357. *The Oxides of Uranium. Part III.* The System* UO_2–MgO–O.

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A study of the binary system UO_2–MgO by means of a high-temperature vacuum furnace and *X*-ray diffraction measurements has revealed no evidence of compound formation at any temperature between 300° and 2350°, but solid solutions of magnesium oxide and uranium dioxide are formed. The solubility of magnesium oxide in uranium dioxide to give a fluorite structure with anion vacancies is only a few moles % even at the highest temperatures unless extra oxygen enters the solid-solution phase. This defect solid solution has a great affinity for oxygen, however, and when it is allowed to take up extra oxygen the solubility of magnesium oxide increases markedly, to as much as 25 moles %. Chemical analysis of these partially oxidised solid-solution phases shows that almost exactly one atom of oxygen is taken up for each molecule of magnesium oxide dissolved in uranium oxide to give a fluorite lattice having no vacant anion sites.

The magnesium oxide phase does not dissolve detectable quantities of uranium dioxide under any of the conditions studied.

THE present work follows that of Part II * on the UO_2–CaO system, and is of some interest in that it involves one of the smallest bivalent cations and one of the largest quadrivalent cations. The Goldschmidt ionic radii are Mg^{2+}, 0·78 Å and U^{4+}, 1·05 Å (cf. Ca^{2+}, 1·06; Ti^{4+}, 0·64; Zr^{4+}, 0·89; Th^{4+}, 1·10). The disparity between the ionic radii of magnesium and uranium is greater than for the comparable double oxide systems previously described in the literature. Magnesium oxide and titanium dioxide form double oxides of the composition $2TiO_2,MgO$ and TiO_2,MgO (v. Wartenberg and Prophet, *Z. anorg. Chem.*, 1932, **208**, 369), and magnesium oxide and zirconia are reported to form $MgZrO_3$ (*idem, ibid.*), although Ebert and Cohn (*ibid.*, 1933, **213**, 321) did not confirm this result. Magnesium oxide and thoria do not interact (v. Wartenberg and Prophet, *loc. cit.*) and neither oxide has a marked solubility in the other. We would therefore expect to find neither compound formation nor an extensive range of solid solutions between magnesium oxide and uranium dioxide. If found at all, solid solutions of magnesium oxide in thorium or uranium dioxides would be expected to have the cubic fluorite structure of the dioxides, with a contracted unit cell (UO_2, $a = 5·457$ kx.u.; ThO_2, $a = 5·5855$ kX.u.) due to the replacement of large ions by smaller ones, each dissolved magnesium oxide " molecule " being associated with an anion vacancy in the lattice.

The ThO_2–MgO system is free from any complications arising from variable valency of the components. On dimensional grounds it would be expected that the solubility of magnesia in thoria and in uranium dioxide should be similar. Whereas, however, the unit cell of thoria undergoes a shrinkage, corresponding to the dissolution of approximately 0·5 mole % of magnesium oxide, when thoria is heated to 2000° in vacuum with an excess of magnesium oxide, our results showed magnesia to have a much greater apparent solubility in uranium dioxide than would be expected on the basis of direct analogy. It became clear that the reason for the difference lay in the variable valency of uranium. This makes it possible for the solid-solution phase to take up sufficient oxygen to fill the lattice vacancies, the electrical neutrality of the crystal being maintained by a corresponding partial increase in charge of the uranium ions from U^{4+} to U^{5+}.† The experimental evidence presented supports the hypothesis that the solubility of magnesium oxide in " uranium dioxide " is, in fact, markedly increased by inclusion of sufficient additional oxygen to fill the anion sites which would otherwise have been vacant. The system corresponds rather

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* Part II, *J.*, 1951, 1352.

† The same result could be achieved by formation of an appropriate proportion of sexavalent uranium ions, but there is evidence to show that in sexavalent uranium compounds the U^{6+} is invariably accompanied by two close O^{2-} ions, forming a structural unit unsuited for inclusion in the cubic fluorite structure of these solid solutions.

closely with the " controlled valency " semiconductors of Verwey and Haijman (*Philips Res. Report*, 1950, **5**, 173), who found, *e.g.*, that Li_2O and NiO would form solid solutions (NaCl type) only if Ni^{2+} could simultaneously be oxidised to Ni^{3+}. The resulting phase, $(Li_x\,Ni^{3+}{}_xNi^{2+}{}_{1-2x})O$, is not anion-deficient.

At high temperatures, the extra oxygen taken up by the solid phase may be provided by dissociation of magnesium oxide, which begins at about 1700° in a vacuum of 10^{-5} mm. (Tiede and Birnbrauer, *Z. anorg. Chem.*, 1914, **87**, 129). For experiments above 1750°, the oxide mixtures used were prepared from the two separate oxides, but for much of the work below this temperature magnesium and uranous hydroxides were coprecipitated from aqueous solutions. The two oxides were thereby very intimately mixed, and the consequent reduction in the necessary diffusion path meant that equilibrium between these two refractory oxides could be attained in a reasonable period of heating at temperatures as low as 650°. In one case good *X*-ray photographs were obtained after heating the precipitated mixture at only 300° in a sealed tube in the presence of moisture. In coprecipitated preparations, heated at lower temperatures, oxygen is provided by the partial atmospheric oxidation which is unavoidable if uranous hydroxide is handled by the ordinary laboratory methods of wet chemistry.

EXPERIMENTAL

The sources of magnesium were the " AnalaR " oxide, which was heated in air to 1300° and stored in a desiccator before use, or the " AnalaR " sulphate. A very pure uranium dioxide was used for making powdered mixtures. " AnalaR " uranyl sulphate was reduced to uranous sulphate by irradiation with ultra-violet light in ethyl alcohol (see Hutchison and Elliott, *J. Chem. Phys.*, 1948, **16**, 920) to obtain the starting material for preparation of coprecipitated oxide mixtures. This uranous sulphate was washed with ethyl alcohol and dried. The magnesium and uranous hydroxides were coprecipitated rapidly in a finely-divided form, by running an aqueous solution of the two sulphates in a stream of fine droplets into mechanically stirred ammonia solution (*d* 0·88). The precipitate is initially green, but becomes black (through brown) during 30 min., owing to partial oxidation of the uranium. By working quickly, and drying the product in a nitrogen stream, this oxidation can be limited but not entirely prevented. These preparations were not normally reduced before use. Oxide mixtures of both types were pressed into pellets ¼″ in diameter and ½″—¾″ long just before they were needed

Furnace.—The high-temperature, high-vacuum furnace used was described by Alberman (*J. Sci. Instr.*, 1950, **27**, 280). The temperature was controlled by adjustment of the power input to the filament at a value determined by previous calibration against the m. p.s of pure nickel, platinum, and rhodium. The fourth-power radiation law was followed very accurately. The ambient pressure in the furnace during the final stages of heating was always close to 10^{-5} mm. Pellets heated to 1750° or less were contained in magnesia crucibles with lids. At the highest temperatures, however, magnesia crucibles disintegrated and in almost all cases the specimens prepared above 1750° were heated in small open tantalum crucibles which made contact with the pellet only at its base. When portions of the same oxide mixture were heated separately to 1950° in magnesia and in tantalum, the products were very slightly different owing, we believe, to the somewhat higher ambient oxygen pressure maintained inside the closed magnesia crucible. Traces of tantalum were detected in a few samples heated above 2000°, but in all cases the lower half of the pellet, at least, was rejected as being most susceptible to contamination by tantalum.

X-*Ray Measurements.*—Samples for *X*-ray diffraction measurements were normally taken from the top of the pellet, although an early experiment showed that there was no difference between such a sample and one from the powdered whole pellet. Finely ground material was loaded into Pyrex *X*-ray capillaries, and diffraction powder photographs were taken on 9-cm. Unicam cameras, filtered copper-$K\alpha$ radiation being used; $K\alpha_1$–α_2 doublets were usually resolved for all lines above $\theta = 60°$. Cell dimensions were calculated by Nelson and Riley's method (*Proc. Phys. Soc.*, 1945, **57**, 160) for graphical extrapolation to the value of a_{100} at $\theta = 90°$. Values quoted are accurate to $\pm 0{\cdot}001$ kX.U. unless otherwise stated.

Chemical Analysis.—The gross composition of the powdered preparations was fixed by weighing the pure oxides. The composition of the coprecipitated samples, however, was determined chemically, because precipitation of magnesium in ammonia solution (*d* 0·880) is incomplete. The composition of the solid-solution phase in two-phase specimens containing free magnesium oxide can be determined by chemical analysis only after removal of free magnesium oxide. Magnesium oxide is soluble in 3M-ammonium chloride solution, while uranium dioxide and solid solutions rich in uranium dioxide are not, so that free magnesium oxide could be leached out from two-phase samples by gently boiling the powdered pellets in 3M-ammonium chloride solution. Leaching and chemical analysis of the solid-solution phase were performed in duplicate in all cases. This leaching was complete in the case of the comparatively well-crystallised samples made by heating the two oxides to high temperatures. The method was unsatisfactory for coprecipitated oxide mixtures which had been heated at temperatures below 1750°; it is presumably difficult to grind the sample down to particles comparable in size with the crystallites formed at these low temperatures, and inclusions of magnesium oxide remain. In the case of coprecipitated samples, therefore, the magnesium content had to be determined from the *X*-ray data, by use of the relationship between cell dimension and dissolved magnesium obtained for the well-crystallised samples, as described later.

For chemical analysis, the materials were dissolved in approximately 8M-nitric acid; 8M-ammonium nitrate solution was added and the uranium was extracted with ether. The method was that described by Rodden (*Analyt. Chem.*, 1949, **21**, 331), except that to obtain accurate results we found it essential to continue the extraction for 3 hr. instead of the 30 min. recommended. The uranium was determined gravimetrically as U_3O_8. The magnesium was determined as 8-hydroxyquinoline complex.

In some cases the solid-solution phase was analysed also for excess of oxygen (*i.e.*, that in excess of a composition represented by xMgO,$UO_{2\cdot00}$), by reducing it for 2 hr. in hydrogen in a silica apparatus, and weighing the water produced. There is some difficulty in obtaining accurate analytical figures for magnesium and oxygen in these solid solutions, as both represent only a small molar fraction of a light element, contained in a small weight of uranium dioxide.

Controlled Oxidation Experiments.—In these, the oxygen uptake of a solid solution of magnesium oxide in uranium dioxide was measured quantitatively, in a Pyrex-glass high-vacuum system of the type commonly used for gaseous adsorption measurements. Pressure measurements in a calibrated volume were made by using a butyl phthalate manometer. The known quantity of gas was expanded into a second known volume containing the sample. The sample tube was mounted horizontally, and the powder shaken out in it to give a very thin layer, so that oxygen uptake would be uniform. It was heated by a small tube furnace, and small corrections were applied for the hot dead space. Samples were removed at intervals for *X*-ray measurements.

RESULTS AND DISCUSSION

The principal features of the high-temperature experimental results are illustrated in the Table. In general, it was found that the *X*-ray photographs could be taken as indicating an equilibrium condition in the heated preparations only when they showed very sharp lines, with good resolution of doublets back to a Bragg angle of 60° or so. Quite good *X*-ray photographs were obtained from some of the specimens heated at 1100°, although further periods of heating showed that slow change occurred for as long as 30 hr. This was taken as evidence that the solid solution was of fairly uniform composition, and that the rate-controlling step in the attainment of equilibrium lies at the interface in this system. It must involve either the slow transfer of MgO or the slow attainment of an oxygen dissociation pressure equal to the ambient oxygen pressure surrounding the pellet in the vacuum. The latter seems the more likely for the following reason. The coprecipitated, partially oxidised MgO–UO_2 mixtures are initially amorphous, but if they are annealed in hydrogen at 650° for a short time (long enough to give a measurable *X*-ray photograph) they show that the original coprecipitated oxide is, in effect, a " supersaturated," though very poorly crystallised, solid solution which separates on heating. This separation occurs much more rapidly at 1000° in hydrogen than it does at 1100° in vacuum, suggesting that removal of oxygen is the rate-controlling factor.

It is convenient to consider the experiments in groups within which the same experimental technique was used throughout.

Preparations below 1750°.—These solid solutions were made by heating the coprecipitated oxides of gross composition 33 MgO : 67 UO_2. *X*-Ray diffraction measurements on this series after being heated to temperatures between 1100° and 1750° (see Table) indicated that the solubility of magnesium oxide in uranium dioxide was large at 1100° and rapidly fell with rising temperature. This is, of course, contrary to the usual effect of temperature on the mutual solubility of solids. The results might at first sight be explained by assuming a slow approach from the "supersaturated" condition of the coprecipitated oxides to a low equilibrium solubility. The rate of approach to equilibrium would be greater at higher temperatures. Long annealing at 1100° showed, however, that the cell dimension changed much more slowly than was observed in a reducing atmosphere at 1000°. It was known that the coprecipitated oxides had taken up some oxygen during preparation, and no attempt had been made to remove this extra oxygen by reduction, since it had been expected that the excess of oxygen would be lost in vacuum—slowly at 1100° and rapidly at higher temperatures, as is the case with β-UO_2 (which has a composition close to $UO_{2\cdot25}$; Alberman and Anderson, *J.*, 1949, S 303). Loss of oxygen on heating was indicated by an abnormally high ambient pressure in the vacuum furnace, and the completion of deoxygenation was inferred from the eventual fall in pressure to 10^{-5} mm. When a portion of the starting material was reduced in hydrogen, the loss in weight corresponded to an initial composition $(MgO)_{0\cdot5}(UO_{2\cdot369})$. When this reduced material was heated to 1100° in a vacuum, its cell dimension indicated a much smaller solubility of magnesium oxide than that of the unreduced material.

Expt. No.	Initial composition, $MgO : UO_2$	Method of prepn.	Crucible.	Temp.	Heating time (hrs.)	a, kX.U.	Solid solution composition :	
							Mg/U	excess O/U
33	33 : 67	Ppt.	MgO	1100°	1·0	5·293	—	—
34	,,	,,	,,	1325	1·0	5·332	—	—
35	,,	,,	,,	1525	1·0	5·390	—	—
36	,,	,,	,,	1750	1·0	5·419	—	—
43	,,	,,	,,	,,	2·0	5·422	0·078 *	0·041
37	,,	,,	,,	1100	2·0	5·292	—	—
38	,,	,,	,,	,,	6·0	5·309	—	—
40	,,	,,	,,	,,	12·0	5·311	—	—
41	,,	,,	,,	,,	30·0	5·319	0·306 *	0·323
44	,,	Ppt. reduced in H_2 at 1000°	,,	,,	2·0	5·406	0·114 *	0·084
26	40 : 60	Powder	Ta	1750	1·0	5·448	—	—
27	,,	,,	,,	,,	2·0	5·448	0·024	—
30	80 : 20	,,	,,	,,	2·0	5·4382	0·039	—
49	30 : 70	,,	,,	1000	1·0	5·448	—	—
51	50 : 50	,,	,,	,,	1·0	5·4424	—	—
54	10 : 90	,,	,,	2150	0·2	5·4502	—	—
50	30 : 70	,,	,,	,,	0·2	5·443	—	—
52	50 : 50	,,	,,	,,	0·2	5·4353	—	—
4	50 : 50	,,	,,	2350	0·1	5·427	—	—
14	50 : 50	,,	,,	1325	6·5	5·417	0·087	—
18	20 : 80	,,	,,	1515	2·0	5·445	0·031	—

* Determined from *X*-ray data.

The solubility of magnesium oxide in uranium dioxide involves replacement of U^{4+} and $2O^{2-}$ by $Mg^{2+} + O^{2-} + \square O$ where $\square O$ represents a vacant oxygen site in the fluorite UO_2 lattice. It seemed possible that incorporation of sufficient oxygen to fill these vacant anion sites might appreciably increase the ability of the uranium dioxide phase to withstand the distortion involved by the inclusion of the much smaller Mg^{2+} ions, and might thus give rise to an increased magnesium oxide solubility. The solid solution phases were accordingly isolated by leaching them with ammonium chloride solution, and were analysed for magnesium, uranium, and excess of oxygen. The oxygen content was in fact, found to be less in solid solutions prepared at higher temperatures, and showed a smooth variation when compared with cell dimensions. Chemical analyses for magnesium on these poorly crystallised coprecipitated samples were not significant. The magnesium content in this series of preparations has therefore been determined from the *X*-ray diffraction values of the cell dimension, a_{100} (see Fig. 3). The justification for this method will appear later, when it will be shown that introduction of excess of oxygen alone, into a solid solution of fixed magnesium content, produces only a comparatively small change in unit-cell size.

There is a close parallel between magnesium oxide content, so determined, and excessive oxygen content, determined chemically, which is shown graphically in Fig. 1. The curve has a slope corresponding to the inclusion of just over one oxygen atom in excess per molecule of dissolved magnesium oxide. Equal proportions are required to maintain a solid solution in which the crystal lattice has no anion vacancies. It is noteworthy that when the anion vacancies are filled with extra oxygen, the solubility of MgO (involving the small Mg^{2+} ion) in UO_{2+x} at 1100° is greater than the solubility of CaO in $UO_{2·0}$ at 1750° (in which case the cationic radii are almost identical, but the lattice is defective).

A marked solubility was observed after a moist precipitate of magnesium hydroxide and uranous hydroxide had been heated in a sealed Pyrex capillary for 2·5 hr. at 300°. A well-crystallised product was obtained, consisting of free U_3O_8, and a UO_2 phase with cell dimensions corresponding to $(MgO)_{0·12}(UO_{2+x})$.

Preparations above 1750°.—A series of mixtures of various proportions of magnesium oxide and uranium dioxide, powdered together, were heated in tantalum to 1750°, 2000°, 2150°, and in one case to 2350° at which temperature the pellet softened. The apparent eutectic is therefore close to 2350°, though, strictly, a true eutectic temperature cannot be obtained in vacuum, where the magnesium oxide is slowly dissociating and volatilising out of the hot zone.

FIG. 1. *Relationship between magnesium content and excess oxygen content of solid-solution phases.*

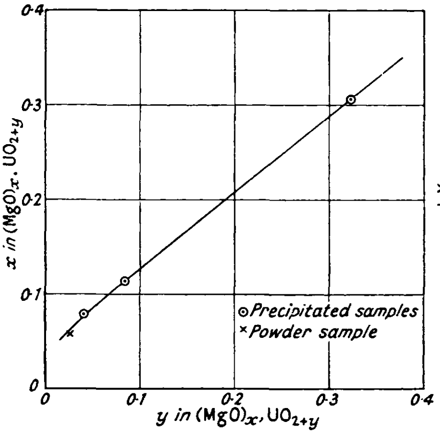
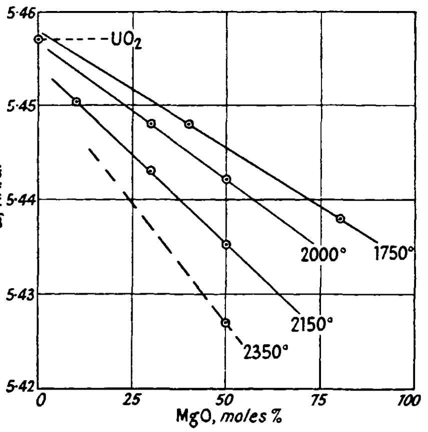


FIG. 2. *Change of* UO_2 *unit-cell dimension after heating mixtures of various gross compositions to* 1750°, 2000°, 2150°, *and* 2350°.



For a normal two-component system, in which component A has a limited range of solubility in component B, a plot of gross composition against the cell dimensions of phase B (containing dissolved A) for a given temperature shows a continuous (usually linear) variation until saturation is reached; the cell dimension then remains constant in the two-phase region, where excess of A coexists with a saturated solution of A in B. The discontinuities in a family of such curves for a series of temperatures give a solubility curve. In this case, however, a constant cell dimension was not obtained in the two-phase region (see Fig. 2), implying that the solubility of magnesium oxide in uranium oxide depended upon the amount of excess of magnesium oxide in contact with the solid solution phase. Further heating showed that this effect was not merely an indication of an increased rate of solution but was a steady-state condition. The slope of the curves was not merely the initial part of the normal plot, since (*a*) chemical analysis showed the presence of ammonium chloride-soluble magnesium oxide, together with a solid-solution phase containing much less magnesium than would be necessary; (*b*) a family of curves was obtained, with different slopes; and (*c*) the *X*-ray diffraction lines of magnesium oxide appear on the photographs of mixtures richer in magnesium oxide than $30MgO : 70UO_2$.

Our interpretation of these results is based on the hypothesis that the oxygen pressure due to the dissociation of magnesium oxide occurring within the pellet was considerably above the ambient pressure maintained by the pumps and the "gettering" action of furnace parts. The resulting incorporation of oxygen led to a solubility of magnesium oxide in uranium dioxide which was favoured by higher temperatures and by the presence of more magnesium oxide. Direct chemical analysis for magnesium, uranium, and excess of oxygen, on one of the samples heated to 2150°, showed that the magnesium : excess of oxygen ratio lay on the curve obtained for the lower-temperature preparations (Fig. 1). The solubility of magnesium oxide in uranium dioxide at the highest temperatures is small, as compared with that observed between 1100° and 1525°.

The fact that the focal point of the family of curves lies so close to the cell dimension of uranium dioxide itself (Fig. 2) indicates that the solubility of magnesium oxide in it would be very small under all conditions if excess of oxygen were completely absent. This conclusion is supported also by the observations that (*a*) the solubility of magnesium oxide in thoria at 2000° as measured by us is only about 0·5 atom %; (*b*) the apparent eutectic temperature is 2350° for a 50 : 50 mixture, and higher still for a 30 : 70 mixture, values which are very close to the m. p. of the more fusible component magnesium oxide (2400°), and indicate very little mutual solubility; (*c*) the solubility of magnesium oxide in uranium dioxide, in a hydrogen atmosphere at 1000°, is very much less than the solubility of magnesium oxide in partially oxidised UO_2 at 1100°.

FIG. 3. *Variation of unit-cell dimension of solid-solution phase with dissolved* MgO *content.*

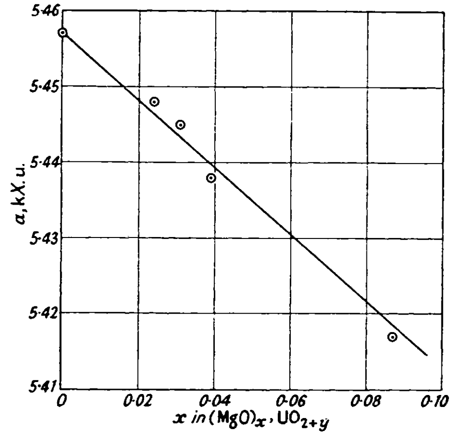
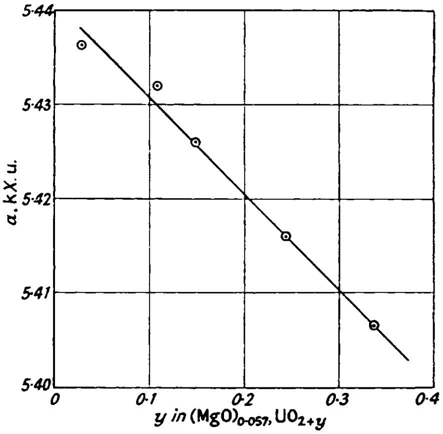


FIG. 4. *Variation of* UO_2 *unit-cell dimension with excess oxygen content, at fixed* MgO *content.*



Oxidation of Solid Solutions.—As is normal in binary oxide systems, it was found throughout that there was a linear relationship between dissolved magnesium oxide concentration and cell dimension for specimens which could be directly analysed for magnesium (Fig. 3). This was very nearly true, irrespective of the treatment given before the high-temperature heating (*e.g.*, reduction in hydrogen or degassing temperature), over a temperature range from 1325° to 2150°. The determination of solubilities in solid systems from *X*-ray cell-dimension measurements is already an accepted technique, but in this case it was necessary to show that increasing the oxygen content by filling anion vacancies did not materially interfere with the method.

A controlled, stepwise oxidation was carried out at 400°, with a solid solution of the composition $(MgO)_{0\cdot057}UO_{2\cdot028}$, as determined chemically, in order to show the effect of varying the oxygen content in the presence of a fixed concentration of dissolved MgO. It was found that the size of the unit cell changed linearly without deviating from cubic symmetry as oxygen was added, up to a composition of $(MgO)_{0\cdot057}\,UO_{2\cdot337}$, at which point the experiment was stopped. The values are presented graphically in Fig. 4. These results show that the change of cell dimension caused by introducing 1 mole % of magnesium oxide into a uranium dioxide phase is approximately 5 times as great as the change caused by introduction of 1 atom % of excess of oxygen. This enables us to estimate the magnesium content of a solid solution phase from its cell dimension, although the accuracy would be reduced if very wide variation of oxygen content also occurred independently.

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