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MINERALOŠKO-KRISTALOGRAFSKE KARAKTERISTIKE DISTENSKO-KORUNDSKE SIROVINE IZ LEŽIŠTA BOBOLOŠ NA RAZLIČITIM TEMPERATURAMA

Ključne reči: Bobolož, sirovina, "pečena" sirovina, opeka, mineralni sastav, mineralne transformacije, dimenzije jediničnih ćelija, sadržaj Al_2O_3.

Izvod: Indicirani su rendgenski difraktogrami praha i određeni su kvalitativni, semikvantitativni sastavi sirovine, "pečene" sirovine i opeke.

Konstatovane su promene mineralnog sastava, mineralne transformacije i prekristalizacije na različitim temperaturama.

Izračunati su i upoređeni parametri jediničnih ćelija distena, korunda, rutila, andaluzita, silimanita i mulita. Kod korunda i rutila su uglavnom nepromenjeni i u okviru standardne greške.

Kod silimanita i mulita, u uzorcima opeke, a_0-ose su veće, a b_0-ose manje nego u uzorcima "pečene" sirovine, pri čemu su c_0-osa i zapremina-V_0 ostale skoro konstantne. To ukazuje na delimično termalno širenje u pravcu a_0-ose na račun b_0-ose i na porast sadržaja Al_2O_3 u strukturi mulita iz opeke u odnosu na mulit iz "pečene" sirovine.

U odnosu na literaturne podatke, manje dimenzije jediničnih ćelija imaju disten, korund i mulit, veće andaluzit i silimanit, dok rutil ima približno podjednake.

Najzastupljeniji mineral u "pečenoj" sirovini i opeci je mulit, što ukazuje na njihove odlične karakteristike i primenu.

Na osnovu mineralnog sastava u "pečenoj" sirovini i opeci procenjen je sadržaj Al_2O_3 od oko 60%.

UVOD

U okviru istraživanja grupe geologa "Geoinstitut"-a na listu OGK Donji Milanovac, na oko 7km JZ od Brze Palanke (lokalnost Bobolož), pronađena je jedinstvena distensko-korundska rudna pojava. Po I l i ć-u (1993), ova distensko-korundska stena se pojavljuje u vidu blokova od kojih je najveći veličine oko 50-60m^3, kao i niza manjih veličine do 2-3m^3.

Područje pojave, strukturno gledano, vezano je za Getsku navlaku. Radi se o tekijsko-sipskoj klipi, nastaloj rasedanjem i erozijom prvobitno jedinstvene šarijske ploče.

Po B o g d a n o v i ć-u i R a k i ć-u (1980) sama navlaka je izgrađena od proterozojskih metamorfita (gnajsevi, mikašisti i amfiboliti), granita, serpentinita, zelenih škriljaca i sedimenata srednje i gornje jure. Uže područje terena na kome je uočena ova stena izgrađeno je uglavnom od proterozojskih gnajseva i mikašista, te podređeno mlađih

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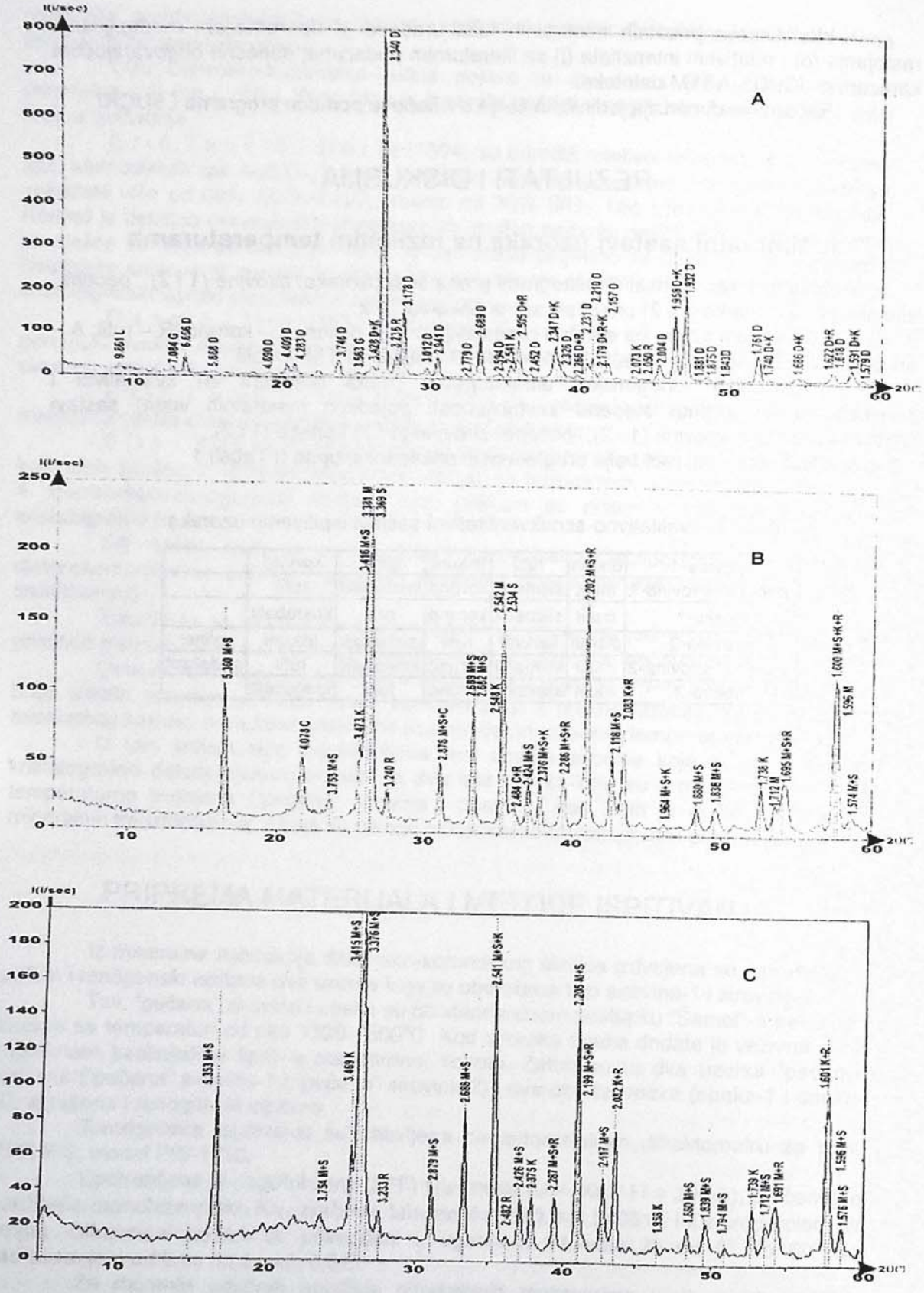
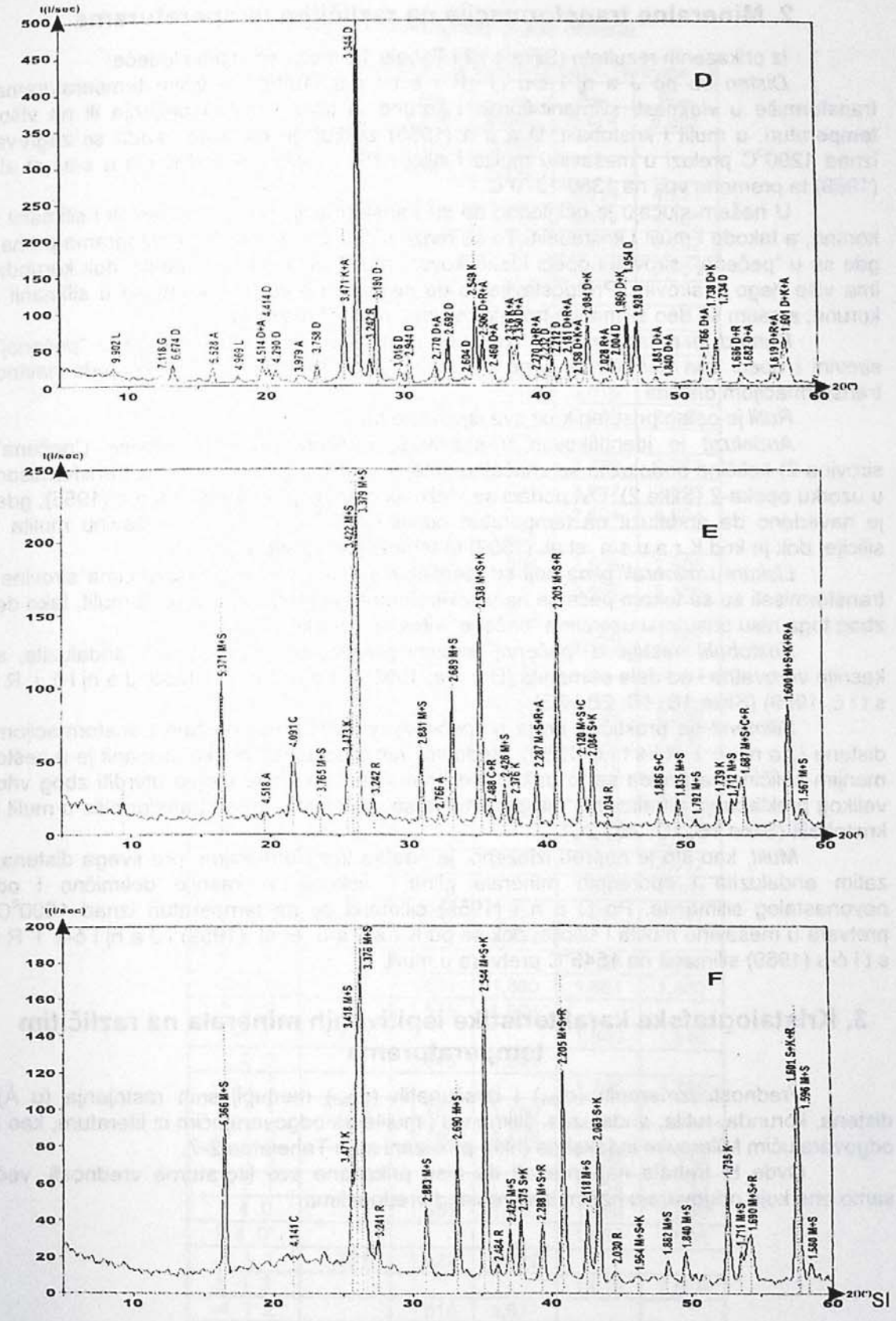


Slika 1: Rendgenski difraktogrami praha sirovine-1 (A), "pečene" sirovine-1 (B) i opeke-1 (C).



Slika 2: Rendgenski difraktogrami praha sirovine-2 (D), "pečene" sirovine-2 (E) i opeke-2 (F).

2. Mineralne transformacije na različitim temperaturama

Iz prikazanih rezultata (Slike 1 i 2 i Tabela 1), može se videti sledeće:

Disten se po J a nj i ć-u i R i s t i ć-u (1989) na višim temperaturama transformiše u vlaknasti silimanit-fibrolit i korund, a tokom dužeg pečenja ili na višoj temperaturi, u mulit i kristobalit. D a n a (1955) zaključuje da disten kada se zagreva iznad 1200°C prelazi u mešavinu mulita i silicije (SiO_2), dok se kod K r a u s-a et al. (1959) ta promena vrši na 1350-1370°C.

U našem slučaju je očigledno da su transformacijom distena nastali i silimanit i korund, a takođe i mulit i kristobalit. To se može videti iz indiciranih difraktograma praha, gde su u "pečenoj" sirovini i opeci identifikovani mulit, silimanit i kristobalit, dok korunda ima više nego u sirovini. Pretpostavljamo da se disten prvo transformisao u silimanit i korund, a zatim se deo silimanita transformisao u mulit i kristobalit.

Korund je ostao prisutan kroz sve ispitivane faze, s tim što ga u "pečenoj" sirovini i opeci ima nešto više nego u sirovini, zbog toga što je deo korunda nastao transformacijom distena.

Rutil je ostao prisutan kroz sve ispitivane faze.

Andaluzit je identifikovan u sirovini-2. Prilikom pečenja sirovine ("pečena" sirovina-2) količina andaluzita se značajno smanjila, dok je praktično skroz transformisan u uzorku opeka-2 (Slika 2). Ovi podaci se slažu sa onim koje je izneo D a n a (1955), gde je navedeno da andaluzit na temperaturi od oko 1400°C prelazi u mešavinu mulita i silicije, dok je kod K r a u s-a et al. (1959) ta temperatura 1390°C.

Liskuni i minerali glina koji su identifikovani kao sporedni u uzorcima sirovine, transformisali su se tokom pečenja na visokim temperaturama pre svega u mulit, tako da zbog toga nisu prisutni u uzorcima "pečene" sirovine i opeke.

Kristobalit nastaje u "pečenoj" sirovini prvenstveno od distena i andaluzita, a kasnije verovatno i od dela silimanita (D a n a, 1995; K r a u s et al., 1959; J a nj i ć i R i s t i ć, 1989) (Slike 1B, 1C, 2B i 2C).

Silimanit se praktično javlja u "pečenoj" sirovini kada nastaje transformacijom distena (J a nj i ć i R i s t i ć, 1989). Međutim, već u uzorcima opeke silimanit je u nešto manjim količinama (mada se to baš sa velikom sigurnošću nije moglo utvrditi zbog vrlo velikog preklapanja difrakcionih maksimumima sa mulitskim), jer se transformiše u mulit i kristobalit (Slike 1B, 1C, 2B i 2C).

Mulit, kao što je napred izloženo, je nastao transformacijom pre svega distena, zatim andaluzita i sporednih minerala glina i liskuna, a kasnije delimično i od novonastalog silimanita. Po D a n i (1955) silimanit se na temperaturi iznad 1600°C pretvara u mešavinu mulita i silicije, dok se po K r a u s-u et al. (1959) i J a nj i ć-u i R i s t i ć-u (1989) silimanit na 1545°C pretvara u mulit.

3. Kristalografske karakteristike ispitivanih minerala na različitim temperaturama

Vrednosti izmerenih (d_{obs}) i izračunatih (d_{calc}) međupljosnih rastojanja (u Å) distena, korunda, rutila, andaluzita, silimanita i mulita sa odgovarajućim iz literature, kao i odgovarajućim Milerovim indeksima (hkl), prikazani su u Tabelama 2-7.

Ovde bi trebalo napomenuti da nisu prikazane sve literaturne vrednosti, već samo one koje odgovaraju našim izmerenim d-vrednostima.

Tabela 2: Difraktogrami praha distena.

disten (JCPDS 11-46)		disten (sirovina-1)		disten (sirovina-2)	
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
1 0 0	6,700	6,656	6,686	6,674	6,686
-1 1 0	5,890	5,868	5,890		
-1 0 1		4,690	4,705		
0 -1 1				4,514	4,521
1 1 0	4,420	4,410	4,411	4,414	4,408
0 1 1		4,283	4,291	4,290	4,292
-1 2 0				3,758	3,761
1 -1 1		3,746	3,748		
-2 1 0	3,440	3,428	3,437		
2 0 0	3,350	3,340	3,343	3,344	3,343
-2 1 1	3,180	3,178	3,178	3,179	3,179
0 2 1	3,020	3,012	3,012	3,016	3,012
-2 2 0	2,947			2,943	2,947
1 2 0		2,941	2,938		
2 1 0	2,782	2,779	2,776	2,770	2,775
2 -1 1	2,699	2,689	2,691	2,692	2,693
-1 1 2	2,612			2,604	2,604
-1 3 0	2,602	2,594	2,598		
-1 -1 2		2,505	2,504	2,506	2,505
2 -2 1	2,460			2,460	2,456
1 2 1		2,452	2,453		
-2 1 2	2,355			2,350	2,351
-2 3 0	2,350	2,347	2,348		
1 -3 1	2,331	2,326	2,324		
-1 2 2	2,272	2,266	2,265	2,269	2,266
-2 3 1		2,231	2,230	2,232	2,231
-3 2 0		2,210	2,211	2,212	2,212
-3 2 1		2,179	2,179	2,181	2,181
1 1 2	2,168	2,157	2,159	2,158	2,160
-1 -3 1				2,084	2,081
3 -1 1	2,006	2,004	2,001	2,003	2,002
-3 1 2				1,960	1,963
-1 4 0	1,962	1,958	1,957	1,954	1,957
-3 3 1	1,930	1,932	1,932		
1 3 1				1,928	1,928
-2 4 0		1,881	1,880	1,881	1,880
-3 2 2		1,875	1,876		
1 -4 1	1,846			1,840	1,840
-1 0 3		1,843	1,844		
-2 -3 1				1,765	1,765
-4 1 1	1,764	1,761	1,760		
-4 1 0		1,740	1,739		
-2 1 3				1,738	1,738
-4 2 1				1,734	1,733
1 4 0		1,686	1,687	1,686	1,686
1 4 0*				1,686	1,686
-4 3 1	1,621	1,622	1,623		
3 -1 2				1,619	1,619
-4 1 2		1,618	1,617		
1 3 2				1,601	1,602
-2 4 2		1,591	1,590		
-4 0 2		1,572	1,572		

*zračenje $CuK\alpha_2$

Tabela 3: Difraktogrami praha korunda.

korund (JCPDS 46-1212)	h k l	0 1 2	1 0 4	1 1 0	0 0 6	1 1 3	2 0 2	0 2 4	1 1 6
	d_{obs}	3,480	2,551	2,379	2,165	2,085	1,964	1,740	1,601
korund (sirovina-1)	d_{obs}	3,428	2,541	2,347	2,179	2,073	1,958	1,740	1,591
	d_{calc}	3,461	2,546	2,359	2,171	2,073	1,950	1,731	1,597
korund ("pečena" sir..-1)	d_{obs}	3,473	2,548	2,376		2,083	1,963	1,738	1,600
	d_{calc}	3,476	2,548	2,377		2,083	1,962	1,738	1,600
korund (opeka-1)	d_{obs}	3,466	2,539	2,373		2,081	1,957	1,737	1,599
	d_{calc}	3,471	2,546	2,372		2,080	1,959	1,736	1,598
korund (sirovina-2)	d_{obs}	3,471	2,549	2,376	2,158	2,084	1,960	1,738	1,601
	d_{calc}	3,476	2,547	2,377	2,161	2,083	1,962	1,738	1,599
korund ("pečena" sir.-2)	d_{obs}	3,473	2,538	2,376		2,084		1,739	1,600
	d_{calc}	3,476	2,546	2,378		2,083		1,738	1,599
korund (opeka-2)	d_{obs}	3,471	2,544	2,375		2,083	1,963	1,738	1,601
	d_{calc}	3,476	2,548	2,377		2,083	1,962	1,738	1,600

Tabela 4: Difraktogrami praha rutila.

rutil (JCPDS 21-1276)	h k l	1 1 0	1 0 1	2 0 0	1 1 1	2 1 0	2 1 1	2 2 0
	d_{obs}	3,250	2,487	2,297	2,188	2,054	1,687	1,624
rutil (sirovina-1)	d_{obs}	3,235	2,505		2,179	2,050	1,686	1,622
	d_{calc}	3,241	2,492		2,189	2,050	1,687	1,621
rutil ("pečena" sirovina-1)	d_{obs}	3,240	2,484	2,286	2,202		1,695	
	d_{calc}	3,244	2,500	2,294	2,195		1,690	
rutil (opeka-1)	d_{obs}	3,230	2,480	2,285	2,198		1,690	
	d_{calc}	3,238	2,494	2,289	2,190		1,686	
rutil (sirovina-2)	d_{obs}	3,242	2,506	2,269	2,181	2,028	1,686	1,619
	d_{calc}	3,225	2,498	2,281	2,191	2,040	1,684	1,613
rutil ("pečena" sirovina-2)	d_{obs}	3,242	2,488	2,287	2,205	2,034	1,687	
	d_{calc}	3,229	2,502	2,283	2,194	2,042	1,686	
rutil (opeka-2)	d_{obs}	3,241	2,484	2,288	2,205		1,690	
	d_{calc}	3,241	2,499	2,292	2,194		1,689	

Tabela 5: Difraktogram praha andaluzita.

andaluzit (JCPDS 39-376)		andaluzit (sirovina-2)	
h k l	d_{obs}	d_{obs}	d_{calc}
1 1 0	5,549	5,528	5,537
1 0 1	4,531	4,514	4,553
1 1 1	3,929	3,979	3,946
2 1 0	3,494	3,471	3,481
2 2 0	2,774	2,770	2,768
1 1 2	2,483	2,506	2,507
3 1 0	2,469	2,460	2,457
0 3 1	2,380	2,376	2,387
3 0 1	2,354	2,350	2,348
2 0 2	2,263	2,270	2,276
2 3 0	2,182	2,181	2,180
3 2 0	2,171	2,158	2,163
4 1 0	1,892	1,881	1,883
3 3 0	1,849	1,840	1,846
2 4 0	1,761	1,765	1,761
2 4 1	1,679	1,682	1,681
0 4 2	1,610	1,619	1,617
4 0 2	1,595	1,601	1,596

Tabela 6: Difraktogrami praha silimanita.

silimanit (JCPDS 38-471)		silimanit ("pečena" sirov.-1)		silimanit (opeka-1)		silimanit ("pečena" sirov.-2)		
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{ob}
1 1 0	5,366	5,360	5,373	5,349	5,372	5,371	5,377	5,36
2 0 0	3,743	3,753	3,757	3,751	3,760	3,765	3,760	
1 2 0	3,415	3,416	3,422	3,412	3,418	3,422	3,424	3,4
2 1 0	3,366	3,369	3,375	3,373	3,377	3,379	3,378	3,3
0 0 2	2,886	2,878	2,879	2,876	2,880	2,881	2,882	2,8
2 2 0	2,680	2,689	2,687	2,686	2,686	2,689	2,689	2,6
2 2 0*	2,680	2,689	2,687					
1 1 2	2,542	2,534	2,538	2,539	2,538	2,538	2,540	2,5
1 3 0	2,421	2,424	2,425	2,424	2,422	2,426	2,427	2,4
3 1 0	2,373	2,376	2,381					
2 0 2	2,289	2,286	2,285	2,285	2,286	2,287	2,287	2,2
1 2 2	2,204	2,202	2,203	2,203	2,202	2,205	2,205	2,2
1 2 2*	2,204			2,203	2,202			
2 3 0	2,112	2,118	2,117	2,115	2,115	2,119	2,118	2,1
2 2 2	1,965	1,963	1,964					1,9
4 0 0	1,872	1,880	1,878	1,879	1,880			1,8
3 1 2	1,833	1,838	1,835	1,838	1,836	1,835	1,836	1,8
3 3 0	1,786			1,792	1,791	1,792	1,792	
2 4 0	1,7070			1,7103	1,7091	1,7117	1,7121	1,7
3 2 2	1,6938	1,6946	1,6958					
4 2 0	1,6821					1,6874	1,6889	1,6
0 4 2	1,5982	1,6000	1,5986	1,5948	1,5968	1,6005	1,5996	1,6
0 4 2*	1,5982							1,6
4 0 2	1,5703	1,5739	1,5732	1,5752	1,5743	1,5760	1,5745	

* zračenje $CuK\alpha_2$

Tabela 7: Difraktogrami praha mulita.

mulit (JCPDS 15-776)		mulit ("pečena" sir.-1)		mulit (opeka-1)		mulit ("pečena" sir.-2)		
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{ob}
1 1 0	5,390	5,360	5,374	5,349	5,372	5,371	5,377	5,36
2 0 0	3,774	3,753	3,757	3,751	3,761	3,765	3,760	
1 2 0	3,428	3,416	3,423	3,412	3,418	3,422	3,424	3,4
2 1 0	3,390	3,381	3,376	3,373	3,377	3,379	3,378	3,3
0 0 1	2,886	2,878	2,881	2,876	2,879	2,881	2,882	2,8
2 2 0	2,694	2,689	2,687	2,686	2,686	2,689	2,689	2,6
2 2 0*	2,694	2,689	2,687					
1 1 1	2,542	2,542	2,539	2,539	2,538	2,538	2,540	2,5
1 3 0	2,428	2,424	2,426	2,424	2,422	2,426	2,427	2,4
3 1 0	2,393	2,376	2,381					
2 0 1	2,292	2,286	2,286	2,285	2,286	2,287	2,287	2,2
1 2 1	2,206	2,202	2,204	2,203	2,202	2,205	2,205	2,2
1 2 1*	2,206			2,203	2,202			
2 3 0	2,121	2,118	2,117	2,115	2,115	2,119	2,118	2,1
2 2 1	1,969	1,963	1,965					1,9
4 0 0	1,887	1,880	1,878	1,879	1,881			1,8
3 1 1	1,841	1,838	1,836	1,838	1,836	1,835	1,836	1,8
3 3 0	1,7954			1,7923	1,7907	1,792	1,792	
2 4 0	1,7125	1,7120	1,7115	1,7103	1,7092	1,7117	1,7121	1,71
3 2 1	1,7001	1,6946	1,6963					
4 2 0	1,6940			1,6897	1,6887	1,6874	1,6889	1,68

mulit (JCPDS 15-776)		mulit ("pečena" sir.-1)		mulit (opeka-1)		mulit ("pečena" sir.-2)		mulit (opeka-2)	
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
0 4 1	1,5999	1,6000	1,5992	1,5948	1,5967	1,6005	1,5996	1,5963	1,5976
0 4 1*	1,5999	1,5998	1,5992						
4 0 1	1,5786	1,5739	1,5735	1,5752	1,5745	1,5760	1,5745	1,5796	1,5771

* zračenje $CuK\alpha_2$

4. Dimenzije jediničnih ćelija ispitivanih minerala na različitim temperaturama

U Tabeli 8 prikazane su skupno, radi bolje preglednosti, izračunate jedinične ćelije ispitanih minerala, zajedno sa literaturnim podacima. Ose a_0, b_0 i c_0 su date u Å; uglovi α_0, β_0 i γ_0 su dati u stepenima (^{0}), a zapremine jediničnih ćelija V_0 su date u Å^3.

Tabela 8: Izračunate jedinične ćelije ispitivanih minerala, zajedno sa literaturnim podacima.

	sirovina-1	"pečena" sirovina-1	opeka-1	sirovina-2	"pečena" sirovina-2	opeka-2	literaturni podaci
disten	a_0=7,107(2) b_0=7,830(3) c_0=5,544(3) α_0=89,84(4) β_0=101,22(3) γ_0=106,16(3) V_0=290,2(2)			a_0=7,109(3) b_0=7,829(3) c_0=5,548(2) α_0=89,86(4) β_0=101,17(3) γ_0=106,24(3) V_0=290,4(1)			a_0=7,112 b_0=7,844 c_0=5,574 α_0=90,09 β_0=101,1 γ_0=105,9 V_0=292,98
korund	a_0=4,72(1) c_0=13,02(6) V_0=251(1)	a_0=4,754(1) c_0=12,979(7) V_0=254,0(1)	a_0=4,745(4) c_0=12,97(2) V_0=253,0(4)	a_0=4,755(3) c_0=12,97(1) V_0=253,9(3)	a_0=4,756(7) c_0=12,96(3) V_0=253,9(5)	a_0=4,754(3) c_0=12,98(2) V_0=254,0(3)	a_0=4,758 c_0=12,99 V_0=254,81
rutil	a_0=4,584(8) c_0=2,97(1) V_0=62,4(3)	a_0=4,59(2) c_0=2,98(2) V_0=62,7(4)	a_0=4,58(1) c_0=2,97(2) V_0=62,3(3)	a_0=4,56(1) c_0=2,98(2) V_0=62,1(4)	a_0=4,57(1) c_0=2,99(2) V_0=62,4(3)	a_0=4,58(1) c_0=2,98(2) V_0=62,6(4)	a_0=4,593 c_0=2,959 V_0=62,43
andaluzit				a_0=7,75(1) b_0=7,91(1) c_0=5,62(1) V_0=344,9(8)			a_0=7,794 b_0=7,897 c_0=5,558 V_0=342,18
silimanit		a_0=7,513(4) b_0=7,688(5) c_0=5,758(4) V_0=332,6(3)	a_0=7,521(4) b_0=7,675(4) c_0=5,759(4) V_0=332,4(3)		a_0=7,520(3) b_0=7,692(3) c_0=5,763(3) V_0=333,4(2)	a_0=7,526(4) b_0=7,688(3) c_0=5,770(4) V_0=333,8(2)	a_0=7,486 b_0=7,675 c_0=5,772 V_0=331,68
mulit		a_0=7,514(4) b_0=7,690(4) c_0=2,881(2) V_0=166,5(1)	a_0=7,522(4) b_0=7,675(4) c_0=2,879(2) V_0=166,2(1)		a_0=7,520(3) b_0=7,692(3) c_0=2,882(1) V_0=166,68(9)	a_0=7,535(4) b_0=7,676(5) c_0=2,884(2) V_0=166,8(1)	a_0=7,545 b_0=7,689 c_0=2,884 V_0=167,35

Iz Tabele 8 može se videti da su dimenzije jediničnih ćelija korunda kroz sve faze praktično nepromenjene, osim u uzorku-1 gde su u sirovini-1 manje vrednosti za a_0 i V_0, a veće za c_0. Pri zagrevanju ("pečena" sirovina-1 i opeka-1) ove vrednosti su se normalizovale.

Rutil ima skoro nepromenjene dimenzije jediničnih ćelija koje su u granicama standardne greške.

Međutim, dimenzije jediničnih ćelija mulita su, kao i kod silimanita, pretrpele određene promene. U uzorcima opeke ose-a_0 su veće nego u uzorcima "pečene" sirovine, dok su ose-b_0 u uzorcima opeke manje nego u uzorcima "pečene" sirovine. To znači da je kod mulita i silimanita prilikom dužeg izlaganja visokim temperaturama, došlo do delimičnog termalnog širenja ovih minerala u pravcu a_0-ose na račun b_0-ose, jer su c_0-osa i zapremina-V_0 ostali praktično konstantnih dimenzija.

Po C a m e r o n-u (1977) ovakva promena dimenzija jediničnih ćelija kod mulita ukazuje na porast ulaska Al_2O_3 u strukturu mulita u opeci u odnosu na mulit iz "pečene" sirovine.

U odnosu na literaturne podatke, manje dimenzije jediničnih ćelija imaju disten, korund i mulit, veće andaluzit i silimanit, dok rutil ima približno podjednake.

5. Sadržaj Al_2O_3 komponente

W e i l l (1966) je prikazao temperaturni dijagram mineralnog sastava u zavisnosti od procentualnog odnosa SiO_2 i Al_2O_3. Sa ovog dijagrama može se videti da se mulit i silimanit javljaju zajedno u temperaturnom opsegu od 932 do 1350°C ako je sadržaj Al_2O_3 od 50-60%, a mulit i korund ako je sadržaj Al_2O_3 od 60-100%.

Prema ovim podacima, a polazeći od toga da naši uzorci "pečene" sirovine i opeke (na temperaturama od 1320-1350°C sadrže istovremeno i mulit i silimanit i korund, to znači da se ovi uzorci nalaze u graničnom području od oko 60% Al_2O_3.

Laboratorijski eksperimenti izvedeni u "Rudnicima i industriji šamota "Šamot" Aranđelovac", gde je sadržaj Al_2O_3 u vatrostalnim opekama određen kao 60-65% (D a n g i ć i I l i ć, 1999), to potvrđuju.

ZAKLJUČAK

U našoj zemlji su prilično retka ispitivanja faznih transformacija, promena mineralnog sastava i parametara jediničnih ćelija pri različitim temperaturama. Zbog toga je u ovom radu pokušano da se ova problematika prikaže i bar delimično objasni.

Da bi se to postiglo, indicirani su rendgenski difraktogrami praha (Slike 1 i 2) i određeni su kvalitativni, semikvantitativni sastavi uzoraka sirovine (1 i 2), "pečene" sirovine (1 i 2) i opeke (1 i 2), koji su prikazani u Tabeli 1.

U Tabelama 2-7 prikazane su kristalografske karakteristike distena, korunda, rutila, andaluzita, silimanita i mulita.

Ispitivane su mineralne transformacije na različitim temperaturama. Obzirom da literaturni podaci o ovoj problematici izostaju, a ne retko su i kontradiktorni (D a n a, 1955; K r a u s et al., 1959; I l i ć i K a r a m a t a, 1978; J a n j i ć i R i s t i ć, 1989; itd.), možemo ipak da izvučemo sledeće zaključke:

Pojava kristobalita, kao i mineralne transformacije i prekristalizacije na nižim temperaturama od literaturnih podataka su verovatno prouzrokovane stavljanjem topitelja pri tehnološkom procesu.

Disten se transformisao prvo u silimanit i korund, a tokom dužeg pečenja nastali su i mulit i kristobalit.

Korund je ostao prisutan kroz sve ispitivane faze, ali ga u "pečenoj" sirovini i opeci ima nešto više nego u sirovini, jer je jedan deo nastao transformacijom distena.

Rutil je ostao prisutan i netransformisan kroz sve ispitivane faze.

Andaluzit se delimično transformisao u "pečenoj" sirovini, a praktično potpuno u opeci, u mulit i kristobalit.

Liskuni i minerali glina su se pri pečenju potpuno transformisali pre svega u mulit.

Kristobalit prvenstveno nastaje od distena i andaluzita, a kasnije i od silimanita.

Silimanit se javlja u "pečenoj" sirovini transformacijom distena, dok se kasnije u opeci najverovatnije delimično transformiše u mulit i kristobalit.

Mulit nastaje transformacijom distena, andaluzita, sporednih liskuna i minerala glina, a kasnije i delimičnom transformacijom silimanita.

Što se tiče dimenzija jediničnih ćelija koje su prikazane u Tabeli 8, može se uočiti da su kod korunda i rutila one praktično nepromenjene (u granicama standardne greške) kroz sve temperaturne promene. Kod distena i andaluzita se eventualne promene nisu ni mogle pratiti obzirom da se i jedan i drugi javljaju samo u sirovini, dok u "pečenoj" sirovini-2 andaluzita ima toliko malo, da se jedinična ćelija nije mogla izračunati na reprezentativnom nivou.

Silimanit i mulit pokazuju promene u dimenzijama jediničnih ćelija, jer su u uzorcima opeke a_0-ose veće, a b_0-ose manje u odnosu na uzorke "pečene" sirovine. To ukazuje da je pri dužem temperaturnom tretmanu došlo do delimičnog termalnog širenja ovih minerala u pravcu a_0-ose na račun b_0-ose, obzirom da c_0-osa i zapremina-V_0 ostaju praktično konstantne. Po C a m e r o n-u (1977) ovakva promena ukazuje na porast sadržaja Al_2O_3 u strukturi mulita u opeci u odnosu na "pečenu" sirovinu.

U odnosu na literaturne podatke, manje dimenzije jediničnih ćelija imaju disten, korund i mulit, veće andaluzit i silimanit, dok rutil ima približno podjednake.

Utvrđeno je da je u uzorcima "pečene" sirovine i opeke najveća zastupljenost mulita koji nastaje prekristalizacijom tri polimorfne modifikacije sastava Al_2SiO_5 (distena, andaluzita i silimanita), kao i liskuna i minerala glina. Ovaj podatak je značajan sa industrijskog aspekta jer po J a nj i ć-u i R i s t i ć-u (1989) mulit karakteriše visoka vatrostalnost (temperatura topljenja od 1825-1850°C), hemijska inertnost i mehanička čvrstoća.

Takođe, utvrđeno je da ovakav mineralni sastav "pečene" sirovine i opeke na 1320-1350°C u kome su zajedno mulit, silimanit i korund može da ukaže i na procentualnu zastupljenost Al_2O_3 (W e i l l, 1966), koja je u ovom radu procenjena na oko 60%.

To je i potvrđeno upoređivanjem sa laboratorijskim podacima firme "Rudnici i industrija šamota "Šamot", Aranđelovac" (D a n g i ć i l l i ć, 1999), gde je zastupljenost Al_2O_3 u opsegu od 60 do 65%.

Na kraju, treba napomenuti da rezultati koji su prikazani u ovom radu još jedanput potvrđuju prednosti rendgensko-kristalografskih ispitivanja u rešavanju ovakvih i sličnih problema i zadataka.

To se posebno odnosi na određivanje mineralnih faza i transformacija na različitim temperaturama.

Takođe, mogu se određivati i eventualne promene hemijskog sastava nekih minerala, kao njihovo i termalno širenje i skupljanje pomoću dimenzija jediničnih ćelija.

Recenzent: Dr. Adam Dangić, redovan profesor

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MINERALOGICALY-CRYSTALLOGRAPHICAL CHARACTERISTICS OF THE KYANITE-CORUNDUM MINERAL RAW MATERIAL FROM THE ORE DEPOSIT BOBOLOŠ AT DIFFERENT TEMPERATURES

by

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Key words: Bobološ, mineral raw material, "baked" mineral raw material, brick, mineral compositions, mineral transformations, unit cell dimensions, Al_2O_3 content.

Abstract: Powder diffraction patterns were indiced and there were determined qualitative, semiquantitative compositions of the mineral raw material, "baked" mineral raw material and brick.

There were established changes of the mineral compositions, mineral transformations and precrystallizations at different temperatures.

There were calculated and compared unit cell dimensions of the kyanite, corundum, rutile, andalusite, sillimanite and mullite. At corundum and rutile they are mostly unchangeable and in the range of the standard error.

Sillimanite and mullite have in the brick samples a_o-axis bigger and b_o-axis smaller than in the "baked" mineral raw material samples, while c_o-axis and volume-V_o remained almost constant. That indicate to the partially thermal expansion in the a_o-axis direction against b_o-axis and to the increase of the Al_2O_3 content in the mullite's structure from the brick at respect to the mullite from the "baked" mineral raw material.

Regard to the literature datas, smaller unit cell dimensions has kyanite, corundum and mullite, bigger andalusite and sillimanite, while rutile has approximatively equal.

The most quantity mineral in the samples of the "baked" mineral raw material and brick is mullite, which indicate to their excellent characteristics and usage.

At basis of the mineral composition in the "baked" mineral raw material and brick samples it was estimated Al_2O_3 content of about 60%.

INTRODUCTION

Geology group from the "Geoinstitute", while researching the sheet OGK Donji Milanovac, at about 7km SW from Brza Palanka (Bobološ locality), found unique kyanite-corundum ore occurence. By I l i ć (1993), this kyanite-corundum rock appears as blocks, from which is largest about 50-60m^3, and also series of the smaller size up to 2-3m^3.

Occurence area, in the structure view, is connected to the Geticum nappe. It is about Tekia klippe which origin was from faulting and erosion of the originally undivided plate.

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By B o g d a n o v i ć and R a k i ć (1980) the nappe is constituted by Proterozoic metamorphites (gneiss, mica schists and amphibolites), granites, serpentinites, greenschists and sediments of Middle and Upper Jurassic. Narrow area on which this rock was detected consists mostly with Proterozoic gneiss and mica schists, and subordinate younger amphibolites, amphibolite shales, granites and aplitic granites. Kyanite-corundum rock lies on the Proterozoic gneiss.

This kyanite-corundum ore occurence is up to date unique discovery of this kind of the mineral raw material in Serbia. Because of that, it challenged many investigators who performed numerous researches.

E r i ć, T a n č i ć and Đ u r i ć (1994) determined relative mineral composition of the rock as: alumosillicates of the Al_2SiO_5 type, corundum, rutile, and also accessory muscovite. Chemical analysis indicated more than 60% Al_2O_3+Cr_2O_3, less than 30% SiO_2, and also less than 1% iron. Corundum was in detail mineralogicaly-crystallographical investigated by several methods. There was obtained corundum participation of about 15%, by what means that this rock (together with the obtained mineral and chemical composition) become significant as mineral raw material for aluminium bricks. Also there was crystallographicaly investigated blue corundum of sapphire type.

D a n g i ć and I l i ć (1995 and 1999), and also C v e t k o v i ć and B o j k o v i ć (1998) confirmed such mineral and chemical composition of the ore and also possibility that this mineral raw material bring into the industrial production of high-aluminious bricks, fireproof blocks, etc.

E r i ć, L o g a r and B a b i č (1997) by the optical, X-ray and chemical methods were investigated alkaline deficit tourmaline from this locality.

E r i ć and B a b i č (1998) separated following mineral associations: 1. kyanite-corundum shale; 2. kyanite-corundum shale with tourmaline; 3. andalusite shale; and 4. muscovite-paragonite shale. At this occasion kyanite and andalusite were chemicaly and crystallographicaly investigated.

Purpose of this paper is to bring out the mineralogical-crystallographicaly characteristics of the kyanite-corundum mineral raw material, "baked" mineral raw material and brick, their compositions and mineral transformations.

Also, it will be observed possible changes of the unit cell dimensions and compositions of present minerals, and it will be estimated the Al_2O_3 content in the "baked" mineral raw material and brick samples.

Such investigations are in our Country very rare and this is one of the attempts for better understanding of the certain processes of phase transformations and precrystallizations, and also changes of the mineral compositions of certain mineral association at different temperatures.

At that sense it will be represented two samples of the mineral raw material which are mineralogicaly-crystallographical determined, and afterwards that same two samples which passed under the order temperature treatments ("baked" mineral raw material and brick) and at which were occured certain mineral transformations, and which were also mineralogicaly-crystallographical determined.

PREPARATION OF THE MATERIAL AND INVESTIGATION METHODS

From the kyanite-corundum shale mineral association there were separated, powdered, and then with the X-ray analysis investigated two samples which are marked as mineral raw material-1 and mineral raw material-2.

So called "baked" mineral raw material and brick were by standard procedure in "Šamot" treated and heated at temperature of about 1320-1350°C. At the brick samples there were added connecting clay (mostly of the kaolinite type) in standard ammount.

Then that two samples of the "baked" mineral raw material ("baked" mineral raw material-1 and "baked" mineral raw material-2) and two samples of the brick (brick-1 and brick-2), were powdered and investigated with the X-ray analysis.

X-ray investigations were performed by automatically diffractometer for powder PHILIPS, model PW-1710.

There was used long-focus (LFF) Cu-anode (U = 40 kV and I = 30 mA), with monochromated $K\alpha_1$ radiation with the wave-length λ = 1,54051 Å and with the Xe proportional counter. Diffraction datas were collected in the angle range 2θ from 5° to 60° with keeping back with 0,5s on every 0,02°.

For measurement of the angle positions of diffraction maximums and their belonging intensities there was used base program PW-1877. Precision of the diffractometer was controled before and after the experiment with metallic Si powder.

Identification of the present mineral phases was done with comparison of the interplanar spacings (d) and relative intensities (I) with the literature datas, that is corresponding card from JCPDS-ASTM database.

Calculation of the unit cell dimensions was accomplished with the LSUCRI programme.

RESULTS AND DISCUSSION

1. Mineral compositions of the samples at different temperatures

Recorded X-ray powder diffraction patterns of six samples: mineral raw material (1 and 2), "baked" mineral raw material (1 and 2) and brick (1 and 2) are represented at Figures 1 and 2.

The marks which are represented at Figures represented: D – kyanite; K – corundum; R – rutile; A – andalusite; L – micas; G – clays; C – cristobalite; S – sillimanite; and M – mullite.

Through these X-ray powder diffraction patterns there were determined qualitative, semiquantitative compositions (by quantity of certain mineral kinds) of the investigated samples of the mineral raw material (1 and 2), "baked" mineral raw material (1 and 2) and brick (1 and 2).

These compositions are, because of better viewness, represented together at Table 1.

Table 1: Qualitative-semiquantitative compositions of the investigated samples.

mineral raw material-1	kyanite	rutile	micas	clays	corundum	
"baked" min. raw material-1	mullite	sillimanite	corundum	cristobalite	rutile	
brick-1	mullite	sillimanite	corundum	rutile	cristobalite	
mineral raw material-2	kyanite	corundum	rutile	andalusite	micas	clays
"baked" min. raw material-2	mullite	sillimanite	corundum	cristobalite	rutile	andalusite
brick-2	mullite	sillimanite	corundum	rutile	cristobalite	

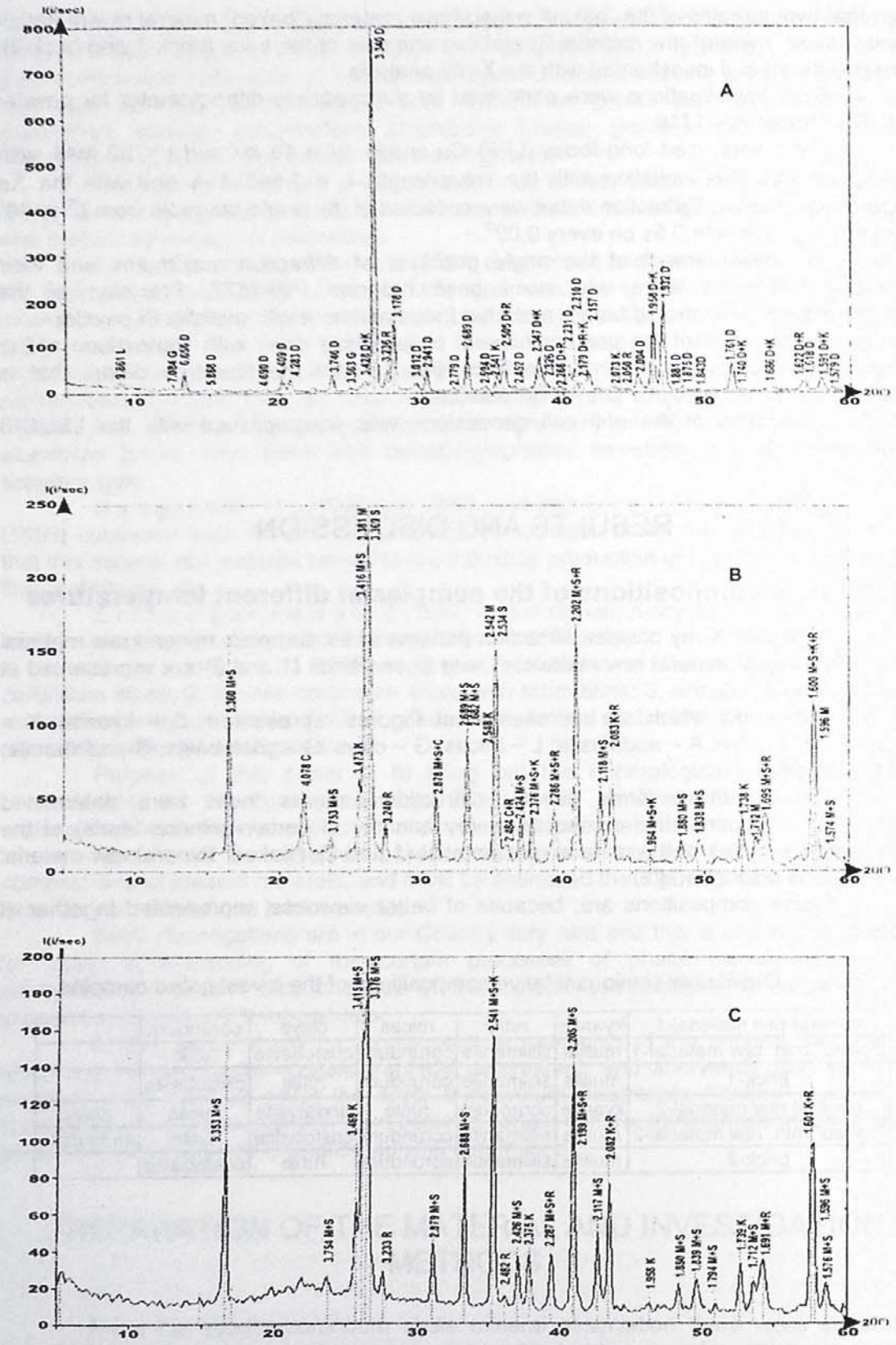

Figure 1: X-ray powder diffraction patterns of the mineral raw material-1 (A), "baked" mineral raw material-1 (B) and brick-1 (C).

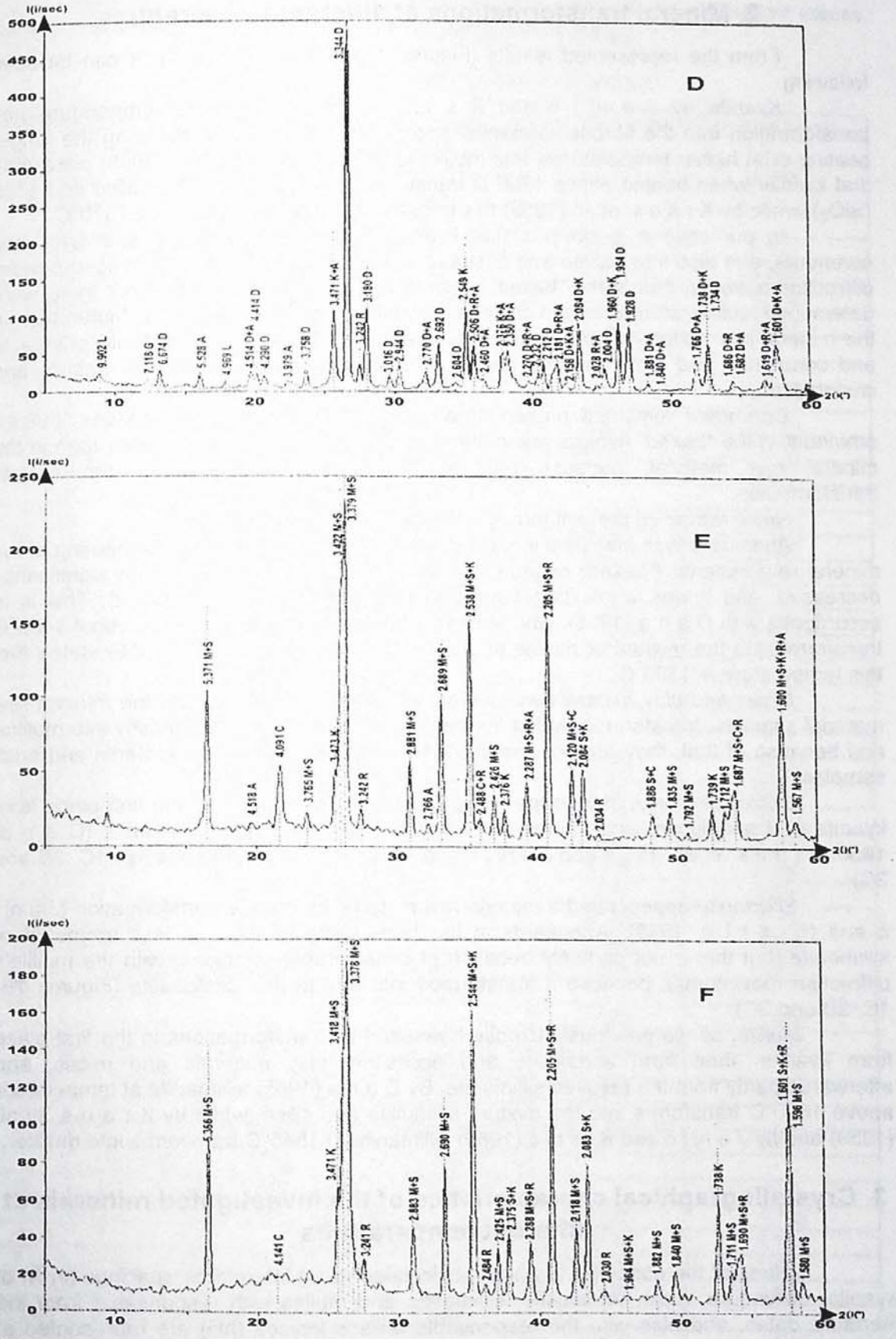

Figure 2: X-ray powder diffraction patterns of the mineral raw material-2 (D), "baked" mineral raw material-2 (E) and brick-2 (F).

2. Mineral transformations at different temperatures

From the represented results (Figures 1 and 2 and Table 1), it can be seen following:

Kyanite by J a nj i ć and R i s t i ć (1989) at higher temperature has transformation into the fibrous sillimanite-fibrolite and corundum, and during the longer heating or at higher temperatures, into mullite and cristobalite. D a n a (1955) concluded that kyanite when heated above 1200°C transforms into the mixture of mullite and silica (SiO_2), while by K r a u s et al. (1959) this transformation performs at 1350-1370°C.

In our case it is obvious that kyanite was transformed into sillimanite and corundum, and also into mullite and cristobalite. It can be seen from the indiced powder diffraction patterns, that in the "baked" mineral raw material and in the brick there were determined mullite, sillimanite and cristobalite, while corundum ammount is higher than in the mineral raw material. We suppose that kyanite was first transformed into sillimanite and corundum, and after that one part of sillimanite was transformed into mullite and cristobalite.

Corundum remained present through all of the investigated phases, but it's ammount in the "baked" mineral raw material and in the brick is some higher than in the mineral raw material, because part of the corundum originated from kyanite transformation.

Rutile remained present through all of the investigated phases.

Andalusite was identified in the mineral raw material-2. During the heating of the mineral raw material ("baked" mineral raw material-2) andalusite ammount significantly decreased, and it was whole transformed in the sample brick-2 (Figure 2). This is in accordance with D a n a (1955), who stated that andalusite at temperature about 1400°C transforms into the mixture of mullite and silica, while K r a u s et al. (1959) stated that this temperature is 1390°C.

Micas and clay minerals which were identified as accessory in the mineral raw material samples, transformed during the heating at high temperature mostly into mullite, and because of that, they are not present in the "baked" mineral raw material and brick samples.

Cristobalite originated in the "baked" mineral raw material in the first place from kyanite and andalusite, and afterwards probably from the part of sillimanite (D a n a, 1955; K r a u s et al., 1959; and J a nj i ć and R i s t i ć, 1989), (Figures 1B, 1C, 2B and 2C).

Sillimanite appears in the mineral raw material by kyanite transformation (J a nj i ć and R i s t i ć, 1989). Afterwards in the brick samples there is less ammount of sillimanite (but this is not certainly because of considerable coinciding with the mullite's diffraction maximums), because it transformed into mullite and cristobalite (Figures 1B, 1C, 2B and 2C).

Mullite, as we previously exposed, resulted by transformations in the first place from kyanite, then from andalusite and accessory clay minerals and micas, and afterwards partly from the resulted sillimanite. By D a n a (1955) sillimanite at temperature above 1600°C transforms into the mixture of mullite and silica, while by K r a u s et al. (1959) and by J a nj i ć and R i s t i ć (1989) sillimanite at 1545°C transforms into mullite.

3. Crystallographical characteristics of the investigated minerals at different temperatures

Values of the observed (d_{obs}) and calculated (d_{calc}) interplanar spacings (in Å) of kyanite, corundum, rutile, andalusite, sillimanite and mullite with responsable from the literature datas, and also with the responsable Miller's indices (hkl) are represented at Tables 2-7.

Here should be mentioned that there isn't represented all of the literature values, but only that which are corresponing to the our observed d-values.

Table 2: Powder diffraction patterns of kyanite.

kyanite (JCPDS 11-46)		kyanite (mineral raw material-1)		kyanite (mineral raw material-2)	
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
1 0 0	6,700	6,656	6,686	6,674	6,686
-1 1 0	5,890	5,868	5,890		
-1 0 1		4,690	4,705		
0 -1 1				4,514	4,521
1 1 0	4,420	4,410	4,411	4,414	4,408
0 1 1		4,283	4,291	4,290	4,292
-1 2 0				3,758	3,761
1 -1 1		3,746	3,748		
-2 1 0	3,440	3,428	3,437		
2 0 0	3,350	3,340	3,343	3,344	3,343
-2 1 1	3,180	3,178	3,178	3,179	3,179
0 2 1	3,020	3,012	3,012	3,016	3,012
-2 2 0	2,947			2,943	2,947
1 2 0		2,941	2,938		
2 1 0	2,782	2,779	2,776	2,770	2,775
2 -1 1	2,699	2,689	2,691	2,692	2,693
-1 1 2	2,612			2,604	2,604
-1 3 0	2,602	2,594	2,598		
-1 -1 2		2,505	2,504	2,506	2,505
2 -2 1	2,460			2,460	2,456
1 2 1		2,452	2,453		
-2 1 2	2,355			2,350	2,351
-2 3 0	2,350	2,347	2,348		
1 -3 1	2,331	2,326	2,324		
-1 2 2	2,272	2,266	2,265	2,269	2,266
-2 3 1		2,231	2,230	2,232	2,231
-3 2 0		2,210	2,211	2,212	2,212
-3 2 1		2,179	2,179	2,181	2,181
1 1 2	2,168	2,157	2,159	2,158	2,160
-1 -3 1				2,084	2,081
3 -1 1	2,006	2,004	2,001	2,003	2,002
-3 1 2				1,960	1,963
-1 4 0	1,962	1,958	1,957	1,954	1,957
-3 3 1	1,930	1,932	1,932		
1 3 1				1,928	1,928
-2 4 0		1,881	1,880	1,881	1,880
-3 2 2		1,875	1,876		
1 -4 1	1,846			1,840	1,840
-1 0 3		1,843	1,844		
-2 -3 1				1,765	1,765
-4 1 1	1,764	1,761	1,760		
-4 1 0		1,740	1,739		
-2 1 3				1,738	1,738
-4 2 1				1,734	1,733
1 4 0		1,686	1,687	1,686	1,686
1 4 0*				1,686	1,686
-4 3 1	1,621	1,622	1,623		
3 -1 2				1,619	1,619
-4 1 2		1,618	1,617		
1 3 2				1,601	1,602

kyanite (JCPDS 11-46)		kyanite (mineral raw material-1)		kyanite (mineral raw material-2)	
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
-2 4 2		1,591	1,590		
-4 0 2		1,572	1,572		

* radiation CuKα_2

Table 3: Powder diffraction patterns of corundum.

corundum (JCPDS 46-1212)	h k l	0 1 2	1 0 4	1 1 0	0 0 6	1 1 3	2 0 2	0 2 4	1 1 6
	d_{obs}	3,480	2,551	2,379	2,165	2,085	1,964	1,740	1,601
corundum (min. raw mat.-1)	d_{obs}	3,428	2,541	2,347	2,179	2,073	1,958	1,740	1,591
	d_{calc}	3,461	2,546	2,359	2,171	2,073	1,950	1,731	1,597
corundum ("baked" min. raw mat.-1)	d_{obs}	3,473	2,548	2,376		2,083	1,963	1,738	1,600
	d_{calc}	3,476	2,548	2,377		2,083	1,962	1,738	1,600
corundum (brick-1)	d_{obs}	3,466	2,539	2,373		2,081	1,957	1,737	1,599
	d_{calc}	3,471	2,546	2,372		2,080	1,959	1,736	1,598
corundum (min. raw mat.-2)	d_{obs}	3,471	2,549	2,376	2,158	2,084	1,960	1,738	1,601
	d_{calc}	3,476	2,547	2,377	2,161	2,083	1,962	1,738	1,599
corundum ("baked" min. raw mat.-2)	d_{obs}	3,473	2,538	2,376		2,084		1,739	1,600
	d_{calc}	3,476	2,546	2,378		2,083		1,738	1,599
corundum (brick-2)	d_{obs}	3,471	2,544	2,375		2,083	1,963	1,738	1,601
	d_{calc}	3,476	2,548	2,377		2,083	1,962	1,738	1,600

Table 4: Powder diffraction patterns of rutile.

rutile (JCPDS 21-1276)	h k l	1 1 0	1 0 1	2 0 0	1 1 1	2 1 0	2 1 1	2 2 0
	d_{obs}	3,250	2,487	2,297	2,188	2,054	1,687	1,624
rutile (mineral raw material-1)	d_{obs}	3,235	2,505		2,179	2,050	1,686	1,622
	d_{calc}	3,241	2,492		2,189	2,050	1,687	1,621
rutile ("baked" mineral raw material-1)	d_{obs}	3,240	2,484	2,286	2,202		1,695	
	d_{calc}	3,244	2,500	2,294	2,195		1,690	
rutile (brick-1)	d_{obs}	3,230	2,480	2,285	2,198		1,690	
	d_{calc}	3,238	2,494	2,289	2,190		1,686	
rutile (mineral raw material-2)	d_{obs}	3,242	2,506	2,269	2,181	2,028	1,686	1,619
	d_{calc}	3,225	2,498	2,281	2,191	2,040	1,684	1,613
rutile ("baked" mineral raw material -2)	d_{obs}	3,242	2,488	2,287	2,205	2,034	1,687	
	d_{calc}	3,229	2,502	2,283	2,194	2,042	1,686	
rutile (brick-2)	d_{obs}	3,241	2,484	2,288	2,205		1,690	
	d_{calc}	3,241	2,499	2,292	2,194		1,689	

Table 5: Powder diffraction pattern of andalusite.

andalusite (JCPDS 39-376)		andalusite (mineral raw material-2)	
h k l	d_{obs}	d_{obs}	d_{calc}
1 1 0	5,549	5,528	5,537
1 0 1	4,531	4,514	4,553
1 1 1	3,929	3,979	3,946
2 1 0	3,494	3,471	3,481
2 2 0	2,774	2,770	2,768
1 1 2	2,483	2,506	2,507
3 1 0	2,469	2,460	2,457
0 3 1	2,380	2,376	2,387
3 0 1	2,354	2,350	2,348
2 0 2	2,263	2,270	2,276
2 3 0	2,182	2,181	2,180
3 2 0	2,171	2,158	2,163
4 1 0	1,892	1,881	1,883

andalusite (JCPDS 39-376)		andalusite (mineral ra	
h k l	d_{obs}	d_{obs}	
3 3 0	1,849	1,840	
2 4 0	1,761	1,765	
2 4 1	1,679	1,682	
0 4 2	1,610	1,619	
4 0 2	1,595	1,601	

Table 6: Powder diffraction patterns of sill

sillimanite (JCPDS 38-471)		sillimanite ("baked" min. raw mat.-1)		sillimanite (brick-1)		sillim min
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{ob}
1 1 0	5,366	5,360	5,373	5,349	5,372	5,37
2 0 0	3,743	3,753	3,757	3,751	3,760	3,76
1 2 0	3,415	3,416	3,422	3,412	3,418	3,42
2 1 0	3,366	3,369	3,375	3,373	3,377	3,37
0 0 2	2,886	2,878	2,879	2,876	2,880	2,88
2 2 0	2,680	2,689	2,687	2,686	2,686	2,68
2 2 0*	2,680	2,689	2,687			
1 1 2	2,542	2,534	2,538	2,539	2,538	2,53
1 3 0	2,421	2,424	2,425	2,424	2,422	2,42
3 1 0	2,373	2,376	2,381			
2 0 2	2,289	2,286	2,285	2,285	2,286	2,28
1 2 2	2,204	2,202	2,203	2,203	2,202	2,20
1 2 2*	2,204			2,203	2,202	
2 3 0	2,112	2,118	2,117	2,115	2,115	2,11
2 2 2	1,965	1,963	1,964			
4 0 0	1,872	1,880	1,878	1,879	1,880	
3 1 2	1,833	1,838	1,835	1,838	1,836	1,83
3 3 0	1,786			1,792	1,791	1,79
2 4 0	1,7070			1,7103	1,7091	1,71
3 2 2	1,6938	1,6946	1,6958			
4 2 0	1,6821					1,68
0 4 2	1,5982	1,6000	1,5986	1,5948	1,5968	1,60
0 4 2*	1,5982					
4 0 2	1,5703	1,5739	1,5732	1,5752	1,5743	1,57

* radiation $CuK\alpha_2$

Table 7: Powder diffraction patterns of m

mullite(JCPDS 15-776)		mullite("baked" min. raw mat.-1)		mullite (brick-1)		mull min.
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}
1 1 0	5,390	5,360	5,374	5,349	5,372	5,37
2 0 0	3,774	3,753	3,757	3,751	3,761	3,76
1 2 0	3,428	3,416	3,423	3,412	3,418	3,42
2 1 0	3,390	3,381	3,376	3,373	3,377	3,37
0 0 1	2,886	2,878	2,881	2,876	2,879	2,88
2 2 0	2,694	2,689	2,687	2,686	2,686	2,68
2 2 0*	2,694	2,689	2,687			
1 1 1	2,542	2,542	2,539	2,539	2,538	2,53
1 3 0	2,428	2,424	2,426	2,424	2,422	2,42
3 1 0	2,393	2,376	2,381			
2 0 1	2,292	2,286	2,286	2,285	2,286	2,28
1 2 1	2,206	2,202	2,204	2,203	2,202	2,20

mullite(JCPDS 15-776)		mullite("baked" min. raw mat.-1)		mullite (brick-1)		mullite("baked" min. raw mat.-2)		mullite (brick-2)	
h k l	d_{obs}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
1 2 1*	2,206			2,203	2,202				
2 3 0	2,121	2,118	2,117	2,115	2,115	2,119	2,118	2,118	2,117
2 2 1	1,969	1,963	1,965					1,963	1,967
4 0 0	1,887	1,880	1,878	1,879	1,881			1,882	1,884
3 1 1	1,841	1,838	1,836	1,838	1,836	1,835	1,836	1,840	1,839
3 3 0	1,7954			1,7923	1,7907	1,792	1,792		
2 4 0	1,7125	1,7120	1,7115	1,7103	1,7092	1,7117	1,7121	1,7110	1,7100
3 2 1	1,7001	1,6946	1,6963						
4 2 0	1,6940			1,6897	1,6887	1,6874	1,6889	1,6895	1,6911
0 4 1	1,5999	1,6000	1,5992	1,5948	1,5967	1,6005	1,5996	1,5963	1,5976
0 4 1*	1,5999	1,5998	1,5992						
4 0 1	1,5786	1,5739	1,5735	1,5752	1,5745	1,5760	1,5745	1,5796	1,5771

* radiation $CuK\alpha_2$

4. Unit cell dimensions of the investigated minerals at different temperatures

At Table 8 there are represented together, because of better viewness, calculated unit cell dimensions of the investigated minerals, together with the literature datas. Axis a_0, b_0 and c_0 are in Å; angles α_0, β_0 and γ_0 are in degreees (^{0}); and unit cell volumes are in $Å^3$.

From Table 8 it can be seen that the unit cell dimensions of corundum through all of the phases are almost unchangeable, except at sample-1 where at mineral raw material-1 there are smaller values for a_0 and V_0, and bigger for c_0. Under the heating ("baked" mineral raw material-1 and brick-1) that values were normalized.

Table 8: Calculated unit cell dimensions of the investigated minerals, together with the literature datas.

	mineral raw material-1	"baked" min. raw mat.-1	brick-1	mineral raw material-2	"baked" min. raw mat.-2	brick-2	literature datas
kyanite	a_0=7,107(2) b_0=7,830(3) c_0=5,544(3) α_0=89,84(4) β_0=101,22(3) γ_0=106,16(3) V_0=290,2(2)			a_0=7,109(3) b_0=7,829(3) c_0=5,548(2) α_0=89,86(4) β_0=101,17(3) γ_0=106,24(3) V_0=290,4(1)			a_0=7,112 b_0=7,844 c_0=5,574 α_0=90,09 β_0=101,1 γ_0=105,9 V_0=292,98
corundum	a_0=4,72(1) c_0=13,02(6) V_0=251(1)	a_0=4,754(1) c_0=12,979(7) V_0=254,0(1)	a_0=4,745(4) c_0=12,97(2) V_0=253,0(4)	a_0=4,755(3) c_0=12,97(1) V_0=253,9(3)	a_0=4,756(7) c_0=12,96(3) V_0=253,9(5)	a_0=4,754(3) c_0=12,98(2) V_0=254,0(3)	a_0=4,758 c_0=12,99 V_0=254,81
rutile	a_0=4,584(8) c_0=2,97(1) V_0=62,4(3)	a_0=4,59(2) c_0=2,98(2) V_0=62,7(4)	a_0=4,58(1) c_0=2,97(2) V_0=62,3(3)	a_0=4,56(1) c_0=2,98(2) V_0=62,1(4)	a_0=4,57(1) c_0=2,99(2) V_0=62,4(3)	a_0=4,58(1) c_0=2,98(2) V_0=62,6(4)	a_0=4,593 c_0=2,959 V_0=62,43

	mineral raw material-1	"baked" min. raw mat.-1	brick-1	mineral raw material-2	"baked" min. raw mat.-2	brick-2	literature datas
andalusite				a_0=7,75(1) b_0=7,91(1) c_0=5,62(1) V_0=344,9(8)			a_0=7,794 b_0=7,897 c_0=5,558 V_0=342,18
sillimanite		a_0=7,513(4) b_0=7,688(5) c_0=5,758(4) V_0=332,6(3)	a_0=7,521(4) b_0=7,675(4) c_0=5,759(4) V_0=332,4(3)		a_0=7,520(3) b_0=7,692(3) c_0=5,763(3) V_0=333,4(2)	a_0=7,526(4) b_0=7,688(3) c_0=5,770(4) V_0=333,8(2)	a_0=7,486 b_0=7,675 c_0=5,772 V_0=331,68
mullite		a_0=7,514(4) b_0=7,690(4) c_0=2,881(2) V_0=166,5(1)	a_0=7,522(4) b_0=7,675(4) c_0=2,879(2) V_0=166,2(1)		a_0=7,520(3) b_0=7,692(3) c_0=2,882(1) V_0=166,68(9)	a_0=7,535(4) b_0=7,676(5) c_0=2,884(2) V_0=166,8(1)	a_0=7,545 b_0=7,689 c_0=2,884 V_0=167,35

Rutile has almost unchangeable unit cell dimensions which are in the limit of the standard error.

However, the unit cell dimensions of mullite, and also of sillimanite, undergo through certain changes. In the brick samples a_o-axis are bigger than in the "baked" mineral raw material, while b_o-axis in the brick samples are smaller than in the "baked" mineral raw material samples. That means that in mullite and sillimanite during the longer exposure at high temperature, realized partly thermal expansion of this minerals at a_o-axis direction regard to b_o-axis, because c_o-axis and volume-V_o remained almost with constant dimensions.

By C a m e r o n (1977) this change of the mullite's unit cell dimensions point at increasing of Al_2O_3 in mullite's structure in the brick relate to the mullite from the "baked" mineral raw material.

Regard to the literature datas, smaller unit cell dimensions has kyanite, corundum and mullite, bigger andalusite and sillimanite, while rutile has approximatively equal.

5. Content of the Al_2O_3 component

W e i l l (1966) represented the temperature diagram of the mineral composition depending at percentual relations of the SiO_2 and Al_2O_3. From this diagram it can be seen that mullite and sillimanite appears together in the temperature range from 932 to 1350°C if Al_2O_3 content is 50-60%, and mullite and corundum if Al_2O_3 content is 60-100%.

According to that datas, and with consideration that our samples of the "baked" mineral raw material and brick (at temperature 1320-1350°C) contain simultaneously mullite and sillimanite and corundum, that means that these samples are situated at border area at about 60%.

Laboratory experiments commited in the "Šamot"-Mines and Industry of Shamotte, Aranđelovac, where Al_2O_3 content in the fireproof bricks was determined as 60-65% (D a n g i ć and I l i ć, 1999), that confirm.

CONCLUSION

In our country there are considerably rare investigations of the phase transformations, changes of the mineral composition and unit cell parameters at different

temperatures. Because of that, in this paper we made attempt that this problem represent and at least partially explain.

To achieve this, powder diffraction patterns were indiced (Figures 1 and 2) and there were determined qualitative, semiquantitative compositions of mineral raw material (1 and 2), "baked" mineral raw material (1 and 2) and brick (1 and 2) samples, which are represented at Table 1.

At Tables 2-7 there are represented crystallographicaly characteristics of kyanite, corundum, rutile, andalusite, sillimanite and mullite.

There were investigated mineral transformations at different temperatures. With regard that the literature datas about this problem are insufficient, and often contradictory (D a n a, 1955; K r a u s et al., 1959; I l i ć and K a r a m a t a, 1978; J a nj i ć and R i s t i ć, 1989; etc.), we can still make following conclusions:

Appearence of cristobalite, and also mineral transformations and precrystallizations at lower temperatures than the literature datas are probably caused by melting components which were added during the technological process.

Kyanite was first transformed into sillimanite and corundum, and during the longer heating mullite and cristobalite also resulted.

Corundum remained present through all of the investigated phases, but in the "baked" mineral raw material and in the brick its ammount is some higher than in the mineral raw material, because one part of corundum resulted from transformation of kyanite.

Rutile remained present and untransformed through all of the investigated phases.

Andalusite partly transformed in the "baked" mineral raw material, and completely in the brick, into mullite and cristobalite.

Micas and clay minerals were during the heating completely transformed mostly into mullite.

Cristobalite was in the first place resulted from transformed kyanite and andalusite, and afterwards from sillimanite.

Sillimanite resulted in the "baked" mineral raw material where transformed from kyanite, and afterwards in the brick most probably was transformed into mullite and cristobalite.

Mullite resulted from transformed kyanite, andalusite, accessory micas and clay minerals, and later from the partly transformed sillimanite.

From the unit cell dimensions which are represented at Table 8, it can be noticed that they are for corundum and rutile almost unchangeable (in the range of the standard error) through all of the temperature changes. At kyanite and andalusite eventually changes couldn't be observed with regard that both of them occurs only in the mineral raw material, while in the "baked" mineral raw material-2 andalusite ammount is too small, and because of that the unit cell dimensions couldn't be calculated at the representative level.

Sillimanite and mullite shows changes in the unit cell dimensions, because in the brick samples a_o-axis are higher, and b_o-axis are smaller related to the "baked" mineral raw material samples. That indicates that during the longer temperature heating there became to the partially thermal expansion of these minerals in the a_o-axis direction regard to the b_o-axis, with consideration that c_o-axis and volume-V_o remained almost unchangeable. By C a m e r o n (1977) change like this indicate to the increasing of the Al_2O_3 content in the mullite's structure in the brick related to the "baked" mineral raw material.

Regard to the literature datas, smaller unit cell dimensions has kyanite, corundum and mullite, bigger andalusite and sillimanite, while rutile has approximatively equal.

It was established that in the "baked" mineral raw material and brick samples there is most quantity of mullite, which resulted by precrystallization from three

polymorphic modification of the Al_2SiO_5 composition (kyanite, andalusite and sillimanite), and also from micas and clay minerals. This data is important at industrial aspect because by J a nj i ć and R i s t i ć (1989) mullite is characterized with high fireproof characteristics (melting temperature at 1825-1850°C), chemical inertness and mechanical hardness.

Also, it was established that such mineral composition of the "baked" mineral raw material and the brick at 1320-1350°C where together are mullite, sillimanite and corundum, could indicate to the percentual Al_2O_3 content (W e i l l, 1966), which was in this paper estimated at about 60%.

That was confirmed by comparing with the laboratory datas from the "Šamot"-Mines and Industry of Shamotte, Aranđelovac, (D a n g i ć and I l i ć, 1999), where Al_2O_3 content is in the range from 60 to 65%.

Lastly, it should be mentioned that results which were represented in this paper once again verificate the advantages of the X-ray – crystallographical investigations in solution of this and similar problems and tasks.

That is especialy related to the determination of the mineral phases and transformations at different temperatures.

Moreover, it can be determined eventualy variations of the chemical compositions of some minerals, and also their thermal expansion and contraction by the unit cell dimensions.

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