Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

The interaction of defects in mayenite structure

Sergey N. Shkerin,[a]* Ekatherina S. Ulyanova,[b] Sergey V. Naumov,[c] Aleksandr N. Shmakov[d,e], Anna S. Tolkacheva,[a,f]

[a] *Institute of High-Temperature Electrochemistry, UB RAS, 620137 Ekaterinburg, Russia*

[b] *Institute of Solid-State Chemistry UB RAS, 620137 Ekaterinburg, Russia*

[c] *Mikheev Institute of Metal Physics, UB RAS, 620990 Ekaterinburg, Russia*

[d] *Boreskov Institute of Catalysis, SB RAS, 630090 Novosibirsk, Russia*

[e] *Novosibirsk National Research State University, 630090 Novosibirsk, Russia*

[f] *INMT Ural Federal University, 620002 Ekaterinburg*

Corresponding author: a.s.tolkacheva@urfu.ru

Table S1. Raman activity of mayenite after air, Ar and H_2 treatment

initial						H_2 treated								ceramic		comments
Ar		Air centre		Air periphery		Ar centre		Ar centre		Air centre		Air periphery		at HT		
ν	D half width	ν	D half width	ν	D half width	ν	D half width	ν	D half width	ν	D half width	ν	D half width	ν	D half width	
						54.3	3.1	53.7	3.7	54.7	3.6	54.2	4.4			L_1
61.7	4.0	61.9	5.3	60.0	7.3	59.4	6.9	59.0	7.8	59.7	7.4	59.8	8.1			
67.5	67.5			67.1	10.7	69.3	11.7			67.9	11.4	68.7	12.1			L_2
75.2	10.7	74.0	16.3	73.4	10.5	76.1	7.8	73.1	18.9	76.7	10.7	77.2	9.4			
84.3	6.4	87.7	12.4	83.6	10.3	83.3	6.9	83.8	5.0	84.3	6.5	84.5	7.2	89.2	7.5	X_1
92.3	6.7	93.4	5.8	93.8	15.9	91.4	8.5	92.7	10.7	92.6	12.1	91.7	8.9	95.1	11.5	X_2
		97.4	5.9			96.4	8.2									
100.7	9.9	101.3	6.1			99.5	5.2	100.6	8.0	101.7	8.4	99.4	10.8			X_3
107.7	7.2	107.3	11.1	107.4	16.4	105.9	9.0			107.7	6.4	108.0	5.4	107.2	19.6	
115.6	11.3	117.1	10.6	118.1	7.1	115.4	4.3	115.4	13.1	113.5	11.4	112.2	32.7	–	–	MO_6
125.1	8.2	125.5	9.8	125.7	28.6			124.2	7.0	125.8	16.9			126.1	21.8	X_4
131.5	7.3	132.0	8.3	133.7	27.3	131.7	48.8	130.6	7.8			136.9	20.8	139.3	30.3	
140.0	14.0	138.1	9.6	141.8	16.0			137.5	8.1	140.8	17.6	140.6	5.0	144.7	14.6	
		144.6	10.1					143.9	12.8			147.8	13.0			
		150.4	7.9													
155.5	24.6	158.1	21.0	154.1	20.0	157.4	14.5	155.4	14.6	159.9	25.4	159.2	15.0	156.4	13.1	X_5
												167.0	24.8	166.1	10.9	
173.3	14.1	175.4	23.2	174.7	25.8	174.7	28.3	173.8	31.5	178.1	17.5	174.0	15.8	175.3	19.0	G_1 E_g T(AlO_4)
180.9	10.1															G_2
186.7	6.1									188.0	12.5	185.9	19.4	192.6	15.7	E_g T(Ca^{2+}) AlO_4
		199.0	15.5	200.3	13.7					198.1	13.4	202.6	14.2			
						227.2	11.7									
237.0	21.5	238.2	20.9	237.8	20.0	239.0	16.7	231.9	16.6							CaO_6
						249.5	11.5	246.8	24.5	243.4	25.7	248.7	28.9	- !	- !	E_g

266.8	29.2	267.7	29.8	267.4	29.7	263.9	19.1	265.4	13.7	265.8	20.4	267.1	13.9	261.6	30.1	G_3 T_{2g} $T(Ca^{2+})$ AlO_4
292.0	21.3	294.4	24.1					283.1	43.9	298.9	34.9			281.3	21.0	G_4
								302.3	18.6			301.7	43.9	298.7	20.7	E_g
310.2	22.2	310.9	20.8	309.2	13.0	309.5	14.2	310.3	13.4	311.6	17.7	312.4	17.5	310.1	7.5	ν_2, AlO_4
				314.0	39.1			318.3	7.8	322.9	9.7			319.0	21.9	
326.0	15.7	327.5	20.1	326.3	53.4	324.3	47.7	328.6	27.5	329.7	16.0	332.6	20.3			G_5 $R(AlO_4)$ A_{1g}
														333.3	38.7	
340.2	25.7	344.2	18.6	346.8	11.5	332.7	14.6			343.8	31.7	347.4	20.1	335.5	4.9	G_6
367.7	26.6					367.2	15.6	360.3	45.4	370.3	39.5	359.8	23.8	379.9	32.6	AlO_4
						384.9	23.0	387.3	16.2	401.7	50.1	377.4	24.3			
								410.8	5.3			396.2	26.5			
								416.4	4.1			414.2	16.0			
										434.4	22.5	431.2	33.4			
										440.4	9.4					
451.3	42.0															
472.0	54.4	476.8	56.3	478.6	66.0											
493.2	28.3	494.7	32.2	494.8	32.7					499.7	34.2					
518.6	19.2	519.3	20.1	519.8	20.2	520.3	12.4	520.2	19.8	516.6	17.1	520.3	17.7	509.0	45.4	G_7 T_{2g}
						521.0	28.0	520.8	10.2	520.8	11.2	520.2	9.8	510.5	24.4	ν_4 AlO_4
								524.1	44.1	525.3	15.3	521.2	32.9	517.2	90.9	
										525.3	32.0					
531.5	53.4															AlO_6
533.1	17.2	534.4	16.4	535.0	16.4											E_g
550.8	13.8	550.4	16.5	550.6	15.9	542.8	78.4			553.1	13.7	552.6	98.4	- !	- !	
568.9	21.1															
576.9	15.8	575.6	28.8	574.9	33.6					575.6	26.3					
588.7	11.0							587.6	41.1							
										601.3	15.4					
612.2	36.0			611.2	15.0					616.1	18.3					
652.7	24.2	653.6	21.3	654.7	23.0											
681.1	20.5	680.8	13.6	680.8	20.0											

		690.4	41.5	710.3	57.0									706.0	6.3	
		719.5	30.1											714.9	14.3	
738.8	12.2	737.6	16.2	740.8	15.4							739.8	10.8	734.1	20.2	incaged oxygen
		749.0	21.5	754.3	15.4	759.0	11.3			754.1	41.2					
769.8	14.7	769.9	14.8	769.6	14.9	770.3	10.7	770.3	9.9	771.3	10.0	770.2	9.8	760.4	27.5	G_8 A_{1g}
773.2	35.6	773.1	35.2	774.3	31.4	772.9	19.0	772.2	19.6	772.6	17.7	772.0	17.4	784.4	35.1	ν_1, AlO_4
								776.5	6.7			775.1	37.0			
						779.1	49.1	776.5	44.9	778.0	32.2					
826.0	45.2	822.1	45.8	838.1	88.0	828.6	29.6	833.3	47.4	832.6	38.5	829.4	52.5	815.8	28.3	G_9
841.9	9.4			848.3	13.1	843.3	16.7	841.4	11.9	843.8	22.2	840.5	13.6			T_{2g} AlO_4
												844.	4.0			
		855.0	40.8			856.7	8.3	859.0	14.8	857.0	7.5	856.6	6.9	843.2	17.7	G_{10}
863.4	12.4	863.6	12.7	863.0	13.3	864.8	19.5			863.4	11.8	864.5	13.8			T_{2g} AlO_4
				871.6	17.5											
879.1	26.2	880.1	28.8	883.0	16.8	884.3	17.2	883.8	11.5	884.3	25.0	883.7	16.5	861.9	19.4	G_{11}
								884.3	24.7	884.7	13.7			877.8	49.7	T_{2g}
				895.4	29.7	898.1	13.1					895.9	47.6			ν_3, AlO_4
		907.7	20.6													
914.3	25.7	919.4	14.5	917.2	21.2	915.5	24.6	916.3	23.5	916.5	17.3	918.6	17.9	+		G_{12} E_g AlO_4
		951.3	13.9													incaged oxygen
		973.6	36.2	972.9	37.2											
		1036.5	10.4													

Table S2. A comparison of bands correlation for calcium silicates and aluminates of garnet structure

Grossular [17]/[18] $Ca_3Al_2(SiO_4)_3$				Mayenite $Ca_{3-x}(Ca, Al)_2(AlO_4)_3$				comment
	A_{1g}	E_g	F_{2g}		A_{1g}	E_g	F_{2g}	
$(Si\text{-}O)_{str.}$			1007 /1000	Si → Al		916		
		904					883	ν_3 AlO_4
	880 /876						863	
			848 /821				830	
			827 /777		770			ν_1 AlO_4
$(Si\text{-}O)_{bend.}$			630 /623	Si → Al			520	ν_4 AlO_4
		592						
			582				340	
	550 /540							
		529 /502						
			512					
			483					
		420						
$R(SiO_4)^{4-}$			389 /405	Si → Al	326		326	
	376	373 /364				311		ν_2 AlO_4
			351					
			333					
		320						
$T(SiO_4)^{4-}$		181 /172		Si → Al		173		E_g T-AlO_4
$T(Ca^{2+})$		186 /194_w		Si → Al		190		
			280 /268				267	

			247 /232					CaO_6
Assumed to be T(Ca^{2+}) [18]			– /135				132	X_4
			– /108				108	X_3

S3. Data on the frequency and half-width of the observed reflections for the luminescence of the studied single crystal samples

Single crystals												comment	Reduced ceramic		IR, air, powder [1]
initial						H_2 treated									
Ar		Air central		Air periphery		Ar		Air central		Air periphery					
ν	D half width	ν	D half width	ν	D half width	ν	D half width	ν	D half width	ν	D half width		ν	D half width	
1224.3	46.7	1224.0	33.7	1225.0	48.3							E_1O			
		1235.1	88.3												
						1257.8	59.0	1245.6	59.9	1251.5	69.0	E_1R			
						1259.0	31.6	1259.9	31.8	1259.5	30.2	$\Delta\nu_o$	1259.3	42.4	
						1271.1	142.7			1268.3	174.0				
1316.9	143.3							1333.2	233.7			$\Delta\nu_1$	1310.8	196.5	
		1347.8	101.4			1357.3	22.2	1343.7	37.7	1353.0	60.1				
						1367.6	76.7	1359.8	26.7	1358.7	25.2		1388.1	72.1	
								1384.4	41.0	1387.6	39.1		1393.2	25.7	
1432.3	54.8			1423.7	278.1	1440.4	43.6					$\Delta\nu_2$			1420
1454.4	43.4	1450.9	82.0	1451.6	70.6	1459.9	93.4	1461.8	83.5	1444.4	75.6		1456.0	42.4	1476
								1490.4	24.8	1504.0	47.5				
		1534.1	57.6	1536.0	56.5			1511.7	38.2				1513.5	125.2	1531
1546.0	27.3	1547.1	25.9	1547.2	26.0	1552.4	29.1	1546.6	37.7	1553.4	36.3	$\Delta\nu_3$	1560.7	50.1	
						1562.7	84.6			1585.7	132.3				
1612.3	36.0	1610.2	82.7	1610.8	78.3	1614.7	192.3	1615.5	163.7	1633.7	476.7		1641.3	73.3	1629
1621.4	405.7														
								1645.1	21.2						
						1680.1	48.9			1684.1	68.5		1673.2	304.8	
1716.1	47.6	1715.1	96.0	1717.6	101.8	1716.1	40.5	-	-	1722.4	33.4	EL1-			1734
				1750.8	26.3					1751.0	62.9				

		1767.0	43.0	1769.7	36.0	1765.0	84.5	1764.8	29.9				1766.0	27.1	
								1786.2	151.3				1773.3	101.7	
1812.1	61.1	1807.3	58.8	1806.4	59.5	1813.1	37.1			1823.8	119.4	E4	1809.2	217.9	
1864.0	44.7	1863.0	79.0	1861.1	86.3	1851.3	60.6	1856.1	89.6	1859.4	37.9	EL2			
										1888.7	35.9				
1928.5	80.5	1929.2	49.8	1930.0	49.8	1919.7	99.6	1935.9	76.7	1931.6	84.6	EL3			
		1966.3	307.4	1961.1	335.8								1977.6	291.3	
2029.6	73.5	2031.2	46.5	2031.4	47.0	2031.1	77.3	2026.5	98.8	2028.9	82.0	EL4			
2129.8	58.5	2133.4	42.7	2133.7	42.7	2126.2	62.1	2133.7	74.3	2127.5	77.3	EL5			
2195								2213.5	73.6						

References

[1] M. M. Rashad, A. G. Mostafa and D. A. Rayan, *J. Mater. Sci.: Mater. Electron.*, 2016, **27**, 2614–2623, DOI: 10.1007/s10854-015-4067-z.