Dec. 7, 1965 H. R. SHELL ETAL 3,222,142

SYNTHESIS OF LARGE CRYSTALS OF FLUORPHLOGOPITE MICA

Filed Sept. 10, 1963

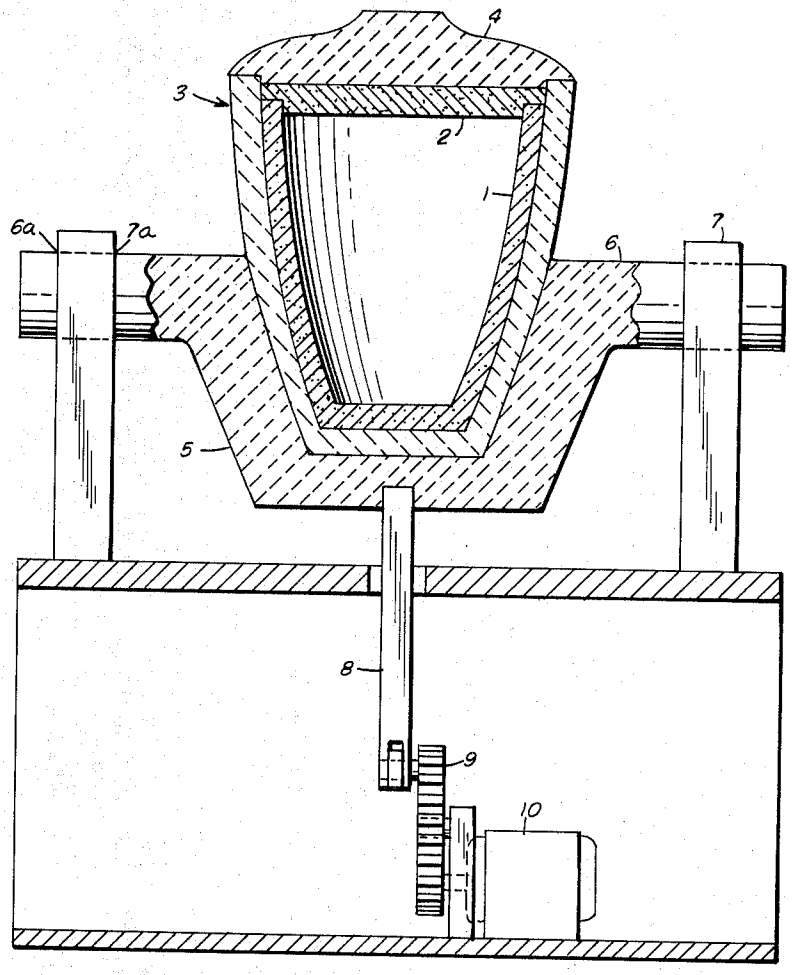


FIG. 1

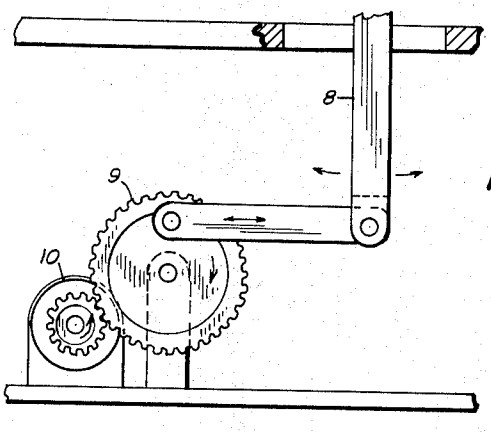


FIG. 2

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United States Patent Office 3,222,142 Patented Dec. 7, 1965

3,222,142

SYNTHESIS OF LARGE CRYSTALS OF FLUORPHLOGOPITE MICA

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Filed Sept. 10, 1963, Ser. No. 308,036
4 Claims. (Cl. 23—302)
(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

This invention relates to synthesis of large single crystals of synthetic minerals or chemicals.

FIGS. 1 and 2 illustrate the apparatus employed in the example.

Previous attempts to synthesize large single crystals of mica, particularly fluorphlogopite, in quantity have invariably met with, at best, partial success. In methods previously employed the liquid phase has been essentially quiescent, whether in crucibles or in 15 ton melts. As a result the growing mica crystals soon develop at their boundaries an environment unfavorable to growth. This situation results from the facts that (1) impurities and non-stoichiometric batch quantities are rejected and (2) the composition of the fluormica is nearly exactly set. For instance, fluorphlogopite crystallizes essentially as $K_2 \cdot Mg_6 \cdot Al_2Si_6 : O_{20}F_4$ even though impurities such as Na^+ and Ca^{++} are present and the batch composition is $F_{4.5}$ (for prevention of forsterite primary crystallization). It has been observed in melts that large crystals are always surrounded by impurity phases including glass and that phases such as CaF_2 and $NaMgF_3$ may be concentrated in masses up to one inch across.

It is therefore the object of the present invention to provide a simple, economical method of producing large single crystals of synthetic minerals or chemicals, particularly mica, in quantity in a high state of purity.

It has now been found that this objective may be accomplished by means of a process in which the vessel containing the melt, from which the crystals are formed, is maintained in a constant state of continuous or periodic motion. The resulting motion of the liquid melt within the vessel produces a continuous or periodic replenishment of the liquid phase about the growing crystals, thus removing excessive accumulations of F^-, Na^+ and Ca^{++} as well as wrong-ratio mica components themselves.

The motion of the vessel may be accomplished by rotating or rolling through 360° or rocking (oscillating) at an angle less than 360° and may be about either a vertical or horizontal axis or any combination thereof. Optimum speed of the motion will vary according to the type of crystals being formed, the composition of the melt and other conditions such as temperature and pressure and is best determined empirically. The motion will generally be rather slow but sufficient to bathe the growing crystals in fresh liquid. Little vibration should accompany the motion of the vessel.

The vessel containing the melt may be of any suitable shape; a generally cylindrical vessel has been found quite satisfactory and the vessel may be in the form of a crucible. It may serve as a furnace for preparing the melt as well as the container during the crystallization. It may also vary greatly in size depending on the quantities of materials, size of crystals, etc. In fact one of the major advantages of the invention is the ready adaptability of the process to large scale production.

The melt may be prepared by any of various means well known in the art. These include internal electric resistance melting, arc furnacing, pouring as from a secondary furnace, etc.

When rolling or rocking of the vessel is employed, provision of a gas space above the melt, as by incompletely filling the vessel with melt, has been found to be highly advantageous. Although the gas is generally air, other gases such as inert gas may be used. Optimum volume of the gas space will vary according to size of vessel, size and type of crystals, etc., and is also best determined empirically. When the vessel is rocked or rolled, as described above, crystals grow upon all inner sides thereof and when crystallization is complete the gas space will be essentially in the center of the vessel. Presence of the gas space has been found to result in optimum liquid phase action during the crystallization.

A back and forth rotational motion of the vessel may also be employed. When such a motion is used provision of a gas space offers little advantage and the melt may fill the vessel completely. In this method the necessary liquid motion is achieved by back and forth rotation so as to take advantage of the liquid inertial flow. The vessel is generally rotated several times in one direction, then the direction of rotation is reversed. While this procedure lacks some of the advantages of the rocking or rolling employing a gas space, it is in some instances preferred because of easier adaptation to present furnacing procedures.

Any of the above procedures results in formation of large crystals of a high degree of purity. Furthermore, warping of crystals caused by pressure is eliminated. In most previous methods of synthesis the central portion is under pressure from cooling and thermal contraction of the outside surfaces, resulting in undesirable warping.

Although the process of the invention has been found to be of particular value in synthesizing fluorphlogopite mica, it may be used to synthesize other types of mica as well as other minerals and chemicals.

The following example will serve to more particularly describe the invention. As will be apparent, however, the invention is in no way limited to the specific details of the example.

EXAMPLE

The apparatus employed is illustrated in the figures. Graphite crucible **1** with lid **2** is contained within fire-clay crucible **3** with lid **4**. This double crucible arrangement is placed in ceramic form **5** having refractory axles **6** and **6***a* and refractory bearings **7** and **7***a*. The crucibles are rocked by means of a motor **10** which drives gear **9** and rocker arm **8**, which is pivotally attached to gear **9**. The specific structure of the apparatus is, of course, not an essential part of the invention and any conventional mechanical arrangement that will provide the required rocking, rolling or rotating motion may be employed.

The batch composition of the material to be crystallized was as follows:

	Grams
K_2SiF_6	466.2
K_2CO_3	97.7
MgO	674.2
Al_2O_3	283.8
SiO_2	879.7

The "batch formula" was, therefore

$$K_2 \cdot Mg_6 \cdot Al_2Si_6 : O_{19.75}F_{4.5}$$

This material was placed in graphite crucible **1** which itself was placed in sealed (by means of high temperature cement) fire-clay crucible **3** to prevent oxidation. This double crucible arrangement was placed in ceramic form **5** which was devised to allow mechanical rocking of the crucible through an angle of 30°. The assembly of crucibles, ceramic form, axles and bearings was placed inside

a furnace which was then heated to 1450° C. Motor **10** and drive wheel **9** are mounted outside the furnace and are connected to ceramic form **5** by means of rocker arm **8**.

The furnace temperature was rapidly lowered to 1400° C., then slowly lowered through the crystallization range (from 1400° to 1370° C.) with rocking taking place during the entire cooling procedure. The furnace was allowed to cool and the product examined. The crystal size of the resulting fluorphlogopite mica was about 2 to 4 times that obtained by use of a stationary crucible to crystallize a melt of the same batch material.

What is claimed is:

1. A method for crystallizing fluorphlogopite mica from a liquid melt in a reaction vessel, said melt being at an elevated temperature, which comprises rocking the vessel at a relatively slow rate of motion through an angle of about 30°, while cooling the melt whereby the fluorphlogopite crystallizes out and the growing crystals are bathed in fresh liquid melt, said rocking motion extending throughout the period of cooling and crystallization.

2. A method for crystallizing fluorphlogopite mica from a liquid melt at an elevated temperature which comprises oscillating the liquid melt through an angle of less than 360° at a relatively slow rate, while cooling the melt to crystallize fluorphlogopite.

3. The method of claim **2** wherein the melt has a batch formula of $K_2 \cdot Mg_6 \cdot Al_2Si_6 : O_{19.75}F_{4.5}$.

4. The method of claim **2** wherein a gas space is provided in contact with the liquid melt.

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