Arab Gulf J. Scient. Res., **9** (2), pp. 35-43 (1991)

The Phase Transition in "U-Nd-O" System

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ABSTRACT. Specimens of the system "U-Nd-O" were prepared by solid reaction containing different Nd-concentrations. The resulting compounds were phase analysed using X-ray powder diffractometry, and a single-phase region with fluorite structure was observed in the Nd_2O_3 molar concentration range (33% - 63%). The lattice parameter also behaved in a manner confirming a preliminary phase diagram deduced earlier. O/U ratios, determined by standard polarographic techniques, exhibited an oxidation stability of the resulting fluorite structure in the concentration region up to 63 mol% Nd_2O_3, suggesting that the fluorite structure observed in the high Nd_2O_3 region is different. Room temperature magnetic susceptibilities of individual compounds exhibited clear regional distinctions which support the suggested phase diagram. The observed behaviour is discussed in terms of the effect of the Nd-ion on the oxidation state of the U-ion.

The importance of UO_2 in the nuclear industry has attracted a considerable amount of interest. In the hope of improving its oxidation characteristics, internal chemistry, thermal stability, and microstructure (Sugisaki and Sueyoshi 1943, 1978, Schmits *et al.* 1971) many have investigated its pseudobinary compounds with rare earth oxides, some of which represent fission products which may result from burning fuel while others were found to affect the above mentioned properties. Thus, investigating these pseudobinaries may consequently suggest some technological implications.

The "U-Nd-O" system has been previously investigated by several authors, whose individual findings seem to have much in common. However the phase relationships individually proposed by Lambertson and Muller (1954), Kolar *et al.* (1962) and Hund and Peetz (1952) seem to disagree in their final details, leading to some contradicting conclusions, as regarding the stabalizing role played by the Nd-ion on the oxidation state of the U-ion.

This work aims at investigating the effect of the Nd-ion on the oxidation state of the U-ion, and its consequential effects on the phase diagram of the "U-Nd-O" system, and on the magnetic state of the uranium ion.

Sample Preparation and Experimental Procedure

Powders of intended compositions $(UO_2)_{1-x}$ $(Nd_2O_3)_x$, with x taking the values 10, 20, 30, 40, 50, 60, 70, 75, 80 mole% Nd_2O_3, were dry-milled for 11 hr, and pelletized at a compacting force of 2 tons for a period of two minutes. The resulting pellets were fired in air for 16 hr at 500 °C and for 18 hr at 1000 °C, then soaked in for 4 hr at 1500 °C followd by furnace - cooling. Attempts were made to prepare these compositions at different thermal conditions, and it was found that preparations made at 1100 °C and under static air conditions have been quite successful in producing single phase fluorite structure material for 50 mol% Nd_2O_3.

Successful compacts were crushed into fine powder and made ready for chemical analysis, X-ray diffraction and measurement of magnetic susceptibility.

Powdered samples of individual compositions were chemically analyzed by standard atomic absorption techniques, the results of which are listed in Table (1). The required phase analysis was made by X-ray powder diffractometry and the respective lattice parameters were accurately determined using computer programms LATCON and APPELMANN (Stewart 1976). The oxidation state of the U-ion present in different members of the series was deduced from the O/U ratios determined by standard polarographic technique.

Magnetic susceptibilities of individual specimens where determined using a magnetic balance (Faraday Technique) at room temperature and Hg Co NCS_4 as standard.

Results and Discussion

Accurately determined lattice parameters which are plotted in Fig. 1, as a function of Nd_2O_3 - Molar Concentration, may suggest a preliminary phase diagram divided into three region: the first of which (region I) indicates the

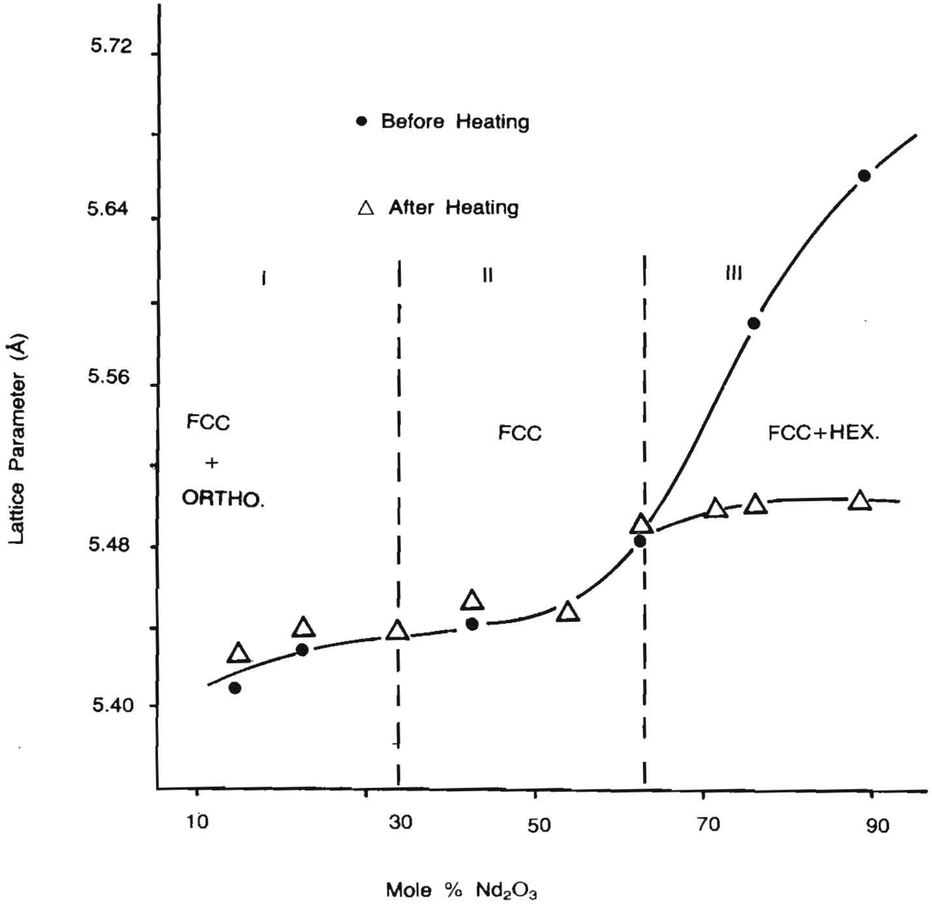

Fig. 1. Preliminary phase diagram of the "U-Nd-O" system constructed from variations of lattice parameter with Nd_2O_3 molar concentration.

formation of a face-centered cubic (fluorite) structure of the "U-Nd-O" system, coexisting with an orthorhombic phase attributed to excess U_3O_8. In the second region (II) a single F C C fluorite - type structure is dominant, with no other phases being detectable. Region (III), on the other hand exhibits a sudden deviation from the pattern, where the lattice parameters of the observed F C C phase increase sharply with increasing Nd_2O_3 content. Moreover, a second phase (of hexagonal crystal structure) was also detected, which might be attributed to the hydrolized Nd_2O_3 (present in excess) (Kolar *et al.* 1962).

Table 1. Molar Composition, lattice parameters and phase analysis of the "U-Nd-O" system

Nominal Mole % of Nd_2O_3	Measured Composition Mole %		Lattice Parameter (A)	Lattice Parameter (A) after heating to 1100 °C	Phases Present
	UO_2	Nd_2o_3			
–	100	–	5.4464	–	FCC
10%	85.06	14.90	5.4138	5.4392	FCC+s ORTH.
20%	77.30	22.30	5.4352	5.4420	FCC+vs ORTH.
30%	66.70	33.30	5.4447	5.4490	FCC
40%	56.60	40.09	5.4480	5.4526	FCC
50%	46.00	54.10	5.4573	5.4560	FCC
60%	36.80	63.10	5.4846	5.4935	FCC
70%	26.80	72.30	5.5053	5.5141	FCC+vs HEX.
75%	23.20	76.80	5.5940	5.5115	FCC+s HEX.
80%	19.00	80.96	5.6636	5.5026	HEX.+s FCC.

All specimens were subjected to a second heat treatment at 1100 °C for a short time and their lattice parameters (shown in Fig. 1 and listed in Table 1), coincided with the original values in regions I and II but greatly differed from those of region III. This may suggest some changes in the oxidation state of the uranium - ions of the compound. In fact this pseudobinary compound is expected to be different from that observed in region I and II, in spite of the fact that its crystal structure is also F C C. However, its determined lattice parameter (5.5141 Å) is quite close to C-type rare earths. Hence the second heat treatment is expected to transform the U^{+4}-ions of the compound into U^{+6}-ions by some oxidation mechanism (Kolar *et al.* 1962, Wilson 1959). Thus the reduction of the unit cell volume becomes logical owing to the smaller observed size of the U^{+6}-ion.

The preliminary phase diagram may suggest that the fluorite structure existing over such a wide concentration range (region I and region II) enjoys a high degree of stability towards oxidation. This may very well be confirmed by the observed polarographic measurements preformed on these compounds, as exhibited in Fig. 2. The O/U ratio seems to be distributed around a general value of 2.57-2.60, which may be taken as evidence of the fact that the mean valency is approximately 5, suggesting that the observed fluorite structure is highly stabilized towards oxidation in spite of multiple heat treatments in static air. Moreover, the U-ion in this unit cell is a mixture of U^{+6} and U^{+4}, with U^{+6} most likely to be dominant in population. The O/U ratio observed in region III may confirm the above suggested

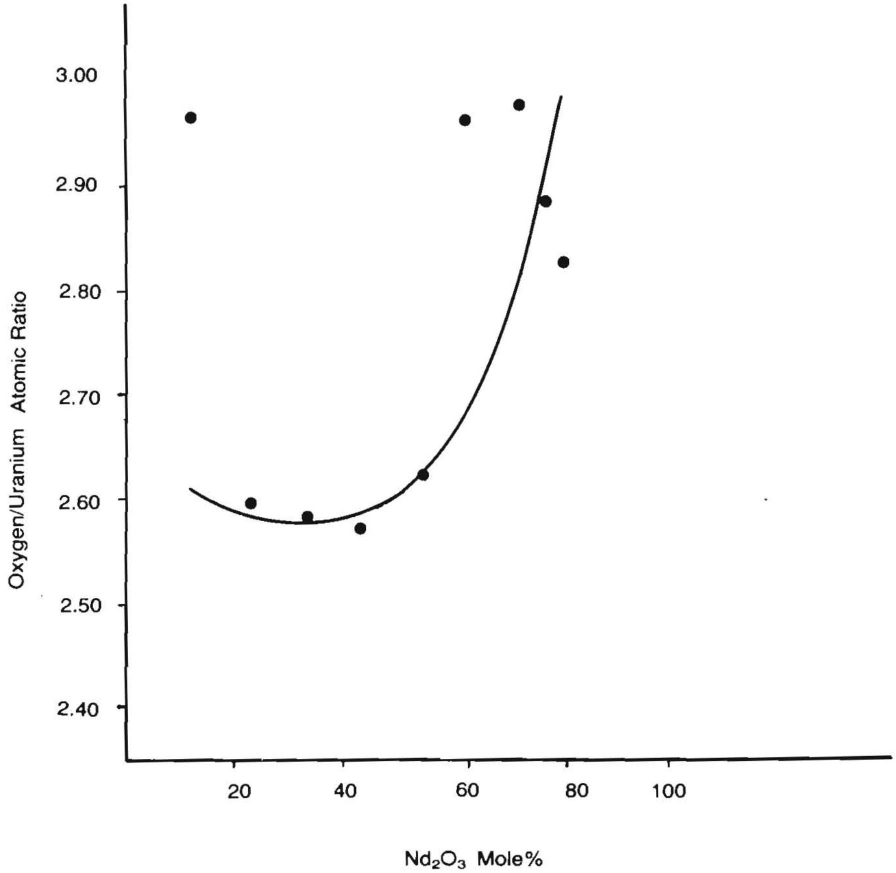

Fig. 2. The variation of O/U ratio with Nd_2O_3 molar concentration.

dissimilarity between the fluorite structures of region III and that of regions I and II. The observed sharp increase may firstly suggest a phase change, and secondly an instability towards oxidation. However, the very large values exhibited may be attributed to the vanishing concentration of U-ion in the compound.

The observed room temperature magnetic susceptibility values plotted in Fig. 3 as a function of Nd_2O_3 concentration also confirm the above suggested phase diagram; exhibiting three separate regions explicitly distinguished by different individual behaviours, which coincide with those of the phase diagram. The smooth steady increase in region I suggests an overall increase in paramagnetism (coming mainly from U^{+4} and Nd^{+3}-ions) and a reduction in the numbers of

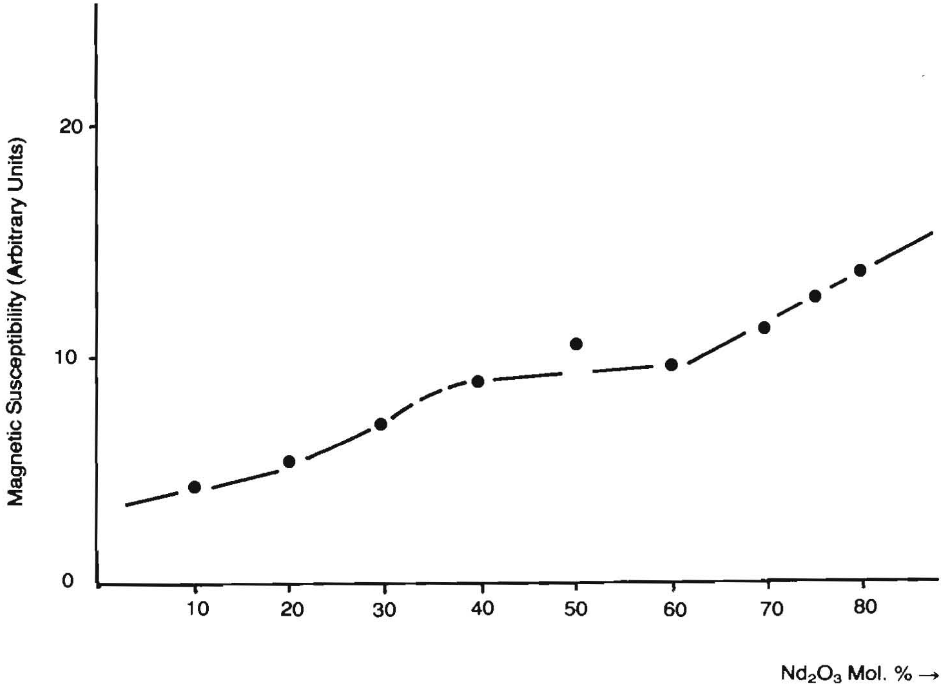

Fig. 3. Variation of the room temperature magnetic susceptibility with Nd_2O_3 molar concentration.

diamagnetic U^{+6}-ions; brought about by the addition of Nd_2O_3 which reacts with U_3O_8 to form the fluorite structure, thus reducing the concentration of U^{+6}-ions. Throughout region II, on the other hand, the susceptibility assumes a constant value which suggests that the added paramagnetic Nd^{+3}-ion is equalized and opposed in value by the creation of diamagnetic U^{+6}-ions. Whenever, a U^{+4}-ion is replaced by a Nd^{+3}-ion, a neighbouring U^{+4}-ion in the lattice is oxidized into U^{+6} to balance the resulting valence (oxygen) deficiency (Kolar *et al.* 1962 and Wilson 1959). Finally, the observed ascent in region III suggests a general enhancement in paramagnetism due to the heavy presence of Nd^{+3}-ion, due to the excessive Nd_2O_3 phase which dominates that of the minority (U^{+4} + U^{+6}) ions.

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(Received 04/09/1990;
in revised form 17/07/1991)

التغاير الطوري للنّظام "U - Nd - O"

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إن الغاية من هذا البحث هو دراسة تأثير أيونات عنصر النيوديميوم (Nd) على حالة الأكسدة لأيونات عنصر اليورانيوم (U)، ومن ثَمَّ دراسة نتائج هذه التأثيرات على المخطَّط الطوري للنظام "U - Nd - O" وعلى الحالة المغناطيسية لأيونات اليورانيوم.

وللوصول إلى هذا الهدف تمَّ تحضير عيّنات من النظام "U - Nd - O" بوساطة التفاعل الصلب الحاوي على تراكيز مختلفة من عنصر النيوديميوم، وبعد ذلك حُلّلت الأطوار البلّلورية المحصول عليها في مختلف العينات المُحضَّرة، وتمَّ التحليل باستخدام تقنية حيود الأشعّة السينية للمساحيق، وبيَّن التحليل بأنَّ المدى التركيزي المَوْلي الواقع مابين ٣٣٪ و ٦٣٪ يُعطي مركبات بللورية أحادية الطور والممّيزة بتركيب الفلورايت المكعّب. وقد سلكت هذه المركبات البللورية سلوكاً يؤكِّد المخطّط الطوري الأولي المستنتج. كما أظهرت معطيّات النسبة U/O التي حُدّدت بطريقة البولاروغرافيا (وهي طريقة متبعة في التحليل الكيميائي) سلوكاً يؤكدِّ استقرارية في الطور لحالة التأكسد للمركبات الواقعة في المدى التركيزي الخاص ببنية الفلورايت. وهذا يؤكد بأن بنية الفلورايت التي لوحظ تواجدها في المدى التركيزي العالي لعنصر النيوديميوم تختلف عن تلك التي تمَّ الكشف عن وجودها في المدى المذكور أعلاه.

وأخيراً أظهرت القياسات التأثيرية المغناطيسية لكل مركب من المركبات والتي أجريت في درجة حرارة الغرفة ـ صفاتاً مميّزةً واضحةً تؤكدّ جميعها المخطط الطوري المستنتج .