Atomic ordering effects and bond indices in quaternary systems Si-(Be,Al)-O-N

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We propose a microscopic method for modeling atomic ordering effects in multi-component solid solutions, which is based on minimizing the number of unfavorable interatomic bonds in the system. Atomic ordering effects are studied in the solid solutions $\text{Si}_{6-x}\text{Al}_x\text{O}_{2x}\text{N}_{8-x}$ ($\beta$-SiAlONs) and hypothetical $\text{Si}_{6-x}\text{Be}_x\text{O}_{2x}\text{N}_{8-2x}$ in the $\beta$-Si$_3$N$_4$-Be-O system. It is established that in $\beta$-SiAlONs, AlO atoms form separate quasi-one-dimensional “channels”. On the contrary, in $\text{Si}_{6-x}\text{Be}_x\text{O}_{2x}\text{N}_{8-2x}$, Be and O atoms constitute a whole cluster. This means that homogeneous solid solutions cannot be formed in the $\beta$-Si$_3$N$_4$-Be-O system under equilibrium conditions.

Keywords: Solid solutions, atomic ordering effects, bond indices, sialon, $\beta$-Si$_3$N$_4$, oxides

I. INTRODUCTION

Atomic ordering effects (AOE) have been discovered in a wide range of non-stoichiometric and multi-component alloys, solid solutions (SS) and compounds. The influence they produce on the properties is great and comparable with the effect of altering the chemical composition of materials

In the majority of theoretical simulations of multi-component materials, atomic ordering effects are studied using integral energy characteristics (for example, free, total or cohesion energies) of a limited number of atomic configurations of a system set a priori. Generally, this approach is applied to binary or ternary compounds, whereas for more complex systems its application is confined by computer power due to rapidly increasing sizes of cells to be considered and the number of atomic configurations.

In the present report, we describe a new method for studying AOE based on comparative analysis of detached techniques of bond characterization can be used as well. The application of this approach can be demonstrated on the four-component SS in the Si-Al-O-N system with the basic structure $\beta$-Si$_3$N$_4$ (the so-called $\beta$-SiAlONs of the formal stoichiometry $\text{Si}_{6-x}\text{Al}_x\text{O}_{2x}\text{N}_{8-x}$, where $x = 0 - 4.2$).

A previous investigation of $\beta$-SiAlONs by the tight-binding method showed that Al and O atoms form extended quasi-one-dimensional (1D) structures constituted by 12-atomic rings — the so-called “impurity channels”, fig. Subsequent studies by the DFT cluster and the band structure full-potential LMTO methods showed that ordered structures exhibited the best stability. Besides, their chemical bonding and electronic properties were examined.

A detailed analysis of bond indices in $\beta$-SiAlONs demonstrated that the most unfavorable bonds are Si-O, which contain the maximum number of FAS. The antibonding states of Al-O bonds are less populated. Si-N and Al-N bonds do not contain any FAS, while COOP(Si-N= 0.58 e) $>$ COOP(Al-N= 0.24 e). Hence, a bonds hierarchy taking into account their stabilizing effects can be represented by the so-called sequence of bonds preferences:

$$P_{\text{Si-O}} < P_{\text{Al-O}} < P_{\text{Al-N}} < P_{\text{Si-N}}, \quad (1)$$

where $P_{A-B}$ reflects the preference of A-B-type bonds presence in the system.

Thus, in order to determine the superstructure of a
multi-component material, it is necessary to choose such distributions of atoms over lattice sites, in which the number of bonds is minimized consecutively in accordance with (5).

For example, for $\beta$-SiAlONs at the first step the superstructures with the minimum number of Si-O bonds are chosen from all possible ones according to (5). Among them we choose the superstructures with the minimum number of Al-O bonds etc. As a result, in a system of a given composition, the superstructures are found, which possess the same number of the same types of bonds, but differ only by their positions in the supercell.

To determine the atomic order type, the following algorithm is applied. The SS $\text{Si}_{6-x}\text{Al}_x\text{O}_2\text{N}_{8-x}$ of a certain composition modelled by a supercell is considered. In this work we make use of the 126-atomic supercells ($3\times3\times1$) analogous to those applied in [3]. For example, the composition of the SS with $x = 2.0$ ($\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$) is described by the $\text{Si}_{36}\text{Al}_{18}\text{O}_{18}\text{N}_{54}$ cell. The following items are fulfilled:

(i) Atoms (Si,Al,N,O) are randomly distributed over the supercell sites so that the result does not depend on initial conditions.

(ii) A random substitution, which is the only permitted one for this system (for example Si→Al, N→O), is performed, while all other types of substitution (Si→O, N→Al) are not considered.

(iii) If the correspondence to (6) improves (the number of favorable bonds increases and the number of unfavorable bonds3 decreases), the step is accepted, otherwise it is rejected.

(iv) Items (ii) and (iii) are repeated until the number of steps denied in succession does not exceed $N_1$.

(v) Items (i-iv) are repeated until the number of structures denied in succession does not exceed $N_2$. This cycle is necessary since the result of cycle (iv) depends on the initial position of atoms and on the first accepted substitution (item iii) defining the subsequent shape of the superstructure.

The choice of $N_1, N_2$ values is determined by the supercell size and composition. In the present work they range from 10000 to 100000 and from 10 to 400 respectively.

An application of the above algorithm for $\beta$-SiAlONs with the same cells and compositions as in (4) shows that the resulting superstructures shapes (1D impurity channels, fig. 1) are in complete agreement with those obtained in a series of complicated calculations of total energies. The formation of impurity channels in $\beta$-SiAlONs leads to the disappearance of the most unfavorable Si-O bonds, while the number of Al-O bonds is minimal.

The evident drawback of the aforesaid scheme concerns condition (4), which reflects only the effect of paired bonds A-B. It should not be excluded that in some cases the formation of $A_mB_m$ clusters is more preferable in spite of low preference of A-B bonds. This restriction may be removed by using a sequence of clusters preferences instead of a sequence of bonds preferences. In respect to $\beta$-SiAlONs, the above restriction does not permit differentiating between distant and adjacent positions of impurity channels.

III. ELECTRONIC STRUCTURE AND ATOMIC ORDERING EFFECTS IN THE $\beta$-Si$_2$N$_4$-BE-O SYSTEM

A. Bond indices and chemical composition

At the first stage of modeling the hypothetical SS in the quaternary system $\beta$-Si$_2$N$_4$-Be-O, we analyzed the electronic properties and bond indices of pure $\beta$-Si$_3$N$_4$ and that containing Be and O impurities, fig. (4). It is seen that in the binary nitride $\beta$-Si$_3$N$_4$ (cell $\text{Si}_{34}\text{N}_{72}$, valence electrons concentration (VEC) equals 576 e/cell), all antibonding states are vacant, while all bonding states are completely occupied.

$O→N$ or Be→Si substitutions (cells $\text{Si}_{54}\text{ON}_{71}$ and $\text{Si}_{53}\text{BeN}_{72}$ respectively) reduce the stability of the $\beta$-Si$_3$N$_4$:O and $\beta$-Si$_3$N$_4$:Be systems. In the first case this is due to partial filling of antibonding states when VEC increases (577 e/cell), while in the second case — due to a depopulation some bonding states when VEC decreases (574 e/cell). A “mutual compensation” of the destabilizing effects of single impurities Be, O can be achieved by choosing a composition, at which the VEC remains 576 e/cell, i.e. when the impurities are introduced in the proportion (Be+20). In this case the type of bands filling (as compared with the basic $\beta$-Si$_3$N$_4$) does not change and the number of filled antibonding and empty bonding states is minimal, fig. (5). Thus, the formal stoichiometry of the SS in the $\beta$-Si$_3$N$_4$:Be-O system is $\text{Si}_{6-x}\text{Be}_x\text{O}_{2x}\text{N}_{8-2x}$.
B. Short-range atomic ordering

When heterovalent substitutions occur in $\beta$-Si$_3$N$_4$, the adjacent arrangement of donor (O) and acceptor (Be) atoms (i.e. the formation of $\{\text{BeO}_2\}$ complexes) is more probable, otherwise the charge screening effect hinders the above mentioned compensation of bonds filling.

C. Long-range atomic ordering

Analysis of separate bonds in the Si$_6$–xBe$_x$O$_2$xN$_8$–2x system shows that Si–O and Be–O bonds consist of filled antibonding states, and their number in Si–O is greater than in Be–O (fig. 2). Determining atomic ordering effects by the proposed algorithm, we search for atomic configurations satisfying the condition of type (2):

$$P_{\text{Si–O}} < P_{\text{Be–O}} < P_{\text{Be–N}} < P_{\text{Si–N}}.$$  

In other words, for the considered series of solid solutions of variable concentrations Si$_6$–xBe$_x$O$_2$xN$_8$–2x ($x \approx 0 – 0.5$), supercells Si$_{53}$Be$_{49}$O$_{46}$N$_{16}$ (fig. 3). As the number of Be, O atoms grows further, the number of Si–O bonds increases linearly and equals the double number of $\{\text{BeO}_2\}$ complexes in the cell. This fact shows that the system has no definite order because, for example, one cluster of 8 complexes $\{\text{BeO}_2\}$ contains the same set of bonds as two

![COOP, arb.un.](image)

FIG. 2: Crystal orbital overlap populations of bonds in Si$_3$N$_4$ (a) and impurity systems Si$_3$N$_4$:O (b), Si$_3$N$_4$:Be (c), Si$_3$N$_4$:(Be+2O) (d) simulated by Si$_{54}$N$_{72}$, Si$_{54}$N$_{71}$, Si$_{53}$Be$_{72}$ Si$_{53}$Be$_{2}$O$_{70}$N$_{70}$ cells, respectively.

| TABLE I: The numbers of different-type bonds in hypothetical SS Si$_6$–xBe$_x$O$_2$xN$_8$–2x as a function of the modelled cell composition. |
|---|---|---|---|
| Cell | Si–O | Be–O | Be–N | Si–N |
| Si$_{53}$Be$_{49}$O$_{46}$N$_{16}$ | 56 | 112 | 0 | 48 |
| Si$_{53}$Be$_{2}$O$_{2}$N$_{12}$ | 58 | 116 | 0 | 42 |
| Si$_{24}$Be$_{30}$O$_{60}$N$_{12}$ | 60 | 120 | 0 | 36 |
separate clusters each containing 4 \{\text{BeO}_2\} complexes (fig. 3). As a result, atomic configurations at a definite supercell composition may have the form of extended, compact or multiple clusters constituted by \{\text{BeO}_2\} complexes, fig. 3.

The analysis of bonds allows us to conclude that the formation of a whole compact cluster with the maximal size is most probable. In this case, the “depopulation” of FAS occurs analogously as in precipitated phases of concentration polytypes in the AlN-Si-O system [7, 8], where antibonding states are present only in “interlayer” bonds Al-O and are absent within the “block of defects”.

In $\text{Si}_{6-x}\text{Be}_x\text{O}_{2x}\text{N}_{8-2x}$, an increase in the size of the “impurity cluster” brings about a growth of the number of “intracluster” Be-O bonds reducing the number of FAS. For example, COOP spectra of “intracluster” and “frontier” Be-O bonds of the $\text{Si}_{46}\text{Be}_8\text{O}_{16}\text{N}_{56}$ supercell are depicted in fig. 4. It can be seen that intracluster bonds do not possess any antibonding states. This indicates that the formation of a compact cluster of the largest size is more advantageous. The growth of a cluster in $\text{Si}_{6-x}\text{Be}_x\text{O}_{2x}\text{N}_{8-2x}$ is not limited meaning the formation of a heterophase state of the system ($\beta$-$\text{Si}_3\text{N}_4$/BeO).

Thus, the proposed semiempirical approach based on quantum-chemical analysis of separate interatomic bonds makes it possible to determine the most probable ef-

FIG. 3: Superstructures in cells of $\text{Si}_{50}\text{Be}_4\text{O}_x\text{N}_{64}$ (a), $\text{Si}_{46}\text{Be}_8\text{O}_{16}\text{N}_{58}$ (b), $\text{Si}_{43}\text{Be}_{11}\text{O}_{22}\text{N}_{50}$ (c,d), $\text{Si}_{41}\text{Be}_{13}\text{O}_{26}\text{N}_{46}$ (e), $\text{Si}_{40}\text{Be}_{14}\text{O}_{28}\text{N}_{44}$ (f) compositions.
stable structures, which were suggested in the framework of the used approach, implies further investigations of their energy states by *ab-initio* methods for the conformation of the presented results. At present, the above studies of Si$_{6-x}$Be$_x$O$_{2x}$N$_{8-2x}$, Si$_{6-x}$Be$_x$O$_x$N$_{8-x}$ and Si$_{6-x}$Be$_x/2$Zr$_{x/2}$O$_x$N$_{8-x}$ SS are being performed by the full-potential LMTO method.

**IV. CONCLUSIONS**

In this paper we proposed a new microscopic semi-empirical method for describing atomic ordering effects in multi-component systems. This method is based on the analysis of interatomic bonds of separate types and includes a procedure of minimizing the number of unfavorable bonds.

The method is used to study AOE in solid solutions of variable compositions: Si$_{6-x}$Al$_x$O$_x$N$_{8-x}$ (β-SiAlONs) and hypothetical Si$_{6-x}$Be$_x$O$_{2x}$N$_{8-2x}$ in the β-Si$_3$N$_4$-Be-O system. It is established that in β-SiAlONs Al, O atoms form separate quasi-one-dimensional “impurity channels”. On the contrary, in Si$_{6-x}$Be$_x$O$_{2x}$N$_{8-2x}$ Be, O atoms trend to form a whole compact cluster. This implies that in the β-Si$_3$N$_4$-Be-O system homogeneous solid solutions cannot be formed under equilibrium conditions.

Potential ways of stabilizing the SS in the β-Si$_3$N$_4$-Be-O system are supposed to be a variation of its stoichiometry (reduction in the oxygen concentration) or partial replacement of silicon by other atoms from the IV-th group, for example, zirconium.

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