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Investigation of a high stable β-cristobalite ceramic powder from $CaO–Al_2O_3–SiO_2$ system

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Abstract

The room temperature stabilized β-cristobalite ceramic powder has great potential for use in production of engineering ceramic materials due to its high resistance to thermal shock, low expansion coefficient, high chemical resistance and low density. However, the use of this material is not common in ceramic industries. The problem is shown to be the instability of β-phase during milling. The applied external force leads to phase transformation to α-cristobalite and thus the material shows poor thermal stability and so on. In this study, a reliable β-cristobalite ceramic powder from $CaO–Al_2O_3–SiO_2$ ternary system was investigated at different compositions and under various sintering temperatures and sintering times. The phase stability of the powder sample was investigated by milling for 50 h using a planetary mill. The crystalline phases were examined by X-ray and FTIR analysis and the results were discussed with respect to the phase homogeneity through the particle mass.

Keywords: A. Powders-solid state reaction; D. SiO_2; E. Refractories

1. Introduction

The crystalline silica ceramic powder takes different polymorphic forms as quartz, tridymite and cristobalite at room temperature. Each crystalline form represents a distinct arrangement of silicon–oxygen tetrahedral into a three-dimensional crystalline network. The cristobalite phase exists in two polymorphic forms as low-cristobalite (α-cristobalite) and high-cristobalite (β-cristobalite). Originally, the β-cristobalite has phase stability above 1470 °C. The phase normally transforms into low-cristobalite form when it is cooled. The temperature range is between 170 and 270 °C. The actual temperature depends on the crystallization conditions.[1–3] This is accompanied by a volume decrease of approximately ∼5%.[4] Because of the large volume change, the α-crystallization causes cracking problems and thus leading to an inferior product. The other stable form of high-cristobalite material is the product obtained at room temperature and it has great importance for use in ceramic fabrication. The promising engineering properties are the high resistance to thermal shock and the low expansion coefficient. The high chemical resistance and the low density are the additional advantages.

The high-cristobalite ceramic powder could be obtained at room temperature by phase stabilization using “stuffing” cations which was first described by Buerger,[5] where the incorporation of foreign ions (Ca, Sr, Cu, Na) in the interstices of silicate structure is charge-compensated by the substitution of Al^{3+} for Si^{4+} in the framework. Saltzberg et al.[6] presented a formula for the high-cristobalite stabilization such as $Si_{1-x}Al_xM_{x/n}{}^{n+}O_2$, where M^{n+} represents the cations occupying the interstices of the framework. It was also noted that the presence of foreign impurities in the interstices presumably inhibits the contraction of the structure during the α ↔ β-cristobalite transformation.[7] Additionally, the best result regarding the yield of a well-crystallized β-cristobalite was investigated for the doping levels ranging from $x = 0.04$ to 0.08. This study also proposed that the doping level should be $x = 0.05$ while Thomas et al.[8] and Alcala et al.[2] indicated different results. They concluded that the composition corresponding to a substitution level should be $x = 0.06$ and $x = 0.07$, respectively.

In spite of the favored properties, the chemically stabilized cristobalite ceramic powders could not been extensively used for manufacturing of industrial ceramics. Two prominent

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problems are: (i) significantly large size of the synthesized β-form powders[7] and (ii) instability of the powder sample during size reduction operations. The applied external force leads to phase transformation of the β- form to α-cristobalite[4,7] and thus the material shows poor thermal stability when the sintering proceeds. The large volume change of α-crystallization produces some cracks thus leading to inferior products.

It is not obvious that the applied external forces with high energy milling always convert the high-cristobalite phase to low form. This may be the result of the insufficient stabilization. In light of this data, it is necessary to synthesize a β-cristobalite ceramic powder with high stability values to enhance use of the ceramic powder in fabrication of high performance engineering ceramic materials. The reliable β-cristobalite ceramic powder from $CaO–Al_2O_3–SiO_2$ ternary system was investigated by changing the concentration of stuffing ions and applying different sintering temperatures and times.

2. Materials and methods

The chemically stabilized β-cristobalite ceramic powder from $SiO_2–Al_2O_3–CaO$ ternary system was examined adopting the chemical composition by the formula given by Saltzberg et al. [6] ($Si_{1-x}Al_{x+y}Ca_{x/2}O_{2+1.5y}$) as stoichiometric ($y = 0$) and non-stoichiometric ($0.02 < y > 0.1$) compositions (see Table 1). The stuffing cations (Al^{3+} and Ca^{2+}) were supplied from aluminum-nitrate-nonahydrate $Al(NO_3)_3·9H_2O$, and calcium-nitrate-tetrahydrate, $Ca(NO_3)_2·4H_2O$. The addition of colloidal silica to such aqueous solutions and stirring for 30 min led to gel formation and then the material was dehydrated at 120 °C for 24 h to obtain amorphous powder. The powder was deaglomerated by using agate mortar (Fritsch Pulverisatte 0) and sintered at the temperature range of 1000–1300 °C for 4 up to 140 h. The heating and cooling rates of the furnace were 5 °C min^{-1}.

The influence of stress inducing on the phase stability of β-form crystallization was investigated by grinding the samples for 50 h by using a planetary ball mill (Retsch-PM 200) with WC jars and grinding balls with a speed of 200 rpm. The crystalline phases of the samples were analyzed between the range of 10–70° using X-ray diffractometer (XRD, Rigaku-miniflex) by using Cu Kα radiation with Ni filter. The scanning speed was 2° min^{-1} and step of 0.01°. Crystalline phases were also analyzed by using FTIR (Burker Vertex 70). The homogeneity of phase distribution on the particle surface was investigated from the surface charges determined by a Zetasizer (Malvern Zeta-Sizer Nano ZS).

Table 1
The chemical compositions of the samples for preparation of the high-cristobalite ceramic powder.

Composition types	Sample code	x	y
Stoichiometric $Si_{1-x}Al_xM_{x/n}{}^{n+}O_2$	S1	0.02	–
	S2	0.04	–
	S3	0.05	–
	S4	0.06	–
	S5	0.07	–
	S6	0.08	–
	S7	0.10	–
Non-stoichiometric $Si_{1-x}Al_{x+y}Ca_{x/2}O_{2+1.5y}$	NS1	0.02	0.02
	NS2	0.04	0.04
	NS3	0.05	0.05
	NS4	0.06	0.06
	NS5	0.07	0.07
	NS6	0.08	0.08
	NS7	0.10	0.10

3. Results and discussions

The room temperature stabilized β-cristobalite ceramic powder from $CaO–Al_2O_3–SiO_2$ ternary system was investigated for producing material with phase stability during high energy milling. The composition of stuffing ions, applied sintering temperatures and times were examined. The experimental results were discussed with respect to X-ray findings and the results of FTIR analysis along with the measurement of surface charge of the particles.

3.1. The phases with X-ray analysis

The β-cristobalite ceramic powder was investigated from the "stoichiometric" and "non-stoichiometric" statement where the x and y values vary from 0.02 to 0.1 (see Table 1). The X-ray phases of the powder samples sintered at 1100 °C for 24 h were determined. The X-ray detected crystallizations are shown to be same for both the stoichiometric and the non-stoichiometric compositions. It is interesting that the non-stoichiometric composition has contained two times higher alumina. The X-ray results for the stoichiometric compositions are given in Fig. 1. The current results are not different than previous literature studies and similar findings of those studies are called surprising.[8] We proposed that the statement asserting there is no influence of the high alumina contamination on the crystallization mechanism is doubtful and thus this type of concept should be discussed with respect to the additional characterizations. In this study, the work was planned as three stages: (i) phase analysis with FTIR, (ii) investigation of the phase homogeneity of particles mass from the surface charge measurements and (iii) the grinding test with high energy milling.

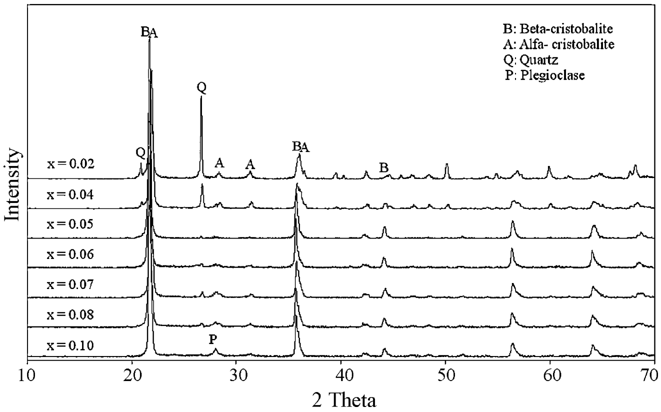


Fig. 1. X-ray analysis of the powder samples sintered at 1100 °C for 24 h for the experiments conducted on stoichiometric compositions.

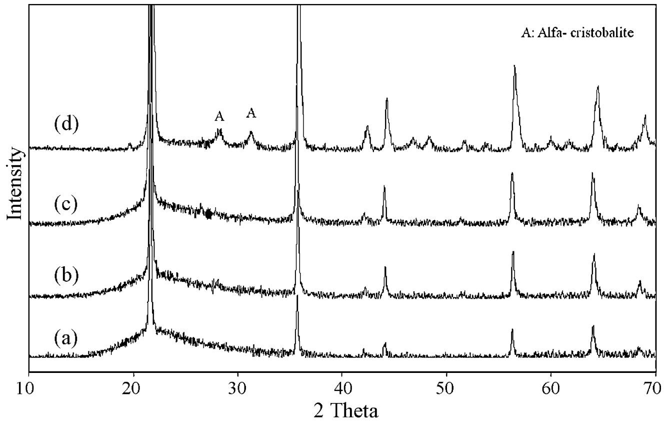


Fig. 2. The X-ray analysis of samples coded as S3; the experiments conducted at low temperature at 1000 °C: (a) 24 h, (b) 48 h, (c) 140 h and high temperature at 1200 °C (d) 24 h.

The amount of doping ions such as Al^{3+} and Ca^{2+} have great influence on the crystallization in which only two states (experiment coded as S3 and NS3) indicate relatively good β-type cristobalite crystallization, the others show impurities such as quartz, plagioclase and α-cristobalite crystallization. Here, the accurate detection of whether the crystallization is α or β is difficult. Diffraction pattern of the α-cristobalite can be distinguished from that of β-cristobalite by the presence in the α-cristobalite pattern of reflection at *d*-spacing of 2.49 and 2.84 Å, which are absent in the β-cristobalite pattern.[9,10] For the low doping level, up to $x = 0.05$, quartz and α-cristobalite phase is present with β-cristobalite crystallization. When the doping level is higher than $x = 0.05$, the plagioclase phase (anorthite) appears with the reaction between the excess stuffing ions and the Si^{4+} ions. The results regarding the yield of a relatively good crystallization were obtained for a doping level of $x = 0.05$ and the result best fitted for the experiments conducted by Saltzberg et al.[6]

Besides some impurities such as quartz and α-cristobalite, the above mentioned two compositions were furthermore investigated for the production of well crystallized β-cristobalite by conducting the experiments at 1000 and 1200 °C for longer soaking times up to 140 h. The results of X-ray analysis are given in Figs. 2 and 3. Fig. 2 presents the experiments conducted at high temperature (at 1200 °C) and low temperature (at 1000 °C) for longer soaking times up to 140 h. And Fig. 3 demonstrates the experiments in which an intermediate temperature (at 1100 °C) was set for less time sintering at about 4 and 12 h. The experiments indicated that the amount of α-cristobalite increased with elevation of the sintering temperature. In this case, the obtained β-cristobalite was retransformed into α-cristobalite. For the low temperature sintering (i.e., at 1000 °C), the X-ray detected amorphous phase appeared with the β-cristobalite crystallization. Increasing of the sintering time decreased the amorphous phase but it remained despite the longer soaking time. On the other hand, the intermediate sintering temperature together with less time sintering, both 4 and 12 h provided well crystallization (see Fig. 3). The observed well crystallization is the only primary finding. The actual crystallization will be explored after IR analysis and so on.

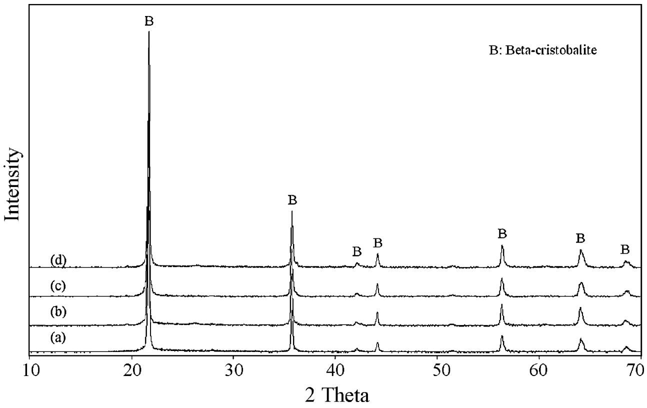


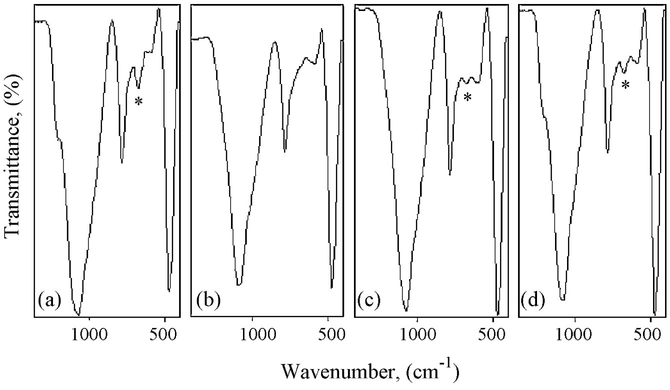
Fig. 3. The X-ray analysis patterns: (a) NS3 sintered at 1100 °C for 12 h, (b) NS3 sintered at 1100 °C for 4 h, (c) S3 sintered at 1100 °C for 12 h and (d) S3 sintered at 1100 °C for 4 h.

3.2. The phases with FTIR analysis

The well β-crystallization observed in X-ray findings (see Fig. 3) was also investigated by FTIR analysis (see Fig. 4). According to the experimental results, only one powder sample was well crystallized (experimental code: NS3) in which the composition was non-stoichiometric and the sintering was applied at 1100 °C for 4 h. The impurities with non-stoichiometric sample sintered for 12 h and with the stoichiometric samples sintered for both 4 and 12 h were shown to be including α-cristobalite-like structures. Whereas the α-cristobalite in IR analysis gave a peak at about 619 nm,[11] here the peak was observed at about 608–610 nm. The slightly different finding was attributed to the occurrence of "cristobalite-like structure".

3.3. The phase homogeneity of particles investigated from surface charge

The above mentioned very small quantity of residual α-like phases (see Fig. 4) might change the surface properties of the powder material. Thus, the zeta-potential of samples was investigated for a wide range of pH values (see Fig. 5). The samples



* Alfa-cristobalite like structure

Fig. 4. The FTIR analysis results: (a) NS3 sintered at 1100 °C for 12 h, (b) NS3 sintered at 1100 °C for 4 h, (c) S3 sintered at 1100 °C for 12 h and (d) S3 sintered at 1100 °C for 4 h.

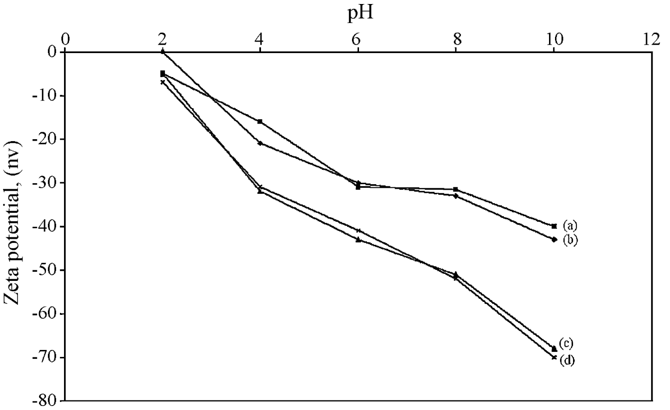


Fig. 5. The surface charges of the samples: (a) S3 sintered at 1100 °C for 12 h, (b) NS3 sintered at 1100 °C for 4 h, (c) NS3 sintered at 1100 °C for 12 h and (d) fully α-cristobalite (reference sample).

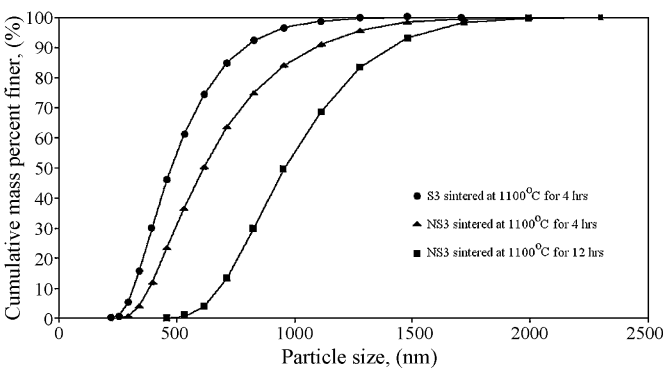


Fig. 6. The particle size distributions after milling for 50 h.

have similar sizes (~15 μm) and thus there is no influence on the surface charge measurement. Irrespective of the experiment on non-stoichiometric sample (NS3) and sintering applied for long time (12 h), the experiments proved the same surface charges for the samples with and without residual α-like phases (experimental code: S3 for 12 h sintering and NS3 for 4 h sintering) determined by IR analysis (see Fig. 4).

The observed different surface charges of the two powder samples are highly interesting; one sample is the high-cristobalite powder (NS3 for 4 h sintering) and the other is the cristobalite-like structure (NS3 for 12 h sintering). The high-cristobalite powder indicates the surface properties are the same through the particle mass. It is well crystallized which is supported by both the X-ray and IR analyses. The surface charge of the cristobalite-like structure is attributed to the differences in formation of the surface phases: the particles have β-type crystallization but the long time sintering may lead to crystallization at the surface as α-cristobalite. The mechanism was a well known process such as the grain growth mechanism like zirconia and other silicates.[7,12–14]

At this point, the same observed surface properties for the fully β-type cristobalite (NS3 for 4 h sintering) and the sample containing residual α-like phases (S3 for 12 h) were very surprising. In this case, the α-like phase was not on the surface, it was in a hiding place, may be located within the grains or grain boundaries.

The above prediction (the occurrence of α-cristobalite at the surface of the β-cristobalite particle mass) is supported by an additional study; a fully α-cristobalite powder was prepared by using colloidal silica particles, which was sintered at 1400 °C for 6 h. Fig. 5 also shows the zeta-potential of the reference material and indicates that the surface charge is close to the previously stated long time sintered non-stoichiometric sample (NS3 for 12 h sintering).

3.4. The grinding test with high energy milling

The above mentioned β-crystallization, with and without residual α-like phases, was investigated with respect to phase stabilities during the milling process. The external forces were applied to the particles through milling for 50 h. The obtained sizes and distributions were different (see Fig. 6) as well as the crystalline phases after milling (see Fig. 7a–c). The particle sizes after milling were smaller than the critical grain size for β–α phase transformation which was about 4–5 μm.[7]

The β-cristobalite was a brittle crystalline phase,[15] thus milling of this type of material produced fine size particles. In the present study, the residual α-like phases influenced the milling performances. While one sample increased the milling performance (S3 for 4 h of sintering) and the other decreased (NS3 for 12 h of sintering). The different milling performance was again an indication of the predicted diversity of crystallization zones. The residual α-like phases at the surface of the particles decreased the milling performance and thus produced coarser size with broad intervals. The crystallization within the grains or grain boundaries increased the area of weak zones depending on the weak crystallization (cristobalite-like structures) and thus finer size with narrow interval could be obtained.

The fully β-cristobalite powder (NS3 for 4 h of sintering) had the same crystalline phase after the milling processes (see Fig. 7a) meaning that the powder sample had promising engineering properties; high performance ceramic materials could be fabricated by the nano-size powder through the sample which has high resistance to thermal shock and low expansion coefficient.

The powders with residual α-like phases showed instabilities after the milling processes (see Fig. 7b and c). The sample having cristobalite-like structures within the grains or grain boundaries (S3 for 4 h sintering) showed amorphous phase with β-cristobalite crystallization (see Fig. 7b). The amorphous phase was not present before the milling processes (see Fig. 3). During the milling operation, the particles broke from the weakest zones leading to the defect areas which were shown as amorphous phases. The milling had different influence on the other sample having the residual α-like phases located on the particle surface (NS3 for 12 h milling); this material indicated the α-crystallization. This result was attributed to the external force on the phase transformation which could only have occurred with the sample having α-cristobalite-like structures depending on the excess sintering. This prediction was supported by experimental findings and fully β-cristobalite crystallization.

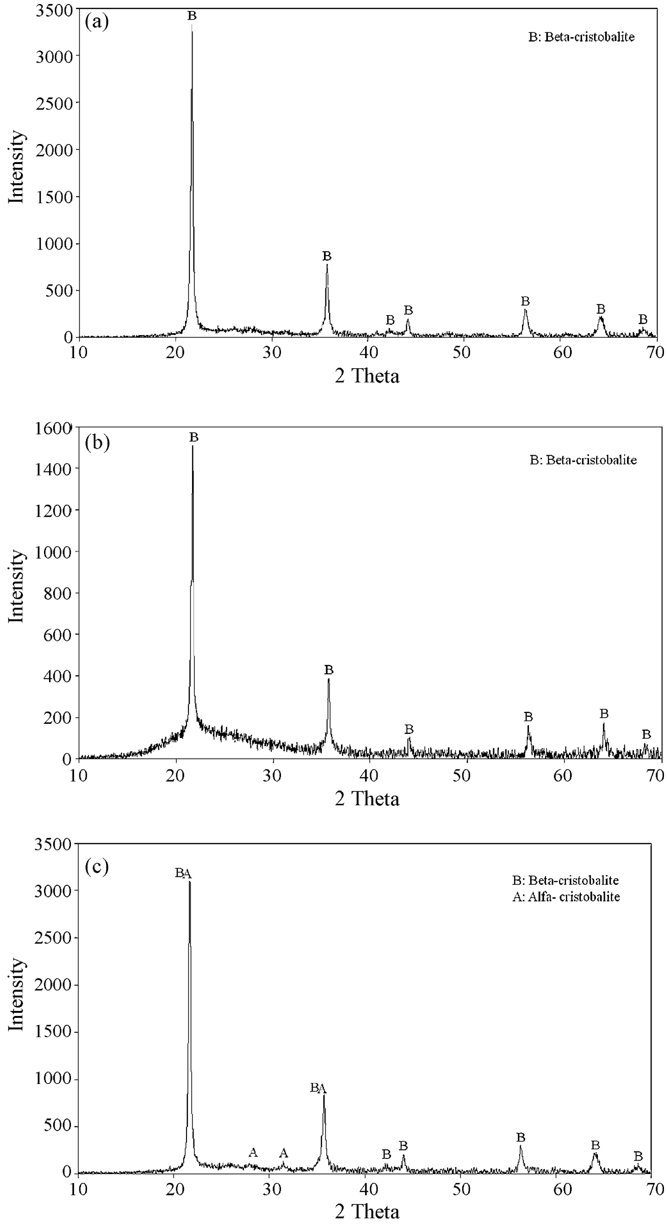


Fig. 7. (a) X-ray analysis of the sample of NS3 sintered at 1100 °C for 4 h after milling for 50 h. (b) X-ray analysis of the sample of S3 sintered at 1100 °C for 4 h after milling for 50 h. (c) X-ray analysis of the sample of NS3 sintered at 1100 °C for 12 h after milling for 50 h.

4. Conclusions

The crystallization of β-cristobalite in SiO_2–Al_2O_3–CaO system was studied and sub-micron size powder was obtained by milling without phase transformation to α-phase. The success can be explained by the crystallization provided without any residual α-like phase. The best crystallization was obtained with the non-stoichiometric composition $38SiO_2 2Al_2O_3CaO$. It was produced by sintering of the powder sample at 1100 °C for 4 h. The applied sintering and cooling rate was 5 °C min^{-1}. The product was powdered for 50 h by using a planetary ball mill and mean particle sizes at about 900 nm were obtained. The external force exposed by the milling did not change the high-cristobalite structure.

The composition produced with stoichiometric type ($38SiO_2Al_2O_3CaO$) had very small amount of residual α-like phase which was detected by FTIR. The X-ray analysis was not sufficient to detect the minor constitutions. The residual phase had great importance on the phase stabilities of the product sample during the milling in which the β- to α-phase samples for long time soaking also led to occurrence of the minor constitution of α-like transformation was determined. The sintering of either stoichiometric or non-stoichiometric phase.

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