Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

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of cubic crystals in phyllites and quartzites of the Wai Miha region, whence also pseudomorphoses of limonite originate.

Quartz was found in limpid and dull-white crystals, attaining a length of 9 cm., found near Pela, situated between the Wai Miha and the Wai Ha. The shapes are the usual combinations of ∞R , R and -R.

Calcite. Elegant skalenhedrons R3 were found in a concretion, originating from the river Kempa, a tributary of the river Wai Miha, and likewise in a cavity of a geode with Macrocephalites. Small rhombohedrons are present in the cavity of the chamosite-rock in the neighbourhood of the mouth of the Wai Najo.

Rhodochrosite occurs in the shape of small rhombohedrons on the walls of the air-chambers of a *Macrocephalites* from the Betino.

Siderite was detected in a boulder of quartzite, originating from the upper-course of the Wai Miha, in the shape of yellowish rhombohedrons. Brown rhombohedrons together with calcite were found in the chambers of an Ammonite from the Wai Galo.

Barite. All the chambers of Macracephalites keeuwenis G. BOEHM are sometimes filled with limpid barite in such a way that the whole mass forms one individual.

Chemistry. — "Studies in the Field of Silicate-Chemistry." II. On the Lithiumaluminiumsilicates whose composition corresponds to that of the Minerals Eucryptite and Spodumene. By Prof. F. M. JAEGER and Dr. ANT. ŠIMEK. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of May 30, 1914).

§ 1. In connection with the study of the ternary system, whose components are: *lithiumoxide*, *alumina* and *silica*, it was necessary for us, to obtain the compounds, whose composition corresponds with that of the minerals *eucryptite* and *spodumene*, in a perfectly pure state, and to investigate their characteristic properties. The third ternary compound, corresponding in its composition with the mineral *petalite*, will be taken in account only afterwards, as for some reasons it is better to deal with it, when the experimental study of the ternary mixtures themselves shall have proceeded some-what further.

The eucryptite: $LiAlSiO_4$ belongs to the series of silicates, whose other members are: *nepheline*, *kaliophilite*, etc. In nature the said compound occurs in the form of microscopical, hexagonal crystals, e.g. in the albite of BRANCHEVILLE (Conn.); albite and eucryptite both take their origin here from spodumene, decomposed by solving agents. The spodumene $LiAlSi_2O_6$ is a monoclinic lithiumpyroxene. The mineral is found in several places, in the form of colourless or feebly tinged, glassy crystals of prismatic habitus, or in the form of opaque, cryptocrystalline aggregations. The transparent or coloured varieties.

which are strongly dichroitic, are used as a beloved precious stone; they are called: *triphane*, *kunzite*, *hiddenite*, etc. Their properties are mentioned further on.

§ 2. As was already pointed out, in a previous paper 1) on lithiumsilicates, the synthesis of the pure compounds offered severe difficulties, caused by the volatilibility of the lithiumoxide at higher temperatures. The composition of the mixture is thus altered during. the synthesis, and the quantities of all three components must therefore afterwards be corrected, after being accurately determined by long and troublesome analysis. A relatively small loss of the lithiumoxide, is of considerable influence on the meltingpoint and other properties of the investigated compound, because of the very small molecular weight of the oxide. The analysis offered many difficulties: for notwithstanding all care and all arrangements ¹), it often happens, that some $Al_{2}O_{3}$ is found in the silica, and some SiO_{2} in alumina, so that afterwards a controlling determination of these admixtures must be made, which takes a lot of time. The small amount of $Li_{s}O$ is furthermore hardly determinable under the colossal excess of $Na_{2}O$ in the liquid; therefore, being determined as the difference of 100°/, with the sum of the percentages for SiO_{2} and $Al_{2}O_{3}$, all mistakes and inaccuracies of those determinations are summed up in the number for Li_2O , so that the correction of the preparation afterwards, often depending on very slight differences in the amount of $Li_{2}O$, is a hazardous and not very amusing task. So it takes much time to obtain products, which will not differ appreciably in their constants and properties from those to be expected for the true pure compounds, the criterium being given by the perfect identity of the products, prepared in several ways.

§ 3.' Synthesis and Properties of the Pseudo-Eucryptite.

The materials for this and other syntheses were the same, whose purity was before tested and described; the alumina used was also provided by BAKER and ADAMSON. It was necessary to heat it for a long time in a platinum dish on the blaze, and often to stir the powder with a platinum-wire, to allow the watervapour and the nitrous gases, which the preparation evolved, to escape completely. The

1) F. M. JAEGER and H. S. KLOOSTER, these Proceedings p. 900, Febr. (1914).

heating was checked when the weight of the dish remained constant after repeated heatings. Analysis then showed, that an almost pure Al_2O_3 (100 °/_o) was_present; even no appreciable trace of iron could be demonstrated with the usual reagents.

To point out the change of composition, taking place on heating mixtures of known composition during the melting of the mass, the numbers here following can serve very well: a mixture of 6,23 gram Li_2CO_3 , 8,61 gram Al_2O_3 and 10,16 gram SiO_2 , was melted in a closed platinum crucible in the FLETCHER-furnace at 1500° C. After crystallisation, the mass was finely ground and sieved, melted again, and this process repeated three times. Instead of the expected composition I, the composition II was found by analysis to be:

	I	II
SiO2	47,7°/。	48,6 °/,
Al_2O ,	40,4 °/,	40,9 °/,
Li_2O	11,9 º/。	10,5 °/,

As there was thus $1,5^{\circ}/_{\circ} Li_2O$ too little, 0,055 gram Al_2O_3 and 0,718 gram dry Li_2CO_3 were added to 18,92 gram of the resulting product, and this mixture was then heated four times in platinum crucibles, by means of small resistance-furnaces, at.900° or 1000° C., the mass being finely ground and sieved after every melting. Then the preparation was again heated once at 1450° C. in a resistance-furnace. Analysis gave:

	Observed ·	Calculated :
, SiO2	47,9 °/。	47,7 °/。
Al_2O_3	40,1 °′	40,4 °/,
Li_2O	12,0 °/,	11,9 °/,

The deviation from the exact composition is so slight, that this preparation could safely be used for the study of the properties of the compound.

§ 4. The meltingpoint of this preparation was determined several times by means of a calibrated thermoelement (N^o. *III*) The mean value of all readings was 14200 M.V. ± 2 M.V.; as the correction of this element with respect to the standard element, which was standardized by means of SOSMAN'S element G, was -12 M.V.; the meltingpoint of the substance, in terms of the *Washington* nitrogengas thermometerscale, can be fixed at **1388**° C.

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The heat-effect on melting is only small; as a result of that, on cooling down the molten mass, one finds a retardation of its crystallisation up to about 12840 M.V.; then crystallisation takes place while the temperature increases only to 1306° C. The point of solidification therefore is found 80° or 90° below the true température of equilibrium : solid \gtrsim liquid, although the velocity of crystallisation can by no means be called very small. From this fact also the discrepancies in the data of different authors are to be explained : 1330° C. (DITTLER and BALLÓ), 1307° C. (GINSBERG), etc. In this case also, the usual method of cooling appears to give no reliable results.

A remarkable fact is the relatively appreciable *increase* of the volume of the molten mass on crystallisation; it is immediately observable by the deformation of the platinum-crucible. (fig. 1). That

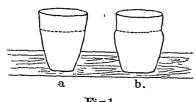


Fig 1. Increase of the volume of molten Eucryptite on crystallisation. really this phenomenon is caused in this case by a volume-change like that of water into ice at the freezing-point, and that it need not be explained in the manner mentioned in the case of the spodumene, can be demonstrated by the determination of the specific gravities of the crystallized

mass, and of that of the beautiful, colourless "glass", obtained by suddenly chilling the liquid. The expansion seems to be about $3^{\circ}/_{\circ}$ of the original volume.

§ 5. The crystallized substance, obtained by slowly cooling the liquid, is opaque and greyish white. Microscopical investigation showed it to be a cryptocrystalline aggregation of irregularly shaped, grain-like crystals, which are so small, that even with an 800-times enlargement, they can hardly be seen; they possess a very weak birefringence. Greater pieces seem to be built up between crossed nicols by innumerable lighting points; such aggregations always show an undulatory extinction. In no case crystals with determinable borders were found. As a "mean" refractive-index the value: $n_p = 1,531 \pm 0,002$ was obtained.

The specific gravity at 13°,6 C. was pycnometrically found to be: $d_{4^0} = 2,365$, and at 25°,1 C: $d_{4^0} = 2,362$; we used orthochlorotoluene (1,0825 at 25°,1 C.) as immersion-liquid.

As follows clearly from those values for the refraction of light and for the specific gravity, the natural *eucryptite* must be another modification of the compound $LiAlSiO_4$; therefore we will distinguish the artificial silicate by the name : *pseudo-eucryptite*.¹).

¹) GINSEERG (Zeits. f. anorg. Chem. **78**. **291** (1911)) describes his preparation in the following manner: completely isotropous, uniaxial negative in convergent polarised light, with a birefingence smaller than that of nepheline. WEYBERG asserts to have obtained an "eucryptite" of rhombic symmetry, by the reaction of Li_2SO_4 on kaoline in solution. Cf. also the experiments of THUGUTT, Zeits. f. anorg. Chemie **2**. **116**. (1892).

§ 6. The glass, obtained by suddenly chilling the molten mass in mercury or cold water, is colourless, perfectly clear and exceedingly hard. It can be removed from the platnum-crucibles in an easier way than the crystallized mass, which fact is connected with the volume-change in crystallizing.

The refractive index of the glass appeared to be. $n_{\rm D} = 1,541$. We have prepared several glasses of varying chemical composition, all in the vicinity of the composition of the pure compound, with the purpose to measure accurately the refractive indices and the dispersion, in order to get information about the influence of the chemical composition on the optical behaviour of these glasses. They were ground in a flat cylindrical form, and in all directions carefully polished; then they were investigated by means of an ABBE-crystalrefractometer in light of different wave-lengths.

For pure *pseudo-eucryptite-glass* of the composition $LiAlSiO_4$, we found:

	Wavelength in $\lambda.U.$	Angle of Total-	Refractive	Δ :
		reflection :	Index :	
Li :	6708	62°11′	1,5450	
	- 000	0.105.11		0,0040
Nu:	5893	61°54′	1,5410	0.0050
Tl:	5350	61°31′	1,5354	0,0056

In the following are summarized the measurements with the glasses :

II. Compos:	47,5º/, Si 02;	40,0°/, Al, O3; 12,5°/, Li2O
III. Compos:	42,5º/o Si O2;	$38,6^{\circ}/_{\circ}$ Al_{2} O_{3} , $18,9^{\circ}/_{\circ}$ Li_{2} $().$
IV. Compos.	48,4°/0 Si O2,	$39,3^{\circ}/_{\circ} Al_{2} O_{3}; 12,3^{\circ}/_{\circ} Li_{2}O.$

	Il.		
Wavelength in	Angle of	Refractive	Δ :
Å. U .:	Total reflection:	Index:	
6708	62°26′	1,5484	
			0,0047
5893	$62^{\circ}5^{1}/_{2}'$	1,5437	0.0044
2950	010471	1 2909	0,0044
5550		1,0090	
Wavelength in	Angle of	Refractive	Δ :
À. U.:	Total reflection :	Index :	
6708	63°36′	1,5647	
			0,0048
5893	63°15′	1,5599	
Koko			0,0039
5350	62°58′	1,5560	
	Å. <i>Ü</i> .: 6708 5893 5350 Wavelength in À. <i>Ü</i> .:	Wavelength in Angle of Å. U.: Totalreflection: 6708 $62^\circ 26'$ 5893 $62^\circ 5^1/_2'$ 5350 $61^\circ 47'$ 111. III. Wavelength in Angle of Å. U.: Totalreflection: 6708 $63^\circ 36'$ 5893 $63^\circ 15'$	Wavelength in Å. U.:Angle of Totalreflection:Refractive Index: 6708 $62^{\circ}26'$ $1,5484$ 5893 $62^{\circ}5^{1/2'}$ $1,5437$ 5350 $61^{\circ}47'$ $1,5393$ $111.$ $111.$ Wavelength in Å. U.:Angle of $63^{\circ}36'$ Refractive $1,5647$ 5893 $63^{\circ}15'$ $1,5599$

		IV.		
	Wavelength in	Angle of	Refractive	Δ :
	Å. U.:	Total reflection :	Index :	
Li	6708	61°50′	1,5400	
				0,0046
Na	5893	61°31′	1,5354	
				0,0053
Tl	5350	61°9′	1,5301	

It is difficult to deduce a simple relation of chemical composition and optical properties from these data. Generally speaking, an increase of the amount of Li_2O seems to cause an increase of the refractive power (except in IV), while a larger amount of SiO_2 appears just to diminish the refractive index, the exceptional case IV could be explained by the superposition of these two causes. This dependence of the quantities of the oxides present, appears to bear some connection with the relatively higher refractive power of the lithiumoxide, and the smaller one of the silica ').

The pseudoeucryptite-glass is, with respect to the opaque, crystallized compound, a typical *metastable* phase: already on heating the glass during a very short time in a BUNSEN-gasburner, the pieces of glass become primarily yellowish, then they become opaque, and finally they appear under the microscope wholly changed into the mentioned cryptocrystalline aggregation of birefringent grains. If heated only for ten minutes at 900° C., they are completely changed, and the same occurs, on heating the finely powdered glass during some time with molten LiCl or LiF in a platinum crucible.

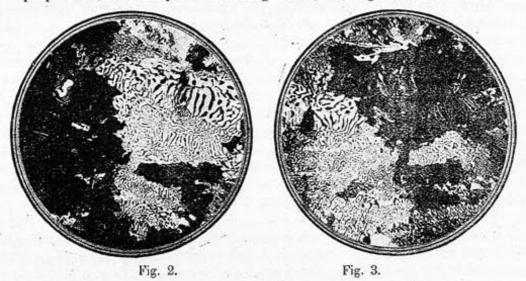
The specific gravity of the pure pseudo-eucryptite-glass was determined by means of the method of swimming, in a mixture of bromoform and benzene, at 13° C.; it was found to be: $d_{40} = 2,429$. Thus both the refractive index and the density of the glass are somewhat higher than for the crystallized compound.

§ 7. Finally we have compared the artificial product with a natural eucryptite of BRANCHEVILLE (Conn.). The mineral, of which a thin section was prepared, looked as an aggregation of cryptocrystalline, homogeneously extinguishing fields: however, although they had superficially some analogy with the artificial product, they must be considered as composed of much larger crystals, showing apparently the kind of structure, somewhat similar to the so-called "schrift"-granite. Locally it is intermixed with a much more strongly

¹) F. M. JAEGER and H. S. VAN KLOOSTER, these Proceedings, loco cit. (1914).

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birefringent mineral; although the eucryptite is here generated from spodume, with deposition of albite, the properties of the inclusions did not agree with those of the two lastnamed minerals. The specific gravity was pycnometrically determined to be $d_{4^0} = 2,667$ at 25° C.; the available data show the composition not to be the proper one, the SiO_q -amount being $0,6^{\circ}/_{\circ}$ too high and that of the



 LiO_{*} about 1 °/₀ less than the theoretical value. The fig. 2 and 3 represent two microscopical preparations of the thin section between crossed nicols; in the fig. 3 the preparation is turned over 30° with respect to that in fig. 2; — this fact pointing to a trigonal twinformation. Also the very peculiar structure of the crystals is shown in fig. 3.

The refractive index was microscopically determined on : $n_D = 1,545 \pm 0,002$. A definite meltingpoint could not be fixed by the usual, dynamical method; at about 1120° C. the mineral gradually changes into a viscous mass, which, on cooling, becomes a glass. The refractive index of this glass appeared to be : $n_D = 1,506 \pm 0,001$; it is thus evidently lower than that for the glass of *pseudo-eucryptite*. On being heated it is devitrified only slightly; there seems to be no doubt, that the natural mineral and its glass are other than the corresponding phases of the artificial product. As also never any indication of an occurring inversion could be found, it is highly probable that eucryptite and pseudo-eucryptite are in relation of monotropic modifications to each other.

§ 8. Synthesis and properties of β -Spodumene. The compound, whose composition is: $LiAlSi_{*}O_{*}$ was prepared

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by us in four different ways, just to get information on the final identity of such preparations:

a. By melting together calculated quantities of Li_2CO_3 , Al_2O_3 and SiO_3 , repeating this manipulation a few times, after thoroughly grinding and sieving the crystallized masses. Analysis and correction were made as usual.

b. By starting from pure Li_2SiO_3 , Al_2O_3 and SiO_2 .

c. From $LiAlSiO_4$ and SiO_2 .

d. From $LiAlO_2$, the lithiumaluminate, and SiO_2 .

The four preparations, thus obtained, were used only for the definitive measurements after it had been proved by repeated analysis and correction, that their composition did correspond, within the limits of error, with that of the formula. All these experiments were made in electrically heated furnaces with oxidizing atmosphere; the preparation of these substances took a long time, because of the volatibility of the Li_2O , and the fact, that only small deviations in the content of Li_2O showed themselves of appreciable influence on the meltingpoint and properties of the compound.

§ 9. The purest preparation we got, was obtained from synthetical eucryptite by admixture of SiO_2 . Analysis gave the following data:

	1.	II.	Calculated :
SiO_{2}	64,39 °/,	64,43 °/,	64,6 °/,
Al_2O_3	27,56 °/,	27,66 °/,	27,4 °/。
Li,O	8,05 °/。	7,91 %	8,0 º/,

The mass was kept during a longer time at a high temperature, to allow it to crystallize totally. Then the meltingpoint was determined in the usual way, by means of thermoelement *III*; we found:

14353	M.	V.
$14\ 341$	М.	V.

Mean: 14 347 M. V. (without correction),

if the rate of heating was about 65 M.V. prominute. As the correction for the thermoelement was -12 M.V. at this temperature, the meltingtemperature is 1400° C, in terms of the nitrogenthermometer.

As a check the meltingpoint was now again determined by the statical method: very small quantities, wrapped in platinum folium were heated during a considerable time (from half an hour to one full hour) at a certain and accurately constant temperature, and then, after suddenly chilling ¹) in cold mercury, investigated by means of

¹) F. M. JAEGER, Eine Anleitung zur Ausfuhrung exakter physiko-chemischer Messungen bei höheren Temperaturen. Groningen, 1913, Seite 73, 74. the microscope. We found that after heating at 14340 M. V. (element III) the whole preparation was again crystalline. although it had the outward appearance of a glassy, half-opaque mass; but on heating at 14360 M. V., all had been changed into a real "glass". The meltingtemperature therefore must be fixed at 14350 M. V. As the correction for the used quenching-system (vid. the determinations of the meltingpoint of natural spodumene of *Madagascar*) was shown to be practically equal to zero, we can conclude from this, that the meltingpoint thus determined is in full agreement with that found by the dynamical method, and can be put at 1401° C. (G Th.). The crystallized product appeared to be identical with the β -modification, later to be described, the refractive index was about: n = 1,521; the specific gravity at 25° C : $d_{4^{\circ}} = 2,411$.

2. In a similar way the preparation, obtained from lithiumaluminate and $Si O_2$ was investigated; analysis gave the following data:

	I	II	Calculated:
Si O2	64,80°/。	64,07°/。	64,6°/。
A 0,	27,83°/,	28,09%/0	27,4°/,
Li, O	7,37°/。	7;84°/。	8,0°/,

This preparation therefore evidently can also be considered as a very good one; it contains ca. $0,4^{\circ}/_{\circ}$ $Li_{\circ}O$ too little, and ca. $0,5^{\circ}/_{\circ}$ $Al_{\circ}O_{\circ}$ too much.

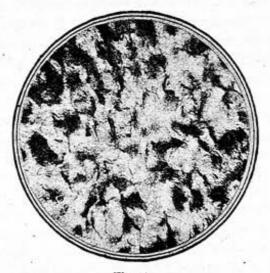


Fig. 4. Artificial β -spodumene, obtained from $LiAlO_2$ and SiO_2 ; melted and slowly cooled. (\times Nicols).

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The meltingpoint, determined after the dynamical method (element III), was found:

Mean 14472 M. V. \pm 10 M. V. (without correction);

after correction, the meltingpoint can be fixed at $1410^\circ \pm 1^\circ$ C. (G.Th.). After 'the statical method, the meltingpoint was determined at 14450 M. V., corresponding to 1410° C. The small excess of Al_2O_3 has evidently caused an *increase* of the meltingtemperature, of about 9° C. The crystallized product again was shown to be β -spodumene (n = 1,519); a photograph of it, taken between crossed nicols is reproduced in fig. 4.

3. An analogous result was, in both ways, obtained with a preparation, prepared from Li_2SiO_3 , Al_2O_3 and SiO_2 . Analysis of this product gave the following data:

	I	II	Calculated :
Si O2	64,7 °/,	64,48 °/。	64,6 °/,
Al_2O_3	28,4 º/o	28,5 °/.	27,4 °/,
Li ₂ O	6,9 °/,	7,1 º/。	8,0 %

The content of SiO_2 is here the right one, but the Al_2O_3 is $1^{\circ}/_{\circ}$ too high. The meltingpoint determinations gave as a mean value: 14456 M.V. (uncorr) after the dynamical method, and about: 14450 M. V. after the statical method. The meltingpoint is therefore: 1409° C. (G.Th.).

4. Most deviating from the composition: $Li \ Al \ Si_2 O_s$, was a preparation, obtained from the melting together of $Li_2 CO_s$, SiO_2 and $Al_2 O_3$. Analysis gave the following numbers:

	I	IĬ	Calculated :	
Si O ₂	64,44 °/,	64,88 °/,	64,6 º/。	-
Al_2O_3	27,09 %	27,17 %	27,4 º/。	
Li_2O	8,47 º/。	7,95 °/,	8,0 °/,	

Evidently it contains about $0,21 \, ^{\circ}/_{0} Li_{2}O$ too much.

After the first method the meltingpoint was found at 14552 M.V. (uncorr.), and after the statical method: 14550 M.V. The true meltingpoint can thus be put at: 1417° C. (G.Th.).

§ 10. Although in most cases perfectly colourless products were obtained, which evidently were identical to and independent of the particular manner of preparing them, and which all represented the β -modification, — we succeeded however in several cases in obtaining beautifully crystallized preparations, which locally or also totally were

tinged with a nice, reddish lilac hue; they were in most cases obtained by longer heating, somewhat *below* the meltingtemperature.

The meltingpoint determination with such an intensively coloured product, prepared from $LiAlO_2$ and SiO_2 and showing by analysis the following composition:

I.	II.	Calculated :
Si O2 64,92 %	64,77 %/	64,6°/,
Al ₂ O ₃ 28,10 °/ ₀	27,94 °/,	27,4 °/。
Li 0 6 98 %	7.29 %	80%

and thus evidently containing about $0.63 \,^{\circ}/_{\circ}$ too much alumina, gave the following results (statical method):

After	heatir	ig at	14660	M.	V.:	alı	glass.
"	,,	,,	14640	M.	v.:	all	glass.
,,	,,	,,	14600	М.	V .:	all	glass.
"	"	,,	14500	M.	V.:	all	crystallized.
,,	,,	,,	14560	М.	V .:	all	crystallized.
		1	at the at a d	- 4	1156		A 37

The meltingpoint is thus situated at 14580 M.V., corresponding with 1420° C. (G.Th.).

Such lilac coloured preparations present in most cases rather larger individuals of the β -modification, which possess a tabular shape with appreciably stronger birefringence than the common cryptocrystalline masses, although the mean refractive index is the same. While commonly this birefringence varies between 0,001 and 0,003, it amounts in these preparations to about 0,007; the principal refractive indices are about: 1,520 and 1,527. In convergent polarized light, at the border of the field an interference-image is partially visible, giving the impression of that of an uniaxial crystal. However on moving the table of the microscope, one can easily observe the curvature and even the hyperbolic form of the dark beams; undoubtedly an optically *biaxial* crystal with a very small axial angle, is present here; while the position of the first bisectrix and the character of the dispersion, point to *monoclinic* symmetry, with a strong tendency to tetragonal forms. This last pecularity can be deduced, — besides from the apparent uniaxity — from the fact, that rectangular plates are not rare, which possess an extinction under right angles or parallel to a diagonal, and a system of cleavage-directions under 45° with the optical sections. The specific gravity, like the refractive , indices, does not differ appreciably from that of the common β -form, and was determined at 25° C.: $d_{1^0} = 2,401 \pm 0,008$, measured with several preparations. We obtained these same apparently uniaxial plates, also from natural spodumenes by melting and slowly crystallizing; there is no doubt whatever about the fact, that these tabular

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crystals are identical with the common β -form, which represents the stable form at the meltingpoint; the plates must be a peculiar kind of crystals of this β -modification.

However we have till now not succeeded in giving a final explanation of the remarkable reddish-lilac colour of many of these preparations. It is quite sure, that it does not depend in any way on the admixture of certain metallic impurities, solved from the cruciblewalls, on the contrary it appears to be connected with the macrocrystalline structure of the preparations. The nearer the chemical composition came to the theoretical one, and the slower the crystallisation of the mass takes place, by heating during a long time at a temperature just below the meltingpoint, the more the appearance of the violet tinge seems to be probable.

The same colour appears, if spodumene-powder or the pulverized "glass" of it, are brought into liquids of about the same refractive index (e. g. into orthochlorotoluene, with n = 1,522); in that case the wellknown phenomenon of the "monochromes" (CHRISTIANSEN) will appear. It is not impossible, that in our case the colour is produced in an analogous way by the presence of the tabular, very thin crystals amidst spodumene-glass, which possesses about the same refractive index (1,519) as the crystal-tables (1,520 till 1,527), or reversely; these tables would be therefore quite invisible in the surrounding medium. It could be understood in this way also, why in the uncoloured mass in some cases locally smaller or larger pink spherolithes are produced, making the impression, as the molten mass were locally inoculated with germs of the violet substance.

By means of the ultra-microscope we were able to show, that the preparation was *not* "optically empty", as a great number of differently coloured lightspots, which do not move however, could be observed; they are manifesting a structure of some particular kind, without it being possible to ascertain of what kind the imbedded particles are.

§ 11. As it follows from these investigations, in connection with the meltingpoint determinations of natural a-spodumene later to be described, that the chemically pure compound $LiAlSi_2O_6$ has a meltingpoint considerably lower than the natural spodumene-minerals, — we made a series of investigations to find out, what admixtures of the natural spodumenes might cause the mentioned increase of the meltingpoint. Therefore to an artificial product, whose composition was:

SiO,	64,7 °/,
Al_2O_3	27,1 %
Li,0	8,2-%

we added successively in concentrations of 1 mol. percentage, the following chemically pure preparations:

	Observed and reduced Meltingpoints:
1. Jadeite: $NaAlSi_2O_{\mathfrak{s}}$, synthetical.	$14415 M.V. = 1382^{\circ}$
2. Leucite: $KAlSi_2O_{\mathfrak{s}}$, synthetical, anhydrous.	$14506 \text{ M.V.} = 1414^{\circ}$
3. Lithiumoxide: Li ₂ O.	$14304 M.V. = 1397^{\circ}$
4. Alumina: Al_2O_3 .	$14585 M.V. = 1420^{\circ}$
5. <i>Silica</i> : <i>SiO</i> , (quartz).	$14530 \text{ M.V.} = 1416^{\circ}$
And in concentrations of 2 mol. perc.:	
6. $Pseudowollastonite: CaSiO_3$, synthetical.	$14357 \text{ M.V.} = 1402^{\circ}$
7. Sillimannite: Al_2SiO_5 , synthetical.	14593 M.V. = 1421°

Keeping in mind, that the pure substance melts at 1417° C. (G. Th.), we can deduce from these experiments, that:

a. An excess of Li_2O lowers the meltingpoint of the compound $LiAlSi_2O_6$, while the influence of an excess of SiO_2 is somewhat uncertain, but seems to produce a *slight increase*.

b. That a *lowering* of the meltingpoint is also produced by an excess of synthetical *jadeite*, *leucite* and *pseudowollastonite*, which can be considered as the principal admixtures of the natural kunzites and spodumenes.

c. That on the contrary, an *increase* of the meltingpoint is produced by an excess of *alumina* and of *alumosilicates*, like e.g. pure sillimannite.

In how far these facts, which of course will be studied more in detail, when the ternary system: $Li_2O_-Al_2O_3-SiO_2$ is investigated completely, can be used for the explanation of the phenomena, observed in the case of the natural spodumenes, will be shown in the next paper.

Groningen, May 1914. Laboratory of Inorganic Chemistry of the University.

Chemistry. — "Studies in the Field of Silicate-Chemistry. III. On the Lithiumaluminiumsilicates, whose composition corresponds to that of the Minerals Eucryptite and Spodumene". By Prof. Dr. F. M. JAEGER and Dr. ANT. ŠIMEK. (Continued). (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated in the meeting of May 30, 1914).

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§ 12. For the purpose of comparison of the properties of the described artificial product with the mineral itself, we have investigated a number of natural *spodumene*-species in an analogous way.