

CRYSTAL CHEMISTRY OF β - Si_3N_4 SOLID SOLUTIONS
CONTAINING METAL OXIDES

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ABSTRACT

Phase equilibrium diagrams of Si_3N_4 -metal oxides systems were reviewed. It was found that the solid solubility limits of different metal oxides in β - Si_3N_4 depends on the size and charge of the metal elements. A misfit factor was suggested to present these variables numerically. For some compositions in the systems Si,Al/N,O, Si,Be/N,O, Si,Al,Be/N,O and Si,Be,Mg/N,O the misfit factors were computed and plotted against the solubility limits. It was found that substantial amount of foreign atoms can be accommodated in the β - Si_3N_4 lattice when the misfit factor is small. When the misfit factor becomes larger, only small amount of foreign atoms enter the lattice. The results suggested that this method can be used to estimate the solid solubility limits of one or more metal oxides and nitrides in β - Si_3N_4 .

Introduction

In the last decade, the compound silicon nitride (Si_3N_4) has attracted much attention because of its potential applications as a high temperature engineering material. Silicon nitride has a high decomposition temperature and good thermal shock resistance. It is also resistant to oxidation and to corrosive environments. Despite these excellent properties, silicon nitride is still not being used extensively today because there are difficulties in

fabricating silicon nitride ceramics. Silicon nitride ceramics with satisfactory mechanical properties can only be obtained by hot pressing which is not economical for mass production. It has been demonstrated that "reaction sintered" silicon nitride does not have mechanical properties comparable to those of the hot pressed materials.

It was found that sintering aids have to be used in preparing silicon nitride ceramics by either hot pressing or reaction sintering. The most effective sintering aids were found to be Al_2O_3 , MgO , Y_2O_3 , etc. The studies of these sintering aids have led to the discovery of a new family of materials - solid solutions of metal oxides in silicon nitride. These solid solutions were reported to have properties comparable to those of $\beta\text{-Si}_3\text{N}_4$. It was reported that these solid solutions can be fabricated by conventional ceramic process, i.e. powder compaction and sintering.

Because of this obvious reason, many silicon nitride - metal oxide systems have been studied in the past few years. Sufficient data on these systems have been collected in the literature. This paper is an attempt to propose a model to predict which oxide or combination of oxides may form solid solution with silicon nitride, and to estimate their solubility limits.

Literature Survey

The first $\beta\text{-Si}_3\text{N}_4$ solid solution was found to exist in the system $\text{Si}_3\text{N}_4 - \text{Al}_2\text{O}_3$, reported by Oyama and Kamigaito (1) in Japan, and Jack and Wilson (2) in Great Britain. Both of these publications reported extensive solid solution formation of Al_2O_3 in $\beta\text{-Si}_3\text{N}_4$. In later publications, the solid solution forming regions were given in ternary systems by these authors. Jack (3) used the ternary system $\text{Si}_3\text{N}_4 - \text{SiO}_2 - \text{Al}_2\text{O}_3$, and Oyama (4), on the other hand, used the system $\text{Si}_3\text{N}_4 - \text{AlN} - \text{Al}_2\text{O}_3$. The phase diagrams of these systems are presented in Figure 1a and Figure 1b respectively. As shown in these diagrams, there are wide ternary solid solution regions in both of these systems. The diagrams in Figures 1a and 1b are isothermal sections of the corresponding systems. Jack (3) reported the 1700° section and Oyama (4) prepared their samples at 1760°C .

The solid solution formation along the join $\text{Si}_3\text{N}_4 - \text{Al}_2\text{O}_3$ requires the existence of non-metal interstitials or metal site vacancies in the $\beta\text{-Si}_3\text{N}_4$ lattice. Oyama (4) has suggested the existence of silicon vacancies as an explanation of his results.

The single-phase $\beta\text{-Si}_3\text{N}_4$ solid solution forming regions in the systems $\text{Si}_3\text{N}_4 - \text{Al}_2\text{O}_3 - \text{Be}_2\text{SiO}_4$, $\text{Si}_3\text{N}_4 - \text{Al}_2\text{O}_3 - \text{Li}_2\text{O}$ and $\text{Si}_3\text{N}_4 - \text{Al}_2\text{O}_3 - \text{MgO}$ were reported by Jack (3). The 1700° isothermal phase diagrams of these systems are given in Figures 1c, 1d, and 1e respectively. The isothermal diagram in the system $\text{Si}_3\text{N}_4 - \text{Al}_2\text{O}_3 - \text{Ga}_2\text{O}_3$, reported by

Oyama (5), is presented in lf. As shown in these diagrams, extensive ternary solid solutions exist in all of these systems.

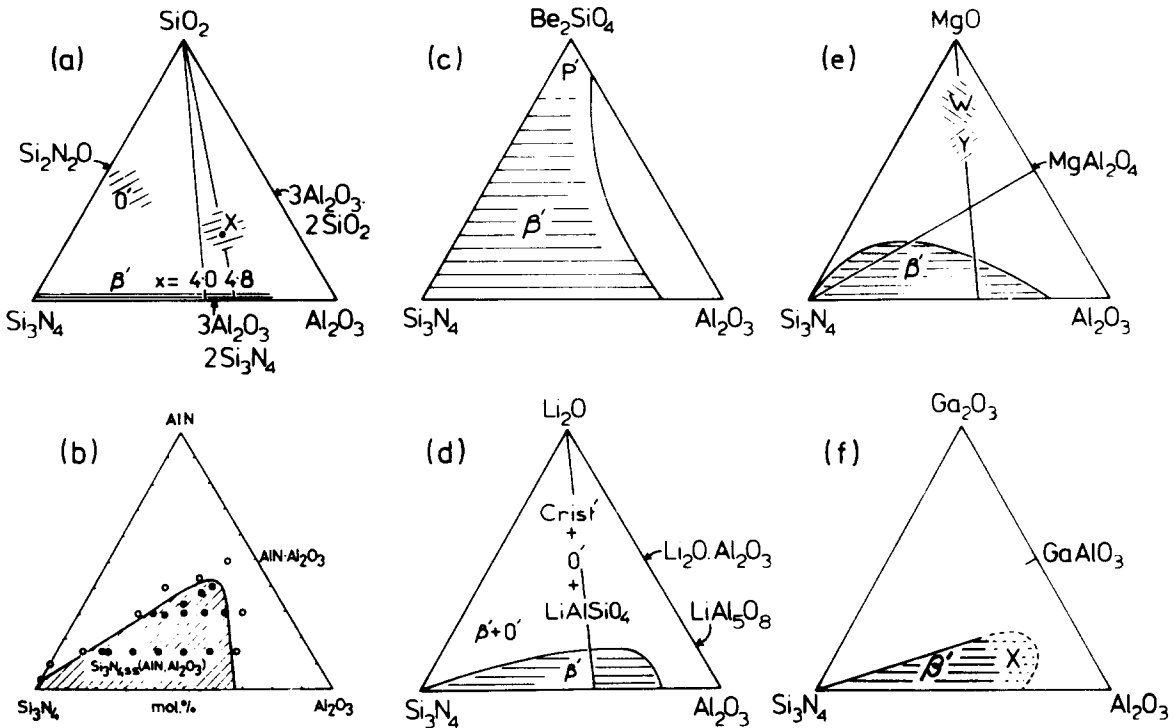


FIG. 1

Isothermal phase diagrams of Si_3N_4 systems. The shaded area indicates solid solution region.

- The system Si_3N_4 - SiO_2 - Al_2O_3 at 1700°C , after Jack (3)
- The system Si_3N_4 - AlN - Al_2O_3 at 1760°C , after Oyama (4)
- The system Si_3N_4 - Be_2SiO_4 - Al_2O_3 at 1700°C , after Jack (3)
- The system Si_3N_4 - Li_2O - Al_2O_3 at 1500 - 1700°C , after Jack (3)
- The system Si_3N_4 - MgO - Al_2O_3 at 1700°C , after Jack (3)
- The system Si_3N_4 - Al_2O_3 - Ga_2O_3 at 1730°C , after Oyama (5).

Gauckler et.al. (6) re-examined the Si_3N_4 - Al_2O_3 system at 1760°C . The results were presented as an isothermal phase diagram of a quasi-ternary reciprocal salts system Si_3N_4 - SiO_2 - AlN - Al_2O_3 . The diagram is presented in Figure 2a. Gauckler et.al. (6) were not able to prepare single phase β - Si_3N_4 solid solution at 1760°C along the join Si_3N_4 - Al_2O_3 . Instead, single phase solid solutions were found to be restricted to a very narrow region along the join Si_3N_4 - $(\text{AlN}:\text{Al}_2\text{O}_3)$. These solid solutions have a definite metal to non-metal ratio of 3:4, hence do not require the existence of extrinsic lattice defects. Five other single-phase regions were found in the system Si_3N_4 - SiO_2 - AlN - Al_2O_3 . All of these solid solutions have definite metal to non-metal ratios.

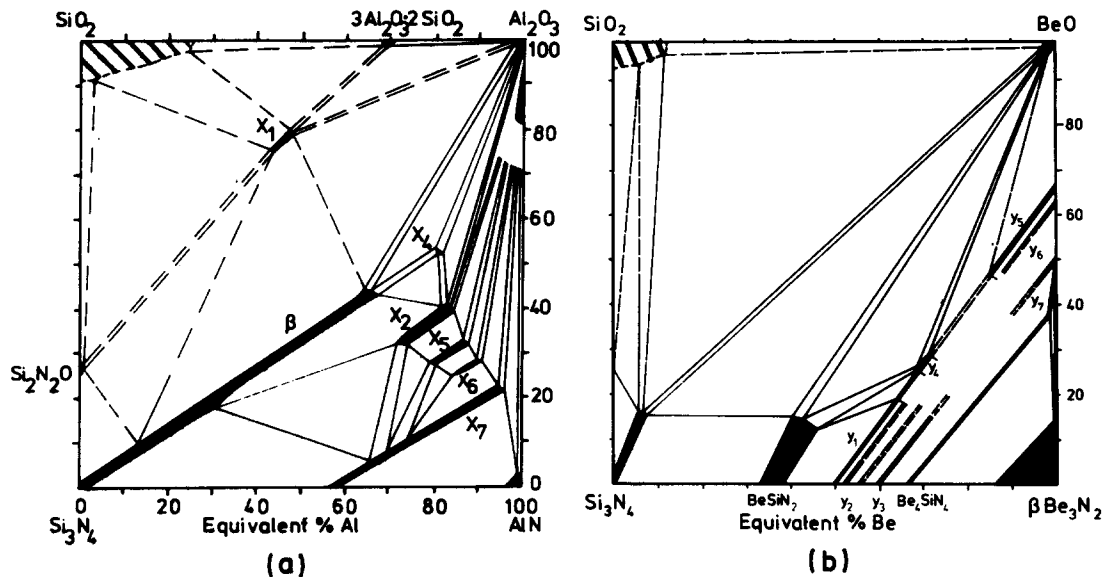
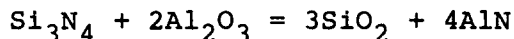


FIG. 2

Isothermal phase diagrams of the reciprocal salts systems containing Si_3N_4 .

- The system Si_3N_4 - SiO_2 - AlN - Al_2O_3 at 1760°C , after Gauckler et.al. (6).
- The system Si_3N_4 - SiO_2 - Be_3N_2 - BeO at 1760°C , after Huseby et.al. (8).

In the system Si_3N_4 - Al_2O_3 , at high temperature under equilibrium, the reaction



might occur. Therefore, Gauckler (6) treated the system Si_3N_4 - Al_2O_3 as a quasi-ternary reciprocal salts system and considered three of the four chemical compounds of the above equation as independent components. The treatment of reciprocal salts systems can be found in the book by Ricci (7). As stated in Ricci's book, in systems containing two metal elements and two non-metal elements, $\text{M}, \text{N}, \text{X}, \text{Y}$ or $\text{MX} + \text{NY} = \text{MY} + \text{NX}$, the compositions are plotted on a square with the four salts as corners, one axis giving the fraction $\text{N}/(\text{M}+\text{N})$ for metal elements (in equivalents) and the other the fraction $\text{Y}/(\text{X}+\text{Y})$ for non-metal elements (in equivalents). The examples are Figures 2a and 2b in this text for the systems $\text{Si}, \text{Al}/\text{N}, \text{O}$ by Gauckler (6) and $\text{Si}, \text{Be}/\text{N}, \text{O}$ by Huseby (8).

Huseby et.al. (8) investigated the Si_3N_4 - SiO_2 - Be_3N_2 - BeO system and the results were reported as a ternary reciprocal salts diagram at 1780°C . The diagram is presented in Figure 2b. As shown in this diagram, only a small amount of Be_2SiO_4 enter the β - Si_3N_4 lattice in contrast to the wide area of solid solution formation reported by Jack (3) in the same system. Note, there are other single-phase materials in this system and all have moderate solubilities along the lines of definite metal to non-metal ratios and small solubilities perpendicular to these lines.

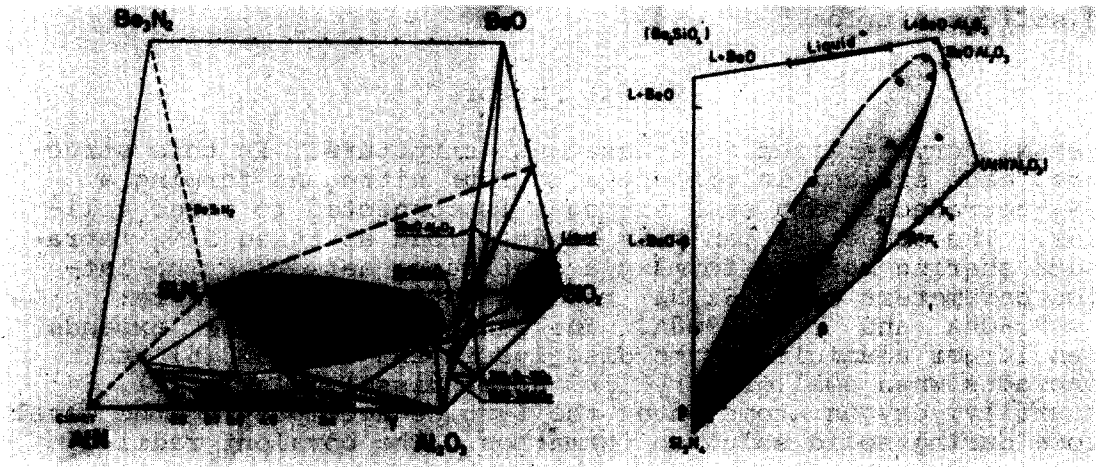


FIG. 3

Phase diagrams of the quaternary reciprocal salts system Si_3N_4 - SiO_2 - AlN - Al_2O_3 - Be_3N_2 - BeO , after Gauckler (9).

- Three dimensional presentation of the system at 1760°C .
- Isothermal section Si_3N_4 - $(\text{AlN}:\text{Al}_2\text{O}_3)$ - $\text{BeO}.\text{Al}_2\text{O}_3$ - Be_2SiO_4 at 1760°C .

The system of silicon nitride containing beryllium- and aluminium oxide can not be expressed as a ternary system, instead it should be presented as a quaternary reciprocal salts system Si_3N_4 - SiO_2 - AlN - Al_2O_3 - Be_3N_2 - BeO . The triangular prism shaped diagram was used by Gauckler (9) as presented in Fig. 3a.

According to Ricci (7), the systems containing three different metal elements and two different non-metal elements (7) (A,B,C/X,Y) are called quaternary reciprocal salts systems. The phase diagram is a triangular prism, where the three different elements are plotted on the ternary diagram on the ends, and two other non-metal elements are plotted on the sides of the square planes. The amounts are again expressed in equivalents.

In the system Si_3N_4 - SiO_2 - AlN - Al_2O_3 - Be_3N_2 - BeO Gauckler (9) found the single-phase solid solutions with β - Si_3N_4 structure are restricted to the plane connecting the points Si_3N_4 , Be_2SiO_4 , BeAl_2O_4 and $\text{AlN}:\text{Al}_2\text{O}_3$. This four points are coplanar in the quaternary diagram. All composition points on this plane have a constant metal to non-metal ratio of 3:4. The plane of 3:4 is presented in Figure 3b. A large area of single-phase region with the β - Si_3N_4 structure is located on this plane. No single-phase solid solution was found either above or below this plane.

The solid solution formation in the systems Si,Al/N,O , Si,Be/N,O and Si,Al,Be/N,O found by Gauckler et.al. (6), Huseby (8) and Gauckler (9) indicated that the lattice β - Si_3N_4 does not

accommodate high concentrations of extrinsic defects. It is reasonable because one does not expect extrinsic defects in excessive quantities to exist in highly covalent compounds such as silicon nitride.

Misfit Factor

β - Si_3N_4 crystallizes in a hexagonal structure. In this structure, each silicon is connected to four nitrogens forming a SiN_4 -tetrahedron and each nitrogen is connected to three silicons. The structure can then be described as three SiN_4 -tetrahedra sharing corners forming a continuous network. The lattice parameters of β - Si_3N_4 reported by Gauckler (9) are: $a = 7.604\text{\AA}$ and $c = 2.908\text{\AA}$. The lattice of β - Si_3N_4 expands when larger aluminium atoms dissolve in the crystal (6) and contracts when smaller beryllium atoms dissolve in it (8). Naturally, oxygen atoms enter the lattice accompanying the metal atoms during solid solution formation. The covalent radii of oxygen is smaller than that of nitrogen. Therefore, oxygen should also effect lattice parameters. When there are more than one kind of metal atoms entering the solid solution, the lattice parameters of β - Si_3N_4 change in a more complex manner.

From these data, one tends to believe that there is an upper limit and a lower limit of lattice distortion that the β - Si_3N_4 can tolerate. It would be very helpful if one could set up a rule using the tabulated values of atomic size to predict the solid solubility limits of different elements in the β - Si_3N_4 . The following is an attempt to do so. Of course, this method can only be applied to substitutional β - Si_3N_4 solid solutions containing no extrinsic vacancy or interstitial. This seems to be true from the results of Gauckler (6), (9), and Huseby (8) in the aluminium and beryllium containing silicon nitride systems.

One can assume that the strongest factors influencing the solid solution formation would be, among others, the size and charge differences between the foreign atoms and the host. One can write an expression to account for the lattice distortion of the host crystal caused by accommodating foreign atoms. The following formula is used to express this differences. Thereby 't' is defined as the "Misfit Factor"

$$t = \frac{\frac{3\sum n_i r_i}{r_{\text{Si}} \sum n_i} + \frac{4\sum n_j r_j}{r_{\text{N}} \sum n_j}}{7} \quad (1)$$

where n_i = fraction of the foreign metal atoms,
 n_j = fraction of the foreign non-metal atoms,
 and r = radii for covalent bonded atoms.

The misfit factor 't' given above includes the influences from both the size and charge from the foreign atoms on the lattice. The size is in the formula as r_i and r_j , however, the charge of the foreign atoms is accounted for by the factor n_j . n_j has different values for the same value of n_i when the charge of the foreign atoms are different. This difference comes from the different number of oxygen atoms needed to balance the total charge brought about by substituting different charged metal atoms for silicon in solid solution. For instance, one oxygen is needed for every aluminum atom and two oxygen atoms are needed for every beryllium atom to form the stoichiometric solid solution of 3:4.

When the misfit factor is plotted against the number of foreign atoms introduced, a map can be drawn to outline the tolerance of the β -Si₃N₄ lattice. The amount of foreign atoms in the mixture can be described by the function:

$$f = \frac{\frac{3\sum n_i}{n_{Si} + \sum n_i} + \frac{4\sum n_j}{n_N + \sum n_j}}{7} \quad (2)$$

where n_{Si} and n_N are the fractions of Si and N atoms respectively.

The logarithm of the Misfit Factor 't' of some compositions in the systems Si,Al,Be/N,O (9) and Si,Be,Mg/N,O (10) were computed and are plotted against the function 'f' in Figure 4. The single-phase compositions were drawn as solid squares and triangles, and the multi-phase compositions were drawn as open squares and triangles. Pauling's tetrahedral covalent radii (11) were used for this computation.

It is clearly shown in Fig. 4 that the single phase region is confined in the center part of the plot where the misfit is the smallest. Substantial amount of foreign atoms can be accommodated in the β -Si₃N₄ lattice when the misfit is small. When the misfit becomes larger, only small amounts of foreign atoms enter the lattice. A curve is drawn in the plot to outline the solubility limit.

It should be noted that all of the data points were taken from isothermal phase diagrams at about 1700°C.

The misfit factors were calculated for the compositions laying on the solubility limits in the system Si₃N₄-Al₂O₃-MgO, reported by Jack (3), and the system Si₃N₄-AlN-Al₂O₃, reported by Oyama (4). These points were plotted in Figure 4. It can be seen that these points fit the curve quite well. It should be noted that only the compositions having a metal to non-metal ratio of 3:4 from the results of Jack (3) and Oyama (4) were used.

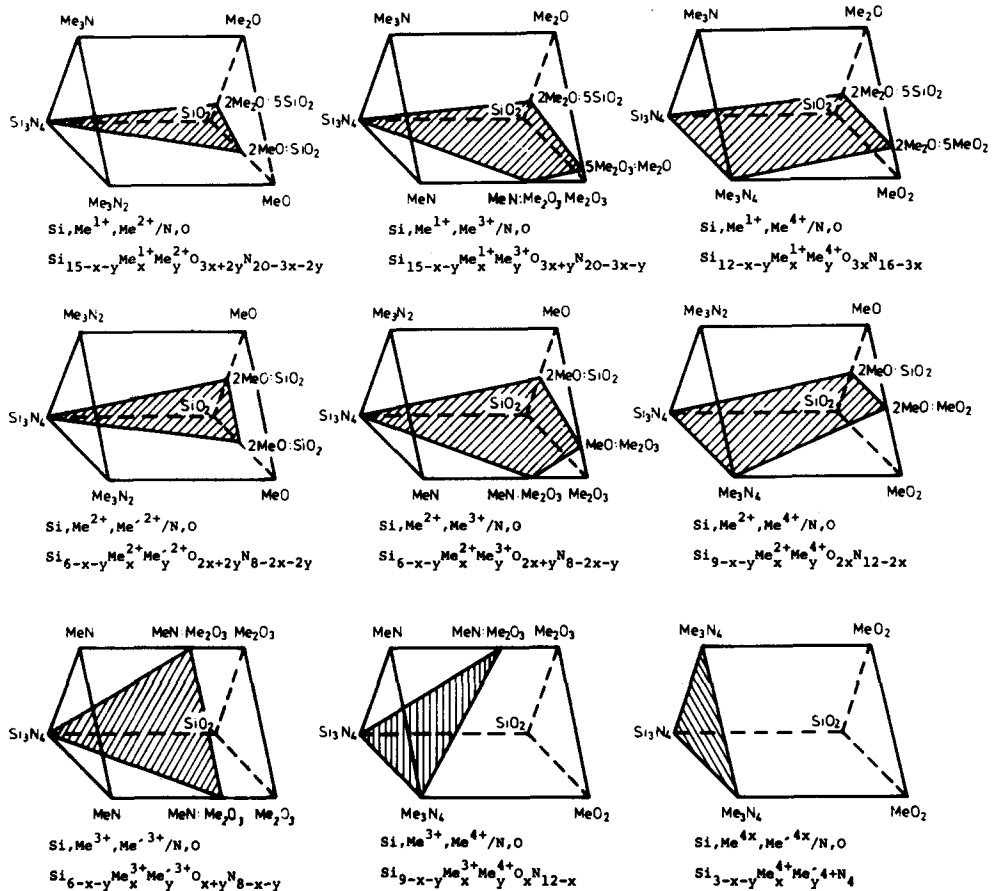


FIG. 4

Logarithm of the misfit factor 't' of foreign atoms in β - Si_3N_4 -metal oxides solid solutions versus amount of foreign atoms function 'f'.

Discussion

More systems should be studied to test the usefulness of the misfit factor. Additional compositions should be chosen among the oxides and nitrides whose metal atoms normally fit in the tetrahedral sites. When we restrict our discussions to the compositions having a constant metal to non-metal ratio of 3:4, and not assuming lattice extrinsic vacancy or interstitial, the compositions should have general chemical formula as given in Fig. 5. The formula are different for different charged cations. When the concept of the reciprocal salts system is used, all compositions should lay on the appropriate joins. These joins are also given in Figure 5.

Combination of three of quasi-ternary reciprocal salts systems will be a quaternary reciprocal salts system. Nine of these systems are given in Fig. 5 as examples. Joins of constant metal to non-metal ratio of 3:4 are drawn in. When these joins are connected, planes are formed in the triangular prism dia-

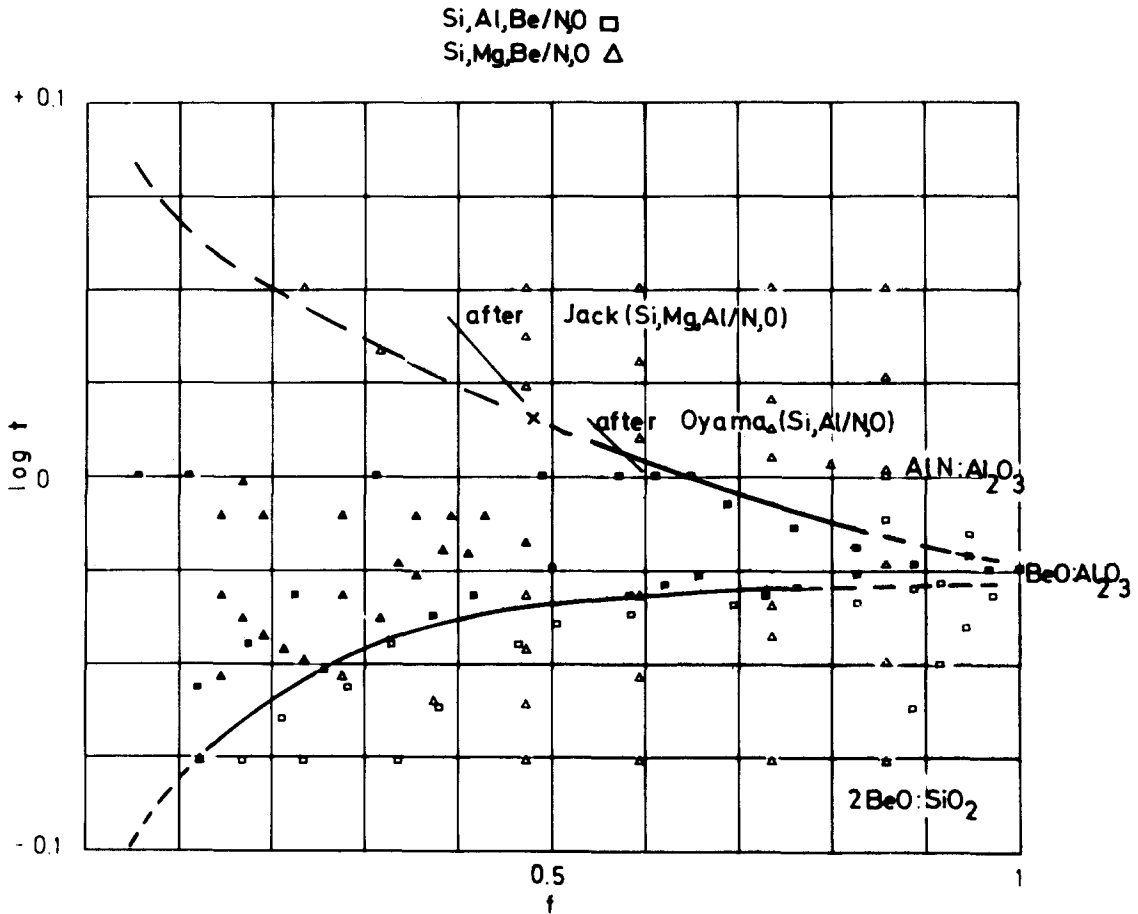


FIG. 5

Phase diagrams of the quaternary reciprocal salts systems showing the planes of the metal to non-metal ratio of 3:4 for different valencies of the metal atoms.

grams. All compositions laying on these planes have a metal to non-metal ratio of 3:4. Generalized formulas of these solid solutions are given underneath the corresponding diagrams. Our hypothesis suggests that compositions on these planes having 't' and 'f' factors inside the boundary in Fig. 4 will form single phase solid solution with β - Si_3N_4 .

The misfit factor should be used with caution. There are other factors which will strongly effect the solid solubility. For example, the character of the chemical bonds in the β - Si_3N_4 - metal oxides solid solutions is an unknown factor which may have strong influence. Solid solubility is also effected by the shape and relative positions of the minimums on the free energy composition curves of both of the phases in equilibrium at a high temperature. That is, the solubility limit of β - Si_3N_4 solid solutions is also affected by the free energy of the phases in equilibrium with it.

Therefore, the calculation proposed in this paper is only the first approximation. However, this calculation will provide a guide to approximate the solubility limits, when the value of the atomic radii can be estimated.

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