

**Compressibility and crystal structure of andalusite at high pressure**

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The unit-cell dimensions and crystal structure of andalusite  $\text{Al}_2\text{SiO}_5$  have been refined from X-ray data on single crystals mounted in a diamond anvil cell at pressures of 12, 25, and 37 kbar. Structure refinements with anisotropic temperature factors yielded weighted  $R$  factors of 3.4, 4.9, and 5.2% respectively. The bulk modulus of andalusite is  $1.35 \pm 0.10$  mbar and the axial compression ratios of orthorhombic unit-cell axes  $a:b:c$  are approximately 2.1:1.5:1.0. The relatively greater compressibility of the  $\text{Al}(1)-\text{O}_D$  bond results in  $a$  being the most compressible axis. Those bonds that compress  $>3\sigma$  between 1 bar and 37 kbar at room temperature, are the bonds that also expand significantly between 25 and 1000°C at room pressure. Polyhedral bulk moduli for the  $\text{Al}(1)$  octahedron, the  $\text{Al}(2)$  trigonal bipyramid and the Si tetrahedron are  $1.3 \pm 0.2$ ,  $1.6 \pm 0.5$ , and  $4.1 \pm 1.5$  mbar, respectively. Thus, the aluminum polyhedra are significantly more compressible than the silicon tetrahedron. The omega step-scanning technique of X-ray intensity data collection results in a significant improvement in accuracy and is recommended for structure determination with the diamond-anvil high-pressure cell.

**Introduction**

High pressure structure determination contain valuable data on the equations of state, interatomic forces and chemical bonding in minerals. The  $\text{Al}_2\text{SiO}_5$  polymorphs, andalusite, sillimanite and kyanite, provide an interesting system where aluminum occurs in three types of coordinations; in addition to the octahedral coordination found in all three minerals, aluminum also occurs in tetrahedral coordination in sillimanite and in five-fold trigonal bipyramidal coordination in andalusite. Knowledge of the response to pressure and temperature of these different types of Al-O bonds in the presence of relatively rigid  $\text{SiO}_4$  tetrahedra is necessary for an understanding of the stability relations and phase transformation within the  $\text{Al}_2\text{SiO}_5$  system. The temperature effects on the crystal structures of andalusite, sillimanite and kyanite have been determined by Winter and Ghose (1979). The elastic constants of andalusite and sillimanite have been determined by Vaughan and Weidner (1978), who used the Brillouin scattering technique. From infrared and Raman

spectroscopic data, the phonon spectra of andalusite and their temperature dependence have been determined and interpreted on the basis of a rigid-ion model by Iishi et al. (1979).

In this paper are presented data on the high pressure structural response of andalusite to 37 kbar, as well as correlations between high-pressure changes and high-temperature response, elasticity, and phonon spectra. It has been possible to observe directly the structural elements of andalusite that are responsible for the compressibility and, hence, the elastic constants. The present data on andalusite at high-pressure, combined with high-temperature data of Winter and Ghose (1979), may be used to test the inverse relationship between structural responses due to temperature versus pressure (Hazen and Finger, 1982). Andalusite is a light-atom structure with a small unit-cell and orthorhombic symmetry and thus also constitutes a test case for the improvement in accuracy of X-ray intensity data collected at high pressure by the omega step-scanning technique. The resulting improvement in









Table 4d. Calculated and observed structure factors for andalusite  
at 37 kbar; continuous scan data.

H OBS		CALC		H OBS		CALC		H OBS		CALC		H OBS		CALC		H OBS		CALC				
H 0 0		H 6 0		H 5 1		H 3 2		H 0 3		H 8 3		H 8 4										
0	0	3200	15	170	178	7	303	307	5	168	169	5	297	289	3	138	136	0	652	666		
2	334	201				8	84	84	6	104	77	7	112	116	5	118	106	1	96	110		
4	377	373	H 7 0		9	272	264	9	79	66	9	141	135	6	132	113	2	93	78			
6	448	441						10	96	92	H 1 3		H 9 3		4	234	229	5	92	93		
8	597	595	1	282	290	H 6 1											6	163	156			
10	69	49	2	71	48	2	133	142	H 4 2		3	312	324	0	82	78	H 9 4					
			3	326	321	4	68	62	0	384	374	4	159	166	3	271	270					
			5	224	228	6	108	108	5	931	950	5	401	385	5	245	239	1	96	107		
			7	183	176	7	120	117	3	101	84	6	68	5	H 10 3		2	222	224			
1	453	434	8	96	115	8	82	79	4	565	579	7	141	142			3	132	124			
2	375	366	9	99	111				5	129	133	8	155	163	3	76	41	4	154	157		
3	534	510	H 8 0		H 7 1					9	70	47	H 11 3		5	168	164					
4	311	318						6	387	383	H 2 3											
5	508	479	4	289	300	0	185	166	7	79	65											
6	272	253	5	115	116	1	275	270	10	295	296	2	135	145	0	82	53					
7	96	107	2	80	18	2	80	18	H 5 2		4	79	67	1	122	124	0	164	166			
8	137	137	3	192	200	3	192	200	1	182	167	6	150	151			1	107	117			
9	103	107	4	162	170	4	162	170	2	470	478	8	140	130	H 1 4		2	258	255			
10	94	102	5	222	229	5	222	229	3	393	400	10	97	90	7	68	77					
11	121	119	6	77	46	6	77	46	5	227	226	H 3 3		8	85	104						
			7	205	217	7	205	217	7	120	135				9	91	83	7	94	67		
			8	92	92	8	92	92	8	150	151	0	280	290	10	92	88					
			9	113	110	9	113	110	10	118	122	1	357	366	H 2 4							
			5	259	269	H 8 1					2	67	74	5	150	143	4	97	86			
0	155	147	6	63	0	1	124	144	0	419	415	3	284	315	6	405	390	6	72	41		
1	407	410	7	144	148	2	193	202	4	246	238	4	246	238	7	77	79	7	195	195		
2	733	734	8	208	212	3	129	127	5	172	175	5	172	175	7	206	207					
3	720	683	9	96	92	6	120	127	7	206	207	8	115	120	9	270	270	8	115	120		
4	48	17	11	96	92	7	82	56	4	497	523	9	234	246	10	241	252	10	241	252		
5	173	173	H 1 1					5	312	336	10	78	59	H 3 4		2	118	120				
6	517	518	0	44	439				7	81	68	H 4 3		4	78	52						
7	113	103	1	316	327				8	295	300				5	81	26					
8	304	335	2	44	45				9	154	149	1	266	282	6	66	64	7	115	109		
9	304	335	3	418	434				H 7 2		2	165	164	7	443	448						
10	324	318	4	373	328	3	314	330	3	162	155	3	162	155	8	138	143					
11	105	75	5	495	488	5	294	289	4	61	32	4	61	32	9	138	143	0	68	61		
			7	189	194	H 10 1					5	178	201				1	190	198			
			8	116	125	2	87	81	1	205	199	6	96	90				2	83	21		
			11	172	173	3	101	74	5	255	261	7	287	279	6	96	90	3	167	156		
			H 2 1					9	251	253	7	200	198	7	200	198	4	163	170			
			1	40	41	4	72	27	9	251	253	9	94	88	9	94	88	5	167	173		
			2	138	148	6	98	60	H 8 2					H 4 4		1	66	93				
			4	93	116				0	166	161	H 5 3		2	76	55						
			6	142	139				2	196	192	0	170	166	4	589	571					
			8	116	121	4	769	735	3	96	89	1	468	452	5	91	73					
			10	126	125	6	569	560	4	263	257	3	140	130	6	185	196	1	136	133		
			11	83	65	8	76	66	5	166	162	4	130	145	7	72	73	2	135	142		
			H 3 1					6	305	291	6	74	68	8	164	157	3	70	71			
			0	389	371	10	247	230	7	74	77	6	74	68								
			1	360	363	H 1 2					7	291	289	H 4 4		1	66	93				
			3	372	344	0	166	161	H 8 2					2	76	55						
			4	278	262	2	196	192	0	166	161	0	170	166	4	589	571					
			9	266	263	3	96	89	2	196	192	1	468	452	5	91	73					
			11	137	147	4	263	257	3	96	89	5	178	201	6	185	196	1	136	133		
			H 4 1					5	166	162	6	96	90	7	72	73	2	135	142			
			0	370	291	6	98	60	6	305	291	7	200	198	8	164	157	3	70	71		
			1	259	265	H 1 2					9	94	88									
			3	372	344	0	166	161	H 8 2					H 5 3		1	66	93				
			4	278	262	2	196	192	0	166	161	0	170	166	2	76	55					
			9	266	263	3	96	89	2	196	192	1	468	452	4	589	571					
			11	137	147	4	263	257	3	96	89	5	178	201	5	91	73					
			H 5 1					5	166	162	6	96	90	6	185	196	1	136	133			
			0	389	371	6	98	60	6	305	291	7	200	198	7	72	73	2	135	142		
			1	360	363	H 0 2					9	94	88	8	164	157	3	70	71			
			3	372	344	0	166	161	H 8 2													
			4	278	262	2	196	192	0	166	161	0	170	166	1	468	452	4	163	170		
			9	266	263	3	96	89	2	196	192	1	468	452	5	91	73	5	167	156		
			11	137	147	4	263	257	3	96	89	5	178	201	6	185	196	4	163	170		
			H 4 1					5	166	162	6	96	90	7	72	73	5	167	156			
			0	370	291	6	98	60	6	305	291	7	200	198	8	164	157	4	163	170		
			1	259	265	H 1 2					9	94	88				5	167	156			
			3	372	344	0	166	161	H 8 2					H 5 3		1	66	93				
			4	278	262	2	196	192	0	166	161	0	170	166	2	76	55					
			9	266	263	3	96	89	2	196	192	1	468	452	4	589	571					
			11	137	147	4	263	257	3	96	89	5	178	201	5	91	73					
			H 4 1					5	166	162	6	96	90	6	185	196	1	136	133			
			0	370	291	6	98	60	6	305	291	7	200	198	7	72	73	2	135	142		
			1	259	265	H 1 2					9	94	88				3	70	71			
			3	372	344	0	166	161	H 8 2					H 5 3		1	66	93				
			4	278	262	2	196	192	0	166	161	0	170	166								