Crystal Chemistry of Gallium(I) in Oxides: Ga^+-β''-Alumina and $GaZr_2(PO_4)_3$

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Ga^+-β''-alumina and $GaZr_2(PO_4)_3$ have been prepared by ion exchange techniques from Na^+-β''-alumina and $AgZr_2(PO_4)_3$, respectively. The structures of both compounds at room temperature are reported along with that for β''-alumina at 11 K. The coordination chemistries of the Ga(I) cations in the two materials are distinctly different: in Ga^+-β''-alumina, the Ga(I) cation displays 3+0-coordination, indicative of a stereochemically active lone pair, with a minimum Ga−O distance of 2.39 Å, but in $GaZr_2(PO_4)_3$, Ga(I) is 6-coordinate with a minimum Ga−O distance of 2.80 Å. Both Ga^+-β''-alumina and $GaZr_2(PO_4)_3$ are stable toward oxidation in air up to ∼500 °C. Crystal data are as follows. $Ga_{1.6}[(Al_{10.7}Li_{0.3})O_{17}]$: rhombohedral, $R\bar{3}m$, $Z = 3$; for $T = 296$ K, $a = 5.5951(1)$ Å and $c = 34.3670(8)$ Å; for $T = 11$ K, $a = 5.5900(1)$ Å and $c = 34.3805(8)$ Å. $GaZr_2(PO_4)_3$: rhombohedral, $R\bar{3}c$, $Z = 6$, $a = 8.72198(4)$ Å, $c = 23.8820(2)$ Å.

Introduction

The chemistry of gallium in an oxidation state of I has been explored by a number of workers. There are well-established halides, coordination complexes, and organometallic species containing Ga(I).[1,2] However, there are no well-characterized examples of oxides that contain Ga(I). The existence and properties of Ga_2O have been explored to a limited extent.[1] It is described as being dark in color and sublimable and there is some structural information for gas phase and matrix-isolated[3] species of this composition, but there is no information regarding the properties or structure of this compound in the solid state. Additionally, Radzilowski[4] has reported the preparation of a Ga(I)-containing β-alumina by ion exchange methods. Subsequently, the electrical properties of Ga^+-β-alumina[5] and its use in the electrochemical purification of gallium[6] were investigated by Fray and co-workers. However, no structural information has been reported for Ga^+-β-alumina.

Radzilowski's strategy of preparing Ga(I)-containing oxide phases by ion exchange is, in principle, readily adaptable for use with a wide variety of materials that display significant ionic mobility at moderate temperatures. The ion exchange chemistries of both β- and β''-aluminas[7−11] and materials with a NZP (sodium zirconium phosphate) framework[12,13] have been extensively investigated, as a consequence of the possible applications of such materials in solid state electrochemical devices.[14,15] β''-Alumina and NZP-like frameworks have been chosen as hosts for Ga(I) in the present study.

β''-Aluminas are typically described as occupying a hexagonal unit cell, space group $R\bar{3}m$. Their structures consist of stacked spinel-like blocks separated by a conduction plane. The neighboring spinel blocks are held together by a combination of the ion exchangeable cations residing between the blocks and an oxygen, usually labeled O(5), that bridges the conduction plane. For β''-aluminas containing only univalent mobile cations, the exchangeable cations sit on some combination of Wyckoff positions 6c and 18h in the conduction plane. The cations on the 18h site, or sites, can be thought of as being displaced away from a 6c site toward one of its three nearest neighbor 6c sites. Cations on the 6c site have a distorted tetrahedral coordination environment.

The NZP $[NaZr_2(PO_4)_3]$ structure consists of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra arranged so that there is a three-dimensional channel system running through the material.[13] There are three distinct types of sites in the NZP channel system that could contain exchangeable cations. However, in NZP itself, only the octahedrally coordinated site is occupied.

The current work reports the preparations, crystal structures, and thermal properties of Ga^+-β''-alumina and $GaZr_2(PO_4)_3$. The crystal chemistry of Ga(I) in these materials is compared with that of other univalent cations in similar hosts, as we are unaware of any other structural studies of Ga(I)-containing oxides.

Experimental Section

A sample of Ga^+-β''-alumina was prepared using a procedure similar to those described by Kummer[16] and Radzilowski[4] for the synthesis of Ga^+-β-alumina. A 13.82 g sample of Na^+-β''-alumina powder ($Na_{1.60}[Al_{10.7}Li_{0.3}]O_{17}$—the composition was determined using the manufacturer's batch analysis to give the Al/Li ratio and the constraint that there should be 17 oxygens), supplied by Ceramatec, was dried by heating at 500 °C for about 45 h (weight loss ∼0.5%). The dry material was placed in a quartz test tube along with 49 g of $AgNO_3$ and heated at 300 °C for 4 days. The molten silver nitrate was decanted from the ion-exchanged β''-alumina and the sample left to cool. The tube was broken open, and the plug of material was heated in 100 mL of distilled water to dissolve the remaining silver nitrate. The product was vacuum-filtered and washed with water until there was no trace of silver in the washings. It was then rinsed with ethanol and dried under vacuum at 200 °C for about 1 h. A chemical analysis of this

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material was performed by Galbraith Laboratories, and X-ray powder diffraction measurements showed it to be almost phase-pure (there was evidence for an unidentified trace impurity that was also present in the Na^+-β''-alumina starting material). A 14.9 g amount of the Ag^+-β''alumina was sealed into a quartz ampule under vacuum along with 45 g of gallium metal and 60 g of iodine. The ampule was gradually heated to 290 °C and held there for about 4 days. The tube was cooled and observed to contain three distinct layers. The bottom layer was olive green, the middle layer was metallic, and the top layer was olive green. The ampule was broken open and the top layer treated with 10% HCl to remove the "GaI".[17,18] The insoluble product **A** (olive green) was recovered by vacuum filtration, washed with distilled water, and dried in air at 120 °C. The bottom layer (subsequently referred to as product **B**) was treated in a similar fashion, and the middle layer, consisting of gallium/silver and containing some large needlelike metallic crystals, was discarded. Product **A** was analyzed by Galbraith Laboratories.

$GaZr_2(PO_4)_3$ was prepared by ion exchange using $AgZr_2(PO_4)_3$[19−21] as a starting material. The latter was prepared from stoichiometric amounts of Ag_2CO_3, ZrO_2, and $(NH_4)H_2PO_4$. The mixed reactants were slowly heated to 600 °C and then removed from the furnace. The product was repeatedly heated (four times) to 900 °C, removed from the furnace, and reground over a period of a few days (total heating time ∼55 h). The resulting sample was heated to 1000 °C for 12 h, reground, and then heated to 1050 °C for a further 55 h. X-ray powder diffraction demonstrated that the product was phase-pure $AgZr_2(PO_4)_3$.

Fifteen grams of $AgZr_2(PO_4)_3$, 40 g of gallium metal, and 53 g of iodine were sealed under vacuum in a quartz ampule. The tube was initially heated to 105 °C; after 4 h, the temperature was raised to 130 °C and the sample heated for a further 20 h. The ampule was then heated to approximately 300 °C for 3 days, after which it was broken open and the residual liquid gallium metal was separated from the product mixture. The green mass containing the desired product, "GaI",[17,18] and some gallium metal was treated with 75 cm^3 of 10% HCl. When hydrogen evolution ceased, almost pure $GaZr_2(PO_4)_3$ was recovered by filtration and washed with water. The crude product was then suspended in water, and after the sample was allowed to settle slightly, the liquid was decanted and filtered. A 7.88 g amount of a fine off-white powder (product **C**) was recovered from the filter, and a further 5.3 g of coarser material (product **D**), which had settled after suspension of the crude product, was recovered. The coarser material still contained a small amount of gallium metal. Product **C** was analyzed by Galbraith Laboratories.

Powder neutron diffraction data were collected for product **A** using the HB4 diffractometer at the HFIR reactor, Oak Ridge National Laboratory. A 5.0 g sample of material was sealed in a 10 mm diameter vanadium can under an atmosphere of helium. The sample can was placed in a Displex cryostat for data collection. A neutron wavelength of 1.417 Å was employed, and data were obtained at both 296 and 11 K over the angular range 11−134.70° in 0.05° steps. The sample transparency (across the diameter of the can) was experimentally determined to be ∼91%.

Powder X-ray diffraction data for the Rietveld refinement of the Na^+-β''-alumina, Ag^+-β''-alumina, Ga^+-β''-alumina (sample **A**), and $GaZr_2(PO_4)_3$ (sample **C**) structures were obtained using a Scintag X1 diffractometer equipped with a Peltier cooled solid state detector. The data were collected in steps of 0.02° over the range 10−150° 2θ. A count time of 8 s/step was employed in the case of $GaZr_2(PO_4)_3$. The program GSAS[22] was used for the Rietveld analysis of both the powder X-ray and the neutron diffraction data sets.

XANES spectra were collected in transmission for samples of both Ga^+-β''-alumina (product **A**) and $GaZr_2(PO_4)_3$ (product **C**). These data were obtained at Beamline X11A, NSLS, Brookhaven National Laboratory, using a three-ion-chamber arrangement, Si(111) double-crystal monochromator, and the spinel $ZnGa_2O_4$ as a reference material. The $ZnGa_2O_4$ sample contained only octahedral gallium(III), as shown by a previous neutron diffraction study.[23]

TGA data were obtained for a 10.387 mg sample of Ga^+-β''-alumina using a Seiko Instruments TGA/DTA 320 analysis module. The sample was heated under flowing (80 mL/min) dry air from 30 to 1000 °C at 10 °C/min and held there for 1 h. TGA data were obtained for a 30.661 mg sample of $GaZr_2(PO_4)_3$ using a Perkin-Elmer 7 series thermal analysis system. The sample was heated in air from 30 to 1000 °C at 10 °C/min.

Results and Discussion

Ag^+ and Na^+-β''-Aluminas. Chemical analysis of the silver-exchanged β''-alumina showed that it contained ∼23.98% Ag and ∼0.06% Na, consistent with ∼99% Ag^+ exchange. Rietveld refinements for the Ag^+- and Na^+-β''-aluminas were carried out using the laboratory X-ray data collected on the starting sodium and the intermediate silver compounds. The lattice constants from these refinements are reported in Table 1; the values obtained for both the silver and sodium compounds are comparable to those determined by other workers. Both refinements showed the presence of a small amount of an unidentified impurity phase.

Ga^+-β''-Alumina. Chemical analysis of the Ga^+-β''-alumina (product **A**) showed that the sample contained ∼17.03% Ga, ∼0.71% Ag, and ∼0.14% Na, consistent with ∼95% Ga^+ exchange, and ∼2.5% residual Ag^+ along with ∼2.5% residual Na^+. The XANES data for the Ga^+-β''-alumina and the reference material $ZnGa_2O_4$ are shown in Figure 1. Both spectra show strong "white line" features; however, the Ga K absorption edge and the "white line" for the Ga^+-β''-alumina sample are at ∼5 eV lower energy than those for the reference material. X-ray absorption edge energies are known to be dependent upon cation oxidation state.[24] For example, it has been shown that there is a difference of ∼3 eV between the Ga K absorption edges of $GaAlCl_4$ and $GaCl_3$,[25] that the Se(IV) and Se(VI) K edge positions in $Er(SeO_3)(SeO_4)_{1/2}\cdot H_2O$ differ by about 3 eV,[26] and that As_2O_3 and As_2O_5 display a separation of about 4 eV between their respective As K edges.[27] The presence of a single white line in the XANES spectrum of the Ga^+-β''-alumina sample, at about 5 eV lower energy than that for $ZnGa_2O_4$, indicates that the majority of the gallium in the sample is in an oxidation state of I.

The TGA experiment performed on the Ga^+-β''-alumina in flowing dry air showed that the material is stable toward oxidative degradation to ∼500 °C. A weight gain of ∼4.07% occurred on heating the sample from room temperature to 1000 °C; this is consistent with the oxidation of all the Ga(I) in a sample of composition $Ga_{1.6}[Al_{10.7}Li_{0.3}]O_{17}$ to Ga(III) (expected weight gain ∼3.8%). Some β''-aluminas are known to hydrate; however, the sample of Ga^+-β''-alumina that was examined did not contain significant amounts of water. The TGA data did not show any low-temperature weight loss indicative of dehydration, and the neutron diffraction data did not display a

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Table 1. Key Structural Parameters for Well-Characterized M^+-β''-Alumina Samples[a]

M^+	type of data[g]	a/Å	c/Å	a/c	6c[e] occ	18h[e] occ	6c coordinates	18h coordinates	stabilizer
Na^+	XP[b]	5.6101	33.6355	0.1668					Li
Ag^+	XP[b]	5.6101	33.3600	0.1682					Li
Ga^+	XP[b]	5.5959	34.3640	0.1628					Li
Ga^+ [c]	NP[b]	5.5900	34.3805	0.1626	1.54		$z = -0.1845$		Li
Ga^+	NP[b]	5.5951	34.3670	0.1628	1.52		$z = -0.1840$		Li
NH_4^+	NS[30]	5.6310	34.378	0.1638	1.56		$z = 0.16967$		Mg
Ag^+	NS[31]	5.6263	33.403	0.1684		1.61		$x = 0.0205$ $z = -0.16947$	Mg
Ag^+	XS[32]	5.63	33.45	0.1683	0	1.64		$x = 0.0186$ $z = -0.1695$	Mg
K^+	NS[31]	5.6253	34.067	0.1651	0.56	1.04	$z = -0.1711$	$x = 0.0837$ $z = -0.1682$	Mg
K^+	XS[33]	5.63	34.01	0.1655	0.61	0.98	$z = -0.1709$	$x = 0.08717$ $z = -0.16784$	Mg
Na^+	XS[33]	5.61	33.54	0.1673	0.67	1.04	$z = -0.1717$	$x = 0.05724$ $z = -0.17241$	Mg
Na^+	NS[31]	5.6230	33.536	0.1677	0.81[f]	1.00	$x = 0.0246$[f] $z = -0.1744$	x=0.0900 z=-0.1694	Mg
Na^+	XS[28]	5.614	33.85	0.1658	2.0		$z = 0.1719$		Mg
Na^+ [d]	NP[29]	5.6071	33.4580	0.1676	0.51	1.16	$z = -0.1726$	$x = 0.104$ $z = -0.1692$	Li
Na^+	NP[29]	5.6101	33.4627	0.1677	0.44	1.23	$z = -0.1717$	$x = 0.104$ $z = -0.166$	Li

[a] Data are from room-temperature studies unless marked otherwise. [b] Data from this study. [c] Measurements made at 11 K. [d] Measurements made at 12 K. [e] Occupancy in atoms per formula unit. [f] A second 18h position not a 6c site. [g] XS = X-ray single-crystal data; NS = neutron single-crystal data; XP = X-ray powder data; NP = neutron powder data.

high background due to incoherent scattering from hydrogen associated with water in the sample. The lack of incoherent scattering also indicates that there was no, or very little, proton exchange during removal of the "GaI" with HCl.

The structural model of Bettman and Peters[28] for Na^+-β''-alumina was used as a starting point for the Rietveld analysis of the powder neutron diffraction data. The lithium was placed on the Al(2) site as indicated by the work of Jorgensen *et al.*[29] A number of different structural models for the Ga(I) distribution in the material were examined, as other studies have shown that univalent cations in β''-aluminas can be distributed in several different ways (see Table 1).[28−33] With the 11 K data, a satisfactory model could be obtained by placing all of the Ga(I) onto a 6c site with $z \sim -0.184$ and refining an anisotropic temperature factor for this atom. The refined values of this temperature factor indicate that there is some static disorder of the exchangeable cations along the crystallographic *c* axis; this may because there is a small amount of residual Na^+ or Ag^+ in the sample and these cations would normally sit on a site with somewhat smaller value of *z* than is observed for the Ga(I). An attempt to develop a split-site model suggested that most of the scattering density was at $z \sim -0.184$ with a smaller amount at a lower value of the *z* coordinate; however, the use of a split-site model did not produce a significantly better fit to the diffraction data. An anisotropic temperature factor was also used for O(5) because in other β''-aluminas there is evidence for static disorder or large amounts of thermal motion for this atom. The refinement of the Ga^+-β''-alumina model based on the 11 K data indicated no significant static disorder for O(5). The absence of disorder for O(5) is probably a consequence of the large gap between neighboring spinel blocks in the Ga^+-β''-alumina. O(5) bridges the gap between two Al(4) atoms in adjacent blocks; as the gap size is reduced below some critical value, the Al(4)−O(5)−Al(4) bond angle will be forced to deviate from 180° and the O(5) atom will become disordered around its ideal position.

With the exception of atoms Ga(1) and O(5), the preliminary refinement was carried out with isotropic temperature factors for all atoms. However, examination of difference Fourier maps indicated that there was excess scattering density near O(2). The use of an anisotropic temperature factor for this atom resulted in a significantly better fit to the diffraction data. The refined values of the temperature factor for this atom indicate static disorder along the crystallographic *c* axis. The presence of static disorder is physically reasonable, because O(2) is coordinated to a site that contains a mixture of Al and Li. The crystallographic details are summarized in Table 2, the final structural parameters obtained from the refinement employing the 11 K neutron diffraction data set are given in Table 3, some selected bond distances are given in Table 4, and the final profile fit is shown in Figure 2a.

The structural model for Ga^+-β''-alumina at 296 K was based on that obtained using the 11 K data. The results from the 296 K refinement are very close to those obtained from the 11 K data, with the exception that the thermal parameters for Ga(1) and O(5) are considerably larger at 296 K than they were at 11 K. It is notable that the material shows very little thermal expansion on going from 11 to 296 K; the *a* axis expands by a small amount and the *c* axis contracts slightly. The crystallographic details are summarized in Table 2, the final structural parameters from the refinement are reported in Table 3, selected distances are given in Table 4, and the final profile fit is shown in Figure 2b.

Some of the important structural parameters for Ga^+-β''-alumina are compared to those of the other structurally characterized M^+-β''-aluminas in Table 1. Ga^+ is reported to have an ionic radius of 113 pm, similar to that of Ag^+ (113

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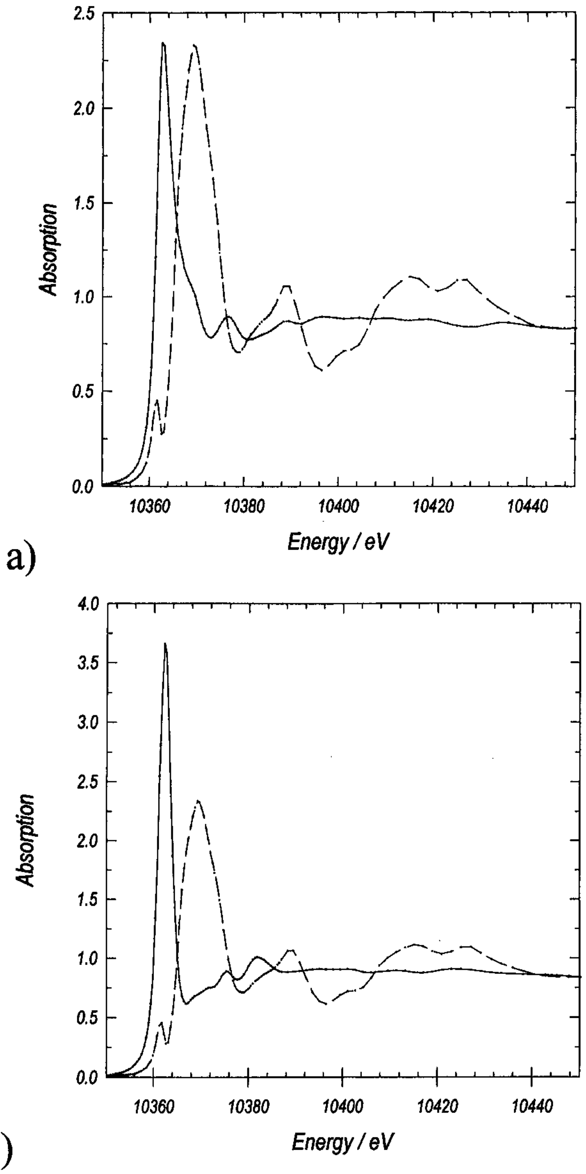

Figure 1. (a) XANES spectra for Ga$^+$-β''-alumina (solid line) and $ZnGa_2O_4$ (broken line). (b) XANES spectra for $GaZr_2(PO_4)_3$ (solid line) and $ZnGa_2O_4$ (broken line).

pm) and between those of Na$^+$ (98 pm) and K$^+$ (133 pm).[34] However, the *a/c* ratio for Ga$^+$-β''-alumina (0.1628) is smaller than that of any other well-characterized β''-alumina, although it is close to that determined for an NH_4^+-containing β''-alumina (0.1638).[30] Additionally, the *z* coordinate for the Ga$^+$ cation is significantly different from those observed for other univalent cations in β''-aluminas. Univalent cations that sit on the 6c site in β''-aluminas (for example, some of the sodium in Na$^+$-β''-alumina) experience a distorted tetrahedral coordination environment. For sodium β''-alumina, the cations on the 6c site have four oxygens at approximately the same distance from them (~2.6 Å). However, the Ga$^+$ cation on the 6c site of the β''-alumina has 3+0-coordination; there are three oxygens on one side of the cation at ~2.39 Å and no other anions within 3.14 Å of the Ga$^+$. The unusual coordination environment of the Ga(I) cation and the small *a/c* ratio suggest that Ga$^+$ in β''-alumina has a stereochemically active lone pair. Main-group metals often have highly irregular coordination environments when they have an oxidation state of 2 less than the group number, and this is attributed to the lone pair of valence electrons occupying some of the solid angle around the cation. For example, Tl$^+$ is known to occur in highly irregular

Table 2. Summary of Crystal Data and Structure Refinement Details for Ga$^+$-β''-Alumina

	11 K refinement	296 K refinement
space group	$R\bar{3}m$	$\mathrm{R}\bar{3}m$
neutron wavelength/Å	1.417	1.417
fw	674.3	674.3
a/Å	5.5900(1)	5.5951(1)
c/Å	34.3805(9)	34.3670(8)
V/Å^3	930.38(5)	931.73(5)
Z	3	3
ρ_x/g cm^{-3}	3.59	3.59
color	olive green	olive green
abs corr	yes	yes
transparency[b]	91	91
angular range (2θ)/deg	11.00−134.70	11.00−134.70
no. of data points	2469	2469
no. of reflections	328	328
no. of refined params	41	41
R_{wp}/%	6.50[a]	5.43[a]
R_p/%	5.40[a]	4.47[a]
χ^2	1.405	1.367
R_{F^2}/%	4.23[a]	4.03[a]

[a] $R_{wp} = \Sigma w(y_{io} - y_{ic})^2/\Sigma w(y_{io})^2$ (weights based on counting statistics); $R_p = \Sigma(y_{io} - y_{ic})^2/\Sigma(y_{io})^2$; $R_{F^2} = [\Sigma(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$ (F_o is estimated from the profile and may be biased by the model). [b] Experimentally measured transparency across the diameter of the sample can.

Table 3. Refined Coordinates and Temperature Factors for Ga$^+$-β''-Alumina[a]

atom	occ	*x*	*y*	*z*	10^2U_{11}[b]	10^2U_{33}[c]
Ga(1)	0.77(1)	0	0	−0.1845(1)	−0.0(1)	1.6(2)
	0.76(1)	0	0	−0.1840(2)	2.2(2)	3.1(3)
Al(1)	1	0	0	0	0.4(2)	
		0	0	0	0.3(2)	
Al(2) + Li(1)	0.85 + 0.15	0	0	0.3494(2)	0.3(1)	
		0	0	0.3499(2)	0.4(1)	
Al(3)	1	0.333(1)	0.1664(5)	0.06916(9)	0.41(6)	
		0.3326(9)	0.1663(5)	0.06918(8)	0.73(5)	
Al(4)	1	0	0	0.4508(2)	0.7(1)	
		0	0	0.4505(2)	0.8(1)	
O(1)	1	0.1566(3)	0.3133(5)	0.03309(6)	0.33(4)	
		0.1561(3)	0.3124(5)	0.03316(5)	0.68(4)	
O(2)	1	0	0	0.2955(1)	-0.4(1)	2.3(3)
		0	0	0.2957(1)	-0.5(1)	2.5(2)
O(3)	1	0	0	0.0930(1)	0.29(9)	
		0	0	0.0932(1)	0.33(8)	
O(4)	1	0.1631(3)	0.3263(6)	0.23612(6)	0.35(4)	
		0.1636(3)	0.3272(6)	0.23599(6)	0.58(4)	
O(5)	1	0	0	0.5	0.8(2)	0.6(3)
		0	0	0.5	2.2(2)	0.0(3)

[a] The results from the 11 K refinement are given above those from the 296 K refinement. [b] Isotropic temperature factor or U_{11} if an anisotropic temperature factor was refined. [c] $U_{11} = U_{22}$, $U_{12} = 0.5U_{11}$, and $U_{13} = U_{23} = 0$.

Table 4. Selected Distances (Å) for Ga$^+$-β''-Alumina

		11 K	296 K
Ga(1)−O(4)	3×	2.374(4)	2.389(5)
Al(1)−O(1)	6×	1.896(2)	1.895(2)
Al(2)−O(1)	3×	1.808(4)	1.809(4)
Al(2)−O(2)	1×	1.851(9)	1.860(9)
Al(3)−O(1)	2×	1.998(3)	1.995(3)
Al(3)−O(2)	1×	1.943(5)	1.949(5)
Al(3)−O(3)	1×	1.807(5)	1.811(5)
Al(3) O(4)	2×	1.867(3)	1.872(3)
Al(4)−O(4)	3×	1.789(4)	1.780(3)
Al(4)−O(5)	1×	1.693(7)	1.701(6)

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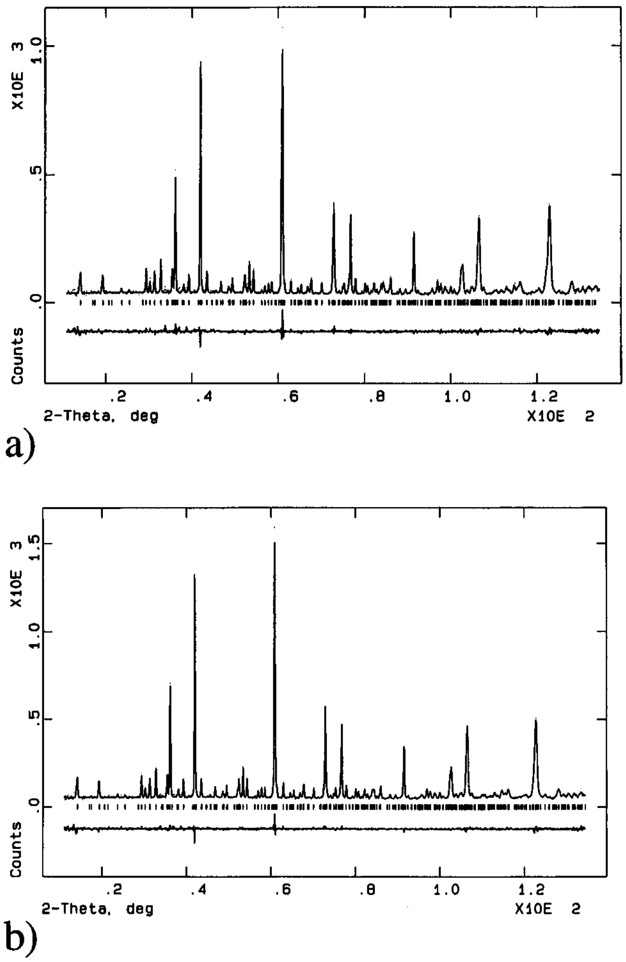

Figure 2. Rietveld refinement fits to the (a) 11 K and (b) 296 K neutron diffraction data for the Ga^+-β''-alumina. The calculated pattern (solid line), observed data (points), difference profile, and calculated reflection positions (vertical tic marks) are shown.

coordination environments like that found for Ga^+ in β''-alumina: in Tl_2O[35] and TlKO,[36] the thallium is 3+0-coordinated, with three oxygens at about 2.5 Å and no other oxygens within 4 Å of the cation. The coordination of In(I) and Tl(I) in the 6c site of β''-aluminas should be similar to that of Ga(I). Unfortunately, there have been no reports of structural studies for Tl^+- or In^+-β''-aluminas. However, there have been studies of Tl(I)-[37,38] and In(I)-β-aluminas.[39] The conduction plane in β-aluminas is different from that in β''-aluminas, and the systems are not strictly comparable; however, it is notable that In^+- and Tl^+-β-aluminas have longer crystallographic *c* axes (~0.2 Å longer) than would expected by comparison with β-aluminas containing alkali metal ions with similar ionic radii.

$GaZr_2(PO_4)_3$. Chemical analysis of product **C** showed that it contained ~33.1% zirconium and ~12.9% gallium, which compare well with the values expected for $GaZr_2(PO_4)_3$ (~34.0% Zr and ~13.0% Ga). The Ga K-edge XANES data for $GaZr_2(PO_4)_3$ (product **C**) and the reference material $ZnGa_2O_4$ are shown in Figure 1b. Both spectra show strong "white line" features; however, the Ga K absorption edge and the "white line" for the $GaZr_2(PO_4)_3$ sample are at ~5 eV lower energy than those for the reference material. The presence of a single white line in the XANES spectrum of the $GaZr_2(PO_4)_3$ sample, at about 5 eV lower energy than that for $ZnGa_2O_4$, indicates that the majority of the gallium in the sample is in an oxidation state of I. The TGA experiment performed on $GaZr_2(PO_4)_3$ in air showed that the material is stable toward oxidation up to ~500 °C. The majority of the weight gain occurred above 650 °C, and it was complete by 800 °C. The observed weight gain of ~3.05% between 450 and 800 °C is consistent with the oxidation of all the Ga(I) in $GaZr_2(PO_4)_3$ to Ga(III) (expected weight gain 2.98%).

Table 5. Summary of Crystal Data and Structure Refinement Details for $GaZr_2(PO_4)_3$

space group	$R\bar{3}c$
neutron wavelength/Å	1.47
T/K	296
fw	537.1
a/Å	8.72198(4)
c/Å	23.8820(2)
V/Å^3	1573.37(2)
Z	6
ρ_x/g cm^{-3}	3.40
color	off-white
abs corr	none required (flat-plate reflection geometry)
angular range (2θ)/deg	10.00−150.00
no. of data points	7000
no. of reflns	734
no. of refined params	30
R_{wp}/%	9.26[a]
R_p/%	6.16[a]
χ^2	4.227
R_{F^2}/%	3.6[a]

[a] $R_{wp} = \sum w(y_{io} - y_{ic})^2/\sum w(y_{io})^2$ (weights based on counting statistics); $R_p = \sum(y_{io} - y_{ic})^2/\sum(y_{io})^2$; $R_{F^2} = [\sum(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$ (F_o is estimated from the profile and may be biased by the model).

Table 6. Refined Structural Parameters for $GaZr_2(PO_4)_3$

atom	*x*	*y*	*z*	10^2U_{11}[a]	10^2U_{22}
Ga(1)	0	0	0	7.4(1)	3.9(2)[b]
Zr(1)	0	0	0.14956(3)	0.32(1)	
P(1)	0.2873(2)	0	0.25	0.51(5)	
O(1)	0.1687(3)	−0.0419(4)	0.1984(1)	0.80(9)	
O(2)	0.1973(3)	0.1717(3)	0.0957(1)	1.00(9)	

[a] Isotropic temperature factor or U_{11} if an anisotropic temperature factor was refined. [b] $U_{11} = U_{22}$, $U_{12} = 0.5U_{11}$, and $U_{13} = U_{23} = 0$.

Table 7. Selected Distances (Å) for $GaZr_2(PO_4)_3$

Ga(1)−O(2)	6×	2.801(3)	P(1)−O(1)	2×	1.531(3)
Zr(1)−O(1)	3×	2.049(3)	P(1)−O(2)	2×	1.535(2)
Zr(1)−O(2)	3×	2.070(2)			

A Rietveld refinement of the $GaZr_2(PO_4)_3$ structure was carried out using Hong's model for $NaZr_2(PO_4)_3$[12] as a starting point. Isotropic temperature factors were employed for all atoms except gallium. The crystallographic details are summarized in Table 5, the final coordinates and temperature factors from this refinement are reported in Table 6, some selected distances are given in Table 7, and the final profile fit is shown in Figure 3.

The coordination environment of Ga(I) in $GaZr_2(PO_4)_3$ is like that found in the alkali metal zirconium phosphates, with six oxygens all at the same distance from the cation, and the unit cell constants for $GaZr_2(PO_4)_3$ are very close to those for $KZr_2(PO_4)_3$.[13] The similarity of the coordination chemistry for Ga(I) and alkali metal ions in the zirconium phosphate host is in stark contrast to the sittuation in the β''-alumina system. Other univalent ions of the group IIIA metals also show this variation in behavior. For example, Tl(I) in Tl_2O, $Tl_3(TlO_3)$, and $Tl(BO_3)$ adopts highly asymmetric coordination environments

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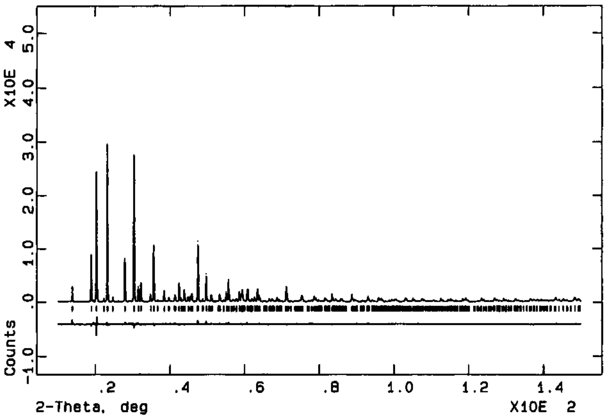

Figure 3. Rietveld refinement fit to the X-ray diffraction data for $GaZr_2(PO_4)_3$. The calculated pattern (solid line), observed data (points), difference profile, and calculated reflection positions (vertical tic marks) are shown.

similar to those found for Ga(I) in the β''-alumina, but Tl(I) in $TlVO_3$, TlH_2PO_4, and $Tl_2S_2O_3$ sits in sites with high coordination numbers.[40] The differences in coordination environment were correlated with the basicity of the oxygens coordinated to the Tl(I) by Brown and Faggiana.[40]

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Supporting Information Available: Complete tables of bond distances and angles (11 pages). Ordering information is given on any current masthead page.

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