

## ON THE SYNTHESIS OF NEPHELINE\*

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Since the procurement of oscillator quartz became progressively worse during the war, and since the synthetic production of quartz did not seem to be proceeding sufficiently well, Professor Carl F. Correns pointed out the possibility that nepheline, which is known to possess piezo-electric properties but occurs in too small size in nature, might be obtained in sufficient purity and size from a melt. In addition, it seemed desirable to attempt to replace sodium by other ions in order to improve the piezo-electric qualities.

Fouqué, Michel-Lévy, Doelter, Bowen, Eitel, and recently, Tilley, have synthesized nepheline,  $\text{NaAlSi}_3\text{O}_8$ . However, in each case the crystals were of microscopic size. Furthermore, in the synthesis of nepheline—as in Bowen's experiments—carnegieite, the high temperature modification, rather than nepheline is first crystallized from the melt; nepheline is stable only below  $1248^\circ\text{C}$ .

Lowering the temperature at which the crystallization of a phase begins can be brought about by the addition of a new component to a system. In addition, it has been known for almost a hundred years that in the synthetic formation of minerals the possibility of crystallization from the melt is enhanced greatly by the addition of suitable materials. These materials are called "agents mineralisateurs," "mineralizers," or, in certain cases, "crystallizers." At first only gases which do not combine with any of the other substances were considered; gases, which merely through their presence, dispose these latter to crystallization. Subsequently the term mineralizer was expanded to include other materials, such as, for example, tungstic acid, boric acid, and the like.

It was proposed to synthesize nepheline by finding a suitable mineralizer, which, when added to a melt, would form a system with the components  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in which nepheline would appear as the primary phase at temperatures below  $1248^\circ\text{C}$ . New experiments had to be undertaken since extremely little is known of the course of the reactions in the presence of any one of the mineralizers, and because the views about them are so much at variance. In these experiments the first object was to secure the clearest and largest nepheline crystals possible, and the second was to obtain some answers to the admittedly very involved complex of questions about the so-called mineralizing effect.

\* English translation by Professor A. C. Swinnerton, Antioch College, Yellow Springs, Ohio, and Mr. Howard M. Schott.

## CRYSTALLIZATION WITH THE ADDITION OF MINERALIZERS

Experimentation started with a mixture of sodium carbonate, aluminum oxide and anhydrous silicon dioxide in the stoichiometric proportions of nepheline,  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2=1:1:2$ . To this mixture were added quantities of the following substances, known to be mineralizers: sodium tungstate, sodium metaborate, vanadium oxide ( $\text{V}_2\text{O}_5$ ), ferrous oxide, to the extent of 15–20% by weight. Since this type of mixture was not completely melted at  $1200^\circ\text{C}$ ., a further addition of LiF, in the proportion of 10% by weight, was made in order to secure a further lowering of the melting point. In this way nepheline crystals were obtained, in some cases at temperatures under  $1200^\circ\text{C}$ ., and in the case of the metaborate plus LiF, crystals which reached the considerable size of  $4\times 2$  mm. But these crystals always grew as "skeletons" with many glassy inclusions; hence still other mineralizers had to be found. It developed that with the addition of fluorides only, nephelines were formed with the fewest glassy inclusions. Therefore, the nepheline-LiF system was investigated more carefully. The diagram of Fig. 1 was obtained which shows not a binary system, but rather a section through a complicated polycomponent system.

Particularly worthy of note is the steep drop in the melting point curve on the nepheline side as the quantity of LiF increases. In the growing of crystals, especially from a melt of the alkali-halogen type, the lowest possible melting point is to be desired for purely practical and material reasons, and especially since the vapor pressure of LiF is quite small at temperatures of less than  $1100^\circ\text{C}$ .

From the diagram it is seen that crystallization of nepheline continues up to the eutectic at 86 mol % LiF (53% by weight). The eutectic is at  $908^\circ$ . The synthetic nepheline has the same structure and the same planar spacings as the natural mineral. Optically its refractive indices  $\omega=1.532$  and  $\epsilon=1.528$  lie within the values that Bannister gives for natural nepheline,  $\omega=1.5299-1.5403$  and  $\epsilon=1.5266-1.5371$ . Double refraction, too, is as low as in natural crystals.

With more than 86 mol % LiF a new alkali-aluminum silicate is formed in hexagonal crystals up to  $3.5\times 4.5$  mm. This was recognized unmistakably as  $\text{LiAlSiO}_4$ , that is, as Li-nepheline. The crystals contained a certain limited amount of LiF but sodium could no longer be detected. The sodium has separated out from the silicate melt and has gone over to the lighter fluoride fraction as NaF. This liquid mixture is indicated in the diagram.

The hexagonal crystals, which show only the faces of a pyramid, and,

more rarely, those of a prism, vary optically from nepheline only in their somewhat lower refractive index:  $\omega = 1.524$  and  $\epsilon = 1.520$ . Li-nepheline is found in nature as an alteration product of spodumene and is known by the name of eucryptite. It occurs only intergrown with albite, without forming independent single crystals. Earlier syntheses have made no crystals suitable for the determination of crystalline structure; hence,

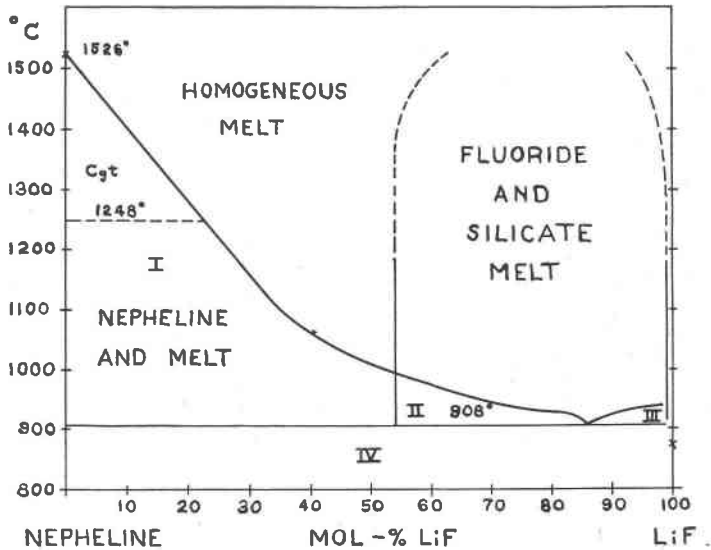


FIG. 1. Melt Diagram of Nepheline-LiF.

- II. Nepheline + Silicate-Fluoride melt.
  - III. Li-Nepheline + Silicate-Fluoride melt.
  - IV. Nepheline + Li-Nepheline + LiF + NaF.
- Cgt. = Carnegieite.

NOTE: The melting points shown must be understood to include the fact that  $\text{CO}_2$  is present in the system, since  $\text{Na}_2\text{CO}_3$  was used initially to obtain the component  $\text{Na}_2\text{O}$ . Although  $\text{CO}_2$  escapes to a considerable degree during the melting, a certain quantity does remain dissolved in the silicate melt and involves a limited lowering of the crystallization temperature of the silicate phase; it may be estimated from other experiments that the lowering of the temperature due to this cause amounts to about  $20^\circ\text{C}$ .

the structure of eucryptite is still entirely unknown. It is not, however, an unimportant point, especially as concerns piezo-electric crystals. For if eucryptite has a polar axis as does nepheline, then it may display the property of piezo-electricity and possibly even in greater degree than nepheline. Therefore, the structural analysis should be carried out.

DEPENDENCE OF THE CRYSTAL SIZE ON THE AMOUNT OF  
LiF IN THE SYSTEM

Upon addition of LiF to the components of the nepheline system, nepheline crystallizes out without difficulty in the form of hexagonal plates with a base and a short prism. So far as the size of the crystals is concerned, with  $15^{\circ}$  to  $30^{\circ}$  undercooling and with the addition of 5.5% by weight of LiF in the system, the crystals achieve a maximum diameter of only 0.8 mm., but with 19% by weight they reach a size of 2–3 mm.; in other words, increasing the LiF content causes the size of the crystals to increase. (See Figs. 2 and 3.)

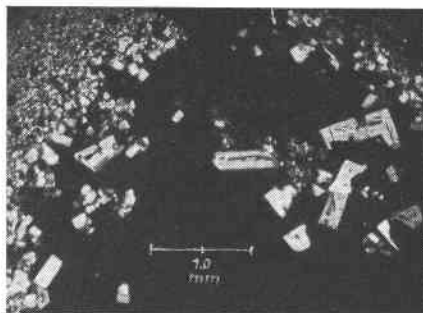


FIG. 2

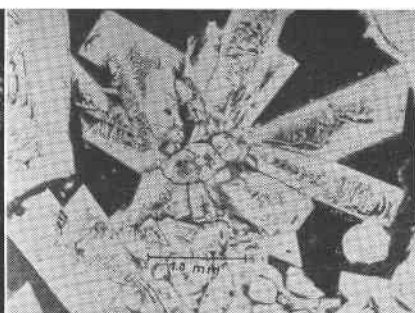


FIG. 3

However, with a LiF content higher than 19%, further increase in crystal size does not take place, although the conditions of the experiment had been so arranged that the growth to a still larger size was not limited by considerations of space or material.

The nepheline which crystallized in the nepheline-LiF system reached the size of a few millimeters, as described above; but the crystals are physically defective, since they crystallized not as skeletons, as was the case in the experiments with the other mineralizers, but rather they contained a considerable quantity of inclusions. Experiments to obtain more homogeneous crystals by slow cooling (one degree C. per hour) were unsuccessful.

## SODIUM SILICOFLUORIDES PLUS LiF AS MINERALIZERS

Recently silicofluorides have been used as mineralizers. Therefore experiments were undertaken in which, to the components of the nepheline system taken as equal to 100% by weight, 10% by weight of LiF and varying quantities of sodium silicofluoride were added. Crystals were obtained which were about 3 mm. in size and which contained somewhat

fewer inclusions. By varying the quantities of  $\text{Na}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ , considerably better results were obtained. When this variation is carried out systematically, a picture is obtained of the extent to which the clarity, the formation of the faces (blockiness, holes, or flawless flat surfaces) and even the crystal size are dependent on the composition of a system, even when the changes in the composition occur within the relatively narrow margin of about 6%. As a result of many experiments in which the addition of 10% by weight of LiF remained constant, the best combinations with  $\text{Na}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  were found, yielding the clearest nepheline crystals up to this time, when 10, 16, or 22.5% of sodium silicofluoride were successively introduced. These crystals had well formed faces (uniform reflection), and reached an optimum diameter and thickness. Crystals were obtained with a diameter of 5, 6, and even 7 mm. with a thickness of 1–2 millimeters. Small crystals of about 1 mm. were completely clear while larger ones had a slight veil of foreign inclusions.

It may now be demonstrated that sodium silicofluoride has no unique effect which furthers crystallization. It is rather the NaF which is formed by simple reaction with the components present in the system that performs this function together with the LiF already present. It can also be shown that neither the  $\text{SiO}_2$  nor  $\text{SiF}_4$ , which are set free by the reaction with the silicofluoride, has an effect on the formation of the crystals.

From this special example of the synthesis of nepheline, one recognizes what conditions are necessary to obtain large clear crystals as free as possible from foreign inclusions. From the knowledge of the quantities of the various elements present in the system, and from the knowledge of all the phases occurring, one can picture the reaction complex presented in this system. Thus one reaches the surprising conclusion that the best crystals are formed from combinations which are almost identical in their chemical composition with only a variance of a few per cent in the amounts of fluorine (and  $\text{CO}_2$ ), although one actually started with three very diverse mixtures. The phases which accompany the formation of nepheline are always the same, and their mutual mass relationships seem to vary only slightly at most. Cryolithionite,  $\text{Na}_3\text{Al}_2(\text{LiF}_4)_3$ , and lithium fluoride (with some  $\text{CO}_2$ ) were identified as phases accompanying nepheline. In addition, a small amount of a crystallized phase appeared which it was not possible to identify. Cryolithionite, LiF, and the unknown phase form a massive aggregate of tiny crystals which can only be determined by  $x$ -rays; the aggregate of tiny crystals is present in re-entrants in the nepheline crystals and on the upper surfaces of the crystallized charges. Taken as a whole, one can estimate the mass of the phases which are formed in an optimum system by weight thus:

80% nepheline	}	(Calculated as a CO <sub>2</sub> free system, equal to 100%.)
10-12% cryolithionite		
5% lithium fluoride		
3-5% unknown phase		

Thus it must be these accompanying phases which permit both the ready crystallization of the components into nepheline, as well as the possibility of growing large crystals. Obviously, the clarity of the crystals depends, for one thing, on the quantities of the components in the system having been so chosen that they agree with the stoichiometric proportions of the phases to be formed. If an excess is present, in general it will not be capable of crystallization and will be inclosed as glass by the growing crystal.

Why exactly these particular accompanying phases work so well in the synthesis of nepheline is a question which cannot as yet be answered.

It can be shown from the special case which has been cited that there are syntheses in which one cannot speak of a vague "mineralizing effect" of certain substances which have been added, even when these are fluorides and silicofluorides, for these substances form new phases within the framework of normal chemical reactions, constituting a complex system difficult to control and direct, but in which the desired crystals can grow flawless and relatively large. The accompanying phases which bring about the best conditions for crystallization can be only empirically ascertained, until the underlying causes have been recognized.