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CHEMISTRY

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1957

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Abstract

Full Text

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ON THE QUESTION OF THE MONOTROPIC TRANSFORMATION OF SPODUMENE

Among the numerous lithium minerals, spodumene more than others has been the object of various investigations. The greatest interest, and the greatest difficulties, were presented by the study of its thermal properties—fusibility and transformations at high temperatures.

As early as 1901-1903, Doelter (⁀1) determined the melting temperature of spodumene and, after many experiments, settled on the value 1080-1090°. These data are greatly underestimated and are completely obsolete. More recent and thorough investigations of spodumene were carried out by Endell and Rieke (⁀2) and by Barlow and Dittler (⁀3).

Endell and Rieke established that, when spodumene is heated to 920°, its specific gravity remains unchanged, but the mineral powder after 6 hours' heating at 980° has the specific gravity of glass; the change in specific gravity was observed over the range from 20° ($d = 3.147$) to 1380° ($d = 2.367$).

Observations of the birefringence of the mineral after cooling of the powders, and also on the heating stage of the microscope, showed that powder heated at 950° for 6 hours is anisotropic (in grains of 300-700 μ) or predominantly isotropic (5-30 μ).

The study of refractive indices made it possible to conclude that if, at 20°, spodumene has an average refractive-index value $n' = 1.66$, and this value is retained up to 920°, then at a higher temperature an instantaneous change in the refractive index occurs, and it assumes the value 1.519 ± 0.004 (at 980°), thereafter remaining constant.

Thus, the regions of instantaneous (discontinuous) changes in the examined properties of spodumene coincide within the rather narrow interval 920-980°, which should be called the region of thermal transformation of spodumene (the region of transition from one modification to another).

Endell and Rieke erroneously called this region the melting region. Independently of the conclusions drawn by the authors themselves, they established the existence of a more highly symmetrical modification of spodumene, which arises at temperatures close to 950° and is accompanied by a sharp increase in volume of 24%. In nature, only monoclinic spodumene has always been found, and its

transition into this unusual modification, differing so sharply in many physical properties, is irreversible.

Brun (⁀4) was the first to point out the inconsistency between the facts and the conclusion of Endell and Rieke, and believed that the change in the structure of spodumene with strong expansion occurs at 1010°; in this process the crystals of the mineral retain their form, but with slight pounding they crumble into a very fine dust.

Barlow and Dittler (⁀3) did not confirm Endell and Rieke' s observations on the disappearance of birefringence in heated natural spodumene; on the contrary, even above 1200° they observed distinct birefringence, which contradicts the opinion that spodumene is isotropic at high temperature. However, in determining the change in the specific gravity of spodumene after heating, Barlow and Dittler definitively established the presence in it of a high-temperature modification and evaluated it as polymorphic and irreversible. They showed that at high temperatures the rate of transformation of spodu-

change is very great: at 1050° in 1.75 hours, 90% of spodumene is transformed into the new modification, and at 1200° in 0.5 hour. Ballo and Ditler proposed the name α-spodumene for natural spodumene (by analogy with α-quartz, which appears at high temperature). This proposal should be considered correct, since β-spodumene does not differ from natural α-spodumene in composition, but only in its physical and optical properties and, consequently, all spodumene minerals occurring in nature should be regarded as metastable phases with respect to the β-form.

A practical consequence of studies of the transformation of spodumene was the use of roasting of spodumene-bearing rock for the purpose of enriching it in lithium ([5], [6], [7]).

It should be noted, however, that in order to obtain β-spodumene, the heating time of α-spodumene is determined not only by the mineral deposit, but also by the batch of ore (other conditions being equal), since pure spodumene does not occur in nature; rather, the most diverse stages of weathering of this mineral are presently represented in it.

As a result of hypergene changes, the kaolinization of spodumene increases, and the process of albitization also occurs; as a result, the heating curve of spodumene shows additional effects, so that thermal analysis, as S. G. Tumanov and G. N. Maslennikova ([8]) state, can serve as a method for determining the degree of kaolinization of spodumene. This is of undoubted practical interest, although, in our opinion, thermal analysis in this case will not be sufficiently accurate. We were interested in the transformation of spodumene itself, and not of the products of its alteration, and in this connection we traced the influence of the heating rate and of various impurities on the temperature of the monotropic transition of α-spodumene into the β-modification.

Table 1

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Composition of α-spodumene samples, wt. %

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Li_2O	Σ
1	64.04	31.18	traces	0.22	traces	0.01	traces	5.12	100.57
2	65.34	30.10	”	0.20	”	0.01	0.14	4.70	100.49
3	66.34	27.58	”	0.22	”	0.12	0.12	6.05	100.43

Table 1 gives the chemical analysis of three spodumene samples on which the present work was carried out (the composition in wt. % is expressed after recalculation to the mineral after ignition). The spodumene was selected under a binocular microscope and freed from foreign minerals.

In addition, general spectral analysis revealed titanium and manganese in all the samples, as well as copper in samples 1 and 3, and tin in sample 2.

The temperature effects for the $\alpha \rightarrow \beta$ transformation, obtained from heating curves recorded at two heating rates, are presented in Table 2.

Table 2

Ranges of the $\alpha \rightarrow \beta$ transformation of spodumene

Sample No.	Heating rate, deg/min	Range of spodumene transformation, °C
1	11	995–1050
1	21	1005–1070
2	10	1025–1070
2	22	1026–1100
3	11	990–1035
3	22	995–1070

As is evident from Table 2, with an increase in the heating rate the temperature at which the transformation begins rises, and the transformation interval broadens. This agrees with the observation of Meissner ([9]), who, it seems, was the first to point out such an influence of the heating rate on the monotrop-

transformation of spodumene. In general, the influence of the rate of heating in solving a number of questions by means of thermal analysis must always be taken into account; unfortunately, in many investigations no importance is attached to this.

Table 3 gives data on the influence of additions of pure quartz and potassium sulfate on the temperature of the $\alpha \rightarrow \beta$ transformation of spodumene at a constant heating rate ($\sim$ 11 deg/min) of the mineral samples. From these data, in comparison with those of Table 2, it is evident that SiO_2 and K_2SO_4, being

mechanically admixed to spodumene, lower the temperature of the $\alpha \rightarrow \beta$ transformation; moreover, with an increase in the content of the added component, its influence increases. It should also be noted that the influence of potassium sulfate proves to be smaller.

Table 3

Influence of additions of SiO_2 and K_2SO_4 on the temperature of the $\alpha \rightarrow \beta$ transformation of spodumene

Sample No.	Additions to spodumene, wt. %	Transformation range, °C
1	5 (SiO_2)	975–1010
1	20 (SiO_2)	915–1000
1	5 (K_2SO_4)	1005–1035
1	50 (K_2SO_4)	965–990
2	5 (SiO_2)	990–1035
2	20 (SiO_2)	925–1020
2	5 (K_2SO_4)	1005–1035
2	50 (K_2SO_4)	975–1010
3	5 (SiO_2)	960–1005
3	20 (SiO_2)	905–1000
3	5 (K_2SO_4)	965–995
3	50 (K_2SO_4)	950–980

It is interesting that the impurities contained in the spodumene itself, i.e., isomorphous substitutes for lithium, of which, according to Gabriel' s observations ([10]), there may be as much as 10 (and probably even more), also exert a very substantial influence on the temperature of the monotropic $\alpha \rightarrow \beta$ transformation of spodumene.

The regularity of this influence is not entirely clear; however, if the data of Tables 1 and 2 are compared, it may be noted that the spodumene richer in lithium undergoes the $\alpha \rightarrow \beta$ transformation at a lower temperature.

This agrees with the observations of Endell and Rieke ([2]), who dealt with the purest of the spodumene samples ever found (7.62% Li_2O) and obtained the lowest value of the temperature of the monotropic transformation.

Such an influence of elements substituting for lithium in spodumene on the temperature range of its transformation is very characteristic, but not unusual, if one accepts that the substitution of lithium by many elements has an isomorphous character ([10]), since usually the formation of solid solutions based on a component possessing a polymorphic transformation lowers the temperature of this transformation. Obviously, the study of the character of the substitution of lithium in spodumene by one or another element should be of independent interest.

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Received
15 X 1956

REFERENCES CITED

1. C. Doelter, *Handb. d. Mineralchemie*, Dresden–Leipzig, **2**, Abt. 2, 1917, S. 193–204.

2. K. Endell, R. Riecke, *Zs. anorg. Chem.*, **74**, 33 (1912).

3. R. Balló, E. Dittler, *Zs. anorg. Chem.*, **76**, 36 (1912).

4. A. Brun, *Zs. anorg. Chem.*, **75**, 68 (1912).

5. M. N. Sobolev, V. V. Plotov, P. I. Assoskov, *Rare Metals*, no. 3, 47 (1932).

6. F. Fraas, O. Ralston, US Dep. Int. Bur. Mines, Rep. Invest., No. 3336 (1937).

7. R. Hader, R. Nielsen, M. Herre, *Ind. and Eng. Chem.*, **43**, 2636 (1951).

8. S. G. Tumanov, G. N. Maslennikova, *DAN*, **107**, 119 (1956).

9. F. Meissner, *Zs. anorg. allg. Chem.*, **110**, 187 (1920).

10. A. Gabriel, M. Slavin, H. Carl, *Economic Geology*, **37**, 116 (1942).

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