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Crystal Structure of Lithium Heptaborate, $Li_3B_7O_{12}$

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$Li_3B_7O_{12}$의 결정구조

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Abstract

Single crystals of lithium heptaborate, $Li_3B_7O_{12}$(M_r=288.49), have been grown and their structure was determined by the x-ray powder diffraction and the single crystal diffraction technique. It is found that the borate anion consists of two $(B_3O_7)^{3-}$ and $(B_3O_8)^{5-}$ groups a unit cell. The space group was determined to be $P\text{-}1(C_i^1)$ with a=6.500(3) Å, b=7.839(2) Å, c=8.512(1) Å, α=92.07(2)°, β=104.97(2)°, γ=99.35(3)°, V=412.0(2) Å^3, Z=2, D_x=2.32 g cm^{-3}, MoKα, λ=0.71069 Å, μ=2.15 cm^{-1}, T=293 K. The structure was refined to R=0.0339 and wR=0.0882 for 2296 unique reflections by the single crystal diffraction. By the x-ray powder diffraction, we could obtain the similar results.

요 약

Lithium heptaborate, $Li_3B_7O_{12}$(M_r=288.49), 단결정을 성장시킨 후, 결정구조를 X-선 분말 회절법과 단결정 회절법을 이용하여 결정하였다. 구조해석 결과 단위포 내에 각각 두개의 $(B_3O_7)^{3-}$와 $(B_3O_8)^{5-}$ 그룹이 있음을 알 수 있었다. 공간군은 $P\text{-}1(C_i^1)$으로 결정되었고, a=6.500(3) Å, b=7.839(2) Å, c=8.512(1) Å, α=92.07(2)°, β=104.97(2)°, γ=99.35(3)°, V=412.0(2) Å^3, Z=2, D_x=2.32 g cm^{-3}, MoKα, λ=0.71069 Å, μ=2.15 cm^{-1}, T=293 K이었다. 최종 구조의 오차인자는 2,296개 회절 점에서 각각 R=0.0339과 wR=0.0882이었다. X-선 분말 회절방법으로 비슷한 결과를 얻을 수 있었다.

1. Introduction

Recently there has been an ambiguity about the presence of $2Li_2O_5 \cdot 5B_2O_3$ phase among the various lithium borate phases. X-ray difffraction intensity patterns of this phase were firstly reported in 1958,[1] without any crystal parameters. Lately Aidong *et al.* proposed that the 2:5 phase of Li_2O-B_2O_3 system in phase diagram should be changed to the new model of the 3:7 phase of lithium borate system. However, it is not clearly identified yet. To clarify this issue, we report the result of the structure analysis of the phase of the $Li_3B_7O_{12}$ crystal which was predetermined by x-ray powder diffraction technique.

2. Experimental

Crystals of the lithium borate were grown by the top seeded solution growth in a platinum crucible by using a vertical electric furnace.

During the growing, it is possible for the grown crystal to have two phases like as $Li_4B_{10}O_{17}$ (Sastry and Hummel,[1] 1958) and $Li_3B_7O_{12}$ (Tang *et al.*,[2] 1991). Firstly to determine approximate composition of the unknown phase, two glass samples (A and B) were made by squeeze quenching method. The composition of sample A was Li:B=2:5 in mole ratio, and the composition of sample B was Li:B=3:7. The glass samples were heat-treated at about 845°C for 24 hours. After the heat-treatment, sample A seemed to be partially decomposed and made liquid phase, but the sample B hardened like a sintered body. However, $Li_3B_7O_{12}$ single crystals were totally decomposed at the same temperature.

Powder samples were prepared from glass samples. Powder XRD pattern of sample A seemed to be overlap of those of sample B and $Li_3B_7O_{12}$ crystal. From this result, the composition of unknown phase could be thought to be near to $Li_3B_7O_{12}$. And so, the sintered body of composition B was used as a seed for crystal growth. The solution composition was Li:B= 10.65 wt%:89.34 wt%, and total batch in 70 cc crucible was 110 g after melting. The growth period was about 5 days after dipping of sintered seed. Several crystals of 2~3 mm in size were obtained.

This structure was solved by direct method and expanded by Fourier techniques. All atoms were refined anisotropically. All computations were performed using SHELXS 86[4] and SHELXL 93[5] crystallographic softwares. The experimental data are listed in Table 1. For Rietveld analysis we measured the 5101 data using the Cu Kα radiation. The scan width and time was 0.02° and 10 sec respectively. The data were refined by the FULLPROF (Rodriguez-Carvajal,[6] 1993).

Table 1. Experimental and refinement details

Crystal data	
$Li_3B_7O_{12}$	MoK_α radiation
M_r=288.49	λ=0.71069 Å
Triclinic	Cell parameters from 25 reflections
P-1	α=92.07(2)
a=6.500(3)	β=104.97(2)
b=7.839(2)	γ=99.35(3)
c=8.512(1)	θ=10-19°
V=412.0(2)	T=293 K
Z=2	sphere
D_x=2.32 g cm^3	0.7 mm(diameter)
μ=0.215 mm^{-1}	
Data collection	
Enraf Nonius CAD4 diffractometer	2,243 observed reflections [I>2σ(I)]
w/2θ scans	R_{int}=0.00
Scan width(°) 0.8 +0.35tanθ	θ_{max}=30.0°
Absortion collection; psi-scan	h=−9~8
intensity decay: none	k=0~11
2,485 measured reflections	l=−12~12
2,296 independent reflections	3 standard reflections monitored every 200 reflections
Refinement	
Refinement on F	$\Delta\rho_{max}$=0.54 eÅ^{-3}
R=0.0339	$\Delta\rho_{min}$=−0.42 eÅ^{-3}
wR=0.0882	Extinction correction: Empirical(Shelxl 93)
S=1.155	Extinction coefficient: 2.06
2,296 reflections	Atomic scattering factors from International Tables Vol. C Tables 4.2.6.8 and 6.1.1.4
200 parameters	
$w=1/\{\sigma^2(F_o^2)+(0.057P)^2+0.1214P\}$	
where $P=(F_o^2+2F_c^2)/3$	

3. Discussion

Atomic parameters and temperature factors from the final refinement are listed in Table 2, and the selective interatomic distances and bond angles are listed in Table 3. The structure is composed of two B_3O_7, B_3O_8 groups a unit cell respectively. This is shown in Fig. 1. In this structure two kinds of the boron-oxygen bonds exist; BO_3 and BO_4 polyhedra. The average bond lengths are 1.333 and 1.412 respectively. This is the same as those of the $Li_2O \cdot 2B_2O_3$ and the LiB_3O_5 compound. The anisotropic thermal parameters are shown in Table 4.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) with e.s.d.'s in parentheses, $B_{eq}=(4/3)\Sigma_i\Sigma_j\beta_{ij}a_i\cdot a_j$

	x	y	z	B_{eq}
O1	0.41056(11)	0.38984(9)	0.31399(10)	1.05(1)
O2	0.32782(11)	0.65749(9)	0.21152(9)	0.73(1)
O3	0.56068(11)	0.80105(9)	0.06956(8)	0.66(1)
O4	0.68442(11)	0.58478(9)	0.24209(9)	0.66(1)
O5	0.26183(11)	0.05632(9)	0.10754(8)	0.60(1)
O6	0.06008(11)	0.23923(9)	0.47433(8)	0.74(1)
O7	0.22529(11)	0.02784(9)	0.36887(8)	0.62(1)
O8	0.72954(11)	0.29573(9)	0.31020(9)	0.68(1)
O9	-0.05004(11)	-0.13684(9)	0.14522(8)	0.64(1)
O10	-0.03589(11)	0.17021(9)	0.18249(8)	0.69(1)
O11	0.06576(11)	0.46737(9)	0.29193(9)	0.82(1)
O12	0.63949(11)	0.86267(9)	0.35775(8)	0.72(1)
B1	0.2678(2)	0.50329(13)	0.27186(12)	0.63(1)
B2	0.0939(2)	0.03618(13)	0.20197(12)	0.51(1)
B3	0.6151(2)	0.42677(13)	0.28741(13)	0.62(1)
B4	-0.0423(2)	0.29068(12)	0.31362(12)	0.52(1)
B5	0.5587(2)	0.72407(13)	0.22309(12)	0.54(1)
B6	0.2150(2)	0.13765(13)	0.49422(12)	0.58(1)
B7	0.2488(2)	0.13224(12)	-0.03663(12)	0.54(1)
Li1	-0.0114(3)	0.6949(2)	0.3146(2)	1.02(2)
Li2	0.5173(3)	0.0760(2)	0.3070(2)	1.25(3)
Li3	0.2156(4)	0.7975(3)	0.0288(2)	

Table 3. Selective bond lengths and bond angles with e.s.d.'s in parentheses

B1-O1	1.378(1)	B4-O11	1.488(1)
B1-O2	1.368(1)	B4-O10	1.449(1)
B1-O11	1.354(1)	B5-O3	1.461(1)
B2-O5	1.506(1)	B5-O2	1.483(1)
B-O7	1.466(1)	B5-O4	1.456(1)
B2-O9	1.494(1)	B5-O12	1.478(1)
B2-O10	1.502(1)	B6-O6	1.363(1)
B3-O1	1.392(1)	B6-O7	1.369(1)
B3-O4	1.353(1)	B6-O12^{viii}	1.367(1)
B3-O8	1.354(1)	B7-O3^{i}	1.366(1)
B4-O6	1.461(1)	B7-O5	1.372(1)
B-O8^{ii}	1.483(1)	B7-O9^{v}	1.388(1)
Li1-O4^{ii}	1.953(2)	Li2-O12^{vii}	1.980(2)
Li1-O6^{iv}	1.968(2)	Li3-O2	1.988(2)
Li1-O9^{iii}	1.985(2)	Li3-O3	2.175(3)
Li1-O11	1.946(2)	Li3-O5^{iii}	2.063(2)
Li2-O5	2.026(2)	Li3-O9^{iii}	2.316(2)
Li2-O7	2.079(2)	Li3-O10^{vi}	1.925(2)
Li2-O8	2.019(2)		
O11-B1-O2	117.97(9)	O4^{ii}-Li1-O11	88.48(9)
O11-B1-O1	121.12(9)	O4-Li1-O6^{iv}	88.10(8)
O-B1-O1	120.89(9)	O11-Li1-O6	116.18(10)
O10-B2-O7	114.87(8)	O4^{ii}-Li1-O9^{iii}	92.29(9)
O10-B2-O9	109.35(8)	O11-Li1-O9^{iii}	126.36(10)
O7-B2-O5	102.13(7)	O6^{iv}-Li1-O9^{iii}	117.46(9)
O10-B2-O5	114.05(8)	O4^{II}-Li1-O2	132.69(9)

Table 3. Continued

O10-B2-O5	114.05(8)	O4^{ii}-Li1-O2	132.69(9)
O7-B2-O9	108.54(8)	O11-Li1-O2	59.10(6)
O5-B2-O9	107.43(7)	O6^{iv}-Li1-O2	135.44(9)
O8-B3-O4	125.27(9)	O9^{iii}-Li1-O2	83.06(7)
O8-B3-O1	115.15(9)	O12^{vii}-Li2-O8	116.85(10)
O4-B3-O1	119.58(9)	O12^{vii}-Li2-O5	116.53(10)
O10-B4-O8^{ii}	109.62(8)	O8-Li2-O5	109.73(10)
O10-B4-O6	112.37(8)	O12^{vii}-Li2-O7	103.69(9)
O8^{ii}-B4-O6	106.57(7)	O8-Li2-O7	132.69(10)
O10-B4-O11	109.50(8)	O5-Li2-O7	68.55(7)
O8^{ii}-B4-O11	108.94(8)	O12^{vii}-Li2-O1	165.77(10)
O6-B4-O11	109.76(8)	O8-Li2-O1	57.36(6)
O4-B5-O2	111.37(8)	O5-Li2-O1	77.26(7)
O4-B5-O3	109.69(8)	O7-Li2-O1	77.35(7)
O2-B5-O3	105.70(7)	O10^{vi}-Li3-O2	154.08(12)
O-B5-O12	113.20(8)	O10^{vi}-Li3-O5^{iii}	92.93(9)
O2-B5-O12	107.96(8)	O2-Li3-O5^{iii}	111.23(10)
O3-B5-O12	108.62(7)	O10^{vi}-Li3-O3	121.37(12)
O6-B6-O12^{viii}	120.93(9)	O2-Li3-O3	68.45(7)
O6-B6-O7	121.35(8)	O5^{iii}-Li3-O3	92.79(9)
O12^{viii}-B6-O7	117.67(8)	O10^{vi}-Li3-O9^{iii}	89.30(9)
O3^{i}-B7-O9^{v}	121.83(8)	O2-Li3-O9^{iii}	91.67(9)
O3^{i}-B7-O5	117.08(8)	O5-Li3-O9^{iii}	66.95(7)
O9^{vi}-B7-O5	121.07(8)	O3-Li3-O9^{iii}	144.90(10)

Symmetry codes: (i) 1-x, 1-y, -z; (ii) -1+x, y, z; (iii) x, 1+y, z; (iv) -x, 1-y, 1-z; (v) -x, -y, -z; (vi) -x, 1-y, -z; (vii) x, -1+y, z; (v) 1-x, 1-y, 1-z; (ix) 1+x, y, z.

Pulverized $Li_3B_7O_{12}$ powder pattern indexed with the following parameters a=6.4941(4) Å, b =7.8454(4) Å, c=8.5151(4) Å, α=92.08(3)°, β= 104.86(4)°, γ=99.44(3)°. The Rietveld refinement of this model converged to R_{wp}=0.143, R_w=0.081, R_B=0.709, R_F=0.909. Observed and calculated differences x-ray powder diffraction profile for $Li_3B_7O_{12}$ is shown in Fig. 2. This model is good agreement with that of the single crystal experiment. The intensity data between the Sastry's and this work are listed in Table 3. The peak position of this model is also good agreement with that of the Sastry's though it is two different compositions.

In this work, we carried out the structure analysis of the $Li_3B_7O_{12}$ phase using the single and powder diffraction technique. From our results we confirmed that the composition is Li $_3B_7O_{12}$ and the space group of this phase is *P-1* which was similar to the Aidong's.[3)]

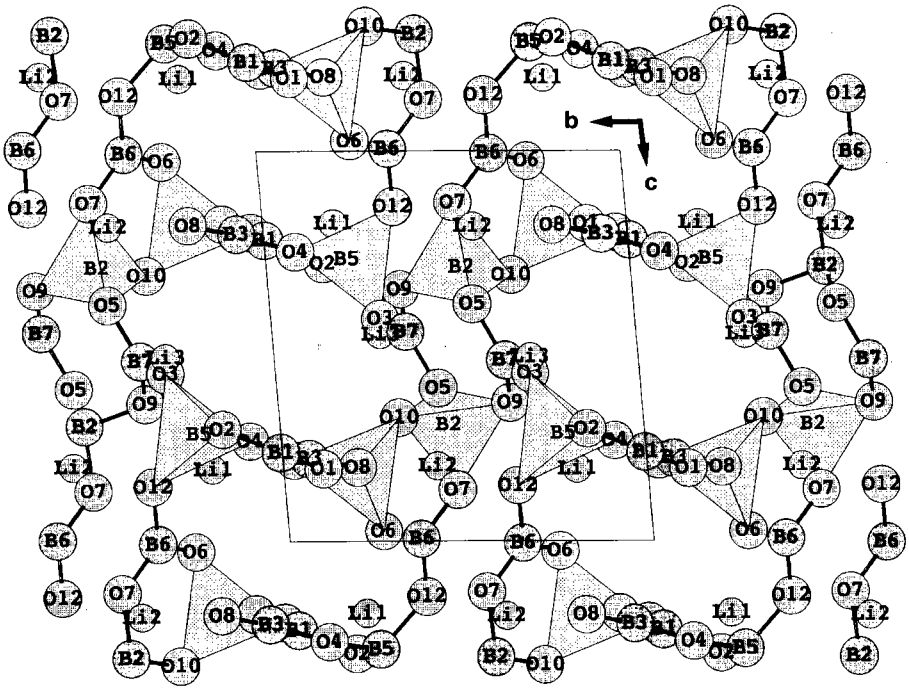

Fig. 1. A projection of the crystal structure of $Li_3B_7O_{12}$ onto the (100) plane.

Table 4. Anisotropic temperature factors (Å^2) with e.s.d.'s in parentheses

	U11	U22	U33	U12	U23	U13
O	0.0073(3)	0.0096(3)	0.0265(4)	0.0083(3)	0.0085(3)	0.0035(2)
O2	0.0051(3)	0.0085(3)	0.0143(3)	0.0047(2)	0.0029(2)	0.0009(2)
O3	0.0060(3)	0.0109(3)	0.0079(3)	0.0036(2)	0.0015(2)	0.0003(2)
O4	0.0058(3)	0.0064(3)	0.0144(3)	0.0029(2)	0.0030(2)	0.0014(2)
O5	0.0063(3)	0.0093(3)	0.0076(3)	0.0023(2)	0.0024(2)	0.0013(2)
O6	0.0090(3)	0.0132(3)	0.0070(3)	0.0013(2)	0.0011(2)	0.0062(2)
O7	0.0083(3)	0.0090(3)	0.0063(3)	0.0010(2)	0.0006(2)	0.0033(2)
O8	0.0048(3)	0.0068(3)	0.0149(3)	0.0028(2)	0.0031(2)	0.0016(2)
O9	0.0063(3)	0.0070(3)	0.0095(3)	0.0020(2)	0.0003(2)	−0.0002(2)
O10	0.0096(3)	0.0095(3)	0.0072(3)	0.0004(2)	0.0006(2)	0.0052(2)
O11	0.0059(3)	0.0070(3)	0.0196(4)	0.0030(2)	0.0057(2)	0.0009(2)
O12	0.0094(3)	0.0088(3)	0.0078(3)	0.0001(2)	−0.0008(2)	0.0033(2)
B1	0.0060(4)	0.0073(4)	0.0112(3)	0.0015(3)	0.0029(3)	0.0012(3)
B2	0.0060(4)	0.0069(4)	0.0064(4)	0.0009(3)	0.0013(3)	0.0013(3)
B3	0.0053(4)	0.0079(4)	0.0103(4)	0.0013(3)	0.0019(3)	0.0015(3)
B4	0.0045(4)	0.0065(4)	0.0089(4)	0.0015(3)	0.0016(3)	0.0012(3)
B5	0.0051(4)	0.0063(4)	0.0089(4)	0.0022(3)	0.0017(3)	0.0007(3)
B6	0.0060(4)	0.0081(4)	0.0078(4)	0.0013(3)	0.0020(3)	0.0013(3)
B	0.0066(4)	0.0061(4)	0.0077(4)	0.0007(3)	0.0019(3)	0.0009(3)
Li1	0.0131(8)	0.0125(8)	0.0143(8)	0.0023(6)	0.0045(6)	0.0046(6)
Li2	0.0116(8)	0.0123(8)	0.0221(9)	0.0032(6)	0.0018(7)	0.0014(6)
Li3	0.0248(10)	0.0142(8)	0.0152(8)	0.0025(7)	−0.0036(7)	0.0062(7)

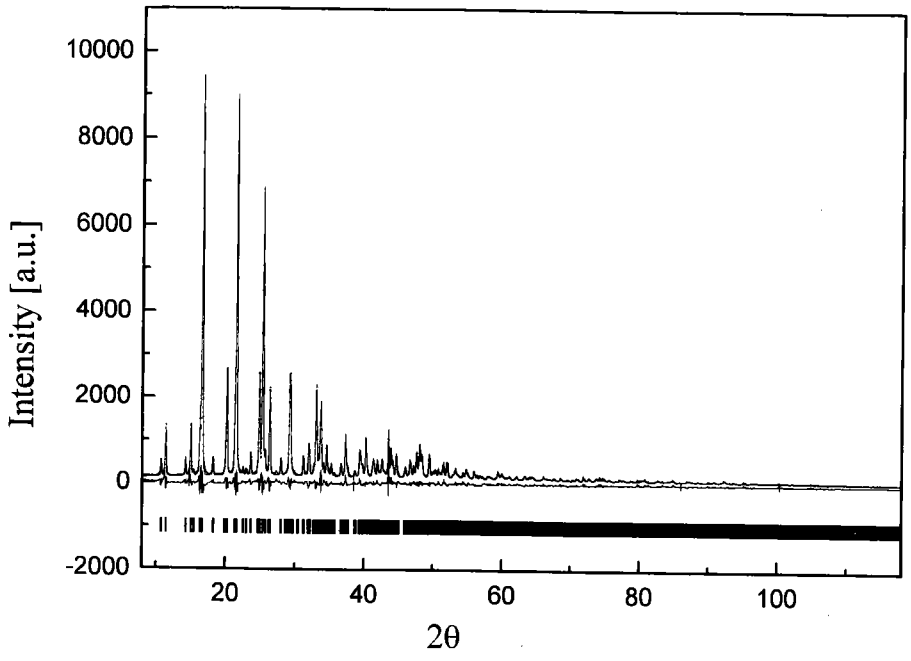

Fig. 2. Rietveld refinement patterns for the conventional x-ray data of pulverized $Li_3B_7O_{12}$ single crystal.

Table 5. Comparison of the reflecting planes by x-ray powder diffraction between Sastry & Hummel and this work

Sastry and Hummel[1]		This work		
d	Intensity	d	h k l	Intensity
		8.1987	0 0 1	4
7.7200	10	7.7087	0 1 0	13
6.2000	5	6.1706	1 0 0	3
5.8800	15	5.8624	0 1-1	14
5.4000	20	5.3984	0 1 1	18
5.3200	60	5.3045	1-1 0	100
4.8700	5	4.8509	1-1-1	3
		4.3993	1 0 1	4
4.3800	35	4.3692	1 1-1	27
		4.1403	1-1 1	16
4.1100	80	4.0994	0 0 2	100
3.7600	5	3.7498	0 1-2	6
3.5750	30	3.5698	1-2 0	16
		3.5656	1 1 1	13
3.5100	100	3.5017	0 1 2	82
3.4620	10	3.4528	1 1-2	7
3.3780	35	3.3703	1-2-1	25
3.1900	5	3.1837	1-2 1	3
3.0510	40	3.0455	1 2-1	24
		3.0333	1 2 0	16
2.8640	7	2.8578	2 0-2	6
2.7940	12	2.7929	2 1-1	3
		2.7889	1 0-3	6
2.7080	40	2.7074	1 1 2	13
		2.6992	0 2 2	14

Table 5. Continued

Sastry and Hummel[1]		This work		
d	Intensity	d	h k l	Intensity
2.6570	20	2.6523	2-2 0	17
		2.6454	0 1-3	5
2.5940	10	2.5892	2 1-2	8
2.5430	5	2.5395	1-3 0	3
2.4830	5			
2.4090	15	2.4067	1-3 1	4
		2.4051	2-2 1	9
2.3270	5	2.3229	2-1-3	1
2.2860	15	2.2837	1 0 3	7
2.2380	15	2.2340	1 3 0	12
2.1800	10	2.1760	2-3 0	5
2.1520	10	2.1495	3-1-1	2
2.1440	10	2.1474	0 2 3	4
2.0780	20	2.0730	3 0-2	15
2.0600	12	2.0569	3 0 0	7
2.0250	10	2.0235	2-3-2	4
		2.0227	0 1-4	3
1.9710	5	1.9701	2 2-3	2
1.9440	8	1.9415	0 1 4	5
1.9260	10	1.9209	2-1-4	4
1.8900	20	1.8870	1-3-3	8
1.8790	15	1.8749	0 2-4	7
1.8390	12	1.8380	2-1 3	7
1.8130	5	1.8096	2-3-3	2
1.7950	5	1.7932	3-3-1	3
1.7740	8	1.7729	2-4-1	4
1.7570	8	1.7543	1-4-2	3

Table 5. Continued

Sastry and Hummel[1)]		This work		
d	Intensity	d	h k l	Intensity
1.7190	5	1.7165	2-4 1	2
1.6850	3	1.6839	3-1-4	2
1.6730	4			
1.6690	2	1.6702	3-3 1	3
1.5880	2	1.5885	2-3-4	1
1.5540	5	1.5518	2 2 3	2
1.5400	5	1.5384	0 5-1	2
1.5160	3	1.5136	3 3-2	1
1.4940	3	1.4903	2-5 0	1
1.4680	3	1.4656	0 4-4	<1
1.4490	4	1.4482	3 1-5	1
1.4130	3	1.4112	2-3 4	1
1.3680	3	1.3665	1-5 3	<1
1.3280	2	1.3268	0 1 6	1
1.3120	2	1.3109	4-3-4	1
1.3010	2	1.2994	3-1-6	<1
1.2840	3	1.2840	0 5-4	<1
1.2760	3	1.2743	5-2-1	1
		1.2342	1-6-2	1
		1.2002	5-3-3	<1
		1.1947	4 3-4	1
		1.1860	0 5 4	<1
		1.0661	2-6 4	<1
		1.0435	1 6-5	<1

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