PREPARATION OF HEXALITHIUM MONOSILICATE, Li₆SiO₅, AS BLANKET MATERIAL FOR BREEDING ENERGY IN FUSION REACTORS

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ABSTRACT

A silicate compound that contains high Li/Si ratio seems to be a candidate material for breeding energy in fusion reactors. A pressable and sinterable powder was prepared by mixing an alcoholic suspension containing 6 moles of LiOH and one mole of SiO₂ (as Aerosil). After being gelled it is dried and then calcined at 420°C for 2 h. Sintering of the pressed powder obtained at temperatures below 700°C results in the formation of the compound hexalithium monosilicate, Li₆SiO₅. This new compound in the lithium silicate family is characterized by six-edges plate crystals that have main x-ray diffraction lines with d-values at 4.407, 3.548, 3.339, 2.419, 2.360, 2.010, 1.421 and 1.418. The Li₆SiO₅ decomposes at temperature above 700°C it decomposes to Li₄SiO₄ and Li₂O. The high lithium content of Li₆SiO₅ permits its usage as blanket material for breeding tritium consequently the energy in forthcoming fusion reactors.

KEY WORDS

Lithium silicate, Hexalithium monosilicate, Blanket material, X-ray diffraction, Tritium, Fusion reactors, Tritium breeding materials and Breeding energy materials.

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INTRODUCTION

Fusion energy will offer a viable alternative energy supply to produce electricity on Earth within the few next decades, with significant environmental, supply and safety advantages over present energy sources. In special reactors of the power plant efficient fusion reactions occur between Deuterium (D or $^2$H) and Tritium (T or $^3$H), with the release of large amount of energy needed for electricity production.

\[
\frac{3}{1}T + \frac{2}{1}D \rightarrow \frac{4}{2}He + n.
\]

Deuterium is abundant as it can be extracted from all forms of water. Tritium does not occur naturally and will be bred from lithium, which is widely available in the earth’s crust. Thus tritium would be made in the fusion power plant from neutrons hitting lithium.

\[
\frac{6}{3}Li + n \rightarrow \frac{4}{2}He + \frac{3}{1}T.
\]

Therefore, once the reaction is established, even though it occurs between Deuterium and Tritium, the external fuels required are Deuterium and Lithium for a power plant [1-3].

Lithium containing substances are becoming important as blanket materials for forthcoming fusion reactor for production of tritium [4]. A variety of Li-containing substances were identified as potential blanket materials including molten lithium, molten LiF - BeF and Pb-Li alloy and solid ceramic materials such as Li$_2$O [5-7]. For the difficulties expected to arise from the usage of these materials, materials such as lithium zirconate, lithium titanate [8], lithium aluminate (LiAlO$_2$), lithium meta silicate Li$_2$SiO$_3$ and lithium orthosilicate Li$_4$SiO$_4$ were developed [9-11].

It has been reported [12] that formation of a compounds such as Li$_6$SiO$_5$ is probable, yet it has been stated afterwards [13] that the formation of such lithium compounds is improbable. Again, the probability of their formation has been emphasized [14]. The reason that these compounds are becoming of interest is that, they have the highest lithium content among the know lithium silicate compounds, which permits their usage as potential blanket materials for breeding tritium, consequently energy in forthcoming fusion reactors. The present work will concern with the preparation of the Li$_6$SiO$_5$ compound and identification of its crystal form, and its x-ray diffraction lines.

EXPERIMENTAL PROCEDURE

Preparation of starting powder

Laboratory reagent grade materials were used for the preparations; involving lithium hydroxide, LiOH (Merck), SiO$_2$, Aerosil. The starting powder was obtained by mixing equivalent weight of one mole of LiOH and 6 moles of SiO$_2$ in alcohol solution. The resulting mix is then heated at 95°C until the alcohol is distilled off. The powder obtained is dried at 110 °C; which will be referred to as "as-dried powder". The later is calcined at 420°C for two hours and the product is considered as the starting powder for preparation of pellet samples.
Pellet samples preparation

The starting powder was pressed at 20 KN/cm² into pellets, that were sintered for 30 min to 2h at different temperatures in the range from 420°C to 1100°C, in order to study the phases which may be formed in this range.

Chemical determination of Li/Si mol ratio

An atomic absorption analyzer, of the Perking Elmer, Model 400, was used for estimating the actual weights of the lithium and silicon elements in the powders and pellets which were sintered at different temperatures and the Li/Si ratios were then calculated.

X-ray and electron microscope analysis

The x-ray diffraction patterns of powders and pellets sintered at different temperatures were obtained by the powder technique method using a Simens - Diffractometer type D-500. The broken surfaces of pellets sintered at different temperatures were analyzed using a JEOL Scanning Electron Microscope type JSM - 35. The as-dried and calcined powder samples were first pressed into pellets then their broken surfaces were also analyzed.

RESULTS AND DISCUSSION

Calcination of the starting powder turned its faint yellow coloration into gray before reaching the intended temperature (420°C); then becomes white at the calcining temperature. It is believed that an organometallic compound was formed which explain such coloration.

Fig.1 shows the x-ray diffraction pattern of the as-dried and samples heat-treated at 420°C /2h, 740°C / 30 min, 1100°C/ 30 min. It can be seen that pattern ( a ) of as-dried powder indicates, the existence of Li₂SiO₃, Li₂CO₃, LiOH and silica in this powder [15-16]. After calcination the x-ray pattern (b), indicates the formation of Li₄SiO₄ [17], in addition to Lithium carbonate lines which can also be observed in this pattern. Lithium carbonate may be formed as a result of the interaction of LiOH with CO₂ from the surrounding atmosphere. The x-ray diffraction patterns of samples that have been sintered at temperatures higher than 700°C show only the lines of the lithium orthosilicate as the main phase formed at these temperatures. Fig.1 (patterns c & d) shows examples of such patterns obtained for pellets treated at 740°C and 1100°C.

Figs.2(a), 2(b) and 2(c) show electron micrographs for the pressed pellets of the as-dried powder and samples calcined at 420°C and 1100°C, respectively. It can be noticed from these figures that the mixed phases in the as-dried powder are reacted and transformed into one phase, lithium orthosilicate - Li₄SiO₄ (Fig.2c).

The above results are in consistent with the chemical analysis data. Fig. 3 shows the chemical analysis results of Li/Si ratios for samples sintered below and above 700°C. Samples sintered at temperatures below 700°C show Li/Si ratios equal to 6, while for those samples sintered at temperatures higher than 700°C the ratio was equal to 4. The later ratio corresponds to the Li₄SiO₄ phase.

The x-ray diffraction patterns, of samples which have been sintered at temperatures below 700°C, are different from those of samples sintered at temperatures above 700°C. Fig. 4 shows such pattern for sample which has been treated at 600°C.
Fig. 4 it can be noticed that the main lines of the lithium orthosilicate, viz, d = 5.730, 5.151, 3.695, 3.167, 2.650, 2.597, 1.873 and 1.537, are disappeared or hardly recognizable. Further more, the orthosilicate lines with d values 4.001 and 3.946 are splitted, each, into more than two lines. On the other hand, a group of new lines are appeared; the main lines of which lie at d values 4.407, 3.548, 3.339, 2.419, 2.360, 2.010, 1.421 and 1.418. These new lines do not belong to any of the known lithium silicate compounds, viz, Li$_2$SiO$_3$ [15], Li$_4$SiO$_4$ [17], Li$_2$Si$_2$O$_5$ [18], Li$_6$Si$_2$O$_7$ [19], and Li$_6$Si$_3$O$_7$ [20].

Fig 5 shows the electron microscope micrograph of pressed sample sintered at 600°C. It can be noticed that the sample is composed mainly of one phase characterized by six-edges plate crystals. By considering the chemical results for samples sintered below 700°C, the x-ray diffraction lines and the six-edged plate phase can be interpreted to be belonging to a new compound in the lithium silicate family, the hexalithium monosilicate (Li$_6$SiO$_5$).

From the chemical data, Fig. 3, it can be noticed that up to 700°C the Li/Si ratio remains 6. Sample heated above 700°C shows Li/Si ratios of 4, which means that at temperatures higher than 700 °C the lithium orthosilicate is the only phase which could be detected. At higher temperatures than 700 °C, the hexalithium monosilicate seems to decompose into lithium orthosilicate, Li$_4$SiO$_4$, and lithium oxide, Li$_2$O. The loss by evaporation of Li$_2$O explains the observed decrease (Fig. 3) in the Li/Si from 6 ratio to 4. The thermal decomposition of the hexalithium monosilicate in this manner is similar to that of the compound Ca$_3$SiO$_5$, where calcium orthosilicate, Ca$_2$SiO$_4$, and calcium oxide, CaO, are formed above its temperature of stability [21]. This similar thermal behaviour between tri-calcium silicate, Ca$_3$SiO$_5$, and the hexalithium monosilicate may suggest a similar structure. However, from the above discussion, the hexalithium monosilicate may be presented by either of the formulas Li$_6$SiO$_5$ or Li$_4$SiO$_4$.Li$_2$O.

CONCLUSIONS

Since the scientific argument about the possibility of the formation of hexalithium monosilicate, Li$_6$SiO$_5$, compound which started at 1913, the present work confirm the possibility of formation of such new compound in the lithium silicate family. The Li$_6$SiO$_5$ is characterized by main x-ray diffraction lines at d values 4.407, 3.548, 3.339, 2.419, 2.360, 2.010, 1.421 and 1.418; and by crystals of six-edges plate like form. It decomposes above 700°C to lithium orthosilicate Li$_4$SiO$_4$, and lithium oxide, Li$_2$O: Li$_6$SiO$_5$ → Li$_4$SiO$_4$ + Li$_2$O. Either of the formula Li$_6$SiO$_5$ or Li$_4$SiO$_4$.Li$_2$O can be used to represent hexalithium monosilicate. However further work is needed to explore its structure.

ACKNOWLEDGMENT

One of the authors, Morsi, M. M., wishes to express his gratitude and thanks for the International Seminar and DAAD, Germany, for financing and giving the chance to cooperate with Kernforschungszenrum Karlsruhe GmbH, Institut fur Material und Festkorperforschung III, D-7500 Karlsruhe, Germany.
REFERENCES

Fig. 1 X-ray diffraction patterns of the as-dried powder and samples heat-treated at 420°C /2h, 740°C /30 min, 1100°C/ 30 min.

Fig. 2 Electron micrographs for pressed pellets of the as-dried powder (a) and samples calcined at 420°C (b) and 1100 °C (d), the later is composed of lithium orthosilicate.
Fig. 3  The Li/Si mole ratios determined by Atomic absorption method for samples sintered below and above 700 °C.

Fig. 4  X-ray diffraction patterns of pressed powder sample treated at 600°C/30 min.
Fig. 5  Electron microscope micrograph of pressed sample sintered at 600°C/30 min