

Die so berechneten Parameter für Sb, Te und I sind in Tabelle 2 den empirisch ermittelten gegenübergestellt. Die Parameterunterschiede wirken sich bei Berechnung der kürzeren Bindungslänge R aus R' in Abweichungen von maximal etwa $0,02 \text{ \AA}$ in den mit Werten belegten Bereichen aus. Für die $\text{Sn}^{\text{II}}\text{-O}$ -Bindungen ist eine solche Abschätzung nicht angebracht, da sich im Falle von SnO die Koordinationszahl 4 nicht in der oben beschriebene Weise von der Koordinationszahl 3 ableitet, sondern zwei Paare gleichlanger *trans*-ständiger Bindungen vorliegen. Für diese berechnen sich die Bindungslänge mit $s = W/4$ in sehr guter Übereinstimmung mit dem Experiment zu $2,22 \text{ \AA}$, während für ein einzelnes Paar *trans*-ständiger Bindungen $2,38 \text{ \AA}$ zu erwarten wären. In Tabelle 2 sind jedoch die abgeschätzten Parameter der Abstandskorrelation für $\text{Xe}^{\text{VI}}\text{-O}$ -Bindungen mit aufgeführt. Aus ihnen errechnet sich für XeO_3 mit *trans*-ständigen Sekundärbindungen von $2,8\text{--}2,9 \text{ \AA}$ eine Verlängerung der Bindungsabstände von $1,74$ auf $1,77 \text{ \AA}$, die den Rahmen der Bestimmungsfehler nicht überschreitet. Insgesamt stellen die Bindungslängen-Bindungsstärken-Beziehungen und - in zweiter Linie - die Abstandskorrelationen zwei Regelmäßigkeiten dar, denen die Bindungslängen in den sonst sehr variablen offenen Sauerstoffkoordinationen von Sb, Te, I und Xe sowie mit Einschränkung auch von Sn gehorchen.

Bei der Sammlung und Auswertung der Strukturdaten war das ICSD-System (Inorganic Crystal Structure Data Base; Bergerhoff, Hundt, Sievers & Brown, 1983) eine wertvolle Hilfe. Die umfangreicheren Rechnungen wurden im Hochschulrechenzentrum Frankfurt ausgeführt.

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The Defect Structure of Reduced CaUO_4

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Abstract

The defect structure of reduced CaUO_4 was postulated on the basis of available thermogravimetric, X-ray powder and transmission electron microscope data. It is proposed that the removal of O takes place in an ordered way forming two types of planar structural units which exhibit, owing to more than one energetically equivalent possibility, a stacking disorder along the threefold axis. The basic building elements of the two different units are a central six-coordinated U cation surrounded by six seven-coordinated Ca cations and a central six-coordinated Ca

cation surrounded by six six-coordinated U cations, respectively, where all six-coordinated polyhedra are deformed octahedra. As a consequence microdomains are formed, based on either type of ordering, with corresponding compositions $\text{CaUO}_{3.67}$ and $\text{CaUO}_{3.50}$, respectively. Owing to a more convenient charge balance the two types of ordering tend to alternate with average composition $\text{CaUO}_{3.58}$, where, unlike the former, nonsymmetrically reduced six-coordinated polyhedra also occur at one of the interfaces between the two alternating domain types. Further reduction to $\text{CaUO}_{3.50}$ is only possible by transforming the less-reduced and keeping from both types

of ordering the more-reduced one only. The composition of CaUO_{4-x} can be continuously changed between CaUO_4 and $\text{CaUO}_{3.50}$ by altering the ratio of reduced to unreduced regions, but there is evidence that oxidation may take place preferentially in the domains containing nonsymmetrically reduced Ca cations.

Introduction

CaUO_4 belongs to the family of alkaline-earth-metal uranates (Loopstra & Rietveld, 1969; Yamashita, Fujino, Masaki & Tagawa, 1981) and the structure, first determined by Zachariasen (1948), is rhombohedral with $a_R = 6.263 \text{ \AA}$, $\alpha_R = 36.04^\circ$ and space group $R\bar{3}m$. It can be obtained from the fluorite-type structure by a slight compression along one of the threefold axes, as shown in Fig. 1. Both the U and the Ca cations are eight-coordinated, but the polyhedra of the latter are slightly enlarged relative to those of the former.

No successful single-crystal X-ray analysis has been reported so far on reduced CaUO_4 , while information obtained from X-ray powder experiments (Anderson & Barraclough, 1963; Holc & Kolar, 1983), where no diffuse streaking or weak superstructure reflections were observed, was not sufficient to draw conclusions from these experiments only.

It is well known that O can be exchanged within a rather wide range of composition in CaUO_{4-x} (Anderson & Barraclough, 1963) and during a recent electron-microscopy investigation (Kraševc, Prodan & Holc, 1984), reduced as well as unreduced regions were observed in such samples. In diffraction pat-

terns, corresponding to the reduced regions, additional sharp superstructure reflections, quadrupling the main reflections along the threefold axis, as well as an ordering in the basal plane, corresponding to a $\sqrt{3}a_H$ superstructure, and being a result of intersecting strongly modulated continuous streaks with the Ewald sphere, were observed. The appearance of these diffraction effects did not, except for intensity, depend on composition. While it was impossible to control the composition during electron-microscopy experiments, it was found by thermogravimetric analysis that reduction of CaUO_4 can proceed until $\text{CaUO}_{3.50}$ with a step at about $\text{CaUO}_{3.55}$, and that the samples oxidized in air can be further oxidized by heating, with another step at $\text{CaUO}_{3.77}$ (Tagawa, Fujino & Yamashita, 1979). The more-reduced specimens take up O immediately when exposed to air, but usually do not oxidize completely into CaUO_4 , so that partly reduced samples are reasonably stable.

Structural consideration

The structure of CaUO_4 can be considered as made up of alternating planes of Ca and U cations, which are separated by double O layers. Each O ion is tetrahedrally coordinated by either three U and one Ca cation (O_I) or *vice versa* (O_{II}). Thus, any reduction will, at least partly, lower the coordination of both kinds of cations (Fig. 1). The smallest possible reduction in cation coordination is from eight to six for U and from eight to seven for Ca, resulting in deformed octahedra and cubes with one corner missing, respectively. Although coordination seven cannot be ruled out for U the polyhedra in such cases are rather different from those described. Besides, in all alkaline-earth-metal uranates, the U atoms are always six-coordinated octahedra, with the exception of unreduced CaUO_4 , where they are eight-coordinated (Loopstra & Rietveld, 1969). The Ca coordination can be further reduced to six. Of the three possible ways, where either the O pair along a body diagonal (symmetrically deformed octahedra), along a face diagonal (nonsymmetrically deformed octahedra), or along an edge of a cube (deformed trigonal prisms) is removed, only the last seems to be ruled out, as shown from the following discussion. As both U- as well as Ca-centred polyhedra in unreduced CaUO_4 are only slightly deformed, both types of O layers can be emptied with the same probability. Further, because of the restriction on coordination and shape of the polyhedra, two O layers of the same type, belonging to O_I or O_{II} layers, *i.e.* next or next-nearest layers to the U layer, must always be emptied simultaneously to a maximum of $\frac{1}{3}$ vacant O sites each. Any further O removal will lower the already reduced coordination of either U or Ca, depending on whether O_I or O_{II} layers are being emptied, respectively. Finally, as O is being removed from the layers in an

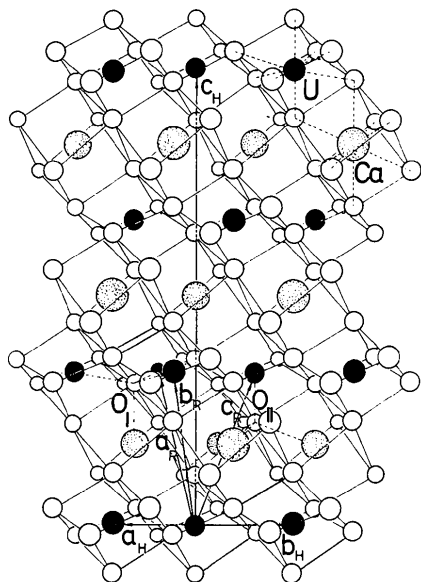


Fig. 1. The structure of CaUO_4 . Rhombohedral as well as hexagonal unit-cell vectors are shown. U and Ca cations and the two types of tetrahedrally coordinated O anions are indicated.

ordered way and as the interaction between vacancies of the same partly emptied O layers is strong as compared to their interlayer interaction, the reduction, once initiated, will proceed in a certain pair of layers until the energetically most convenient concentration of vacancies is reached, leaving at the same time other regions unreduced. The ratio of reduced to unreduced layers will depend on the stage of reduction until full reduction is reached.

Regarding the intrinsic order of the reduced units, there are basically two possibilities, independent of one another.

First, two O_{II} layers are partly emptied by removing from the eight anions surrounding one U the two along the inversion triad. This, type *A* ordering, is shown in Fig. 2. From all possible superlattices the one which belongs to the highest possible concentration of vacancies in one O layer is $\sqrt{3}a_H$. The coordination of every third U cation is changed from eight to six, while at the same time the coordination of all Ca cations in both adjoining cation layers is changed from eight to seven. A direct consequence of removing in this way one third of the O from both O_{II} layers is that no next-nearest O layer to both adjoining U layers can be emptied at all, because the resulting six-coordinated Ca polyhedra would be the already mentioned deformed trigonal prisms, while removing O from the nearest layers to the adjoining U layers would automatically mean a change-over into the second possible type of ordering.

In this, type *B* ordering, one of the remaining equivalent O pairs, belonging to two O_I layers, is removed. Once one of the three possible pairs at a certain U site is chosen, the rest of the ordering is completely determined, so that $\frac{1}{3}$ of the vacant O sites form a $2a_H$ superstructure in both O_I layers. In the

resulting net of deformed octahedra all three possible orientations are equally included. The vacancies reduce the coordination of $\frac{3}{4}$ of the U cations from eight to six and those of $\frac{1}{4}$ of the Ca ones in adjoining layers from eight to seven, so that further reduction is possible! Either the coordination of the remaining $\frac{1}{4}$ U is reduced by removing adjacent O_{II} anions, reducing at the same time the remaining $\frac{3}{4}$ Ca and again preventing U from the next layers from being reduced at all, or the as-reduced layer is not further changed, but the reduction is repeated around the next U layer in exactly the same way, but symmetrically with regard to the previous U layer, thus reducing the Ca coordination also from eight to six, similar to the way U is reduced. The net reduction is the same in both cases and all additional vacancies, belonging either to the O_I or O_{II} layers, form $2a_H$ superstructures in each of these partly reduced layers. However, for reasons discussed later, only the second of the two possibilities takes place and this, type *B* ordering, is shown in Fig. 3. Thus, the basic element is a central six-coordinated Ca cation surrounded by six six-coordinated U cations. The reason for the appearance of only seven-coordinated polyhedra in type *A* ordering, while in type *B* the Ca coordination can be reduced from eight to six, is the fact that the six-coordinated polyhedra, which would result as the next step during O removal in type *A* ordering, would have to be deformed trigonal prisms with Ca cations placed way off their centres, while in type *B* they remain at the very centres of the resulting deformed octahedra.

Two possible situations must be considered. The reduced regions, which coexist with the unreduced ones, can include either nonrelated type *A* and type *B* parts or these alternate over equal, $2[00.3]_H$ -thick layers. The second possibility must occur, because it gives the only answer to the diffraction effects, while

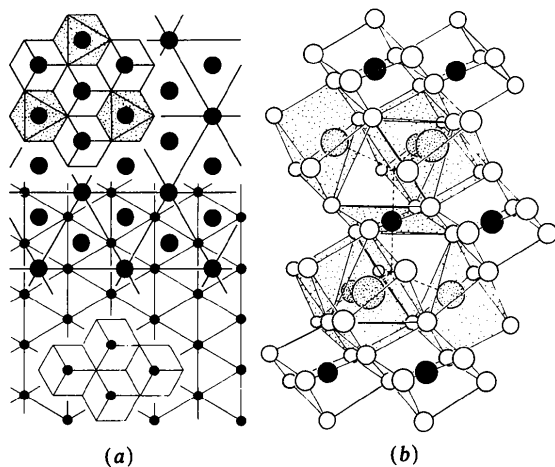


Fig. 2. Two subsequent U layers with the corresponding anion polyhedra (only partly shown) as seen along the threefold axis (a) and a complete detail as seen perpendicular to it (b) for type *A* ordering. The dotted polyhedra are those with reduced coordination (crosses indicate the missing O). U, Ca and O ions are indicated in the same way as in Fig. 1.

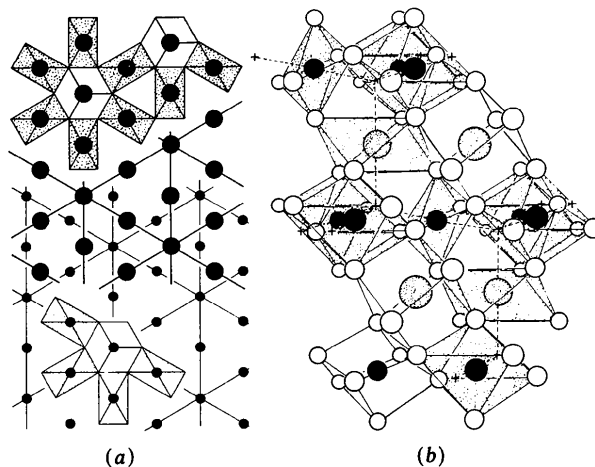


Fig. 3. Type *B* ordering as seen (a) along and (b) perpendicular to the threefold axis. For details see the caption of Fig. 2.

the first cannot be ruled out, as its resulting diffraction will overlap that of the related layers.

In type *A* regions $2[00.3]_H$ -thick layers are stacked in a disordered way along the threefold axis, while in type *B* the corresponding regions are only $[00.3]_H$ thick, reducing CaUO_4 to $\text{CaUO}_{3.67}$ and $\text{CaUO}_{3.50}$, respectively. Thus, if complete ordering were to take place, periodicities $2c_H$ and c_H , respectively, would be achieved. Finally, if both types alternate, the stacking along the inversion triad is disordered again but the regions become $4[00.3]_H$ thick, reducing CaUO_4 to $\text{CaUO}_{3.58}$. As both sides of type *A* regions are not equivalent if only two U layers thick, the coordination of one quarter of the Ca cations, forming one of the two interfaces between type *A*/type *B* regions, will be changed from eight to six by removing O pairs along face diagonals of the cubes. The overall reduction, obtained by averaging all three possible types of ordering O vacancies, is equal to the last mentioned, *i.e.* $\text{CaUO}_{3.58}$. Any further reduction requires a rearrangement of the already reduced layers, so that only type *B* will remain, extending the reduction limit as far as $\text{CaUO}_{3.50}$. No further reduction is possible.

During oxidation of the reduced CaUO_{4-x} samples, the process is expected to be completely reversible, *i.e.* unreduced regions should grow at the expense of the reduced ones, regardless of whether the reduced regions are of type *A*, type *B* or mixed type *A*/type *B* origin.

Discussion and comparison with the experiments

The expectations, based on structural considerations, are in qualitative agreement with the experimental results. With the picture given none of the U ions, whether eight or six coordinated, will be significantly displaced during reduction. The same is valid for those Ca ions for which the coordination is also symmetrically reduced from eight to six, while the nonsymmetrically reduced ones, for which the coordination is changed either from eight to seven only, or from eight to six, will have to be displaced. Regarding O, the structure factor is weak as compared to those of U and Ca, so that minor shifts, if any at all, can be ignored. Due to the stacking disorder of the reduced layers, the existing ordering of vacancies in layers perpendicular to the inversion triad is completely smeared out. The net result is that only the average structure factor of O is changed, depending on the reduction of particular layers, but the hexagonal base of the average unit cell of the O sublattice remains equal to that of the subcell. Thus, O can only contribute to the weak but sharp reflections joining the subcell reflections. The symmetrically reduced U and Ca ions do not contribute to any superlattice reflections, while the nonsymmetrically reduced Ca ions contribute to the diffuse superlattice streaks only. During type *A* ordering these ions are

displaced along one of the body diagonals of the unreduced deformed cubes. Because of the stacking disorder of such reduced Ca layers these represent very thin diffraction objects, which generate long spikes in reciprocal space (Fig. 2 in Kraševc *et al.*, 1984).

Since no $2a_H$ superstructure reflections are present in electron diffraction patterns, type *B* ordering must be such that not only U but also Ca cations are not displaced from the centres of their polyhedra. This is the reason why of the possibilities mentioned only that shown in Fig. 3 can be accepted. The second possibility contradicts this requirement.

The whole reasoning given for type *A* and type *B* ordering is also valid for the alternating combination of both, with the only difference that the coordination of Ca cations forming one of the nonsymmetrically reduced layers between type *A* and type *B* ordering is partly reduced to six and not to seven only. The net result is, besides the $4[00.3]_H$ periodicity, the appearance of similar streaking to that of type *A* ordering only.

The reciprocal space of reduced CaUO_4 , constructed on the basis of electron diffraction experiments (Kraševc *et al.*, 1984), is shown in Fig. 4(a), while Fig. 4(b) is a copy of the first with the modulated streaking decomposed into reflections which, when strongly streaked themselves, combine to form the observed intensity distribution. The centres of enhanced intensity along the streaks, with corresponding periodicities $12c_H/(9n+9/2)$, are in fact a result of the overlapping of two close-lying strongly streaked reflections, with corresponding periodicities $12c_H/(9n+3)$ and $12c_H/(9n+6)$, with $n=0, (1, 2), 3, 4, \dots$. The numbers in parentheses belong to the weak parts of the streaks, where second-order reflections are overlapped. Thus, for example, the streaking centred at $\frac{1}{3}\frac{1}{3}\frac{3}{8}$ is a result of two overlapped reflections at $\frac{1}{3}\frac{1}{3}\frac{3}{12}$ and $\frac{1}{3}\frac{1}{3}\frac{6}{12}$. All reflections in the reciprocal space are obtained by repeating, due to multiple scattering, a certain arrangement of sharp and streaked satellite reflections around each subcell reflection. However, only those satellites for which the Ewald sphere is intersecting at the same time these very satellites as well as their originating subcell reflections are visible. Thus, for example, only the sharp reflections along the threefold axis, belonging to the 100, 010 and 001 reflections, are visible, while the corresponding streaked reflections are not. If present, they would, because they are displaced by $\frac{1}{3}111$ along the threefold axis, alter the observed modulation along the streaks. The intensity of the satellites decreases rapidly and can mostly be neglected after the second-order reflections, indicating that the ordering present extends over relatively short distances only. Further, the arrangement of the satellites around each subcell reflection can best be described by constructing two equivalent rhombohedral 'unit cells',

rotated by 60° around the threefold axis which, strictly speaking, are not unit cells in a normal sense, but rather a useful construction to explain the complicated distribution of satellites. The two equivalent 'unit cells' are a result of the fact that different type A structural units, being part of the reduced CaUO_{4-x} , and which are the origin of the diffuse streaking, can be statistically rotated by 60° with respect to one another. It should be pointed out that, although all three possible types of ordering have so far been equally considered, there is strong evidence that the one where type A and type B alternate is the more favourable (Fig. 1 in Kraševc *et al.*, 1984). A possible reason is a more convenient charge distribution with the two different types alternating. Calculations following Pauling's electroneutrality rules clearly show that in unreduced CaUO_4 the eight-coordinated U and Ca cations carry a $6+$ and a $2+$ charge, respectively, which is compensated by the $4-$ charge of the

surrounding electrons. Although there may be more possibilities, the best compensation of charges can be achieved in the following way. If type A and type B alternate, $\frac{1}{6}$ of the $\text{U}^{6+}(8)$ in type A layers is changed into $\text{U}^{5+}(6)$ while $\frac{7}{8}$ of the $\text{Ca}^{2+}(8)$ are changed into $\text{Ca}^{2+}(7)$ and $\frac{1}{8}$ into $\text{Ca}^{2+}(6)$. At the same time the negative charges around reduced cations are changed from $4-$ (coordination 8) into $3-$ (coordination 6) and $\frac{7}{2}-$ (coordination 7), so that the average positive and negative charges become $\frac{47}{6}+$ and $\frac{349}{48}-$, respectively. As a result, the net charge per unit of such a layer is $\frac{9}{16}+$. It can be found with the same reasoning that the net charge per unit of the corresponding type B layer is $\frac{9}{16}-$ if $\frac{1}{8}$ of the $\text{Ca}^{2+}(8)$ is changed into $\text{Ca}^{2+}(6)$ and $\frac{1}{8}$ into $\text{Ca}^{2+}(7)$, while $\frac{3}{4}$ $\text{U}^{6+}(8)$ is changed into $\text{U}^{4+}(6)$. This way of balancing the charges must be compared with those of type A and type B ordering separately. In type A the charge compensation is only possible if $\frac{1}{3}$ of the $\text{U}^{6+}(8)$ remains unchanged, while $\frac{1}{2}$ is changed into $\text{U}^{5+}(8)$ and $\frac{1}{6}$ into $\text{U}^{5+}(6)$ and if $\text{Ca}^{2+}(8)$ is changed completely into $\text{Ca}^{2+}(7)$. In contrast, in type B, $\frac{3}{4}$ of the $\text{U}^{6+}(8)$ must be changed into $\text{U}^{5+}(6)$ and $\frac{1}{4}$ into $\text{U}^{5+}(8)$, again with $\frac{1}{4}$ of $\text{Ca}^{2+}(8)$ changed into $\text{Ca}^{2+}(6)$.

Finally, the appearance of a step at about $\text{CaUO}_{3.77}$ in the TGA oxidation curve is somewhat strange, because it means that reduction and oxidation are not two completely equivalent processes. By analogy with reduction, a step can only be attributed to a situation where the whole sample takes on a certain order. The only possibility seems to be that oxidation from $\text{CaUO}_{3.58}$ takes place preferentially in type A domains, which contain nonsymmetrically reduced Ca cations, resulting in $\text{CaUO}_{3.75}$. As this contradicts the existence of reduced/unreduced regions during reduction it must be possible that rearrangements of the existing domains take place during subsequent cycling.

Concluding remarks

For a compound with a highly ionic character, which CaUO_4 certainly is, it would practically be impossible to explain the large variation in stoichiometry by the existence of a structure able to accommodate a large percentage of point defects. The interaction between point defects in ionic compounds at concentrations several orders of magnitude lower from those in question is effective enough either to force the vacancies to order or to eliminate them (*e.g.* Adams, 1974). Thus, the existence of microdomains, different in structure and composition, is not surprising. By analogy with the formation of extended defects (crystallographic shear, block structures and twinning) in some transition-metal oxides, energetically favoured microdomains, as compared to a high concentration of point defects, where a metal to oxygen ratio is varied by the ratio of six to eight and seven to eight

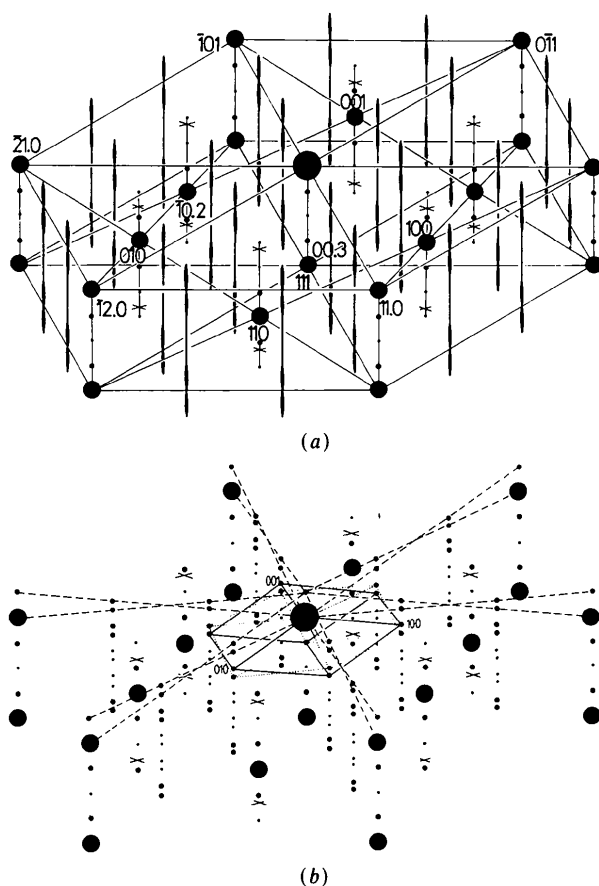


Fig. 4. (a) The reciprocal space of reduced CaUO_4 . Rhombohedral as well as hexagonal indexing for the subcell is given. The weak lines and the crosses indicate the positions of the subcell and satellite reflections, while the strong and nonuniform lines show the streaking along the triad. (b) The decomposition and the modulated streaking shown in (a). The interrupted lines and crosses show the positions of sharp and streaked satellites. Full and dotted lines show the two 'unit cells' (one indexed), rotated by 60° to each other, which can account for all satellites present.

coordinated cations, can account for practically any stoichiometry in the composition range between CaUO_4 and $\text{CaUO}_{3.50}$.

The given explanation is not only in agreement with all known experimental data, but also with the results of Thornber & Bevan (1970), who studied mixed oxides of the type MO_2 (fluorite)- M_2O_3 , which can accommodate large departures in stoichiometry in fluorite-related structures. The defect complex in these compounds, which enables the variation in composition, is equivalent to type A ordering, one of the possible ways of reducing CaUO_4 .

There is a perfect intrinsic order in the arrangement of O vacancies in both types of microdomains and the observed disorder is only a result of more than one energetically equivalent possibility of stacking the reduced layers along the original inversion triad. If the nearest-neighbour interaction between reduced layers could be extended to the next-nearest neighbours at sufficiently low temperatures, a complete three-dimensional ordering would be achieved. As the favoured alternation of both types of ordering can only be explained on the basis of the most convenient charge balancing during reduction, it is obvious that this kind of ordering is conditioned by the possibility of U taking on a whole series of

different ionization states with close ionization energies.

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Crystallographic Relations between the β and γ Forms of $(\text{Ca}_2, \text{Ca}_{1.8}\text{Sr}_{0.2})\text{SiO}_4^*$

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Abstract

Crystal associations of β and γ forms of synthetic $(\text{Ca}_2, \text{Ca}_{1.8}\text{Sr}_{0.2})\text{SiO}_4$ showing a paramorphosis relationship are studied by optical microscopy and X-ray diffraction. The mutual crystallographic orientation is unequivocally established. The cell parameters are: $(a \sin \beta)_\beta = 5.48$, $a_\gamma = 5.08$; $b_\beta = 6.74$, $b_\gamma = 6.76$; $c_\beta = 9.30$, $c_\gamma = 11.23 \text{ \AA}$. On the basis of experimental evidence the structural relationships

between the β and γ forms are analyzed both qualitatively and quantitatively. An atom-by-atom correspondence is established between the two structures and the transformation mechanism from the β into the γ form is discussed. The reconstructive and displacive components of the semi-reconstructive atomic rearrangement are singled out.

Introduction

The structural relationships among the five phases: α , α'_H , α'_L , β , and γ of calcium orthosilicate, the atomic mechanisms of transformation and their connections with equilibrium solid-phase relations are

* Editorial note: An independent study of the polymorphs of Ca_2SiO_4 has appeared recently [Barbier & Hyde (1985). *Acta Cryst.* **B41**, 383-390].