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Crystal Structure of Li_3ABO_5 (A = Al,Ga; B = Si,Ge): A Novel Wurtzite Superstructure

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The crystal data for lithium aluminogermanate, Li_3AlGeO_5, are M_r 200.386, orthorhombic, $P2_1nb$, a = 4.881(1), b = 5.404(3), and c = 15.841(7) Å, V = 417.9 Å^3, Z = 4, D_x = 3.184 g cm^{-3}, λ(Mo$K\alpha$) = 0.71069 Å, $F(000)$ = 376.0, T = 298 K, R = 0.043, and R_w = 0.045 for 553 independent reflections. The structure consists of hexagonal close-packed oxide ions with cations ordered over one set of tetrahedral sites. It may also be described as a cristobalite-like sheet structure. The phases Li_3AlSiO_5, Li_3GaSiO_5, and Li_3GaGeO_5 are isostructural, as confirmed by Rietveld refinement.

Introduction

The new phase, Li_3AlGeO_5, was synthesized during a study of the system Li_2O–Al_2O_3–GeO_2 (*1*). From its stoichiometry, it was considered likely to be composed of infinite $(AlGeO_5)^{3-}$ sheets; since its X-ray powder diffraction pattern was unlike that of other layer phases, such as $Li_2Si_2O_5$, a full crystal structure determination was carried out. Subsequently, three other isostructural phases were synthesized and the structures of two, Li_3GaGeO_5 and Li_3GaSiO_5, confirmed by Rietveld refinement of X-ray powder data.

Experimental

Crystals of Li_3AlGeO_5 were grown by heating a mixture of $LiAlO_2$ and Li_2GeO_3 in the molar ratio 35 : 65 at 1200°C for 1 hr and then cooling to 1100°C at 1°C/min. Crystals were extracted from the cooled, crushed preparation under the petrographic microscope. X-ray diffraction data were obtained from a suitable small crystal (ca, 0.16 × 0.5 × 0.1 mm) on a Nicolet P3 four-circle diffractometer with Mo$K\alpha$ radiation (λ = 0.71069 Å; graphite monochromator). The orthorhombic unit cell dimensions were determined as a = 4.881(1), b = 5.404(3), and c = 15.841(7) Å using 14 reflections at 26–30° 2θ. Data were collected using the ω-scan method for 2θ in the range 0°–60° for a primitive set of unique reflections with $0(0,0) \leq h(k,l) \leq 7(8,23)$.

Prescan intensities (I_p) were used to select ω scan rates in the range 1.0 to 29.3° ω min^{-1}, the limiting values corresponding to $I_p < 150$ and $I_p > 2500$, respectively. The ω-scan width was 0.6° and backgrounds were measured at ±1° for each reflection.

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TABLE IA

Li_3AlGeO_5 COORDINATES

	x/a	y/b	z/c	U_{eq}
Ge	0^a	0.1610(1)	0.0975(1)	7(1)
Al	0.505(2)	0.3255(3)	0.2016(1)	5(1)
O(1)	0.596(2)	0.6395(9)	0.2119(4)	12(1)
O(2)	0.647(2)	0.190(1)	0.1097(3)	10(1)
O(3)	0.111(2)	0.3166(9)	0.0084(4)	10(1)
O(4)	0.103(2)	0.855(1)	0.1028(3)	11(1)
O(5)	0.142(2)	0.3133(9)	0.1902(4)	11(1)
Li(1)	0.99(1)	0.165(2)	0.3020(8)	$17(3)^b$
Li(2)	0.486(8)	0.343(2)	0.9955(8)	$15(3)^b$
Li(3)	0.51(2)	0.819(3)	0.0982(7)	$19(3)^b$

Note. e.s.d's are in parentheses. U × 10^3. $U_{eq} = (\frac{1}{3}) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

[a] Invariant to define origin.

[b] U_{iso}.

The resulting data contained 677 unique reflections, which were converted to structure amplitudes in the usual way. The intensities of the 00*10* and 320 reflections monitored at intervals of 50 measurements showed no significant variation. ψ-scans on the 200, 400, and 600 reflections revealed significant variation in intensity, and an absorption correction was applied (maximum and minimum transmission factors of 0.2855 and 0.0923, respectively).

Initial atomic parameters for the germanium and aluminum atoms were obtained by Patterson methods. The structure was subsequently solved using Fourier techniques and refined by full matrix least-squares with non-Li atoms anisotropic and Li atoms isotropic. Final $R = 0.043$, $R_w = 0.045$ for 553 reflections, and $I > 2.5\sigma(I)$. Maximum shift/e.s.d. in final least-squares cycle = 0.297 (for Al U_{12}). Maximum and minimum peak heights in the final difference map were 1.61 and -1.78 eÅ^{-3}. Scattering factors for neutral atoms were from the "*International Tables for X-Ray Crystallography*" (*2*). SHELX/SHELXS crystallographic programs were used for all calculations (*3, 4*). All figures were plotted using STRUPLO (*5*). A Honeywell DPS8/70 of the Computing Centre of the University of Aberdeen was used for computations.

Analogues, Li_3ABO_5 (A = Al,Ga, B = Ge,Si), were prepared by heating mixtures of $LiAO_2$ and Li_2BO_3, in a 1 : 1 molar ratio, at 1050°C for 2 days. Powder XRD analysis showed all except Li_3AlSiO_5 to be phase pure. X-ray diffraction data for Rietveld refinements were collected for these pure phases with a STOE STADI/P diffractometer in transmission mode using a small linear position sensitive detector, with Cu$K\alpha_1$ radiation (λ = 1.54056 Å; germanium monochromator). Scan ranges of $5° \leq 2\theta \leq 110°$ in steps of 0.02° were used in the refinements. The program used was the Pattern Fitting Structure Refinement

TABLE IB

ANISOTROPIC TEMPERATURE FACTORS × 10^3

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge	9(1)	9(1)	4(1)	0(1)	0(1)	1(1)
Al	8(1)	4(1)	2(1)	0(1)	2(2)	−1(2)
O(1)	16(3)	11(2)	9(2)	−4(2)	2(3)	−3(2)
O(2)	4(3)	16(2)	10(3)	−1(2)	2(2)	2(2)
O(3)	11(3)	13(2)	6(2)	2(2)	4(2)	−1(2)
O(4)	14(3)	10(2)	7(3)	3(2)	−1(2)	2(2)
O(5)	9(3)	13(2)	10(2)	−2(2)	−3(2)	1(2)

Note. e.s.d's are in parentheses.

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR Li_3AlGeO_5

Coordinations of cations			
Ge–O(4^1)	1.728(6)	O(4^1)–Ge–O(3)	114.5(3)
Ge–O(3)	1.730(6)	O(4^1)–Ge–O(2^2)	111.5(3)
Ge–O(2^2)	1.742(8)	O(4^1)–Ge–O(5)	106.4(2)
Ge–O(5)	1.820(6)	O(3)–Ge–O(2^2)	110.9(3)
		O(3)–Ge–O(5)	108.6(3)
		O(2^2)–Ge–O(5)	104.3(3)
Al–O(1^3)	1.757(6)	O(1^3)–Al–O(1)	114.5(4)
Al–O(1)	1.762(6)	O(1^3)–Al–O(2)	107.8(4)
Al–O(2)	1.772(7)	O(1^3)–Al–O(5)	108.0(4)
Al–O(5)	1.78(1)	O(1)–Al–O(2)	112.1(4)
		O(1)–Al–O(5)	107.2(4)
		O(2)–Al–O(5)	106.9(4)
Li(1)–O(4^4)	1.90(2)	O(4^4)–Li(1)–O(1^3)	114(2)
Li(1)–O(1^3)	1.95(5)	O(4^4)–Li(1)–O(5^4)	112(2)
Li(1)–O(5^4)	2.04(2)	O(4^4)–Li(1)–O(5^5)	111(2)
Li(1)–O(5^5)	2.08(2)	O(1^3)–Li(1)–O(5^4)	107(1)
		O(1^3)–Li(1)–O(5^5)	106(1)
		O(5^4)–Li(1)–O(5^5)	107(1)
Li(2)–O(3^6)	1.85(4)	O(3^6)–Li(2)–O(3^7)	113(1)
Li(2)–O(3^7)	1.94(2)	O(3^6)–Li(2)–O(4^7)	109(1)
Li(2)–O(4^7)	1.98(2)	O(3^6)–Li(2)–O(2^6)	104(1)
Li(2)–O(2^6)	2.14(2)	O(3^7)–Li(2)–O(4^7)	114(1)
		O(3^7)–Li(2)–O(2^6)	106(1)
		O(4^7)–Li(2)–O(2^6)	111(1)
Li(3)–O(3^8)	1.91(2)	O(3^8)–Li(3)–O(4)	110(2)
Li(3)–O(4)	1.98(8)	O(3^8)–Li(3)–O(1)	122(2)
Li(3)–O(1)	2.09(2)	O(3^8)–Li(3)–O(2^9)	110(2)
Li(3)–O(2^9)	2.13(3)	O(4)–Li(3)–O(1)	103(2)
		O(4)–Li(3)–O(2^9)	103(2)
		O(1)–Li(3)–O(2^9)	107(2)
Coordinations of oxygen			
O(1)–Al^{10}	1.756(6)	Al^{10}–O(1)–Al	124.0(4)
O(1)–Al	1.762(6)	Al^{10}–O(1)–Li(1^{10})	107(1)
O(1)–Li(1^{10})	1.95(5)	Al^{10}–O(1)–Li(3)	111(1)
O(1)–Li(3)	2.09(2)	Al–O(1)–Li(1^{10})	108(1)
		Al–O(1)–Li(3)	108(1)
		Li(1^{10})–O(1)–Li(3)	95(2)
O(2)–Ge^5	1.742(8)	Ge^5–O(2)–Al	121.1(4)
O(2)–Al	1.772(7)	Ge^5–O(2)–Li(3^1)	103(1)
O(2)–Li(3^1)	2.13(3)	Ge^5–O(2)–Li(2^{11})	107.7(7)
O(2)–Li(2^{11})	2.14(2)	Al–O(2)–Li(3^1)	109(1)
		Al–O(2)–Li(2^{11})	113.0(7)
		Li(3^1)–O(2)–Li(2^{11})	100(1)
O(3)–Ge	1.730(6)	Ge–O(3)–Li(2^{11})	116.0(8)
O(3)–Li(2^{11})	1.85(4)	Ge–O(3)–Li(3^{12})	117(1)
O(3)–Li(3^{12})	1.91(2)	Ge–O(3)–Li(2^{13})	112.9(8)
O(3)–Li(2^{13})	1.94(2)	Li(2^{11})–O(3)–Li(3^{12})	102(2)
		Li(2^{11})–O(3)–Li(2^{13})	104(1)
		Li(3^{12})–O(3)–Li(2^{13})	104(2)
O(4)–Ge^9	1.728(6)	Ge^9–O(4)–Li(1^{14})	118(1)
O(4)–Li(1^{14})	1.90(2)	Ge^9–O(4)–Li(2^{13})	113.4(8)
O(4)–Li(2^{13})	1.98(2)	Ge^9–O(4)–Li(3)	116.0(8)
O(4)–Li(3)	1.98(8)	Li(1^{14})–O(4)–Li(2^{13})	104(1)
		Li(1^{14})–O(4)–Li(3)	105(2)
		Li(2^{13})–O(4)–Li(3)	102(2)
O(5)–Al	1.78(1)	Al–O(5)–Ge	118.5(4)
O(5)–Ge	1.820(6)	Al–O(5)–Li(1^{14})	108.4(9)
O(5)–Li(1^{14})	2.04(2)	Al–O(5)–Li(1^2)	106.1(9)
O(5)–Li(1^2)	2.08(2)	Ge–O(5)–Li(1^{14})	109.5(9)
		Ge–O(5)–Li(1^2)	112.3(9)
		Li(1^{14})–O(5)–Li(1^2)	100(1)

Note. Symmetry operations: (1) $x, y - 1, z$; (2) $x - 1, y, z$; (3) $x, y - \frac{1}{2}, \frac{1}{2} - z$; (4) $x + 1, y - \frac{1}{2}, \frac{1}{2} - z$; (5) $x + 1, y, z$; (6) $x, y, z + 1$; (7) $x + \frac{1}{2}, 1 - y, 1 - z$; (8) $x + \frac{1}{2}, 1 - y, -z$; (9) $x, y + 1, z$; (10) $x, y + \frac{1}{2}, \frac{1}{2} - z$; (11) $x, y, z - 1$; (12) $x - \frac{1}{2}, 1 - y, -z$; (13) $x - \frac{1}{2}, 1 - y, 1 - z$; (14) $x - 1, y + 1, \frac{1}{2} - z$.

(PFSR) (Rietveld method) with starting parameters obtained from the single-crystal study of Li_3AlGeO_5. Refinement was carried out using the Pearson VII function with exponent $m = 2$ to model peak shape; peak full width at half maximum was described by the function

$$\mathrm{FWHM} = A*T(0,x) + B*T(1,x) + C*T(2,x),$$

where A, B, and C are refinable parameters and the $T(n,x)$ are shifted Tchebychev polynomials of degree n and $x = (2\theta - 2\theta_{\min})/(2\theta_{\max} + 2\theta_{\min})$. Cell parameters for Li_3AlSiO_5 were evaluated using the cell refinement program LATREF, based on 38 peaks.

Results and Discussion

Tables IA, IB, and II report final atomic coordinates, bond distances, and bond angles for the crystal structure of Li_3Al

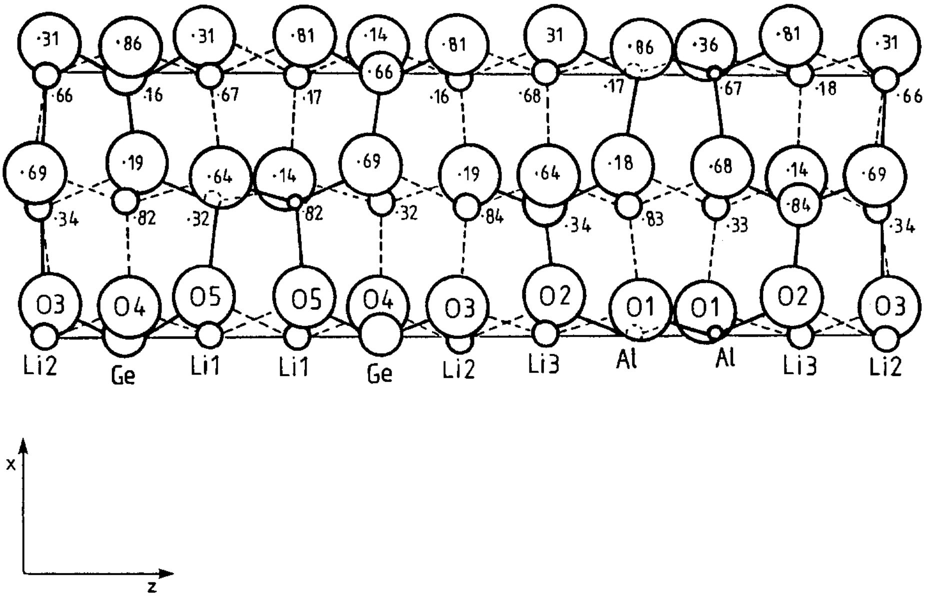

FIG. 1. Projection of the Li_3AlGeO_5 structure in the xz plane; the unit cell is outlined. The heights of the atoms are given as fractional coordinates; circles in decreasing order of size represent O, Ge, Li, and Al.

GeO_5.[1] A projection of the structure on the xz plane is shown in Fig. 1. Layers of oxide ions in an *AB* stacking sequence occur perpendicular to x. Cations are ordered over one set of tetrahedral sites; hence the structure may be described as a wurtzite superstructure.

Alternative structural descriptions may be obtained by considering the pattern of atomic linkage. All the atoms have tetrahedral coordination, with varying degrees of distortion. The AlO_4 tetrahedra share two corners with adjacent AlO_4 tetrahedra, to form infinite pyroxenoid chains parallel to y. Adjacent chains are linked, via Ge, to form sheets in the xy plane. Lithium atoms are of two types: those that act to link together adjacent aluminogermanate sheets, Li(2) and Li(3), and those that are located entirely within individual sheets, Li(1). Figure 2 presents a projection of the aluminogermanate sheets viewed along the

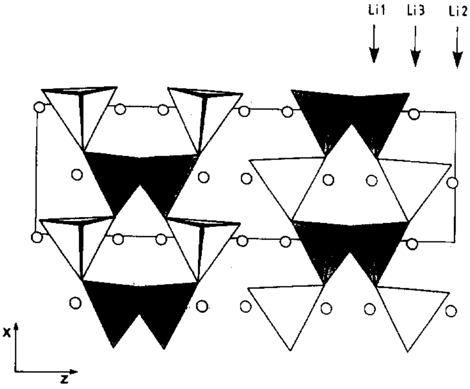

FIG. 2. Projection of the Li_3AlGeO_5 structure in the xz plane. The shaded triangles represent AlO_4 tetrahedra, unshaded GeO_4 tetrahedra.

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[1] Lists of structure factors have been deposited with the British Library Document Supply Centre. Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

TABLE III

CRYSTAL DATA FOR Li_3ABO_5 (A = Al,Ga; B = Si,Ge)

A,B	Ga,Ge	Ga,Si	Al,Ge	Al,Si
Spacegroup	$P2_1nb$	$P2_1nb$	$P2_1nb$	$P2_1nb$
Z	4	4	4	4
F.W.	243.13	190.63	200.39	147.89
a (Å)	4.9283(2)	4.8536(2)	4.8711(2)	4.7703(2)
b (Å)	5.4656(3)	5.4066(3)	5.3953(2)	5.3260(3)
c (Å)	15.8617(8)	15.6854(8)	15.8221(7)	15.5355(8)
V (Å^3)	427.25	411.61	415.82	394.70
D_x	3.740	3.232	3.186	2.623
$F(000)$	448.0	376.0	376.0	304.0
R	6.42	4.56	5.63	—
R_{wp}	8.31	6.95	7.50	—

y direction. The aluminate chains are connected via the germanate tetrahedra to form six-membered rings. Hence, each aluminate tetrahedron is bonded to two other aluminate tetrahedra via O(1) and to two germanate tetrahedra via O(2) and O(5), and may be classified as Q^4 in condensed aluminosilicate notation (*6*). Germanate tetrahedra, by contrast, are bonded to two aluminate tetrahedra and are therefore Q^2. Thus, each six-membered ring in the structure is composed of four quaternary, Q^4, aluminate tetrahedra and two binary, Q^2, germanate tetrahedra, as opposed to six Q^3 tetrahedra which is more common for phyllosilicates and phyllogermanates (*6*). An additional difference from such families of sheet structures is the presence of intralayer lithiums, giving an overall sheet stoichiometry $(LiAlGeO_5)^{2-}$.

Another way of looking at the structure is provided by a comparison with the cristobalite framework of SiO_2 or, in its stuffed derivative form, of Na_2BeSiO_4 (*7*). The

TABLE IV

FRACTIONAL COORDINATES FROM RIETVELD REFINEMENTS

	Li_3GaGeO_5			Li_3GaSiO_5			Li_3AlGeO_5		
	x/a	y/b	z/c	x/a	y/b	z/c	x/a	y/b	z/c
A	0.50(2)	0.331(2)	0.2009(7)	0.51(2)	0.327(1)	0.2015(3)	0.49(2)	0.323(3)	0.202(2)
B	0.000(†)	0.161(2)	0.0963(6)	0.000(†)	0.163(2)	0.0957(8)	0.000(†)	0.161(1)	0.0983(8)
O1	0.59(1)	0.66(1)	0.203(3)	0.60(1)	0.642(5)	0.214(2)	0.58(1)	0.651(9)	0.212(3)
O2	0.63(1)	0.185(8)	0.102(4)	0.654(9)	0.185(5)	0.106(2)	0.632(9)	0.196(6)	0.112(3)
O3	0.11(1)	0.307(8)	0.004(3)	0.10(2)	0.271(5)	0.014(2)	0.10(2)	0.322(8)	0.009(3)
O4	0.11(1)	0.852(9)	0.098(4)	0.103(9)	0.858(5)	0.094(2)	0.095(9)	0.860(6)	0.106(3)
O5	0.10(1)	0.31(1)	0.182(3)	0.14(1)	0.315(6)	0.201(2)	0.13(1)	0.300(8)	0.192(3)
Li1	0.99(7)	0.17(2)	0.307(8)	0.96(2)	0.17(1)	0.292(6)	0.99(6)	0.16(2)	0.303(7)
Li2	0.49(6)	0.33(2)	0.99(1)	0.51(5)	0.34(2)	0.994(4)	0.46(2)	0.36(2)	0.99(1)
Li3	0.50(9)	0.82(2)	0.095(8)	0.66(2)	0.63(2)	0.008(7)	0.51(5)	0.81(1)	0.093(9)

Note. Forty-five parameters varied in final refinement. e.s.d.'s are in parentheses.

[†] Invariant to define origin.

TABLE V

Calculated Bond Valences for Li_3ABO_5

	Al,Ge	Ga,Ge	Ga,Si
B–O1	0.8259	0.8280	1.1163
–O2	1.0731	1.0386	1.1382
–O2	1.1963	0.9429	0.9347
–O5	0.9353	1.2582	0.5485
Sum	4.0306	4.0677	3.7377
A–O2	0.8556	0.7700	0.9067
–O3	0.6160	0.7120	0.7338
–O4	0.7856	0.6617	0.6393
–O5	0.6843	0.5252	0.5429
Sum	2.9416	2.6689	2.8227
Li1–O1	0.2247	0.2065	0.2548
–O4	0.3011	0.3043	0.1780
–O5	0.2219	0.2074	0.2897
–O5	0.1979	0.1612	0.2151
Sum	0.9456	0.8794	0.9376
Li2–O2	0.1442	0.2546	0.2794
–O3	0.3536	0.2675	0.3111
–O3	0.3101	0.2081	0.2304
–O4	0.1901	0.2674	0.3448
Sum	0.9982	0.9976	1.1657
Li3–O1	0.3478	0.2417	0.1609
–O2	0.2121	0.1766	0.2376
–O3	0.1845	0.3638	0.3990
–O4	0.1571	0.2510	0.1161
Sum	0.9015	1.0331	0.9136

linkage of $(Al,Ge)O_4$ tetrahedra within the sheets of Li_3AlGeO_5 is very similar to that in Na_2BeSiO_4. The difference is that in Li_3AlGeO_5 the cristobalite-like component of the structure is confined to two dimensions, whereas it is three dimensional in Na_2BeSiO_4. On introduction of sodium vacancies into Na_2BeSiO_4, in solid solutions such as $Na_{1.8}(Ga_{0.2}Zn_{0.8})SiO_4$, high sodium conductivity results (*7*); it remains to be seen whether Li_3AlGeO_5 can be similarly modified to obtain high Li^+ conductivity.

The results of Rietveld refinements on Li_3AlGeO_5, Li_3GaGeO_5, and Li_3GaSiO_5 are given in Tables III and IV. Results on Li_3AlGeO_5 served to provide a comparison with the single-crystal results; lattice parameters showed small differences which might indicate a slightly different composition of the powder and single-crystal samples. Atomic coordinates agreed to within two e.s.d's, although the Rietveld e.s.d's were generally an order of magnitude greater than the single-crystal e.s.d's.

As a further check of the Li_3ABO_5 structure solution, a study of bond lengths/bond valences was carried out. Initially, bond valences, S, were calculated from the bond lengths, R, using the equation

$$S = \exp((R_0 - R)/B),$$

where R_0 and B are tabulated parameters (*8*). The calculated values are reported in Table V. Had there been any errors in the structure solution, the bond valence sum around each atom would differ greatly from its atomic valence; however, the results show the sums to be in good agreement with the oxidation state of each atom.

Rietveld results in Li_3GaGeO_5 and Li_3GaSiO_5 showed them to be isostructural with Li_3AlGeO_5. Li_3AlSiO_5 appears to be isostructural, although Rietveld refinement was not attempted since the sample contained additional phases.

Acknowledgment

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