130.3	12	1	1.0 (30°)	1 mol/L $\text{Al}(\text{NO}_3)_3$ ($\delta=0$)
^{31}P	202.4	12	60	4.3 (90°)	$\text{NH}_4\text{H}_2\text{PO}_4$ ($\delta=1.12$)
^{29}Si	99.3	8	60	6.0 (90°)	Tetrakis (trimethylsilyloxy) silane

3 Results and discussion

Fig. 1 shows the XRD patterns of $x\text{Bi}_2\text{O}_3-\text{AlPO}_4-\text{SiO}_2$ ($x=0.025, 0.100, 0.150$) glasses. At a low content of Bi_2O_3 ($x \leq 0.1$), a broad hump at $2\theta=20^\circ-30^\circ$ and the absence of sharp crystalline diffraction peaks confirm an amorphous character of the prepared samples. When $x=0.15$, a peak at 21° corresponding to AlPO_4 (JSPDS 11-0500) can occur, indicating the formation of AlPO_4 clusters.

Fig. 2 shows the ^{27}Al , ^{31}P and ^{29}Si MAS NMR spectra of $x\text{Bi}_2\text{O}_3-\text{AlPO}_4-\text{SiO}_2$ glasses. The spectra were analyzed by DMFIT using the Gaussian

lineshape (see Fig. 3). When Bi_2O_3 is not added, a relatively broad leftward oblique ^{27}Al spectrum can appear, which contains a signal at about 40 and two shoulder peaks at 20 and 0, which can be assigned to Al(IV), Al(V) and Al(VI) aluminum environments, respectively. A signal (~ -25) and a shoulder (~ -15) occur in the ^{31}P spectrum, which can be assigned to the $\text{P}^0_{4\text{Al}}$ and $\text{P}^0_{3\text{Al}}$ phosphate units (P^n_{mAl} represents the phosphorus oxygen tetrahedron, which contained n bridging oxygen atoms and connected with m aluminum atoms), respectively. A signal (~ -107) and a shoulder (~ -99) were observed on the ^{29}Si spectrum, which belong to the Q^4 and Q^3 structural units, respectively (Q^n represents the silicon oxygen

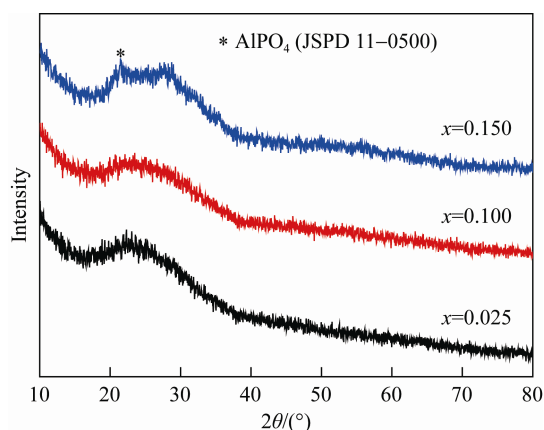


Fig. 1 X-ray diffraction patterns of $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ ($x=0.025, 0.100, 0.150$) glasses

tetrahedral unit with n bridging oxygen atoms). With increasing Bi_2O_3 contents, the content of Al(V) and Al(VI) units decreased gradually, but two signals (a broad one and a sharp one) attributed to Al(IV) units appeared. Accordingly, a new sharp signal at about -30 can be observed in ^{31}P spectra. The signal can be ascribed to $\text{P}_{4\text{Al}}^0$ phosphate units. The sharp Al(IV) signal indicates the formation of nanocrystals. This is consistent with the XRD results, as shown in Fig. 1. From the ^{29}Si spectra, the Q^3 content increases, and a new signal attributed to Q^2 units appears with increasing Bi_2O_3 contents.

Fig. 4 shows the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR and $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR decay curves for representative samples. The REDOR decay curves of Al(IV) units are similar for the glasses with different Bi_2O_3 contents. Al(IV) and P form four Al—O—P bonds, which are in close analogy to the network structure of SiO_2 ^[21]. As Bi_2O_3

content increases to 0.15, a relatively sharp Al(IV) appears, but the strength of the REDOR effect between this new Al(IV) (labeled as $\text{Al(IV)}^{\text{II}}$) and P does not change, indicating that $\text{Al(IV)}^{\text{II}}$ also forms four Al—O—P bonds with P. In Fig. 4(b), there is little change in $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR results as Bi_2O_3 content increases. Although an intense sharp signal at -30 appears in ^{31}P MAS spectra, the strength of the REDOR effect is the same as the $\text{P}_{4\text{Al}}^0$ signal at -25 , reflecting that the phosphorus atom corresponding to this new ^{31}P signal is also connected to four aluminum atoms to form $\text{P}_{4\text{Al}}^0$ units. Based on the results above, this new Al(IV) and new $\text{P}_{4\text{Al}}^0$ from AlPO_4 nanocrystals. A silica-like polymeric structure is formed based on alternating Al(OP)_4 and P(OAl)_4 tetrahedra^[14]. The relatively sharp ^{27}Al and ^{31}P resonance is dominated due to the presence of the nanocrystals. The broad Al(IV) and $\text{P}_{4\text{Al}}^0$ signals are also derived from the AlPO_4 amorphous domains^[21], so the NMR signals of ^{27}Al and ^{31}P are broad.

Fig. 5 shows the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR effect of Al(IV), Al(V), and Al(VI) of sample $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ ($x=0.05$). The $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR effect of Al(IV) is much stronger than that of Al(V) and Al(VI). It can be concluded that the second coordination spheres of Al(V) and Al(VI) are not all P^{5+} . If the second coordination spheres of Al(V), Al(VI) are all P^{5+} , that is, all Al(V) and Al(VI) coordinate with P to form five and six Al—O—P bonds, the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR effect of Al(V) and Al(VI) then should not be weaker than that of Al(IV). Whereas, herein their effect is obviously weaker than that of Al(IV). Therefore, the second coordination sphere of Al(V) and Al(VI) is not all P^{5+} , there are other cations. This is consistent with the results of ^{31}P MAS spectra, as shown in Fig. 3. In

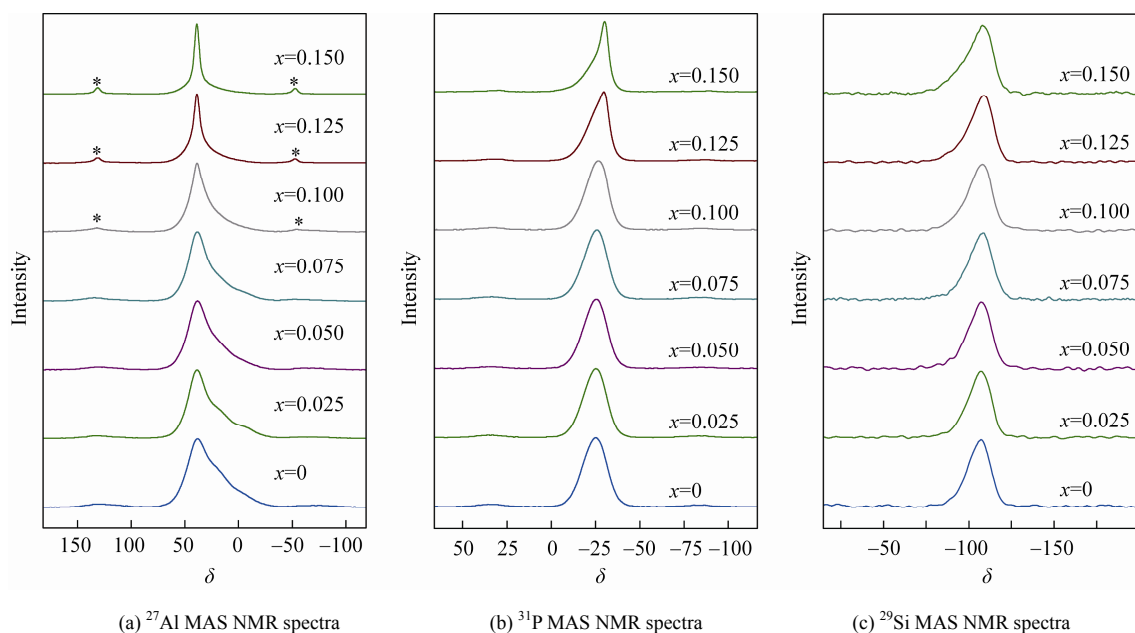


Fig. 2 High-resolution ^{27}Al , ^{31}P , and ^{29}Si MAS NMR spectra of $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses

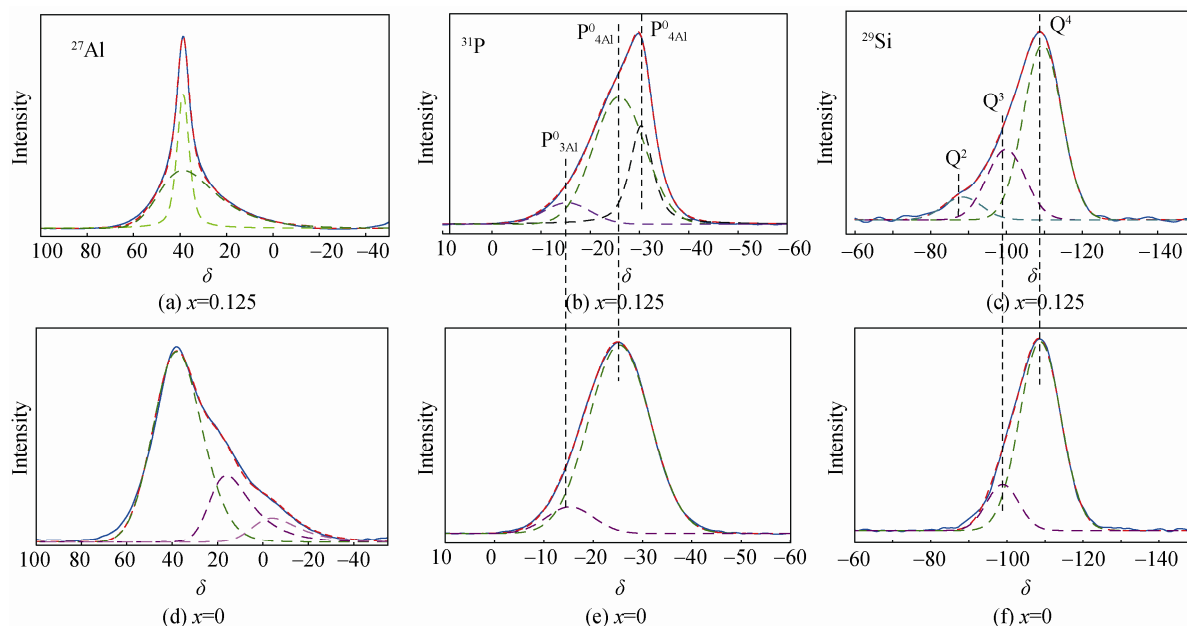


Fig. 3 Deconvolutions of ^{27}Al (left), ^{31}P (middle), and ^{29}Si (right) MAS NMR spectra of glasses with the compositions of $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$

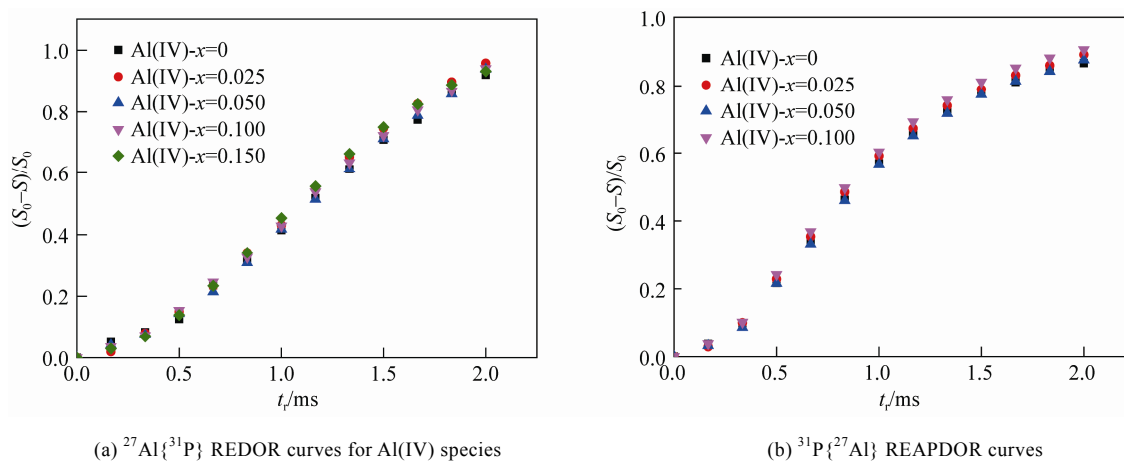


Fig. 4 $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR and $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR results of $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses

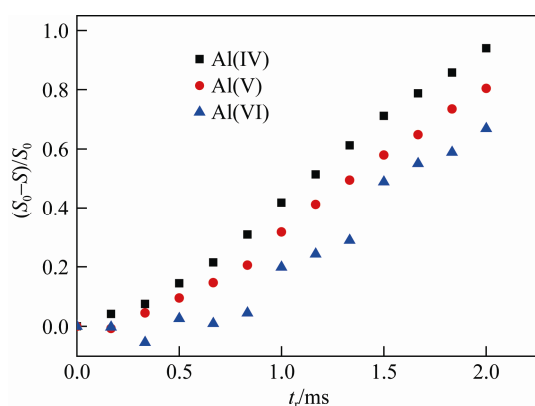


Fig. 5 $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR curves for Al(IV), Al(V), and Al(VI) species of sample $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ ($x=0.05$)

the ^{31}P MAS spectra, there is a small amount of $\text{P}^0_{3\text{Al}}$ in addition to $\text{P}^0_{4\text{Al}}$, indicating that phosphorus units

are not all connected to Al^{3+} , and there are also a small amount of other cations. This indicates the similar results with $\text{GaPO}_4\text{--SiO}_2$ glasses synthesized by a sol-gel method^[30]. In $\text{GaPO}_4\text{--SiO}_2$ glasses, Ga(V) and Ga(VI) both act as linkages connecting phosphorus oxygen tetrahedron with silicon oxygen tetrahedron, and play a role of connecting GaPO_4 and SiO_2 clusters. As GaPO_4 clusters increase, the ratio of Ga(V) and Ga(VI) decreases. In the $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses, we also observed that Al(V) and Al(VI) disappear eventually with the increase of Bi_2O_3 content. In order to determine the change in the size of AlPO_4 domains, ^{31}P CT-DRENAR experiments (see Fig. 6) were performed. The results of the ^{31}P CT-DRENAR show that the dipole interaction between $^{31}\text{P}\text{--}^{31}\text{P}$ is enhanced with the increasing Bi_2O_3 content, indicating that the size of AlPO_4 domains increases. In ^{29}Si MAS NMR spectra (see Fig. 3), when Bi_2O_3 is not added, there are

Q^3 units. The unit should be a silicon tetrahedron formed by a Si--O--H bond and three Si--O--Si bonds. It is a $\text{Q}^3_{1\text{H}}$ unit. When Bi_2O_3 content increases to more than 0.125, the signal of ^{29}Si obviously shifts to a higher chemical shift, the content of Q^3 increases, and new Q^2 units form. It may be due to that Bi^{3+} ions react with SiO_2 to form Bi--O--Si bonds. The Q^3 may contain both $\text{Q}^3_{1\text{H}}$ and $\text{Q}^3_{1\text{Bi}}$ units, and the newly formed Q^2 should be $\text{Q}^2_{2\text{Bi}}$ units.

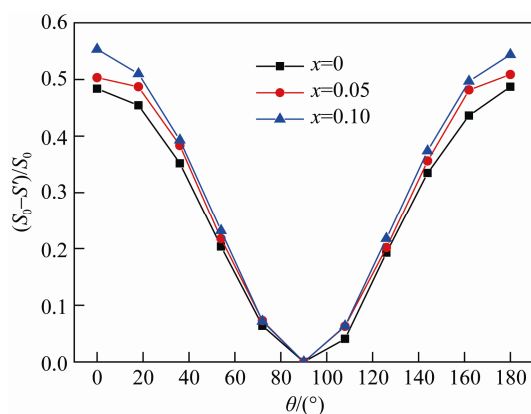


Fig. 6 ^{31}P -CT-DRENAR-BABA-xy16 decay curves of $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses

Fig. 7 shows the XPS results of Bi element in $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses. Clearly, the positions of Bi 4f peaks of $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses do not change obviously as Bi_2O_3 content increases. The 4f peaks of Bi are independent of the content of Bi_2O_3 . Compared with that of the $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses, the positions of Bi 4f peaks shift toward low binding energies in crystalline Bi_2O_3 , indicating the absence of Bi--O--Bi connectivity in all as-prepared glasses. It is difficult to determine whether P--O--Bi or Bi--O--Al bonds are formed from the ^{31}P and ^{27}Al

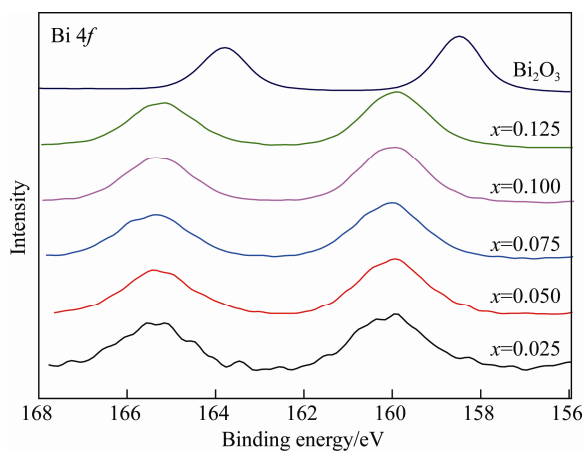


Fig. 7 X-ray photoelectron spectra of glasses in the system $x\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ and the crystalline Bi_2O_3 standard sample

MAS NMR spectra. However, if Bi^{3+} present only in the SiO_2 phase, take the sample ($x=0.125$) for example, there should exist 0.75 Bi--O--Si . However, from the line shape analysis and deconvolution results (see Fig. 3), there are apparently a few Bi--O--Si bonds. This indicates that some Bi^{3+} present in AlPO_4 phase. The amount of Bi^{3+} in AlPO_4 phase is too low to be clearly observed from the ^{27}Al and ^{31}P MAS NMR spectra.

The presence of P--O--Bi bonds is unclearly demonstrated. Although no Al(V) and Al(VI) appear in the sample ($x=0.125$), $\text{P}^0_{3\text{Al}}$ is still seen on the ^{31}P spectra. There is no clear evidence to confirm the remaining non-bridged oxygen in this unit is connected to Bi^{3+} or H^+ . Some ^1H -related solid-state NMR experiments can be carried out to confirm these inferences in a future work.

4 Conclusions

$\text{Bi}_2\text{O}_3\text{--AlPO}_4\text{--SiO}_2$ glasses were prepared by a sol-gel route. Based on the results by the solid-state NMR and XPS, the structure of these glasses was composed of SiO_2 and AlPO_4 nano-domains. The increase of Bi_2O_3 content led to the increase of AlPO_4 domains and finally the crystallization of AlPO_4 . Bi_2O_3 was distributed in the both domains, but there was no effective technique to determine the quantitative distribution in the two clusters. A further work on the determination of the linkage of H^+ , Bi^{3+} and phosphorous tetrahedron was suggested to provide insights into the structural framework organization of bismuth-aluminophosphosilicate glasses.

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