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Sintering behavior of feldspar rocks

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ABSTRACT - *Sintering behaviour as dependence of water absorption, flexural strength and firing shrinkage of dry pressed test samples made from three different types of feldspar rocks on the firing temperature (1120 – 1300 °C) was determined. Potassium, potassium-sodium and sodium-calcium industrially milled feldspars with similar granulometry according to equivalent mean spherical diameter of the grains d(0.5) in the range of 16.6 – 20.8 μm were used. The sintering process was described according to changes in mineralogical composition of the fired test samples too. During the sintering process, feldspars gradually disappear in phases – first of all alkali feldspars (albite, microcline); anorthite (calcium feldspar) is more resistant to melting thanks to its higher melting temperature and it increases the sintering temperature of feldspar. Sodium-potassium feldspar Z43NaK50 with the lowest content of alkalis (3.35 % of K_2O and 2.67 % of Na_2O) and the highest equivalent 2mean spherical diameter d(0.5) showed the most intensive sintering activity. An explanation of this unexpected fact can be found in the equilibrium phase diagrams and in the formation of low melting eutectic mixtures.*
Keywords - *feldspars, sintering, porosity, mineralogical composition*

I. INTRODUCTION

Feldspars are silicoaluminates of alkaline and alkaline-earth metals. Feldspars create about 60 % of earth and form part of rocks as fundamental mineralogical components. From the chemical point of view, feldspars are divided into the following fundamental types [1], [2]:

- Potassium feldspars (K-feldspars) $K(AlSi_3O_8)$ – Orthoclase, Microcline,
- Sodium feldspars (Na-feldspars) $Na(AlSi_3O_8)$ – Albite,
- Calcium feldspars (Ca-feldspars) $Ca(Al_2Si_2O_8)$ – Anorthite.

Feldspars or feldspar rocks [3] are used in the fine ceramic industry as a flux to form a glassy phase in bodies, thus promoting vitrification and translucency. They are also used as a source of alkalies and alumina in glazes [4]. An appropriate choice of feldspar type can significantly influence the properties of the fired ceramic body [5] and optimal firing temperature or soaking time. Particle size distribution of feldspar influences densification of green body, cleanability and the stain resistance of polished porcelain tiles [6].

The ternary equilibrium phase diagram K-feldspar – Na-feldspar – Ca-feldspar (fig. 1) provide useful information on melting temperatures of different compositions of feldspar.

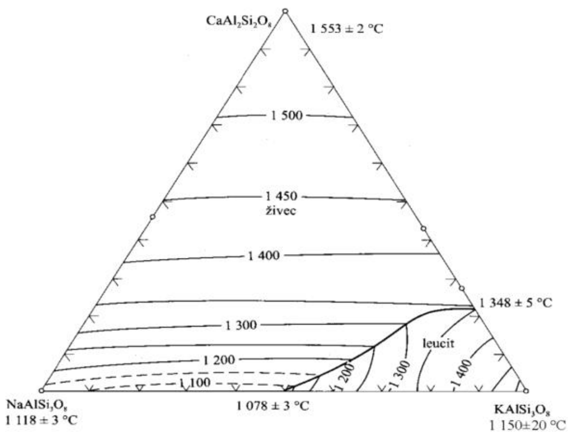

Fig. 1: Melting equilibrium phase diagram of the ternary system $NaAlSi_3O_8$ – $KAlSi_3O_8$ – $CaAl_2Si_2O_8$ [2]

The article uses the marking of feldspars according to the Czech standard: e.g. Z45KNa50 means that this feldspar contains 45 % mass of pure potassium (K)-sodium (Na) feldspar (Table 1) and maximally 0.50 % mass of Fe_2O_3.

Table 1: Classification of feldspars according to Czech standard CSN 72 1370

Type of feldspar	Marking	$K_2O:(K_2O+Na_2O)$		$CaO:(CaO+Na_2O-K_2O)$	
		min.	max.	min.	max.
Potassium	K	0.75	1.00		
Potassium-sodium	KNa	0.60	0.75		
Sodium-potassium	NaK	0.40	0.60		
Sodium	Na	0.00	0.40		
Sodium-calcium	NaCa			0.16	0.63
Calcium-sodium	CaNa			0.63	1.00

Feldspar rocks are necessary raw material for the production of ceramic tiles, whitewares, glazes etc. There is very important knowledge of their sintering activity for economical firing process. This problem has not been discussed for specific types of feldspar. The aim of the article is to describe the sintering ability of three different industrially milled feldspars with similar granulometry. The change of porosity (bulk density, water absorption), flexural strength, firing shrinkage and mineralogical composition in dependence on the firing temperature (1120 – 1300 °C) were determined on the test samples made from dry granulate prepared from the pure tested feldspars.

II. MATERIALS AND METHODS

Three different industrially milled feldspars from Czech quarries were used for the experiments:

- Sodium-potassium feldspar Z43KNa50 – alkali feldspar. Approximate mineralogical composition according to chemical composition (Table 2) and XRD patterns (Fig. 2): potassium feldspar (microcline) 20.0 %, sodium feldspar (albite) 22.6 %, calcium feldspar (anorthite) 2.4 % and quartz 55.0 %.
- Potassium feldspar Z75K13 – alkali feldspar. Approximate mineralogical composition according to chemical composition (Table 2) and XRD patterns (Fig. 2): potassium feldspar (microcline) 57.2 %, sodium feldspar (albite) 16.0 %, calcium feldspar (anorthite) 1.5 %, mica (muscovite) 4.0 % and quartz 21.3 %.
- Sodium-calcium feldspar Z80NaCa40 – plagioclase feldspar (oligoclase). Approximate mineralogical composition according to chemical composition (Table 2) and XRD patterns (Fig. 2): muscovite 4.9 %, sodium feldspar (albite) 60.3 %, calcium feldspar (anorthite) 21.0 % and quartz 13.8 %.

The chemical composition of feldspars (Table 2) reflects their mineralogical composition and volume of different types of pure feldspars (potassium, sodium or calcium).

Table 2: Chemical composition of used feldspars

Feldspar	Content [%mass]										
	SiO_2	Al_2O_3	Fe_2O_3	MnO	TiO_2	CaO	MgO	K_2O	Na_2O	LOI	sum
Z43KNa50	79.76	12.37	0.42	0.00	0.05	0.48	0.10	3.35	2.67	0.80	100.00
Z75K13	70.96	16.10	0.10	0.00	0.04	0.30	0.06	10.36	1.90	0.20	100.02
Z80NaCa40	66.67	20.11	0.26	0.00	0.04	4.23	0.07	0.83	7.13	0.74	100.00

Granulometry of milled feldspars was determined according to particle size distribution (laser particle size analyzer Malvern Mastersizer 2000). Particle size distribution and the equivalent mean spherical diameter d(0.5) of the milled feldspars were very similar (Fig. 3). The properties of fired test samples based on the feldspars are influenced to a very low extent by their granulometry in the presented experiment.

Industrially milled raw materials (feldspars) were moistened by 8 % mass of solution of carboxymethylcellulose CMC (3 % mass solution = 3 g CMC in 100 g of water). The moistened mixtures were pressed through the 1 mm sieve. The pressing granulate was thus prepared and subsequently mixed for 12 hours in the closed plastic vase of the homogenizer to reach a homogenous moisture. Testing samples with a green body size of 100 x 50 x 10 mm were uniaxially pressed to the steel mould at 20 MPa with 30 seconds soaking time at the maximal pressure.

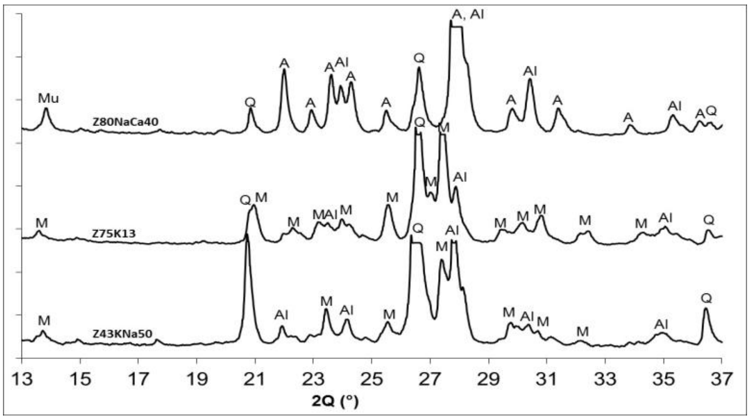

Fig. 2: XRD patterns of used feldspars Z43KNa50, Z75K13 and Z80NaCa40. Mu-muscovite, M-microcline, Q-quartz, Al-albite, A-anorthite

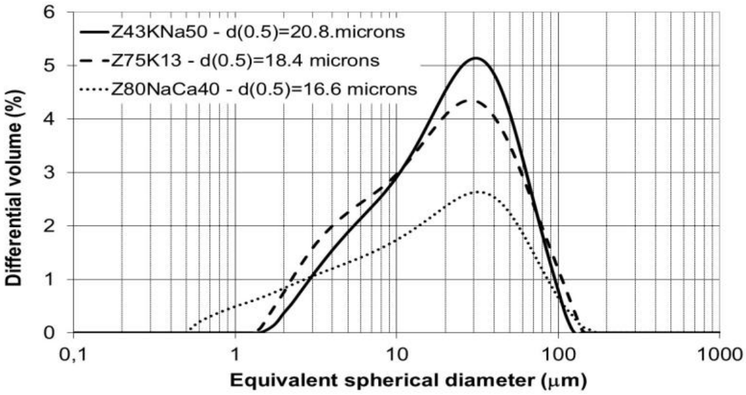

Fig. 3: Granulometry (particle size distribution) of used feldspars

The green bodies were fired in the electric laboratory furnace at temperatures of 1000, 1050, 1100 and 1150 °C with the heating rate 10 °C/min and 30 minutes soaking time at the maximum temperature. The subsequent cooling proceeded spontaneously following the natural cooling rate of the furnace. After firing, the body properties (6 test samples) were defined according to the official standard EN ISO 10545 (water absorption E, bulk density B, flexural strength R). Mineralogical composition of pure feldspars and fired bodies was determined by X-Ray diffraction (XRD). The XRD analysis was performed with the diffractometer Phillips PW 1170 with Cu anticathode ($\lambda\alpha 1$ = 0.15406 nm), accelerating voltage 40 kV, beam current 25 mA and scanning rate 1° 20' min^{-1}.

III. Results

Sintering activity of dry pressed test samples based on different kinds of feldspars Z43KNa50, Z75K13 and Z80NaCa40 according to dependence of water absorption on the firing temperature was determined. The most intensive sintering of the feldspar body is visible (Fig. 4) when feldspar Z43KNa50 was used – the test samples have the lowest water absorption (Fig. 4), the highest bulk density (Fig. 5) and flexural strength (Fig. 6) in all firing temperatures in the range of 1120 – 1210 °C. Sodium-calcium feldspar Z80NaCa40 begins sintering at much higher firing temperatures. The most exact parameter for sintering process description is sintering temperature, which is defined as temperature when the fired body has water absorption E = 2 % (Fig. 4). Sintering temperature of tested alkali feldspars Z43KNa50 and Z75K13 is significantly lower than oligoclase Z80NaCa40.

It was found that:

- The same bulk density (about 2300 $kg.m^{-3}$) is shown in all test samples after firing at sintering temperature (visible in Fig. 5).
- The lowest firing shrinkage FS (Fig. 7) at sintering temperature (Table 3) was found for the sample from feldspar Z43KNa50 with the lowest content of pure feldspars and the highest content of quartz.
- Mixed sodium-potassium feldspar Z43KNa50 with a lower content of feldspar substance (45 %) is characterized by a lower melting point (sintering temperature) than pure potassium feldspar Z75K13 with higher content of feldspars (75 %).

The highest content of quartz in feldspar Z43KNa50 caused high expansion of the body during firing in the range of 500 – 600 °C (Fig. 8) in comparison with other tested samples based on feldspars Z80NaCa40 and Z75K13. After exceeding the temperature of 900 °C dry pressed body from feldspar Z43KNa50 has the best ability to create the most compact body of all with the highest firing shrinkage (about 4.5 % after firing at 1180 °C without soaking time – Fig. 8).

The quartz transformation at 573 °C during the firing and cooling of test samples (Fig. 8) is visible depending on quartz content in individual tested feldspars. This transformation is most visible when the Z43KNa50 feldspar with 55 % content of quartz is used.

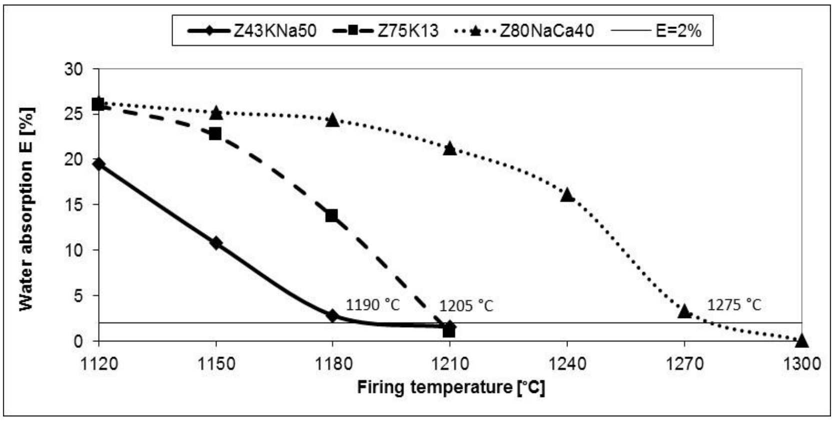

Fig. 4: Dependence of water absorption on the firing temperature and determination of sintering temperature

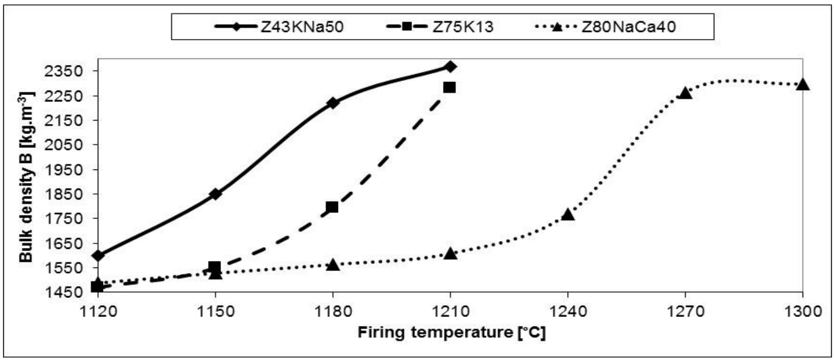

Fig. 5: Dependence of bulk density on the firing temperature

The feldspar Z43KNa50 with the lowest sintering temperature based on microcline and albite is typical for the quickest disappearing of feldspars during the firing. After firing at 1180 °C it is possible to find (fig. 9) only a small indication of albite. Sintering temperature (1190 °C) means the existence of only quartz and amorphous glassy phase without any feldspars. It is surprising that leucite (main XRD patterns 3.266 (1), 3.438 (0.85), 5.39 (0.8)) generated during the potassium feldspars melting was not detected even in sintered bodies Z43KNa40 and Z75K13 (based on the potassium feldspar microcline) despite the theoretical assumptions [1].

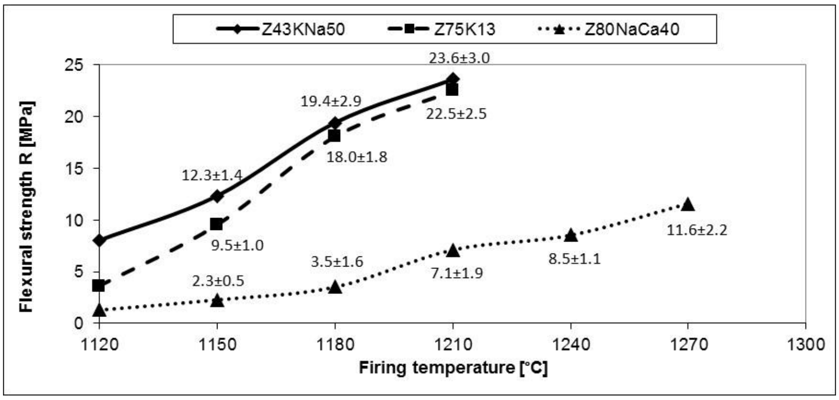

Fig. 6: Dependence of flexural strength on the firing temperature

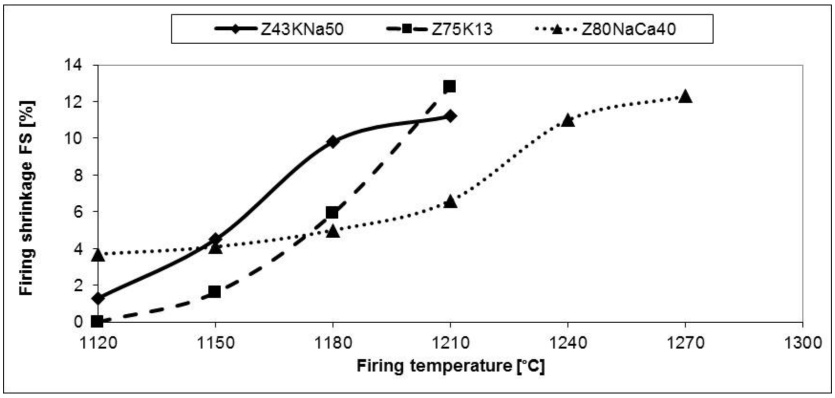

Fig. 7: Dependence of firing shrinkage on the firing temperature

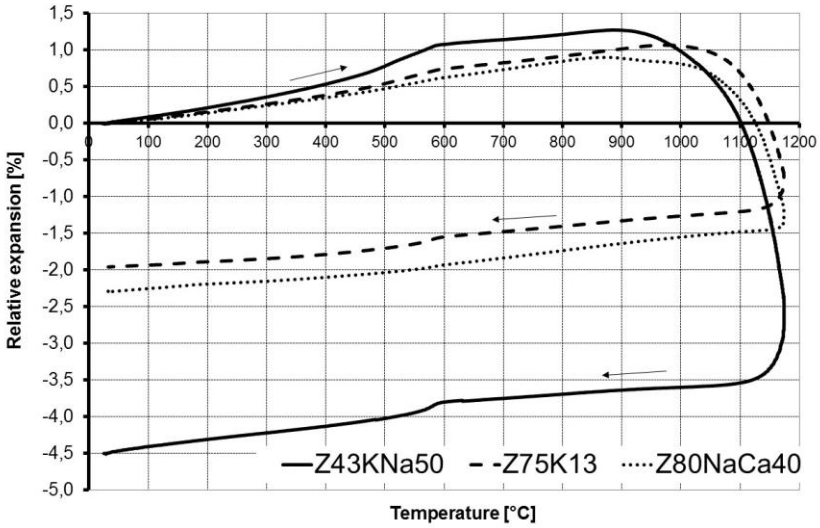

Fig. 8: Thermodilatometric curves of the feldspar samples (10 °C/min without soaking time on the maximal temperature)

Test samples based on potassium feldspar Z75K13 with dominant microcline phase lost albite content after firing at 1180 °C but the content of microcline was not significantly reduced (Fig. 10). Quartz, amorphous glassy phase and microcline were represented in the body after the firing at sintering temperature (1205 °C). There was a considerable difference in Z43KNa50 samples, where feldspar phase was not found after the firing at sintering temperature (Fig. 9). It is not possible to find an explanation of this fact in granulometry parameters of used feldspars, which significantly influence sintering and melting of feldspars, but it is possible to find in the equilibrium phase diagram (Fig. 1). Mixed sodium-potassium feldspars generated low melting eutectic melts, which accelerate the sintering and melting process of feldspars. The same situation is repeated for test samples based on the sodium-calcium feldspar Z80NaCa40 (Fig. 11). After firing at sintering temperature (1275 °C) the body contains anorthite with high melting temperature of about 1550 °C and small content of albite (Fig. 11).

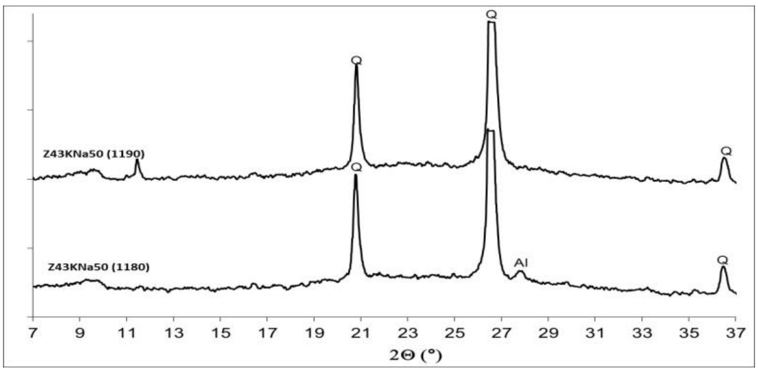

Fig. 9: XRD patterns of the test samples from feldspar Z43KNa50 fired at 1180 °C (for comparison) and 1190 °C (sintered body): Al-albite, Q-quartz

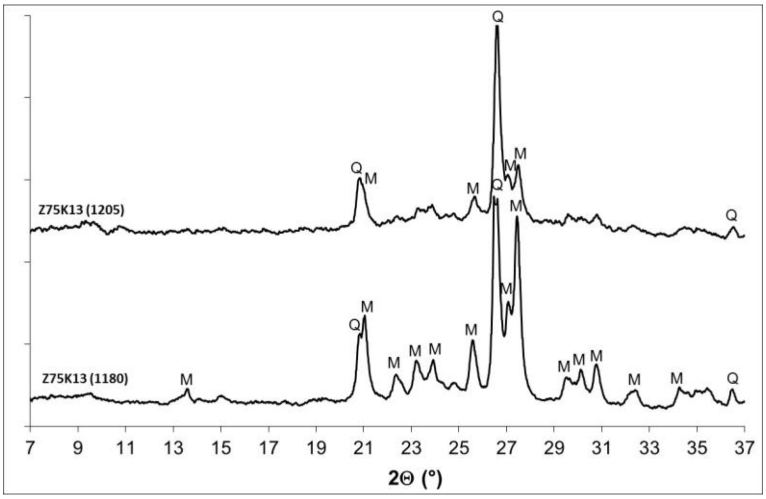

Fig. 10: XRD patterns of the test samples from feldspar Z75K13 fired at 1180 °C (for comparison) and 1205 °C (sintered body): M-microcline, Q-quartz

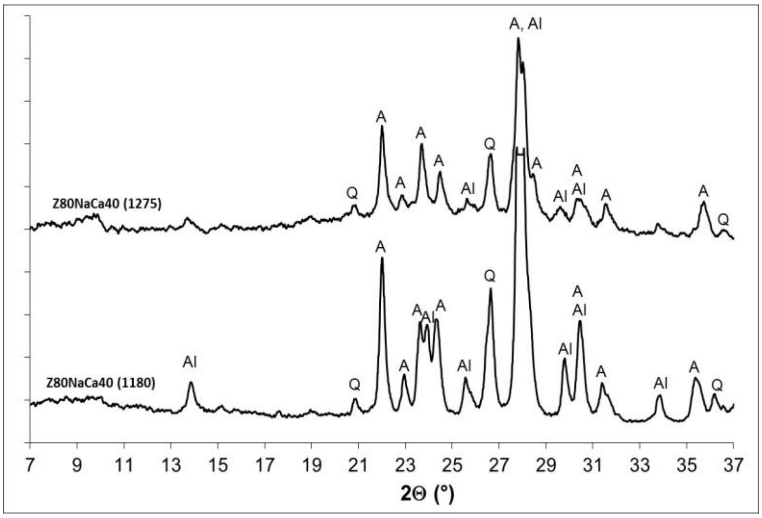

Fig. 11: XRD patterns of the test samples from feldspar Z80NaCa40 fired at 1180 °C (for comparison) and 1275 °C (sintered body): Al-albite, A-anorthite, Q-quartz

IV. CONCLUSION

Sintering and melting of feldspars are dependent on many aspects, such as the granulometry, the rate of heating and finally on the content of alkali oxides because it directly creates the melting effect. Three different feldspars with different content of K-feldspar, Na-feldspar and Ca-feldspar from the Czech quarries were compared. The performed comparison test showed that the highest sintering activity was reflected in Z43KNa50 feldspar, which is characterized by the lowest sintering temperature (1190 °C). The least favourable results in terms of flux were achieved by using sodium-calcium feldspar Z80NaCa40 whose sintering temperature is above 1240 °C. The sintering temperature of Z80NaCa40 is high due to the requirements of fast-firing ceramic materials with a relatively high content of feldspar.

For sintering and melting of feldspars, not just the total content of feldspar components are important, but also the ratio between potassium and sodium feldspar (i.e. between K_2O and Na_2O). At the appropriate ratio, low-melting eutectics can be expected to appear, with a melting temperature substantially lower than the theoretical melting temperature of pure feldspars is set. The presence of calcium feldspar significantly reduces sintering ability and melting of feldspars.

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