

The thermal behavior of albite as observed by DTA

Lois A. Johnson, Ronald A. McCauley*

Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA

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Abstract

There is a range in the melting point of albite ($\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-6\text{SiO}_2$) at 1 atm reported in the literature. An experimental evaluation of the melting point of albite was conducted using differential thermal analysis (DTA). A melting point of 1134°C was determined by this method that is higher than the reported values. In the DTA method, continuous heating in a flowing gas atmosphere removes any volatiles formed by heating. It is suggested that the evaporation of soda (Na_2O) during heating can lead to a raising of the melting point of albite.

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1. Introduction

The melting point of albite ($\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-6\text{SiO}_2$) has been the subject of numerous studies and there is uncertainty about its true value [1]. The commonly accepted value of $1118 \pm 3^\circ\text{C}$ [2] was lowered to $1100 \pm 3^\circ\text{C}$ by Boettcher et al. [3]. This lower value was determined by constructing a pressure–temperature fusion curve that fit the experimental data obtained from reversed experiments. Navrotsky et al. [4] have shown that there can be a range in the melting interval from about 1105 to 1145°C . Their results were based on phase equilibria data which suggested that there might be some solid solubility of excess nepheline (NaAlSiO_4) in albite. Their maximum melting composition was more NaAlO_2 -rich than albite and melted at 1145°C . The solidus for stoichiometric albite was 1105°C and the liquidus was 1125°C . A more silica-rich albite would melt at an even lower temperature. Enthalpy measurements by drop calorimetry also indicated that albite did not melt quickly until about 100 – 150 K above its melting point [5].

The equilibrium melting point can be obtained by DTA if the melting points of a series of different heating rates are

plotted as a function of heating rate and then extrapolated to zero heating rate.

2. Experimental

A fine-grained powder albite SRM (NBS no. 99 Soda–Feldspar) was chosen for study. X-ray diffractometry (XRD) was performed to determine its phase purity. Particle sizes were observed using a field emission scanning electron microscope (FESEM). Since the FESEM data indicated that some large grains existed, this SRM was milled to obtain a uniform $1\ \mu\text{m}$ diameter powder. The SRM was ball-milled (5 g albite, 90 g ZrO_2 , 0.5 cm balls, and 25 mL water in a 250 mL plastic bottle) using ZrO_2 milling media in deionized water for 12 h, poured into a porcelain evaporating dish, and then oven dried at 200°C . The proper choice of milling parameters was determined empirically for the production of micron-sized albite powder. The powder was heated in an electric resistance box furnace to 800°C for 6 h in an alumina (Al_2O_3) crucible to remove any hydroxyl contamination on the surfaces of the grains that might be introduced by the long milling time. An energy dispersive spectroscopy (EDS) spectrum was obtained to check for possible contamination by impurities that may have occurred during the milling process. Microprobe analysis of the sample was performed to

* Corresponding author.

E-mail address: mccauley@rci.rutgers.edu (R.A. McCauley).

check for any excess silica. A TA Instruments model SDT 2960 thermal analyzer was used to determine the melting point of the albite. Gold was chosen for temperature calibration because its melting point (1064 °C) is close to that of albite and it does not oxidize readily. A gold wire was heated in an alumina sample cup and formed into a sphere, which was then positioned in the center of the cup. The ball-milled albite was heated in platinum cups to avoid reaction with the alumina. Sample weights of 2.78 mg were used for both the gold and the albite. The DTA reference material used for all measurements was an alumina powder standard. Nitrogen (N₂) was used as a purge gas for all DTA runs.

3. Results and discussion

3.1. Powder characterization

The as-received albite was found by XRD to be phase pure and identifiable as ordered albite (JCPDS card 9-0466) except for one minor peak at 26.75° 2 θ . This is very close to the major peak for quartz (JCPDS card 33-1160). A Guinier pattern of ordered albite (JCPDS card 19-1184) does include a peak at this angle, indexed as a (221) reflection. Both cards for ordered albite designated this albite as triclinic with space group *C* 1. Therefore, it is possible that this peak was truly a reflection of albite and not from an impurity of quartz. To confirm this conclusion, a microprobe chemical analysis was performed to check for any excess silica by a comparison with a natural albite [6] and stoichiometric albite (Table 1). None was found.

In order to determine the particle size and distribution, the as-received albite powder was examined by FESEM. One can see from Fig. 1a that this SRM contained a wide distribution of particle sizes. This photomicrograph shows a range of sub-micron to micron-sized particles surrounding a larger 9 μ m sized grain. In order to have a more uniform sized powder for melting point studies, this SRM was ball-milled until a much more uniform 1 μ m material was obtained (Fig. 1b).

An EDS spectrum on the ball-milled powder was obtained to determine if any contamination had occurred during milling. There were some minor impurities of magnesium

(Mg), calcium (Ca), potassium (K), and zirconium (Zr), but they were all present below the 1% level as measured by a standardless quantitative analysis program. The Zr level was very low, and therefore, very little contamination had occurred by the milling operation.

3.2. DTA calibration

The DTA curves of the gold calibration sample for one set of heating rate runs (three measurements were made) are shown in Fig. 2a. The onset temperatures exhibited a continuous decrease in the melting point as the heating rate was decreased. The sizes and the widths of the endotherms also decreased with a decrease in heating rate. The minimum of the endothermic peaks is the temperature at which the reaction is completed, and the minimums also shifted to lower temperatures as the heating rate was decreased. These are all expected variations. The endotherms shift to lower temperatures with a decrease in heating rate because the temperature step has greater resolution with a smaller time step. The decrease in the size and breadth of the endotherms also decrease because the signal, which is the temperature difference between the sample and the reference material, becomes more equilibrated as the heating rate is lowered.

The equilibrium melting point of gold as measured by DTA was determined to be 1063.27 °C (an average of three measurements). A plot of the melting point versus heating rate is shown in Fig. 2b. The melting point was determined by extrapolation to zero heating rate using a linear fit to the data. The difference in the measured melting point and that of the reported value was -0.73 °C. This is larger than the largest standard deviation of about 0.10 °C. When the 1 and 3 °C heating-rate data were excluded, the melting point was determined to be 1063.34.

3.3. Melting point study

An attempt was made to use the same sample morphology for both the gold and the albite. The albite powder was placed into the platinum cup by pressing the powder in the center of the cup so that it melted to form one large bead of albite glass after heating. This, however, produced a very

Table 1

Microprobe analysis of the ball-milled albite and comparison with the chemical composition of albite pegmatite, Amelia County, VA [6] and stoichiometric albite

Sample measurement	Weight % oxide					
	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	SiO ₂ /Al ₂ O ₃
1	67.67	18.87	0.03	2.27	11.16	3.59
2	68.55	18.20	0.02	0.44	12.79	3.77
3	69.72	20.04	0.00	0.17	10.07	3.48
4	65.83	18.66	0.00	0.18	15.31	3.53
Average	67.94	18.94	0.02	0.77	12.33	3.59
Albite pegmatite	67.84	19.65			11.07	3.45
Stoichiometric albite	68.73	19.45			11.82	3.53

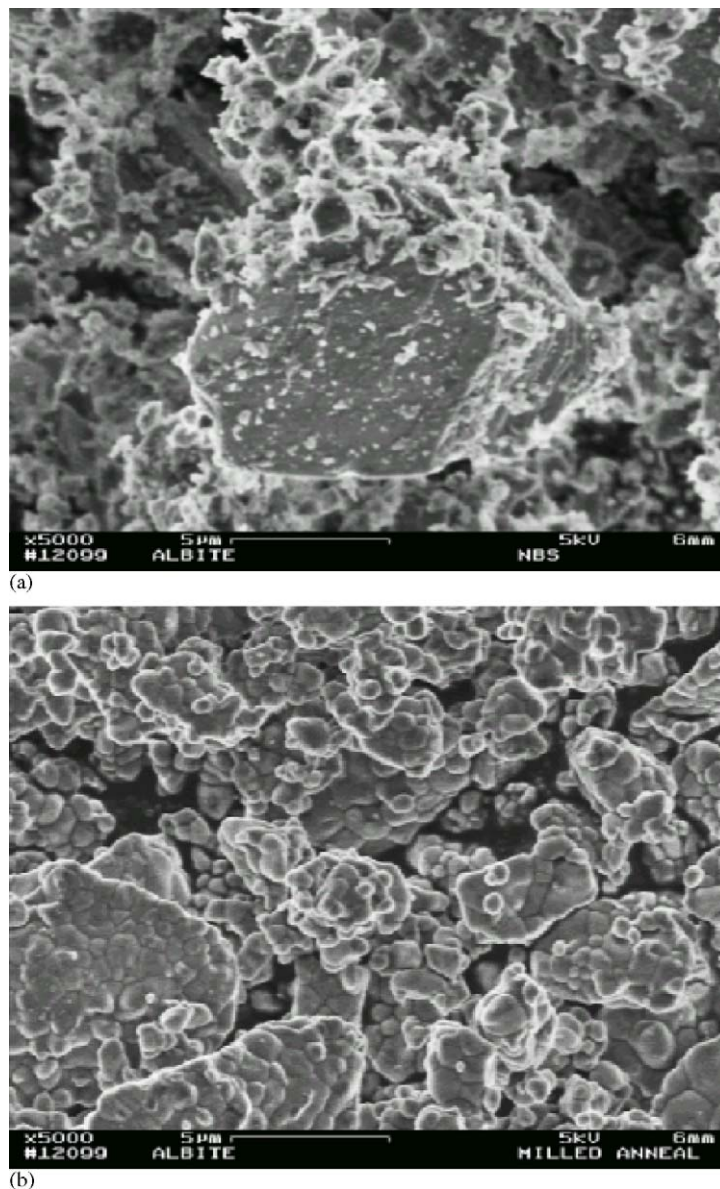


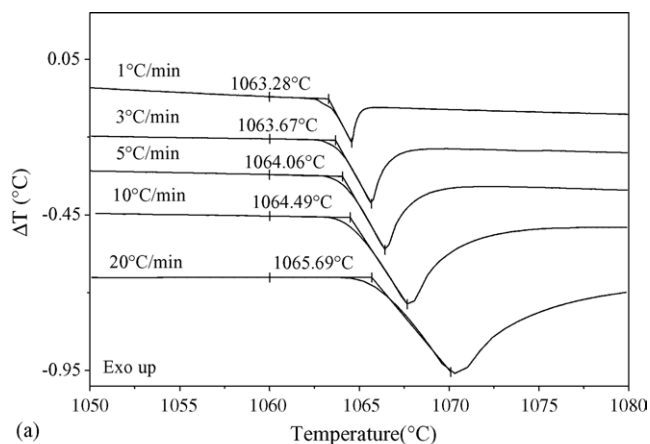
Fig. 1. FESEM micrographs of (a) the NBS no. 99 Soda-Feldspar, and (b) the ball-milled albite.

weak DTA signal. The amount of powder was then doubled but this still produced a weak signal. In order to obtain acceptable signals, the powder had to be loosely packed and spread over the entire bottom of the cup. This resulted in the production of many small beads of albite glass after heating.

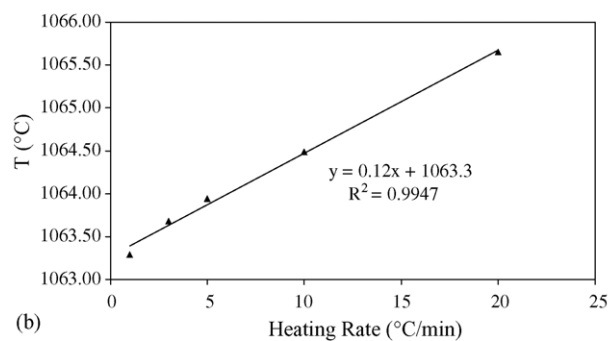
The DTA curves of albite showed a remarkably different heating pattern than those of the gold (Fig. 3a). The endotherms were very broad, indicating that the melting of albite occurred over a very large temperature interval. When the ΔT was plotted as a function of time (Fig. 4), the slopes of the melting curves indicated that the gold melted about 22-times faster than the albite, and that the time of melting was also much less than that required to melt all the albite. At a heating rate of $10^{\circ}\text{C}/\text{min}$, it took approximately 10 min to

totally melt the albite, whereas it took only 0.4 min to totally melt the gold.

The DTA curves of the gold sphere are much sharper, narrower, and smoother than those of albite. There are also oscillations in the ΔT of parts of some of the albite curves. These features can be most readily understood by a consideration of the sample geometry and its effect upon the recording of temperature by the thermocouple. The thermocouple, which records the sample temperature, is positioned to be in contact with a platinum foil over which the sample cup is placed. The sample and the sample cup are heated in a tube furnace so that the sample top surface is heated first and then the heat is conducted into the sample. At the same time, the sample cup is being heated from the sides and the heat is conducted inwards towards the sample. The heat of the sam-



(a)



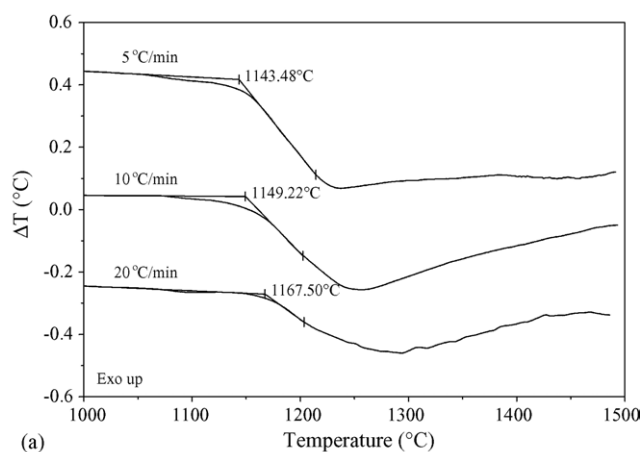
(b)

Fig. 2. (a) DTA curves of the gold sphere used for temperature calibration. Melting points are plotted as a function of heating rate. (b) The determination of the melting point of gold from heating rates.

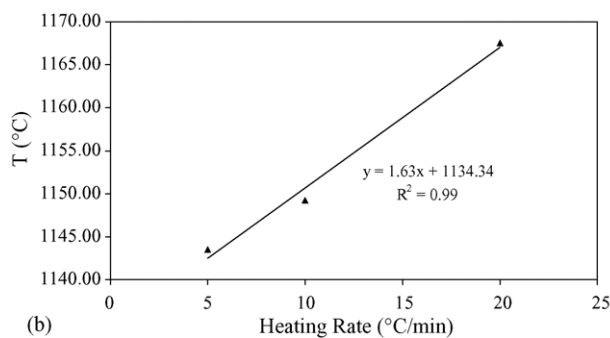
ple must be conducted through the bottom of the sample cup, through the foil, to the thermocouple. The onset temperature is then determined to be the initial deviation of the temperature difference between the gold and the alumina reference material.

An investigation of the effect of sample geometry showed that the position of the sample affected the results. The DTA curves of two very different geometries of the gold sample are shown in Fig. 5. The upper curve was obtained using the gold sphere that was used for the temperature calibration of the thermal analyzer. The lower curve was obtained using two different lengths of gold wire placed randomly into the alumina sample cup. This was done merely to get the gold wire to melt into spheres so that a suitable gold sample could be formed that would be reusable for the calibration study. It was found that the position of the sample in the cup would shift the DTA curve and the weight of the sample would affect the magnitude and the slope of the ΔT curve. Therefore, it was determined that in order to have consistency, a constant weight, morphology, and position of the gold sample had to be maintained throughout the measurements. It was concluded that it was this effect that dominated the lowering of the melting point of the gold in this study compared to that of the reported literature value.

Typically the melting of a material by the DTA technique uses a method in which the material is quickly heated to about



(a)



(b)

Fig. 3. (a) DTA curves of albite. Melting points are plotted as a function of heating rate. (b) The determination of the melting point of albite from heating rates.

100 °C below its melting point, allowed to equilibrate (which is typically 15 min) and then the desired heating rate begins. This aids in cutting down the time required for the data to be obtained. In the case of the gold sphere, the results obtained by using this equilibrate method and that of simply heating the material at the desired heating rate, beginning at room temperature, showed no significant difference. However, in the case of albite, the results were very different. It was not possible to obtain any endotherm by using the equilibrate method. This indicated that the albite must be slowly heated in order to obtain a result.

The onset temperatures of the albite samples exhibited a consistent decrease going from 20 to 5 °C/min. There are no data for the 1 and 3 °C/min heating rates because the method of equilibrating the sample before melting could not be used for albite, i.e., the measurement would take too long. However, the effect of eliminating the 1 and 3 °C/min heating rates for determining the melting point of gold was shown previously to not seriously affect the graphical result. Therefore, only data for the heating rates of 5, 10, and 20 °C/min were used to determine the melting point of the albite. The melting point was determined to be 1034.34 °C (Fig. 3), which was about 16 °C above the reported literature value. This could be interpreted as showing that albite can be superheated.

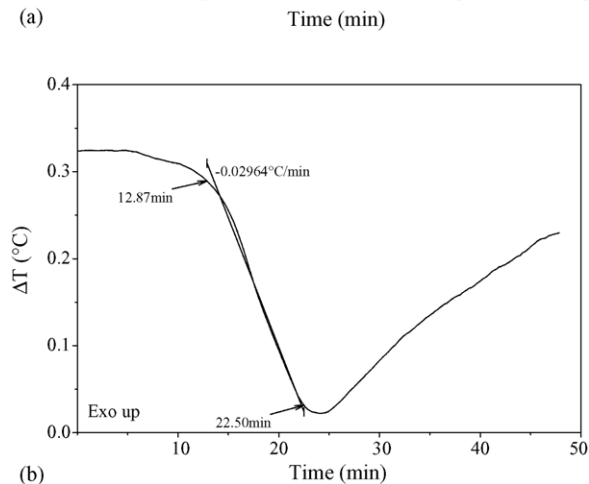
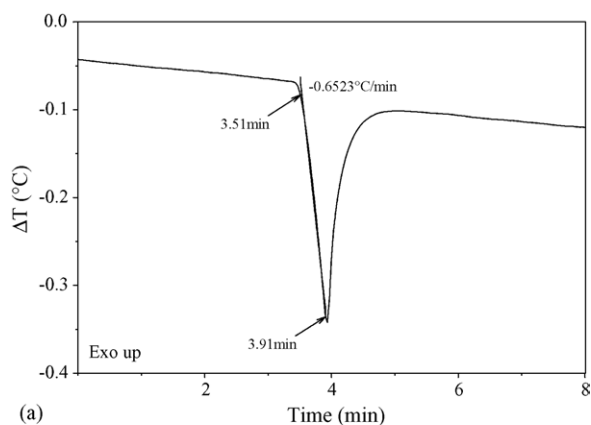


Fig. 4. DTA curves of (a) the gold sphere, and (b) the albite powder plotted as a function of time for the heating rate of $10^{\circ}\text{C}/\text{min}$. Zero time was arbitrarily set for ease of graphical analysis.

The melting points determined using heating rates of 5, 10, and $20^{\circ}\text{C}/\text{min}$ were 25, 31, and 50° above the reported melting point of albite, respectively. It took about 22, 10, and 7 min to totally melt the albite at 5, 10, and $20^{\circ}\text{C}/\text{min}$, respectively. The higher the temperature of melting, the faster the albite melted.

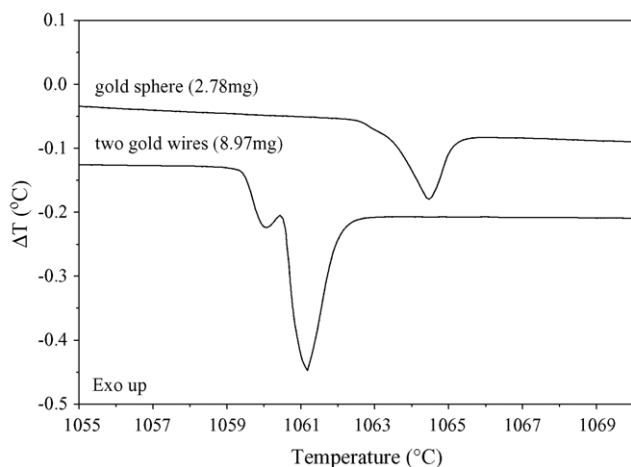


Fig. 5. The DTA curves of gold wire (two pieces) and the gold sphere used for temperature calibration. Heating rate is $1^{\circ}\text{C}/\text{min}$.

It was previously remarked that it was difficult to obtain a reasonable signal unless the albite powder was evenly distributed and loosely packed in the sample cup. Since two gold wires distributed in different areas of the sample cup gave two different endotherms, it is reasonable to assume that some of the broadening of the endotherms of the albite could be attributed to the much wider distribution of the powder in the sample cup and that the peaks represented a convolution of different endotherms. The oscillations observed in the ΔT curves after melting have been attributed to a collapsing of the sample [7]. The thermal contact, and therefore, the heat exchange between the sample with its surroundings has changed, and so the return to baseline is not smooth.

The results for the melting of albite indicated the possibility that albite could be superheated. Morse [8] has commented that although the superheating of crystals is rare, only those that melt to very viscous liquids, such as quartz or albite, have been reported in the literature. Navrotsky et al. [5] determined the enthalpy of albite at 1000–1773 K (727 – 1500°C) starting with both crystalline and glassy samples. The enthalpy values for the crystalline sample at 1400 and 1500 K (1127 and 1227°C) fell between the curves for crystal and liquid, even though these temperatures were above the melting point of albite. Since the calorimetric drop experiments last about 10 min, it was suggested that albite did not melt quickly. A mixture of glass and crystals of albite was found in the sample that started out all crystalline, whereas the glassy sample did not produce crystals. Since the samples were cooled for several hours to room temperature, it was suggested that the crystals represented incomplete melting and not crystallization from the melt.

In addition to the problems discussed above, there is one more that may play a role in the determination of the melting point of albite. What happens to albite and its melting point if substantial soda vaporizes during heating? A reasonable answer to that question can be obtained by examination of the phase diagram of the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system [9]. This diagram (Fig. 6) gives the melting point of stoichiometric albite as 1118°C . If soda vaporizes, the composition shifts towards the albite–mullite liquidus boundary curve. An immediate consequence of this is that the solidus temperature (i.e. first melting) changes to 1050°C and the liquidus decreases from 1118 to about 1104°C . Once the boundary curve is crossed, the liquidus temperature begins to increase, although the solidus will remain at 1050°C . So, if any soda vaporizes, the point of complete melting will first decrease to about 1104°C , but then increase and reach about 1200°C by the time that about 10–12% of the soda has vaporized. This vaporization of soda could easily explain the variation in the melting points reported in the literature and could also explain why the present study indicated melting point 15 – 50°C higher than literature data. Thermogravimetric (TGA) data that was collected simultaneously with the DTA run at a heating rate of $10^{\circ}\text{C}/\text{min}$ showed a weight loss of 1.09% from 1273 up to 1500°C that may indicate the vaporization of soda from the melt (Fig. 7). This weight loss occurred

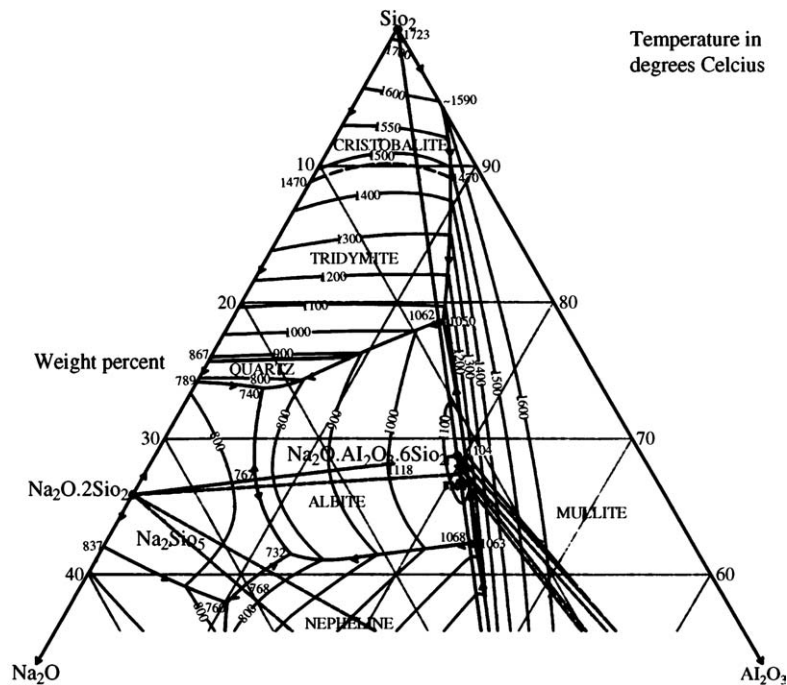


Fig. 6. The $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ diagram from Phase Diagrams for Ceramists, Fig. 501, 1964 [9].

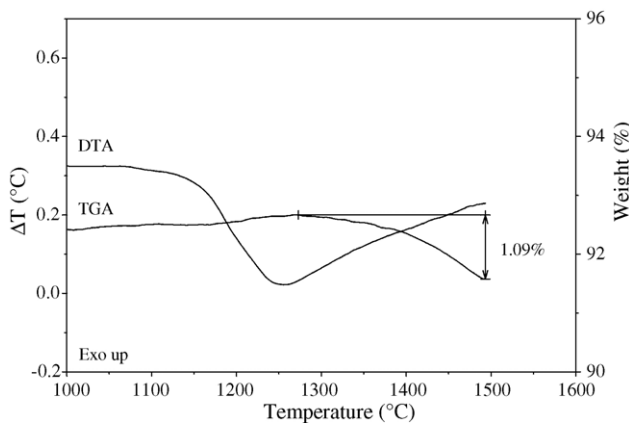


Fig. 7. DTA–TGA curves of albite using heating rate of $10^\circ\text{C}/\text{min}$.

after the temperature of complete melting of the albite. However, probably, the evaporation rate initially was slow, and therefore, small compared to the heating rate, so that no measurable weight loss occurred until the higher temperatures were reached.

4. Conclusion

The melting point of albite cannot be accurately determined from DTA measurements. The albite appeared to superheat about $30\text{--}50^\circ\text{C}$ above the reported melting points of 1118 [2] and 1100°C [3]. An alternative explanation could be the increase in liquidus temperatures caused by the vaporization of soda. Albite was totally melted in 10 min using

a heating rate of $10^\circ\text{C}/\text{min}$ and melting began at an onset temperature of 1134°C .

Acknowledgements

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