Supporting Information

Sol-Gel derived Mesoporous GaAlPO₄ Glasses for Heavy Metal Ion Sequestration

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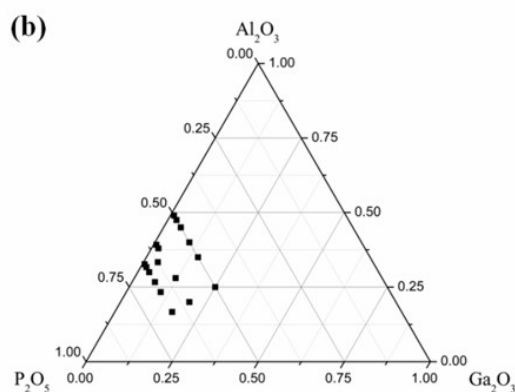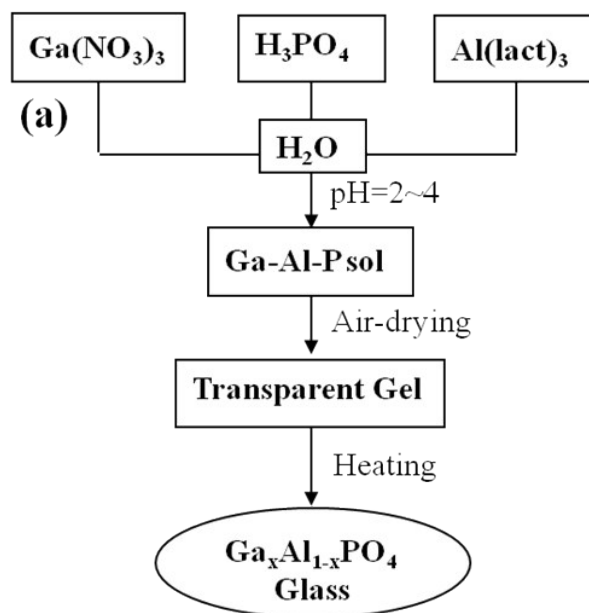**Preparation of GaAlPO$_4$ mesoporous glasses**

Fig. S1 (a) Flow chart of the sol–gel route of gallium-aluminum-phosphate glass; (b) Ternary phase diagram of the compositions of glass samples via sol-gel route in mol%.

Gallium aluminum phosphate gels and glasses were prepared via a sol-gel route shown in Fig. S1a, using aluminum lactate (98%, Fluka), gallium nitrite (99%, sigma) and H$_3$PO$_4$ (98%, Fluka). In a typical preparation, the desired amount of aluminum lactate and gallium nitrate added up to 0.004 mol were dissolved in distilled water, followed by the addition of H$_3$PO$_4$ (1M) solution prepared by dissolving solid H$_3$PO$_4$ (98%, Fluka) in distilled water, the volume of which was adjusted to the desired P/Al+Ga molar ratio in the mixture. The pH of the mixing solutions was controlled within 0.01 units by a pH meter (Mettler Toledo pH s20k, Switzerland). After stirring for 4h, the resulting clear solution was spread onto a flat surface and then gelled in the open air for 2–3 days at room temperature. The clear and free-flowing properties of the precursor sols also offer some potential applications as inert coating materials. Upon air-drying the sols, transparent colorless gallium aluminum phosphate xerogels were prepared. After heating the xerogels at 600 °C for several hours in ambient atmosphere,

homogeneous Ga_2O_3-Al_2O_3-P_2O_5 glasses (GAPs) pieces were finally obtained. Their non-crystalline state was confirmed by X-ray powder diffraction patterns (Guinier method, Cu Kα1 radiation), revealing the typical response of glassy samples.

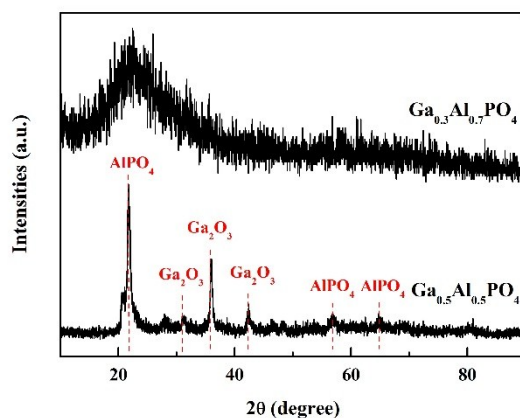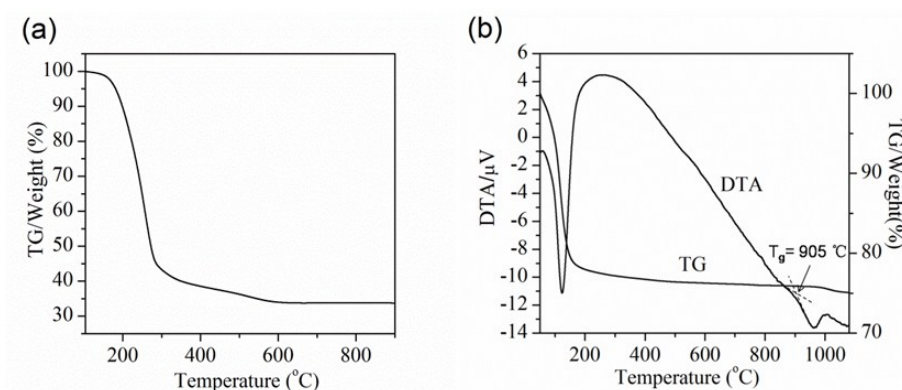Fig S2. The XRD of calcined $Ga_{0.3}Al_{0.7}PO_4$ and $Ga_{0.5}Al_{0.5}PO_4$

Fig. S3 (a) The thermogravimetric (TG) traces of $Ga_{0.1}Al_{0.9}PO_4$ xerogel formed at room temperature. (b) TGA and DTA of $Ga_{0.1}Al_{0.9}PO_4$ glass after annealing at 600 ℃ for 6 h.

Table S1 Real composition, Glass Transition (T_g) and Crystallization Temperatures (T_x) of the Annealed Glassy Materials

Sample	Ga(a.t.%)	Al(a.t.%)	P(a.t.%)	T_g (℃)	T_x (℃)
$Ga_{0.01}Al_{0.99}PO_4$	0.00208	0.2063	0.1973	992	1058
$Ga_{0.02}Al_{0.98}PO_4$	0.00407	0.1992	0.1982	995	1060
$Ga_{0.05}Al_{0.95}PO_4$	0.0103	0.1956	0.1980	980	1042
$Ga_{0.1}Al_{0.9}PO_4$	0.0206	0.1835	0.1997	905	1088
$Ga_{0.2}Al_{0.8}PO_4$	0.0402	0.1606	0.2049	807	900
$Ga_{0.25}Al_{0.75}PO_4$	0.0513	0.1538	0.1997	890	988

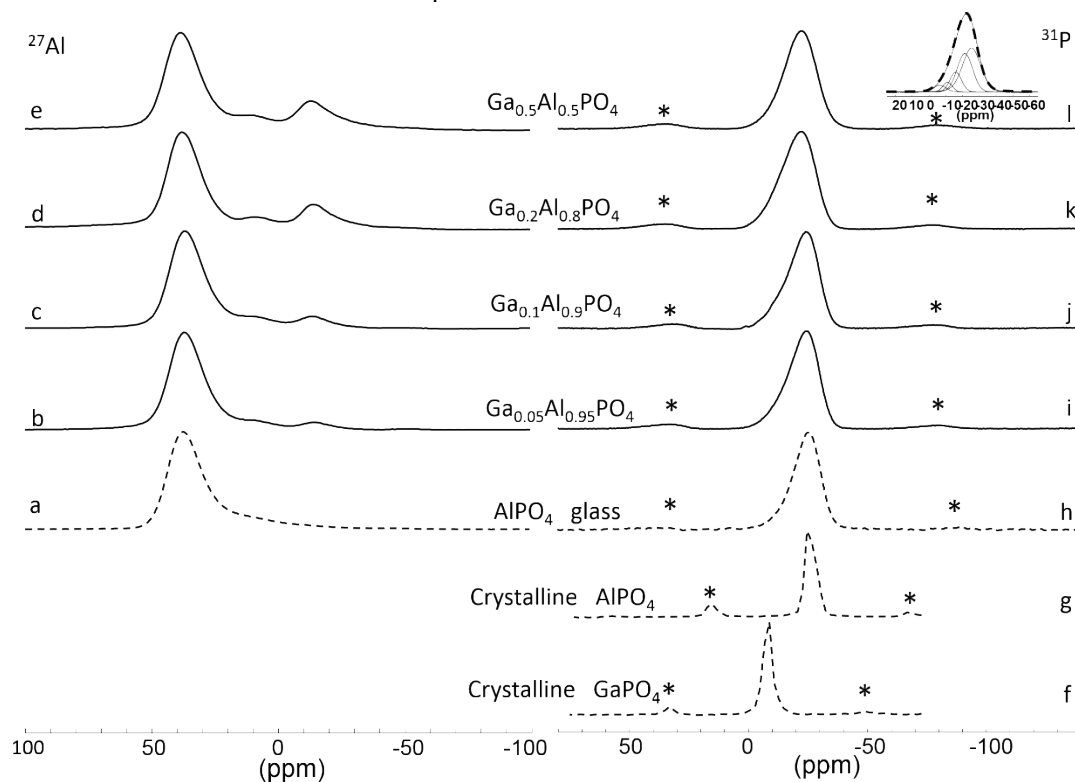**The structural disscussion of GaAlPO$_4$ Glasses**

Fig. S4 104.3 MHz ^{27}Al (left) and 162.4 MHz ^{31}P (right) MAS-NMR spectra of gallium aluminum phosphate glasses along the compositional line Ga$_x$Al$_{1-x}$PO$_4$. For contrast, Trace a and h are from gallium-free AlPO$_4$ glasses. Trace f and trace g are from crystalline GaPO$_4$ and AlPO$_4$ respectively. Spinning sidebands are indicated with asterisks.

Table S2 ^{27}Al and ^{31}P isotropic chemical shift (δ_{iso}) via ^{27}Al and ^{31}P MAS spectra data for some representative samples in the present study

Samples	^{31}P (ppm)	AlO$_4$(ppm)	AlO$_5$(ppm)	AlO$_6$(ppm)
AlPO$_4$	-25.4	37.5	—	—
Ga$_{0.02}$Al$_{0.98}$PO$_4$	—	37.6	9.0	-12.0
Ga$_{0.05}$Al$_{0.95}$PO$_4$	-24.5	37.3	9.0	-12.7
Ga$_{0.1}$Al$_{0.9}$PO$_4$	-23.4	39.4	9.3	-14.1
Ga$_{0.2}$Al$_{0.8}$PO$_4$	-22.7	37.6	9.1	-13.7
Ga$_{0.25}$Al$_{0.75}$PO$_4$	—	38.1	9.3	-13.9
Ga$_{0.3}$Al$_{0.7}$PO$_4$	—	37.5	8.8	-13.6
Ga$_{0.5}$Al$_{0.5}$PO$_4$	-22.2	38.0	9.0	-13.7

Fig. S4 shows the ^{31}P (right) and ^{27}Al (left) MAS spectra of some representative sol-gel derived glasses annealed at 600-700 °C. All the glasses were obtained through heating the corresponding xerogels formed at 50 °C from the sols with pH around 2.8-3.2. The isotropic chemical shifts (δ_{cs}) of both ^{31}P and ^{27}Al are listed in Table S2. The data of Fig. S4 permit a comprehensive structural

discussion of the ternary $Ga_xAl_{1-x}PO_4$ glass system. The spectra of $AlPO_4$ are also shown in the bottom of these figures.

^{31}P NMR chemical shift values for phosphates are decided by a number of parameters like (a) the electronegativity and charge to radius ratio of nearest and next nearest neighbours, (b) O-P-O angles, (c) P-O-M angles, (d) P-O bond order, etc [1]. The nearest neighbours and their number around P are same for both $AlPO_4$ and $GaPO_4$. As the radii of Ga^{3+} and Al^{3+} are 0.05 and 0.062 nm, respectively, and the Pauling's electro-negativities of Ga^{3+} and Al^{3+} are approximately 1.5 and 1.6, respectively. The average P-O-M angles are found to be significantly different, namely, 145 and 132° for $AlPO_4$ and $GaPO_4$, respectively, and for intermediate compositions this angle varied in a systematic manner which is consistent with the monotonic variation of chemical shift with composition [2]. As the P-O-M angle decreases, the s character of bridging oxygen atoms decreases, which results in the reduced shielding around P nuclei thereby increasing chemical shift values. Both $AlPO_4$ and $GaPO_4$ show a significant difference in their chemical shifts (δ) [3]. The value of δ is -25.4 ppm for $AlPO_4$, and the chemical shift value for crystalline $GaPO_4$ is -8.5 ppm. This increase in the chemical shift value for $GaPO_4$ is arising due to the decreased cationic field strength, $\{(Z_{eff}/r)q\}$, electron affinity of Ga^{3+} as compared to that of Al^{3+} ions and the decreased value of Ga-O-P bond angle as compared to that of Al-O-P as revealed by the crystal structure of these two compounds (Fig. S4).

The origin of the ^{31}P signal shifts towards higher frequency for $Ga_xAl_{1-x}PO_4$ glasses can be understood in terms of the structural configurations of ^{31}P with varing number of Al^{3+} and Ga^{3+} as its next nearest neighbours. For $Ga_xAl_{1-x}PO_4$ glasses, the four oxygen atoms of PO_4 tetrahedral units are connected either to Al^{3+} or Ga^{3+} cations. Depending on the contents of Al^{3+} and Ga^{3+} in the glasses, the relative concentration of such structurally different configurations of ^{31}P will change. For $Ga_xAl_{1-x}PO_4$ glass, the ^{31}P NMR are complex due to the superposition of five individual patterns whose relative intensity is found to vary systematically with variation of Al/Ga ratio. In crystalline phosphates, the ^{31}P chemical shift increases by $\approx$4 ppm for each replacement of Al^{3+} by Ga^{3+}. The line widths (Γ) for glasses in general tend to be broader than those in crystals due to more asymmetric in amorphous environments [4]. So in the spectra (Fig. S4), the single peaks could not be distinguished separately.

As illustrated from Table S2, the compositional dependence of the structural speciation can be clearly viewed in term of a competition of gallium and aluminum species for the phosphorus. The effect of moving the main peak upfield was found to significantly depend on an increase of Ga contents in theses phosphate glasses. As Ga contents increases from 5% to 20%, the ^{31}P chemical shift moves to -22.7 ppm. It indicates that one aluminum sites was replaced by gallium constantly. These $P(OAl)_4$ and $PO_4(1Ga3Al)$ units become the overwhelming majority of phosphorus sites. The structure which is based on alternating of the two units is similar with the gallium-free "ideal" $AlPO_4$ network. This is the reason that the mesoporous structure remains intact. Whereas 30% difference of gallium contents between $Ga_{0.2}Al_{0.8}PO_4$ and $Ga_{0.5}Al_{0.5}PO_4$ shows a little difference (0.5 ppm) in their chemical shifts (δ). The deconvoluted ^{31}P spectra of $Ga_{0.5}Al_{0.5}PO_4$ reveals the fact that $P(OAl)_4$ and $PO_4(1Ga3Al)$ units keeps as major species even the amount of gallium adds to 50%. It can be clearly seen that there is some competition between the two cations but that the tendency of the Al^{3+} to occupy the next nearest sites of P^{5+} is a bit larger than that of the Ga^{3+}. It gives the clear evidence that the phase separation occurs as the amount of gallium increases. The fact that the glasses turns out to be opaque when gallium add up to 30% ascribed to macroscopic phase separation. The surface areas significantly decreases as the gallium reaches 20% percent can be corresponded to the phase separation which destroys the "ideal" $AlPO_4$ three-dimensional network. The ^{27}Al NMR spectrum (Fig. S4 left) indicates the formation of additional five- and six-coordinate aluminum species as Ga contents increases. The excess of phosphorus due to the larger tendency of Al^{3+} to occupy the next nearest sites of P^{5+} is used for the conversion of additional aluminum into $Al(OP)_5$ and $Al(OP)_6$ units; furthermore, the same chemical shift of four-, five- and six- coordinated (Al(IV), Al(V) and Al(VI)) aluminum compared

with Al_2O_3-P_2O_5 binary system confirm that the Al-O-Ga linkages are largely absent in these glasses [5].

The leaching behavior of $Ga_{0.1}Al_{0.9}PO_4$ Glass

The leaching test was carried out by using the ASTM standard MCC-1 leaching method [6]. The standard pH buffer solutions were employed as fixed pH leachant, the ratio of glass surface area to leachant volume (SA/V) was 2000 m^{-1}, and the leaching temperature was at room temperature. Test duration is 7 d which is longer than the saturated absorption time of heavy metal ions on GAPs. The leachate was analyzed by using inductively coupled plasma spectrometry (ICP) for the three main glass elements: Al, Ga, P. The mass of glass specimen was measured before and after leaching; then the total mass loss *ML* and the element leached fraction *LF$_i$* were calculated as follows:

$$ML = (m_0 - m_1)/(SA)$$

$$LF_i = (C_i \times V)/(m_0 \times f_i)$$

Where $m_0(g)$ and $m_1(g)$ are mass of original unleached sample and sample after leaching, respectively; $C_i(g$ m$^{-3})$ indicated the concentration of element *i* in leachate; f_i is the mass fraction of element *i* in the unleached sample.
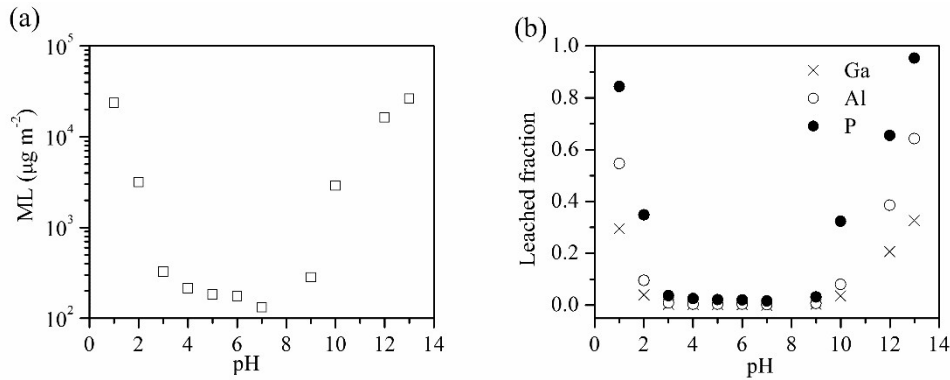

Fig S5. (a) *ML* and (b) *LF$_i$* vs. pH (MCC-1, *SA/V*=2000 m^{-1}, 7d, standard buffers).

The total mass loss and the leached fraction of three ions depicted in Fig. S5 indicate that the GAPs are the most durable from pH 3 to pH 9. The rate of leached fraction increases dramatically above pH 9 and below pH 3. The variations of leaching behavior always seem as a function of its composition. The chemical durability of phosphate glasses would be improved by introducing a number of other glass formers and modifiers such as Al_2O_3, MoO_3, Ga_2O_3, In_2O_3, Sb_2O_3 [7]. For example, it was well known that the Al_2O_3 affects the phosphate glass properties in ways that imply an increase in the extent of structural polymerization, inhibiting hydration reactions [8]. It should be noticed that the leached fraction of GAPs in a wide pH range from 3 to 9 is rather low (<10%) which is attributed to the high Al_2O_3 and Ga_2O_3 content. The high chemical durability of GAPs benefits its application in harsh environment.
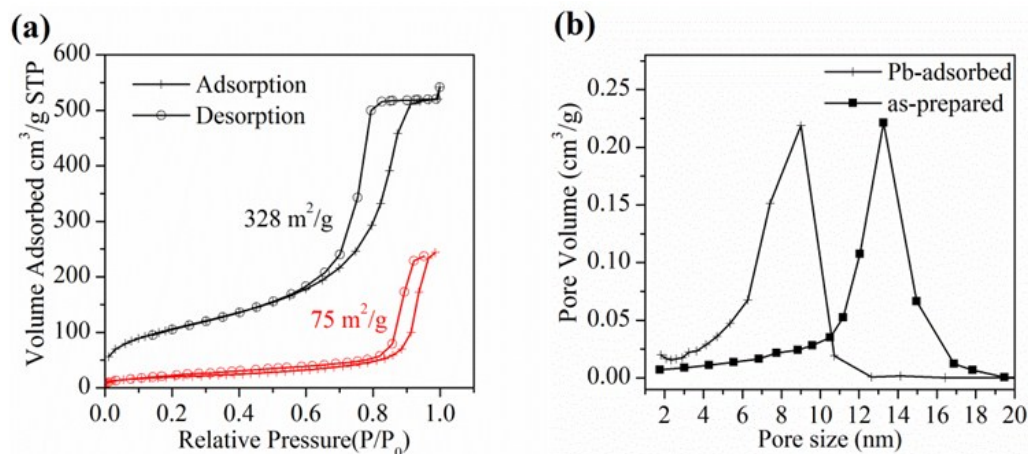
Fig. S6 (a) Adsorption–desorption isotherms (b) Pore size distribution of $Ga_{0.1}Al_{0.9}PO_4$ mesoporous glass before and after Pb adsorbed.

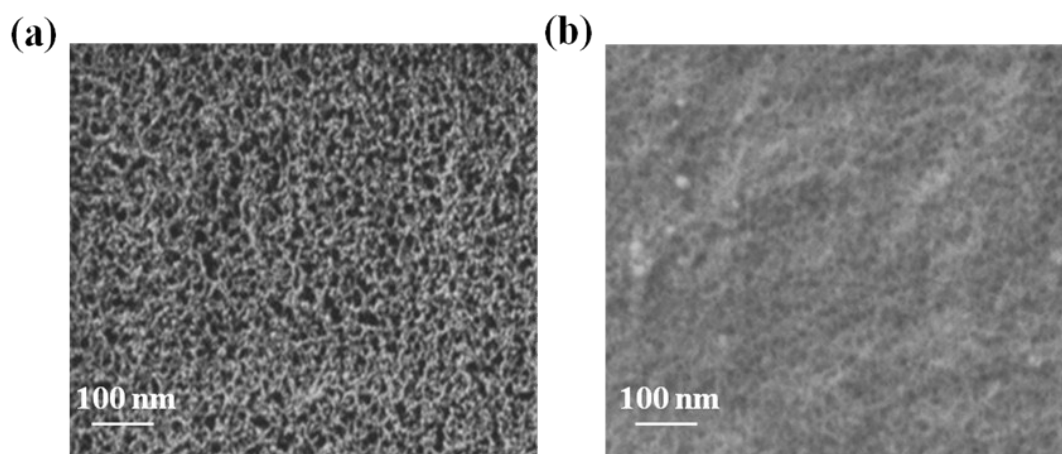Fig. S7 SEM of (a) as-prepared and (b) Pb-adsorbed $Ga_{0.1}Al_{0.9}PO_4$ mesoporous glass

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