

碱铝磷酸盐玻璃的近程结构及化学稳定性

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摘 要: 为了揭示碱金属、玻璃结构及化学稳定性之间的内在联系, 以及对未来核废料基质玻璃的发展及化学稳定性的评估, 本工作通过熔融淬冷法制备了一系列不同碱金属组成的铝磷酸盐玻璃, 其组成为 $[x\text{Na}_2\text{O}-y\text{K}_2\text{O}-(41.6-x-y)\text{Cs}_2\text{O}]-16.7\text{Al}_2\text{O}_3-41.7\text{P}_2\text{O}_5$ 。采用产品一致性测试 B 方法研究了这些玻璃的化学稳定性, 并使用先进的固体核磁共振技术对玻璃的原子尺度结构进行了精确解析。结果表明, 碱金属种类的改变不仅通过调节对非桥氧的电场吸引力影响了玻璃网络的致密性, 而且明显改变了玻璃的网络结构。在这些玻璃中, 不同配位数的铝都只被磷氧四面体(PO_4)所包围。随着碱金属离子场强的增大, 高配位铝的含量增加, 导致铝与磷氧四面体的化学键连接增多。这种结构变化进一步增强了玻璃网络的致密性, 最终提高了其化学稳定性。

关键词: 碱金属; 铝磷酸盐玻璃; 结构; 化学稳定性; 固体核磁共振

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磷酸盐基质玻璃是一种非常重要的材料, 它在生物医药、激光增益介质、密封以及核废料固化等领域具有广泛应用^[1-9]。纯磷酸盐玻璃的化学稳定性非常差, 这严重影响了它的工业应用^[10], 但是, 在掺入某些金属氧化物(如 Fe_2O_3 和 Al_2O_3)后, 玻璃的化学稳定性会显著提升, 这主要得益于加入的金属元素提高了玻璃网络的聚合度并且形成了更稳定的 $\text{M}-\text{O}-\text{P}$ 键(M 为金属元素)^[11-13]。事实上, 碱金属也会显著影响玻璃的化学稳定性。Minami 等^[14]对含不同碱金属的磷酸盐玻璃的腐蚀研究表明, 玻璃的化学稳定性按照 Li, Na, K, Rb, Cs 的顺序降低。Bunker 等^[15]对不同碱钙磷酸盐玻璃的研究表明, 含 Li 玻璃的化学稳定性要比含 Na 玻璃的更强。Peng 等^[16]也研究了 Na_2O 和 K_2O 在磷酸盐玻璃中的作用, 他们认为高场强离子可以增加其与非桥氧之间的结合强度, 从而提高玻璃的化学稳定性。基于这些研究结果, 场强论的观点常被用来解释碱金属对玻璃化学稳定性的影响。然而, Binhgham 等^[17]对碱铁磷酸盐玻璃的研究表明, 玻璃的化学稳定性按照

Li, Na, K 的顺序增加。Fang 等^[18]和 Yang 等^[19]在对碱铁磷酸盐玻璃的腐蚀研究中也观察到低场强碱离子取代高场强碱离子会提高玻璃的化学稳定性。显然, 这些研究结果无法通过上述的场强论来解释, 但他们也没有给出合理的解释。碱金属对磷酸盐玻璃化学稳定性的影响还需要进一步研究。

在先前的工作中, 本课题组已对摩尔组分为 $41.6\text{K}_2\text{O}-16.7\text{Al}_2\text{O}_3-41.7\text{P}_2\text{O}_5$ 的玻璃腐蚀机理进行了详细研究, 发现腐蚀玻璃表面的结晶相是溶解的大分子基团在溶液中饱和和沉积的产物^[20]。玻璃的组分会对玻璃的溶解行为及化学稳定性产生显著的影响。然而, 作为玻璃组分不可或缺的一部分, 碱金属对于玻璃结构及化学稳定性的影响还缺乏更深入的研究。

本工作设计了一系列含不同碱金属的铝磷酸盐玻璃, 其组分为 $[x\text{Na}_2\text{O}-y\text{K}_2\text{O}-(41.6-x-y)\text{Cs}_2\text{O}]-16.7\text{Al}_2\text{O}_3-41.7\text{P}_2\text{O}_5$ (x, y 为摩尔分数), 通过先进的固体核磁共振(SSNMR)技术在原子尺度上解析了玻璃的内部结构, 深入研究了碱金属对磷酸盐玻璃内

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部结构及化学稳定性的影响。

1 实验

1.1 样品制备

通过传统的熔融冷却方法制备了 $[x\text{Na}_2\text{O}-y\text{K}_2\text{O}-(41.6-x-y)\text{Cs}_2\text{O}]-16.7\text{Al}_2\text{O}_3-41.7\text{P}_2\text{O}_5$ 的4个玻璃,详细的玻璃组成见表1, x 和 y 对应表1中相应氧化物括号中的理论值。为描述方便,将含有碱金属Na、K、Na/Cs和K/Cs的初始铝磷酸盐玻璃分别标记为玻璃样品NAP、玻璃样品KAP、玻璃样品NCAP和玻璃样品KCAP。使用相同的方法也制备了仅含Cs的铝磷酸盐玻璃,但是由于它在空气中就表现出很强的吸水性,无法获得其精确的内部结构。玻璃制备所需要的原料包括 $\text{Al}(\text{OH})_3$ 、 $\text{Al}(\text{PO}_3)_3$ 、 NaPO_3 、 KPO_3 、 Cs_2CO_3 和 $\text{NH}_4\text{H}_2\text{PO}_4$,这些原料均购自阿拉丁试剂有限公司,除原料 NaPO_3 的纯度是高于95%外,其余原料的纯度均高于99%。根据玻璃组分称取总量为20.0 g的原料,并在玛瑙研钵中充分研磨使其混合均匀。将装有混合原料的铂金坩埚置于1250~1300℃的高温炉中保温30 min,随后将熔体倒在平整的钢板上快速压制以获得大块玻璃。玻璃中的Na、K、P和Al元素都通过电感耦合等离子体原子发射光谱法(ICP-AES)进行了定量分析(表1)。需要说明的是,ICP-AES无法分析Cs元素,表格中 Cs_2O 的实际含量是基于其他氧化物的测量值所推断出来的。

表1 初始玻璃的ICP-AES结果(括号中的数值为理论含量)
Table 1 ICP-AES results of the pristine glasses (The values in parentheses denote the theoretical content)

Glass	Al_2O_3	P_2O_5	Na_2O	K_2O	Cs_2O
NAP	15.9 ^a (16.7) ^b	42.4 (41.7)	41.7 (41.6)		
KAP	16.2 (16.7)	41.1 (41.7)		42.7 (41.6)	
NCAP	16.6 (16.7)	40.8 (41.7)	22.0 (20.8)		20.6 (20.8)
KCAP	17.2 (16.7)	41.6 (41.7)		21.0 (20.8)	20.2 (20.8)

^a and ^b represent the measured and nominal value, respectively, with an error margin of $\pm 2\%$; The content of Cs_2O is deduced from the measured values of other oxides.

1.2 腐蚀实验

不同碱铝磷酸盐玻璃的化学稳定性通过产品一致性测试B方法(PCT-B)来评估^[21]。根据该方法的要求,对玻璃样品进行研磨,并使用100目(孔径为150 μm)和200目(孔径为75 μm)的筛网筛选介于两者之间的玻璃粉末(粒径在75~150 μm),使用去离子

水和酒精清洗这些玻璃粉末并干燥。取1.0 g干燥的玻璃粉末和10.0 mL中性去离子水混合后置于密闭的聚四氟乙烯容器中,在90℃恒温环境中静置7 d。所有样品的腐蚀实验一式2份且均设置有空白对照组。腐蚀实验完成后,对过滤后的渗滤液进行ICP-AES分析以获得渗滤液中各浸出元素的浓度(Cs元素除外)。玻璃内部各元素的归一化质量损失可通过式(1)获得^[21]。玻璃样品NAP、玻璃样品KAP、玻璃样品NCAP和玻璃样品KCAP的密度分别为2.6、2.5、3.1 g/cm³和3.1 g/cm³。玻璃粉末的粒径 d 和最终浸出液的体积 V 分别设置为0.011 25 cm和0.01 L。玻璃样品KCAP腐蚀后全部形成了凝胶状产物,未得到可供检测的渗滤液。

$$\Delta m_i = \frac{c_i(\text{sample}) - c_i(\text{blank})}{f_i \cdot (A/V)} = \frac{[c_i(\text{sample}) - c_i(\text{blank})] \cdot V \cdot \rho \cdot d}{f_i \cdot 6 \cdot m} \quad (1)$$

式中, Δm_i 为玻璃中元素 i 的归一化质量损失,g/m²; $c_i(\text{sample})$ 和 $c_i(\text{blank})$ 分别为元素 i 在玻璃腐蚀后的渗滤液和空白对照组渗滤液中的浓度,g/L; A 为玻璃粉末的总表面积,cm²; V 为最终浸出液的体积,L; ρ 为玻璃的密度,g/cm³; d 为玻璃粉末的粒径,cm; f_i 为元素 i 在玻璃中的质量分数; m 为玻璃粉末的总质量,g。

1.3 样品表征

所有的SSNMR实验均是在德国布鲁克公司生产的配备有11.7 T磁场的Bruker Avance III HD 500 M谱仪上进行的。实验包括³¹P魔角旋转(MAS)、²⁷Al MAS、²⁷Al{³¹P}旋转回波双共振(REDDOR)、³¹P{²⁷Al}绝热通道双共振(REAPDOR)和³¹P重聚焦双量子技术(refocused INDEQUATE),这些实验都是在1个4 mm探头上完成的,转子的转速为12 kHz; ³¹P和²⁷Al的共振频率分别为202.5 MHz和130.3 MHz; ³¹P和²⁷Al的化学位移参照物分别为85%的 H_3PO_4 和1 mol/L的 $\text{Al}(\text{NO}_3)_3$ 溶液;使用 $\text{NH}_4\text{H}_2\text{PO}_4$ 作为³¹P的二级定标物,化学位移定标 1.1×10^{-6} ;化学位移为样品共振频率与标准物频率的差值除以标准物的频率。所有实验脉冲的初始部分均添加有饱和梳状脉冲以获得稳定的信号采集,具体的实验方法和参数设置如下: ³¹P MAS实验的脉冲长度和弛豫时间分别为2.5 μs(90°固体翻转角)和160.0 s。 ²⁷Al MAS实验的脉冲长度和弛豫时间分别为0.7 μs(10°液体翻转角)和1.0 s。实验完成后获得的³¹P MAS谱和²⁷Al MAS谱都通过DMFIT软件进行了

拟合, 所使用的模型分别为 Gaussian 和 Czjzek 模型^[22-23]。

$^{27}\text{Al}\{^{31}\text{P}\}$ REDOR 实验采用由 Gullion 和 Schaefer 发明而后由 Chan 和 Eckert 改进的脉冲序列^[24-25]。 ^{27}Al 和 ^{31}P 的 180° 脉冲长度均设置为 $9.0\ \mu\text{s}$ 。弛豫时间为 $0.5\ \text{s}$ 。偶极二阶矩 $M_2^{\text{Al-P}}$ 可通过短初始演化时间内 ($0 \leq \Delta S / S_0 \leq 0.3$) 的 REDOR 曲线获得, 拟合公式如下所示:

$$\frac{\Delta S}{S_0} = \frac{4}{3\pi^2} (NT_r)^2 M_2^{\text{Al-P}} \quad (2)$$

式中: $\Delta S = S_0 - S$, 表示相对信号衰减。 S_0 和 S 分别为不加载和加载 ^{27}Al - ^{31}P 偶极相互作用时 ^{27}Al 的信号强度; N 和 T_r 分别为转子旋转的圈数和转子旋转一周的时间。

$^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR 实验采用由 Garbow 和 Gullion 发明的脉冲序列^[26], 加载到 ^{31}P 通道的 180° 脉冲长度为 $9.0\ \mu\text{s}$, 加载到 ^{27}Al 通道上的再耦合脉冲长度为 $27.8\ \mu\text{s}$ (转子的三分之一转速周期), 对应相同能量下的液体章动频率为 $23.3\ \text{kHz}$, 弛豫时间设置为 $40.0\ \text{s}$ 。

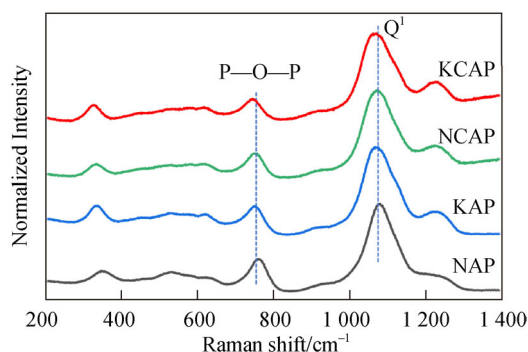
^{31}P 1D refocused INADEQUATE 实验通过 1 个 $\pi/2 - \tau - \pi - \tau - \pi/2$ 脉冲序列激发 ^{31}P - ^{31}P 双量子相干^[27-28], τ 表示 2 个脉冲之间的时间间隔。此实验可检测到含有 P—O—P 的 Q^n (Q 表示磷氧四面体, n 表示每个 P 基团(磷氧四面体)中 P—O—P 键的数量, $n \neq 0$) 信号, 而有效压制不含 P—O—P 的 Q^0 信号。加载到 ^{31}P 核上的 90° 脉冲长度为 $2.5\ \mu\text{s}$ 。弛豫时间设置为 $40.0\ \text{s}$ 。玻璃 NAP 和 KCAP 优化后的 τ 值为 $7.5\ \text{ms}$ 。

Raman 光谱是在英国雷尼绍公司生产的 Renishaw inVia 光谱仪上获得的, 所使用的激光波长为 $488\ \text{nm}$ 。

2 表征结果

2.1 Raman 光谱

图 1 所示为各初始玻璃的 Raman 光谱, 这些玻璃的 Raman 谱峰形状相似, 位置相近, 均在约 $750\ \text{cm}^{-1}$ 和 $1080\ \text{cm}^{-1}$ 处存在 2 个不同的谱峰。前者来自于短链 P—O—P 的对称伸缩振动, 后者与 Q^1 基团中末端氧的对称 PO_3 基团的伸缩振动相关, 都对应玻璃中的 Q^1 基团^[29-30]。此外, 这些玻璃在约 $1150\ \text{cm}^{-1}$ 处还存在 1 个微不可察的弱峰, 这与 Q^2 基团中的对称 PO_2 基团的伸缩振动相关^[29], 但其含量极少, 可忽略不计。



Note: KCAP is the glass that contains only the alkali metals K and Cs; NCAP is the glass that contains only the alkali metals Na and Cs; KAP is the glass that contains only the alkali metal K; NAP is the glass that contains only the alkali metal Na.

图 1 初始玻璃的 Raman 光谱

Fig. 1 Raman spectra of the pristine glasses

2.2 ^{31}P MAS NMR 谱

图 2 为各初始玻璃的 ^{31}P MAS 谱。所有玻璃的 ^{31}P 谱均坐落在 $10.0 \times 10^{-6} \sim -30.0 \times 10^{-6}$ 范围内, 主要对应玻璃中的 Q^1 基团。此外, 这些玻璃的 ^{31}P MAS 谱均为非对称的宽包络谱, 说明其内部包含有多种不同的 Q^1 基团。为解析这些 ^{31}P MAS 谱, 对代表性玻璃 NAP 和 KCAP 进行了 ^{31}P 1D refocused INADEQUATE 实验, 并与它们的 ^{31}P MAS 谱进行了对比, 结果如图 3a~图 3d 所示。玻璃样品 NAP 的 ^{31}P MAS 谱中的 ^{31}P 信号均可通过 INADEQUATE 实验检测到, 并可由 4 个 ^{31}P 信号去卷积拟合, 基于其化学位移(表 2), 这 4 个 ^{31}P 信号可分别归属于 $Q_{0\text{Al}}^1$ 、 $Q_{1\text{Al}}^1$ 、 $Q_{2\text{Al}}^1$ 和 $Q_{3\text{Al}}^1$ 基团。此处 $Q_{m\text{Al}}^1$ 中的 m 表示 P—O—Al 键的数量。玻璃样品 KCAP 的 INADEQUATE 谱仅可由位于约 -9.5×10^{-6} 和 -15.8×10^{-6} 处的 2 个 ^{31}P 信号去卷积拟合, 分别对应 $Q_{1\text{Al}}^1$ 和 $Q_{2\text{Al}}^1$ 基团。玻璃样品 KCAP 中位于约 -1.7×10^{-6} 处的 ^{31}P 信号在 INADEQUATE 谱中消失, 基于其化学位移, 可将其归属于 $Q_{2\text{Al}}^0$ 基团。

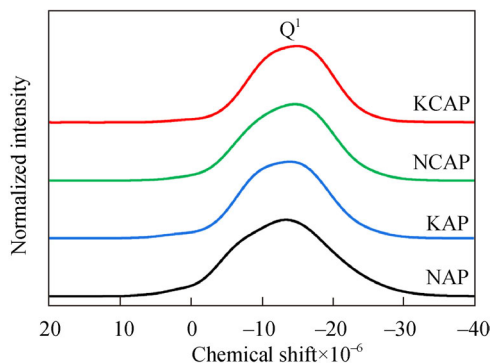


图 2 初始玻璃的 ^{31}P 魔角旋转(MAS)谱

Fig. 2 ^{31}P magic angle spinning (MAS) spectrum of the pristine glasses

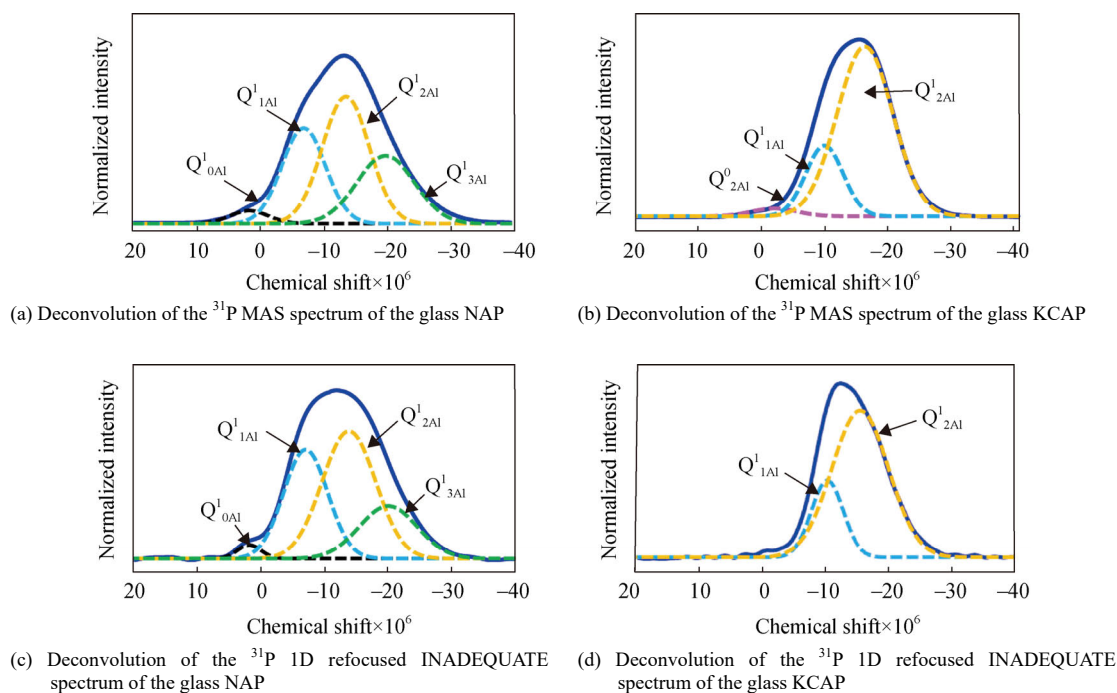


图3 玻璃样品 NAP 和玻璃样品 KCAP 的 ^{31}P MAS 和 ^{31}P 1D refocused INADEQUATE 谱的去卷积
Fig. 3 Deconvolutions of the ^{31}P MAS and the ^{31}P 1D refocused INADEQUATE spectra of the glasses NAP and KCAP

表2 初始玻璃的 ^{31}P MAS 去卷积谱的详细参数
Table 2 Deconvolution parameters of the ^{31}P MAS spectra of the pristine glasses

Glass	P unit	$\delta/10^{-6}$	FWHM/ 10^{-6}	Area/%
NAP	$\text{Q}^1_{0\text{Al}}$	1.6	7.2	2.9
	$\text{Q}^1_{1\text{Al}}$	-7.0	8.2	29.9
	$\text{Q}^1_{2\text{Al}}$	-13.7	8.8	40.9
	$\text{Q}^1_{3\text{Al}}$	-20.0	10.8	26.3
KAP	$\text{Q}^0_{2\text{Al}}$	-1.0	9.3	3.4
	$\text{Q}^1_{1\text{Al}}$	-8.3	6.8	22.4
	$\text{Q}^1_{2\text{Al}}$	-14.7	10.2	67.6
	$\text{Q}^1_{3\text{Al}}$	-21.9	9.4	6.6
NCAP	$\text{Q}^1_{0\text{Al}}$	-0.8	7.1	2.3
	$\text{Q}^1_{1\text{Al}}$	-8.2	7.5	23.6
	$\text{Q}^1_{2\text{Al}}$	-15.3	10.5	68.5
	$\text{Q}^1_{3\text{Al}}$	-22.3	10.9	5.6
KCAP	$\text{Q}^0_{2\text{Al}}$	-1.7	8.5	1.8
	$\text{Q}^1_{1\text{Al}}$	-9.5	6.9	23.1
	$\text{Q}^1_{2\text{Al}}$	-15.8	10.3	75.1

Note: δ denotes the chemical shift with an error margin of $\pm 0.3 \times 10^{-6}$; FWHM refers to the half-peak width with an error margin of $\pm 0.3 \times 10^{-6}$, and the Area indicates the proportion of P unit with an error margin of $\pm 5\%$.

为验证上述归属,对玻璃样品 NAP 和玻璃样品 KCAP 进行了 $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR 实验和 SIMPSON 模拟^[31],结果如图 4 所示。玻璃样品 NAP 和玻璃样品 KCAP 中 $\text{Q}^1_{1\text{Al}}$ 和 $\text{Q}^1_{2\text{Al}}$ 信号的 $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR 曲线分别与 P-1Al 和 P-2Al 曲线相吻合,

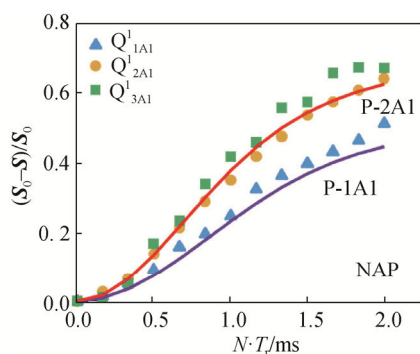
玻璃 NAP 中 $\text{Q}^1_{3\text{Al}}$ 信号的 $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR 曲线高于 P-2Al 曲线。此处的 P-1Al 和 P-2Al 分别表示 P 基团键连 1 个和 2 个 Al 原子。这些结果说明上述对玻璃 NAP 和 KCAP 中 P 基团的归属是正确的。需要说明的是,玻璃 NAP 中 $\text{Q}^1_{3\text{Al}}$ 信号和 $\text{Q}^1_{2\text{Al}}$ 信号的 $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR 衰减曲线相差较小是由于与 $\text{Q}^1_{3\text{Al}}$ 化学位移重叠的少量 $\text{Q}^2_{0\text{Al}}$ 信号的存在,其导致 $\text{Q}^1_{3\text{Al}}$ 信号的 $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR 衰减减弱,与上述的 Raman 谱结果一致。基于这些分析结果,对各初始玻璃的 ^{31}P MAS 谱进行了去卷积拟合,结果如图 5 所示,详细的拟合参数总结在表 2 中。基于这些玻璃的 ^{31}P MAS 去卷积谱,获得了单位摩尔玻璃中 Al—O—P 键的含量,并将结果总结在表 3 中。随着碱金属离子场强的增加,玻璃内部 Q^1 基团和 Al 的连接也在增加。

2.3 ^{27}Al MAS NMR 谱

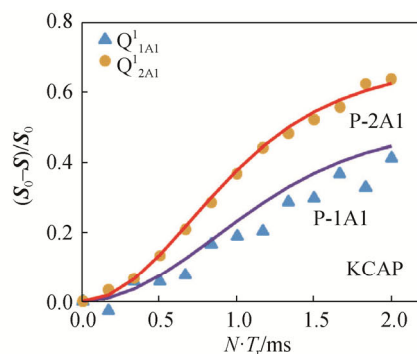
图 6 所示为各初始玻璃的 ^{27}Al MAS 谱。所有玻璃均在约 50.0×10^{-6} 、 18.5×10^{-6} 和 -10.0×10^{-6} 处存在 3 个不同的 ^{27}Al 信号,分别对应 4、5 和 6 配位 Al 基团,标记为 Al(4)、Al(5)和 Al(6)。各初始玻璃 ^{27}Al MAS 谱的去卷积结果展示在图 7 中,详细的拟合参数总结在表 3 中。不同碱铝磷酸盐玻璃中 3 种 Al 基团的占比存在明显差别,玻璃样品 NAP 中 Al(6)基团的占比最高,而玻璃样品 KAP、玻璃样品 NCAP 和玻璃样品 KCAP 则主要以 Al(4)基团为主。为探

究这些玻璃中不同 Al 基团周围的 P 原子分布, 对它们进行了 $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR 实验, 相对应的各 Al 基团的 $M_2^{\text{Al-P}}$ 值总结在表 4 中。图 8a 和图 8b 展示了代表性玻璃样品 NAP 和玻璃样品 KCAP 的 $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR 结果。玻璃样品 NAP、玻璃样品 KAP 和玻璃样品 NCAP 中各 Al 基团的 $M_2^{\text{Al-P}}$ 值与标准晶体样品相近, 说明这些玻璃中不同 Al 基团的第一配体均为磷氧四面体。玻璃样品 KCAP 中各 Al 基团的 $M_2^{\text{Al-P}}$ 值较标准晶体样品较小, 这是由于玻璃内部

半径较大的 K 和 Cs 原子的共同存在导致 Al 和 P 原子之间的距离变大, 事实上, 玻璃样品 KCAP 中所有 Al 基团第一配体也均为磷氧四面体。基于 ^{27}Al MAS 谱分析结果, 获得了单位摩尔玻璃中 Al—O—P 键的含量, 并将结果总结在表 3 中。该结果与基于 ^{31}P MAS 谱获得的 Al—O—P 键含量相近, 进一步说明这些玻璃内部所有 Al 基团的第一配体均为磷氧四面体。值得注意的是, 单位摩尔的样品 NCAP 和样品 KCAP 中 Al—O—P 键的数量相当。



(a) $^{31}\text{P}\{^{27}\text{Al}\}$ REDPDOR curves of different P units within the glass NAP

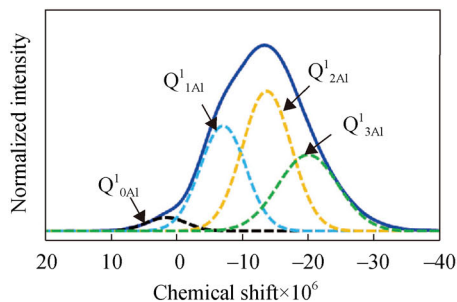


(b) $^{31}\text{P}\{^{27}\text{Al}\}$ REDPDOR curves of different P units within the glass KCAP

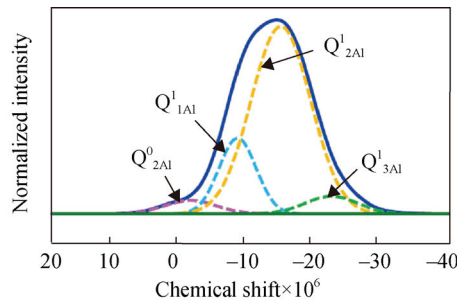
Note: S_0 and S denote the amplitude without and with the ^{31}P - ^{27}Al dipolar interaction, respectively; The vertical axis represents the normalized $^{31}\text{P}\{^{27}\text{Al}\}$ dephasing intensity, and the horizontal axis denotes the evolution time; N represents the number of rotations of the rotor, while T_i denotes the rotation period; In the simulation, a P-Al distance of 3.1 Å and a ^{27}Al C_Q value of 4.0 MHz were used; The terms "P-1Al" and "P-2Al" represent the P units with one and two Al atoms bonded to them, respectively; In the P-2Al simulation, a Al-P-Al angle of 109° was used.

图 4 初始玻璃的 $^{31}\text{P}\{^{27}\text{Al}\}$ REDPDOR 曲线和 SIMPSON 模拟结果

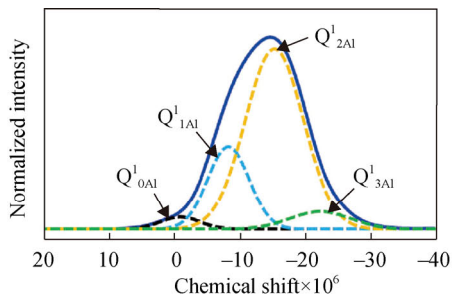
Fig. 4 $^{31}\text{P}\{^{27}\text{Al}\}$ REDPDOR curves of the pristine glasses along with the SIMPSON simulations



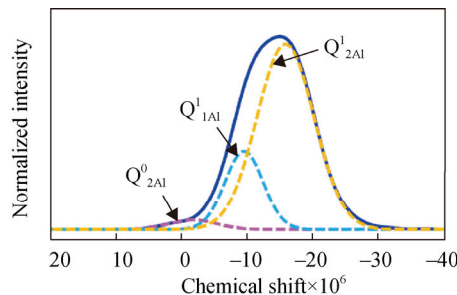
(a) Deconvolution of the ^{31}P MAS spectrum of the glass NAP



(b) Deconvolution of the ^{31}P MAS spectrum of the glass KAP



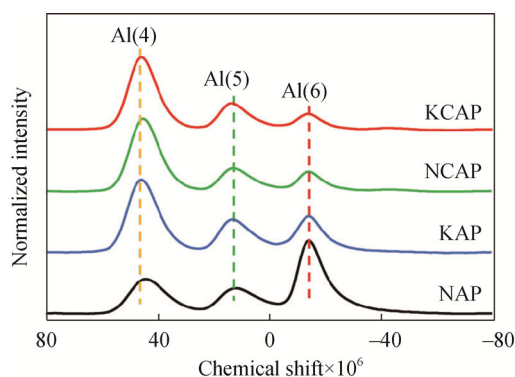
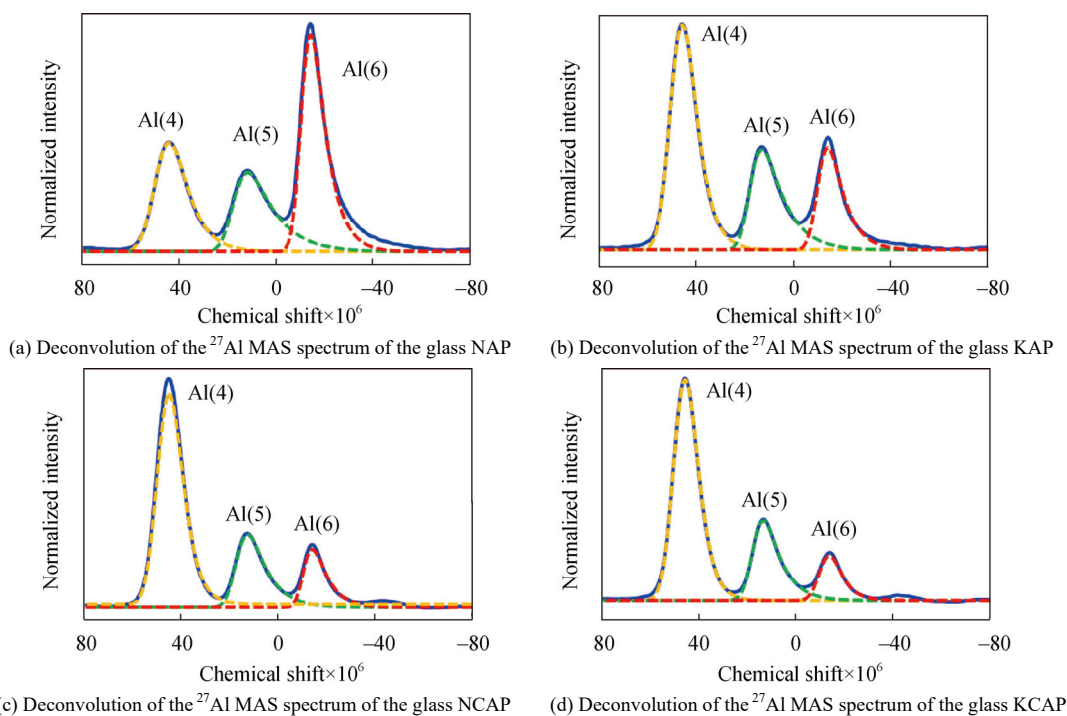
(c) Deconvolution of the ^{31}P MAS spectrum of the glass NCAP



(d) Deconvolution of the ^{31}P MAS spectrum of the glass KCAP

图 5 初始玻璃的 ^{31}P MAS 谱去卷积

Fig. 5 Deconvolution of the ^{31}P MAS spectra of the pristine glasses

图6 各初始玻璃的 ^{27}Al MAS 谱Fig. 6 ^{27}Al MAS spectra of different pristine glasses图7 初始玻璃的 ^{27}Al MAS 谱去卷积Fig. 7 Deconvolution of the ^{27}Al MAS spectra of the pristine glasses表3 初始玻璃的 ^{27}Al MAS 去卷积谱的详细参数以及单位摩尔玻璃中 Al—O—P 键的含量Table 3 Deconvolution parameters of the ^{27}Al MAS spectra of the pristine glasses, along with the content of Al—O—P bonds per mol of glass

Glass	Al species	$\delta/10^{-6}$	C_Q/MHz	Area/%	$n(\text{Al—O—P})/\text{mol}$
NAP	Al(4)	49.9	4.4	30.2	1.72 ^a (1.59 ^b)
	Al(5)	18.5	5.4	25.7	
	Al(6)	-10.0	4.1	44.1	
KAP	Al(4)	50.3	3.8	50.9	1.57 ^a (1.54 ^b)
	Al(5)	18.6	4.9	27.1	
	Al(6)	-9.6	4.2	22.0	
NCAP	Al(4)	49.2	3.6	62.9	1.51 ^a (1.48 ^b)
	Al(5)	17.9	4.5	22.9	
	Al(6)	-10.1	4.0	14.2	
KCAP	Al(4)	50.0	3.4	62.8	1.50 ^a (1.47 ^b)
	Al(5)	18.1	4.3	25.3	
	Al(6)	-10.0	3.6	11.9	

^a The content of Al—O—P bonds per mol of glass is determined from the ^{27}Al MAS spectra; $\text{Al—O—P} = [\text{Area}(\text{Al}(4)) \times 4 + \text{Area}(\text{Al}(5)) \times 5 + \text{Area}(\text{Al}(6)) \times 6] \times 0.167 \times 2$; ^b The content of Al—O—P bonds per mol of glass is determined from the ^{31}P MAS spectra. $\text{Al—O—P} = [\text{Area}(\text{Q}^0_{2\text{Al}}) \times 2 + \text{Area}(\text{Q}^1_{1\text{Al}}) + \text{Area}(\text{Q}^1_{2\text{Al}}) \times 2 + \text{Area}(\text{Q}^1_{3\text{Al}}) \times 3] \times 0.417 \times 2$; n is in mole; C_Q denotes the quadrupolar coupling constant with an error margin of ± 0.3 ; δ has an error margin of ± 0.3 , and Area has an error margin of $\pm 5\%$.

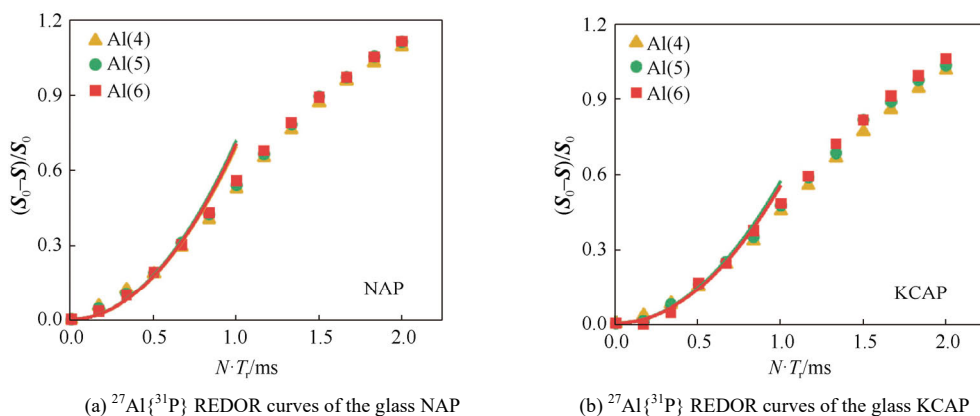


图 8 初始玻璃的 $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR 曲线
Fig. 8 $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR curves of the pristine glasses

表 4 不同样品中不同 Al 基团的二阶偶极矩值 $M_2^{\text{Al-P}}$
Table 4 Dipolar second moment $M_2^{\text{Al-P}}$ values of the different Al species within different samples

Samples	$M_2^{\text{Al-P}} / (\text{rad}^2 \cdot \text{s}^{-2})$		
	Al(4)	Al(5)	Al(6)
AlPO_4	5.0×10^{-6}		
$\text{Al}(\text{PO}_3)_3$			4.5×10^{-6}
NAP	5.1×10^{-6}	5.3×10^{-6}	5.2×10^{-6}
KAP	4.9×10^{-6}	5.0×10^{-6}	5.1×10^{-6}
NCAP	4.7×10^{-6}	4.9×10^{-6}	4.8×10^{-6}
KCAP	4.1×10^{-6}	4.2×10^{-6}	4.1×10^{-6}

2.4 玻璃的化学稳定性

玻璃的腐蚀实验完成后, 根据各渗滤液中浸出元素的浓度, 获得了玻璃样品 NAP、玻璃样品 KAP 和玻璃样品 NCAP 内部各元素的归一化质量损失 (表 5)。玻璃 KCAP 浸泡后的腐蚀产物为凝胶状, 不存在可供检测的渗滤液, 玻璃样品被完全腐蚀。玻璃样品 NAP 在浸泡过程中各元素的归一化质量损失都很小, 玻璃的内部元素几乎没有浸出, 表现出很好的化学稳定性。相比之下, 玻璃样品 KAP 和玻璃样品 NCAP 内部碱金属和 P 都表现出显著的

表 5 初始玻璃浸泡后各元素的归一化质量损失详细数据
Table 5 Detailed data of normalized mass loss of each element in the pristine glasses

Glass	Δm_{Al}^a	Δm_{P}^a	Δm_{Na}^a	Δm_{K}^a
NAP	0.2	0.7	1.0	
KAP	0 ^b	15.2		19.2
NCAP	0.2	21.1	26.6	

^a The error is expressed using the standard deviation of the data; The values within parentheses represent the maximum error for each corresponding vertical axis data in the table; Both of Δm_{Al} and Δm_{K} have an error margin of ± 0.3 , while both of Δm_{P} and Δm_{Na} have an error margin of ± 0.4 ; ^b the actual value is approximately 0.02 g/m²

浸出, 化学稳定性相对较差。此外, 由同等碱含量的 Cs 组成的铝磷酸盐玻璃在空气中就表现出较强的吸水性, 化学稳定性非常差。结合这些玻璃在浸泡过程中 P 的归一化质量损失, 不同碱金属组成的铝磷酸盐玻璃的化学稳定性由强到弱的顺序为 Na, K, Na/Cs, K/Cs, Cs。显然, 随着碱金属离子场强的增加, 玻璃的化学稳定性也增强。

3 结果与讨论

基于上述不同碱金属组成的铝磷酸盐玻璃化学稳定性的分析结果, 化学稳定性按照 Na, K, Na/Cs, K/Cs 的顺序减弱。玻璃的化学稳定性与其内部结构密切相关。根据上述不同碱铝磷酸盐玻璃的 ^{31}P MAS 谱解析结果, 这些 O/P 为 3.6 的不同玻璃的内部 P 基团主要是 Q^1 结构, 与过往的研究结果一致^[32-34]。这意味着不同碱铝磷酸盐玻璃中 P—O—P 键在所有化学键中的占比是相同的, 碱金属的变化对玻璃内部的 P—O—P 键影响不大。但是, 根据这些玻璃的 ^{27}Al MAS 谱的解析结果, 碱金属的变化会对玻璃内部的 Al 基团产生显著影响。随着碱金属离子场强的增大, 玻璃中高配位 Al 的占比增多。在这些玻璃中, 不同配位数的铝都只被磷氧四面体 (PO_4) 所包围, 即所有配位的 Al 都只存在 Al—O—P 键。更多的 Al—O—P 键连接会导致更致密的玻璃网络, 这种致密的玻璃网络会阻碍玻璃内部元素的溶解浸出以及溶液中 H 物种向玻璃内部的扩散, 从而提高玻璃的化学稳定性。玻璃网络的致密性可由玻璃摩尔体积的倒数 ($1/V_{\text{mol}}$) 来表征。 $1/V_{\text{mol}}$ 值越大, 说明单位体积中所包含的原子数越多, 玻璃网络的致密性越高。表 6 中总结了不同碱铝磷酸盐玻璃的 $1/V_{\text{mol}}$ 值以及玻璃内部 Al—O—P 键的占比 (F)。不同碱金属组成的铝磷酸盐玻璃的 $1/V_{\text{mol}}$ 值和 F 值均

按照 Na, K, Na/Cs, K/Cs 的顺序减小, 与化学稳定性的减弱顺序一致。这些数据充分证实了碱金属离子场强的增加会导致玻璃内部 Al—O—P 键占比上升, 从而提高玻璃网络的致密性, 使玻璃表现出更好的化学稳定性。此外, 值得注意的是, Na/Cs 组成的玻璃中 Al—O—P 键的占比与 K/Cs 组成的玻璃相当, 但是前者的结构更致密。这是因为 Na 的离子半径比 K 小, 相应的离子场强要比 K 大。较小的碱金属离子半径会导致玻璃网络的结构间隙更小, 而较大的离子场强会提高其对非桥氧的电场吸引力。这都会导致玻璃网络致密性的增加, 从而使玻璃表现出更好的化学稳定性。

表 6 初始玻璃的摩尔体积的倒数($1/V_{\text{mol}}$)和 Al—O—P 键在总化学键中占比(F)

Table 6 Reciprocal of the molar volume ($1/V_{\text{mol}}$) and the proportion of Al—O—P bonds in the pristine glasses (F)

Glass	$\frac{1}{V_{\text{mol}}} / (\text{mol} \cdot \text{L}^{-1})$	$F/\%$
NAP	2.6×10^{-4}	54.5
KAP	2.2×10^{-4}	52.6
NCAP	2.1×10^{-4}	50.7
KCAP	2.0×10^{-4}	50.5

4 总结

研究了包含 4 种不同碱金属氧化物(Na、K、Na/Cs 和 K/Cs)的铝磷酸盐玻璃的结构与化学稳定性, 其化学稳定性由强到弱的顺序为 Na, K, Na/Cs, K/Cs。随离子场强的增加, 玻璃的化学稳定性提升。离子场强对化学稳定性的提升具有双重作用。

首先, 增加场强会加强玻璃修饰体对非桥氧的电场吸引力, 从而提高玻璃结构的致密性和强度。其次, 离子场强的增加会引起玻璃网络结构的改变。在这些玻璃中, Al 的 3 种配位体 Al(4)、Al(5)和 Al(6)都存在, 只与 PO_4 四面体连接。随着碱金属离子场强的增加, 玻璃中高配位 Al[Al(5)和 Al(6)]的含量增加, 使得 Al 与 PO_4 四面体的化学键连接增多。这种结构变化进一步提高了玻璃网络的致密性, 从而使玻璃表现出更好的化学稳定性。

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Short-Range Structure and Chemical Stability of Alkaline Aluminum Phosphate Glass

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Extended Abstract

Introduction The chemical stability of phosphate glass is vital for its applications in various fields, i.e., biomedicine, laser gain media, sealing, and high-level nuclear waste solidification. Alkali metals affect the chemical stability of phosphate glass. Some studies indicate that alkali metals with a higher ionic field strength can enhance the chemical stability of glass via reinforcing the ionic crosslinking between alkali ions and non-bridging oxygen atoms. However, a few studies indicate that certain phosphate glasses containing low-field strength alkali metals exhibit a better chemical stability, compared to the glasses containing high-field strength alkali metals. These results cannot be explained based on the simple field strength. It is thus necessary to further investigate the influence of alkali metals on the chemical stability of phosphate glass. In this study, we utilized various advanced solid-state nuclear magnetic resonance (SSNMR) techniques to analyze the network structure of the aluminum phosphate glasses containing different alkali metals in an atomic scale. The intrinsic correlation among alkali metals, glass structure, and chemical stability was discussed.

Methods The glasses with molar compositions of $[\text{xNa}_2\text{O}-\text{yK}_2\text{O}-(41.6-\text{x}-\text{y})\text{Cs}_2\text{O}]-16.7\text{Al}_2\text{O}_3-41.7\text{P}_2\text{O}_5$ were synthesized by melt quenching methods. The values of (x, y) used were (41.6, 0), (0, 41.6), (20.8, 0), and (0, 20.8), respectively. The raw materials required for glass preparation were $\text{Al}(\text{OH})_3$ (purity>99%), $\text{Al}(\text{PO}_3)_3$ (purity>99%), NaPO_3 (purity>95.0%), KPO_3 (purity>99%), Cs_2CO_3 (purity>99%), and $\text{NH}_4\text{H}_2\text{PO}_4$ (purity>99%). Each batch, consisting of 20 g of mixed raw materials, was loaded into a platinum crucible and subjected to a high-temperature furnace at 1250–1300 °C for 30 min to melt raw materials. Thereafter, the melt was poured onto a steel plate and quickly pressed to obtain a bulk glass.

The chemical stability of these glasses was assessed by the Product Consistency Test B (PCT-B) method. 1 g of dried glass powder with particle sizes of 75–150 μm was mixed with 10 mL of neutral deionized water in a sealed polytetrafluoroethylene (PTFE) container. The container was then placed in a constant temperature environment at 90 °C for 7 d. After the corrosion experiments, the concentrations of leached elements in the leachates were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), thus calculating the normalized mass loss (NL) of each element within the different glasses.

All the SSNMR measurements were performed on a model Bruker Avance III HD 500 MHz spectrometer in a magnetic field of 11.7 T at room temperature. The measurements included ^{27}Al magic-angle spinning (MAS), ^{31}P MAS, $^{27}\text{Al}\{^{31}\text{P}\}$ rotational echo double resonance (REDOR), $^{31}\text{P}\{^{27}\text{Al}\}$ rotational echo adiabatic passage double resonance (REAPDOR), and ^{31}P 1D refocused

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The Raman spectra were determined by a model Renishaw inVia spectrometer, with a laser wavelength of 488 nm.

Results and discussion The NL of phosphorus (P) in the glasses containing alkali metals Na, K, and Na/Cs are 0.7, 15.2, and 21.1 g/m², respectively. The glass containing K/Cs exhibits a complete corrosion without detectable leachate obtained. These findings indicate that the chemical stability of the aluminum phosphate glasses with varying alkali metal compositions follows a decreased order of Na, K, Na/Cs, K/Cs. The P units within the different glasses are predominantly Q¹ units (Qⁿ, “n” represents the number of P—O—P bonds per P unit), indicating a consistent proportion of P—O—P bonds in these glasses. The variation in alkali metals does not affect the P—O—P bonds within the glasses. However, the variation in alkali metals significantly affects the Al species within the glasses. Specifically, the glasses containing alkali metals with a high ionic field strength exhibit a higher proportion of high-coordinated Al. In these glasses, the Al species with different coordinations are exclusively surrounded by phosphorus oxygen tetrahedra (PO₄), indicating that all Al species exist solely in the form of Al—O—P bonds. The compactness of the glass network increases with the proportion of Al—O—P bonds. The compact glass network can impede the dissolution and leaching of glass elements, as well as the diffusion of hydrogen species from solution into glass, thereby enhancing the chemical stability of the glass. The compactness of the glass network can be characterized by the reciprocal of the molar volume (1/V_{mol}). A higher value of 1/V_{mol} indicates a greater number of atoms per unit volume, corresponding to a higher compactness of the glass network. The values of 1/V_{mol} (×10⁴ mol/L) in these glasses containing alkali metals Na, K, Na/Cs, and K/Cs are 2.6, 2.2, 2.1, and 2.0, respectively. Correspondingly, the proportions of Al—O—P bonds are 54.5%, 52.6%, 50.7%, and 50.5%, respectively. A decreasing order of Na, K, Na/Cs, K/Cs is consistent with a decreasing order of the chemical stability. These results provide an evidence that the proportion of Al—O—P bonds increases as the ionic field strength of alkali metal increased, resulting in an enhanced compactness of the glass network and improved chemical stability. Furthermore, it is noteworthy that the proportion of Al—O—P bonds in the glass containing Na/Cs is comparable to that in the glass containing K/Cs. The former demonstrates a denser glass network. This can be attributed to the smaller ionic radius and higher ionic field strength of Na, compared to K. The smaller ionic radius results in narrower structural gaps within the glass network, while the higher ionic field strength enhances its electric field attraction to non-bridging oxygen.

Conclusions The chemical stability of the aluminum phosphate glasses containing different alkali metals decreased in an order of Na, K, Na/Cs, K/Cs. The chemical stability increased as the ionic field strength of alkali metals increased. The change in alkali metals affected the compactness of the glass network *via* modulating the electric field attraction to non-bridging oxygen, and substantially modified the network structure of the glass. In these glasses, the Al species with varying coordination numbers were exclusively surrounded by phosphorus oxygen tetrahedra (PO₄). The proportion of high-coordinated Al increased with increasing the ionic field strength of alkali metals, resulting in an augmentation of the chemical bond connections between Al and PO₄. This structural adjustment further enhanced the compactness of the glass network, ultimately improving its chemical stability.

Keywords alkali metals; aluminum phosphate glass; structure; chemical stability; solid-state nuclear magnetic resonance