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STABILIZING EFFECTS OF OXIDE ADDITIONS  
TO URANIUM OXIDE

by

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# STABILIZING EFFECTS OF OXIDE ADDITIONS TO URANIUM OXIDE

Wendell B. Wilson and Arnold F. Gerds

*An investigation of the stabilizing influence of oxide additions to uranium oxide was continued. These additions are employed for two purposes: (1) to eliminate the phase transformation to  $U_3O_8$  which occurs when  $UO_2$  is exposed to an oxidizing environment at elevated temperatures, and (2) to reduce the volatility or transpiration losses of uranium oxide which become appreciable in air at temperatures in excess of 1200 C.*

*Previous work has shown that solid solutions of  $UO_2$  containing nominally 60 mole per cent of trivalent oxides such as  $La_2O_3$  are stable at temperatures to at least 1750 C. In the present work a partial substitution of CaO for  $La_2O_3$  and  $Y_2O_3$  was attempted, to reduce the large amount of additive required for stabilization. The substitution also permits use of additives of lower thermal-neutron cross section.*

*The results show that CaO may be successfully employed in partial substitution for  $La_2O_3$  and  $Y_2O_3$ . The resulting solid solutions exhibited high-temperature stability comparable to that of the "binary" solid solutions of  $UO_2$  containing  $La_2O_3$  or  $Y_2O_3$ . On the basis of these and other results some alternative approaches are possible to reduce the amount and cross section of additive required for stabilization.*

## INTRODUCTION

Uranium dioxide has received considerable attention as a high-temperature nuclear fuel because of its excellent refractory characteristics. In practice, however, its use is problematical because of its oxidation characteristics. If exposed to an oxidizing environment at elevated temperatures, either as a result of operational failure or as a normal condition, it will transform to  $U_3O_8$ . The resulting volume expansion is sufficient to be disruptive to  $UO_2$ -containing fuel elements. In addition,  $U_3O_8$  exhibits appreciable vapor pressure at temperatures in excess of 1200 C.

Solid solutions of  $UO_2$  containing certain rare-earth and other oxide additions can withstand oxidation without undergoing a phase transformation. In addition, the loss of uranium oxide by volatility may be significantly decreased by such additions. Solid-state studies of the  $UO_2$ - $La_2O_3$  and the  $UO_2$ - $Y_2O_3$  systems were undertaken to provide a better understanding of the stabilizing influence of such additions. The results have been given previously.<sup>(1,2)</sup> However, since they are pertinent to the present work, a brief review for  $La_2O_3$  appears warranted.

Previous work has shown that  $UO_2$  forms extensive solid solutions with  $La_2O_3$  to beyond 50 mole per cent  $La_2O_3$ . These solid solutions are oxygen deficient since the trivalent  $La_2O_3$  is incorporated into the fluorite structure of  $UO_2$ . Oxidation of the  $UO_2$ - $La_2O_3$  solid solutions results in a decrease in lattice parameter which tends to produce the equivalent of the "anomalous" fluorite-structure solid solutions of Hund<sup>(3)</sup> obtained by reacting  $U_3O_8$  and  $La_2O_3$ . As Hund has shown,  $U_3O_8$  and  $La_2O_3$  form solid solutions of fluorite structure from 33 to 68 mole per cent  $La_2O_3$ . From this it may be seen that

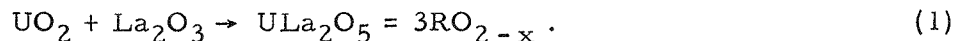
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(1) References are at end.

UO<sub>2</sub> containing in excess of 33 mole per cent La<sub>2</sub>O<sub>3</sub> will, even when oxidized, retain the fluorite structure, although there is an associated lattice-parameter decrease.

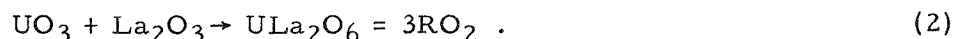
An explanation for this unusual phase stability has been advanced, based upon the concept of valence compensation. The term "compensation" arises from the fact that when foreign atoms having more electrons than the base crystal are present simultaneously with foreign atoms having fewer electrons, they tend to compensate for each other. The explanation of the effects of valence compensation or balanced valence in crystals has been given by Kroger and Vink<sup>(4)</sup>.

In the uranium-oxygen system, when UO<sub>2</sub> is oxidized a valence change occurs as the uranium goes from U<sup>+4</sup> to the U<sup>+6</sup> state. This is analogous to adding foreign atoms containing more electrons to UO<sub>2</sub> and as such can be compensated for by foreign atoms containing fewer electrons, such as La<sub>2</sub>O<sub>3</sub>. This is true, of course, only if the additive reacts to form solid solutions with the uranium oxide. The resultant solid solutions may be represented by the following reactions:



(Oxygen-deficient fluorite solid solution)

Reaction (1) becomes upon oxidation:



(Stoichiometric fluorite solid solution)

Examination of Reaction (2) above indicates that if equimolar amounts of UO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> are not involved, the resulting solid solutions deviate from stoichiometry. Study of the uranium-lanthanum-oxygen system indicates that a shift from p- to n-type electrical conductivity occurs at the equimolar composition for both Reactions (1) and (2) and for all degrees of oxidation between.\* This is interpreted as indicative that the Fermi level remains constant in the solid solution despite the variable oxygen content. The detailed study, by Kroger and Vink, of the effects of imperfections and foreign atoms in solid solution has led to a possible explanation of the mechanism by which the Fermi level can be kept constant with variable composition.

Studies of solid solutions, represented by Reaction (2), have indicated that a trivalent additive may be used to produce stable solid solutions which do not undergo a phase change upon oxidation. An equivalent reaction can also be written for a divalent additive, such as CaO as:



(Stoichiometric, fluorite structure)

Examination of the phase diagrams of divalent oxide additions to UO<sub>2</sub> indicates that the solubility is too limited to be equivalent to Reaction (3). Comparison of Reaction (2) with Reaction (3) shows that on a per-atom basis, a divalent additive would be more effective for valence compensation than a trivalent additive.

\*The results of the study of the "oxidized" solid solutions have not as yet been given. They will be presented elsewhere.

The present work was undertaken to substitute a divalent additive, in part, for a trivalent additive, in an attempt to reduce the total additive content and to use additives of lower cross section. Solid solutions of uranium oxide containing  $Y_2O_3$  and CaO, and  $La_2O_3$  and CaO were evaluated in the present work.

## EXPERIMENTAL WORK

### Fabrication

The general technique of fabrication employed was similar to that reported previously.<sup>(1,2)</sup> In the present work, however, two alternative fabrication techniques were used which resulted in some variation of the composition of the solid solutions.

The first technique employed, involved vacuum drying the oxide powders to remove absorbed water. The dried powders were mixed in an argon-filled dry box to appropriate compositions. The binary oxide solid solutions of  $UO_2-La_2O_3$  and  $UO_2-CaO$  were mixed initially and then compacted hydrostatically at 100,000 psi using a binder of 1 w/o beeswax. Following compaction these binary solid solutions were sintered in vacuum at temperatures ranging from 1650 to 1750 C for periods up to 4 hr. Following the sintering, the compacts were recrushed and reprocessed to obtain better homogeneity.

After preparation of the binary solid solutions the "ternary" compositions were prepared by mixing appropriate amounts of the binaries and reprocessing. In this way an attempt was made to obtain ternary solid solutions of  $UO_2-La_2O_3-CaO$  and  $UO_2-Y_2O_3-CaO$ .

The second technique employed in the present work involved the direct mixing of the ternary oxides followed by compaction, sintering, and reprocessing.

The ternary compositions prepared in the present work are given in Table 1. These have been subdivided into two groups. Group I samples were prepared to determine whether stable solid solutions could be formed and retained after air oxidation at elevated temperatures. Group II samples, consisting of the more stable compositions, were those from which more complete chemical and structural analysis, electrical characteristics, and high-temperature stability were obtained.

A further distinction between the Group I and Group II compositions is made on the basis of their fabrication. With the exception of the first sample (Sample 63) the Group I samples were prepared by the direct-sintering technique. The relative instability of these samples, compared with that of Sample 63, suggested that the direct sintering had altered the composition. Analysis of the last series (Samples 125, 126, 128, and 129) of the Group I samples disclosed that CaO had been preferentially lost from solid solution, possibly resulting in understabilized materials. The Group II samples were subsequently fabricated by preparation of the binaries as was Sample 63.

Table 1 also contains samples of  $UO_2-La_2O_3-ThO_2$ . The objective of this was to evaluate the stability of  $ThO_2$ -containing stabilized  $UO_2$ , i. e.,  $UO_2$  containing 60 mole per cent  $La_2O_3$ . Previous work had shown that  $UO_2-ThO_2$  solid solutions decomposed to

TABLE 1. COMPOSITION AND SINTERING LOSSES OF THE TERNARY SOLID SOLUTIONS

| Sample          | Intended<br>Composition,<br>mole per cent |       |                 | First Sintering   |             |                          | Second Sintering  |             |                          |
|-----------------|---|-------|-----------------|-------------------|-------------|--------------------------|-------------------|-------------|--------------------------|
|                 | R <sub>2</sub> O <sub>3</sub>             | RO    | RO <sub>2</sub> | Temperature,<br>C | Time,<br>hr | Weight Loss,<br>per cent | Temperature,<br>C | Time,<br>hr | Weight Loss,<br>per cent |
| <u>Group I</u>  |   |       |                 |                   |             |                          |                   |             |                          |
| 63              | 20 La                                     | 20 Ca |                 | --                | --          | --                       | --                | --          | --                       |
| 86              | 30 La                                     | 5 Ca  |                 | 1700              | 2           | 11.10                    | 1750              | 3           | 7.11                     |
| 87              | 30 La                                     | 10 Ca |                 | 1700              | 3           | 14.40                    | 1700              | 3           | 2.56                     |
| 88              | 40 La                                     | 5 Ca  |                 | 1750              | 3           | 18.70                    | 1700              | 3           | 2.89                     |
| 90              | 25 Y                                      | 15 Ca |                 | 1700              | 3           | 3.70                     | 1700              | 4           | 1.90                     |
| 91              | 20 Y                                      | 20 Ca |                 | 1700              | 3           | 5.80                     | 1750              | 3-1/2       | 3.70                     |
| 92              | 30 Y                                      | 10 Ca |                 | 1700              | 3-1/4       | 2.20                     | 1750              | 3-1/4       | 6.40                     |
| 125             | 20 La                                     | 20 Ca |                 | 1700              | 2           | 6.20                     | 1750              | 3           | 3.9                      |
| 126             | 30 La                                     | 5 Ca  |                 | 1700              | 2           | 4.20                     | 1750              | 3           | 3.8                      |
| 128             | 30 La                                     | 10 Ca |                 | 1700              | 2           | 10.70                    | 1750              | 3           | 3.1                      |
| 129             | 40 La                                     | 5 Ca  |                 | 1700              | 2           | 9.30                     | 1750              | 3           | 12.8                     |
| <u>Group II</u> |   |       |                 |                   |             |                          |                   |             |                          |
| 134             | 20 La                                     | 20 Ca |                 | 1650              | 4           | 2.12                     |                   |             |                          |
| 135             | 25 Y                                      | 25 Ca |                 | 1650              | 4           | 0.76                     |                   |             |                          |
| 136             | 25 La                                     | 25 Ca |                 | 1650              | 4           | 1.63                     |                   |             |                          |
| 137             | 20 Y                                      | 20 Ca |                 | 1650              | 4           | 0.76                     |                   |             |                          |
| 154             | 25 La                                     | 25 Ca |                 | 1650              | 4           | 1.80                     |                   |             |                          |
| 155             | 20 La                                     | 20 Ca |                 | 1650              | 4           | 1.00                     |                   |             |                          |
| 156             | 20 Y                                      | 20 Ca |                 | 1650              | 4           | 0.75                     |                   |             |                          |
| 157             | 25 Y                                      | 25 Ca |                 | 1650              | 4           | 0.66                     |                   |             |                          |
| 64              | 30 La                                     |       | 50 Th           | 1700              | 4           | --                       |                   |             |                          |
| 89              | 30 La                                     |       | 50 Th           | 1750              | 3           | --                       |                   |             |                          |
| 93              | 30 La                                     |       | 50 Th           | 2000              | 1-1/2       | --                       |                   |             |                          |



powder and lost uranium oxide when exposed to oxidizing conditions at elevated temperatures. Thus, these samples were prepared for direct comparison with the  $\text{UO}_2$ - $\text{ThO}_2$  solid solutions.

The sintering losses which occurred during preparation of the solid solutions are also given in Table 1. These losses are associated with the preferential loss of CaO previously mentioned, as well as vaporization of the oxides during sintering. A comparison of the sintering losses is also of interest in that they indicate the relative stability of the materials in vacuum to the stability in high-temperature air.

### High-Temperature Air Oxidation

The compositions of Table 1 were subjected to air oxidation in dry flowing air at 1650 and 1760 C for periods up to 20 hr. Initially, the materials were placed on BeO slabs placed in a recess in an Alundum block. The samples and holder were heated in a  $\text{ZrO}_2$  resistance furnace to the desired temperature. In several instances the sample came into contact with the Alundum and apparently dissolved yielding inconclusive results. The final series of air-oxidation samples was placed completely in a BeO thimble placed in the Alundum setter to circumvent this difficulty. In spite of such precautions, however, some further, but less catastrophic, reaction between the "stabilized" oxide and the BeO occurred since the BeO became discolored with continued use.

It was the purpose of the air-oxidation experiments to determine the relative stability of the ternary compositions for comparison with the binary compositions such as  $\text{UO}_2$ -60 mole per cent  $\text{Y}_2\text{O}_3$ . The tendency to crack or pulverize during oxidation together with the phase stability were also of significance in addition to evaluation of uranium loss through volatility from the materials.

The weight changes resulting from heating the solid solutions to 1650 and 1760 C in air are given in Table 2.

The lattice parameters of the ternary compositions before and after air oxidation are given in Table 3 and the chemical analyses of the ternary oxides as prepared and after air oxidation are given in Table 4. The shift in composition occurring with oxidation is also shown graphically in Figure 1.

## RESULTS

The analyses of the results, given in the series of tables and Figure 1, show that CaO may be partially substituted for the trivalent additives of  $\text{La}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . The lattice parameters in Table 3 show that, in general, solid solutions were formed, with the exception of the  $\text{UO}_2$ - $\text{La}_2\text{O}_3$ - $\text{ThO}_2$  composition (Samples 64, 89, and 93). In some instances minor phases were detected having slightly different lattice parameters. These possibly resulted from oxidation on the surface of the materials upon exposure to air after sintering. In addition, two of the samples (63 and 137) of Table 3 exhibited two distinct lattice parameters which may have resulted from inhomogeneity as well as oxidation.

TABLE 2. WEIGHT CHANGES RESULTING FROM HEATING TERNARY OXIDES OF  $\text{UO}_2\text{-La}_2\text{O}_3\text{-CaO}$   
AND  $\text{UO}_2\text{-Y}_2\text{O}_3\text{-CaO}$  IN AIR AT 1650 AND 1760 C

| Sample          | Mixed-Oxide Composition,<br>mole per cent |       |               | Oxidation<br>Temperature, C | Weight Change <sup>(a)</sup> , per cent,<br>After Indicated Time |          |       |        | Setter <sup>(b)</sup> | Remarks  |
|-----------------|---|-------|---------------|-----------------------------|--|----------|-------|--------|-----------------------|----------|
|                 | $\text{R}_2\text{O}_3$                    | RO    | $\text{RO}_2$ |                             | 1 Hr   | 3-1/2 Hr | 5 Hr  | 20 Hr  |                       |          |
| <u>Group I</u>  |   |       |               |                             |  |          |       |        |                       |          |
| 63              | 20 La                                     | 20 Ca | --            | 1650                        | +0.98  | --       | --    | +1.71  | 1                     | Stable   |
| 86              | 30 La                                     | 5 Ca  | --            | 1650                        | (c)  | --       | --    | -9.30  | 2                     | Powdered |
| 87              | 30 La                                     | 10 Ca | --            | 1650                        | +0.70  | --       | --    | -3.90  | 2                     | Stable   |
| 88              | 40 La                                     | 5 Ca  | --            | 1650                        | +1.30  | --       | --    | +1.50  | 2                     | Cracked  |
| 90              | 25 Y                                      | 15 Ca | --            | 1650                        | -4.00  | --       | -4.40 | --     | 2                     | Cracked  |
| 91              | 20 Y                                      | 20 Ca | --            | 1650                        | -4.40  | --       | -5.60 | --     | 2                     | Powdered |
| 92              | 30 Y                                      | 10 Ca | --            | 1650                        | +1.90  | --       | +0.39 | --     | 2                     | Powdered |
| 125             | 20 La                                     | 20 Ca | --            | 1760                        | 0  | -2.08    | -3.75 | --     | 2                     | --       |
| 126             | 30 La                                     | 5 Ca  | --            | 1760                        | (c)  | +0.13    | -3.48 | --     | 2                     | --       |
| 128             | 30 La                                     | 10 Ca | --            | 1760                        | -3.14  | -1.64    | --    | --     | 2                     | --       |
| 129             | 40 La                                     | 5 Ca  | --            | 1760                        | (c)  | +1.52    | --    | --     | 2                     | --       |
| <u>Group II</u> |   |       |               |                             |  |          |       |        |                       |          |
| 134             | 20 La                                     | 20 Ca | --            | 1760                        | +0.44  | --       | -3.24 | -14.90 | 3                     | Stable   |
| 135             | 25 Y                                      | 25 Ca | --            | 1760                        | -2.95  | --       | -15.8 | -3.41  | 3                     | Stable   |
| 136             | 25 La                                     | 25 Ca | --            | 1760                        | +1.60  | --       | -6.35 | -0.26  | 3                     | Stable   |
| 137             | 20 Y                                      | 20 Ca | --            | 1760                        | +0.82  | --       | -0.68 | -3.37  | 3                     | Stable   |
| 154             | 25 La                                     | 25 Ca | --            | 1760                        | +1.67  | --       | +1.35 | +0.10  | 3                     | Stable   |
| 155             | 20 La                                     | 20 Ca | --            | 1760                        | -0.03  | --       | -1.58 | -5.96  | 3                     | Stable   |
| 156             | 20 Y                                      | 20 Ca | --            | 1760                        | +1.66  | --       | -0.05 | -3.95  | 3                     | Stable   |
| 157             | 25 Y                                      | 25 Ca | --            | 1760                        | +2.44  | --       | +2.36 | +0.59  | 3                     | Stable   |
| 64              | 30 La                                     | --    | 50 Th         | 1650                        | +0.75  | --       | --    | +6.28? | 1                     | --       |
| 89              | 30 La                                     | --    | 50 Th         | 1650                        | (c)  | --       | --    | -1.20  | 2                     | Powdered |
| 93              | 30 La                                     | --    | 50 Th         | 1650                        | --   | --       | --    | -1.20  | 2                     | Powdered |

(a) Plus sign indicates weight gain, minus sign indicates loss.

(b) 1 - Heated in an Alundum setter.

2 - Heated on a BeO slab in an Alundum setter.

3 - Heated in a BeO thimble in an Alundum setter.

(c) These samples were partially lost, reacted with the  $\text{Al}_2\text{O}_3$  setter or dissolved in it.

TABLE 3. LATTICE PARAMETERS OF TERNARY COMPOSITIONS OF  $\text{UO}_2\text{-La}_2\text{O}_3\text{-CaO}$   
AND  $\text{UO}_2\text{-Y}_2\text{O}_3\text{-CaO}$  BEFORE AND AFTER AIR OXIDATION

| Sample          | Lattice Parameter<br>After Final<br>Sintering, A | Oxidation<br>Temperature, C | Lattice Parameter After Oxidation Time Shown, A |          |      |       |
|-----------------|--|-----------------------------|---|----------|------|-------|
|                 |  |                             | 1 Hr  | 3-1/2 Hr | 5 Hr | 20 Hr |
| <u>Group I</u>  |  |                             |   |          |      |       |
| 63              | 5.542  | 1650                        | (a)   | --       | --   | (a)   |
| --              | 5.511  | --                          | --  | --       | --   | --    |
| 86              | 5.525  | 1650                        | 5.51  | --       | --   | 5.52  |
| 87              | 5.50   | 1650                        | 5.51  | --       | --   | 5.51  |
| 88              | 5.55   | 1650                        | 5.52  | --       | --   | 5.53  |
| 90              | 5.35   | 1650                        | 5.36  | --       | 5.36 | --    |
| 91              | 5.36   | 1650                        | 5.35  | --       | 5.36 | --    |
| 92              | 5.36   | 1650                        | 5.34  | --       | 5.35 | --    |
| 125             | 5.50   | 1760                        | (a)   | --       | (a)  | --    |
| 126             | 5.535  | 1760                        | --  | --       | 5.51 | --    |
| 128             | 5.54   | 1760                        | 5.51  | --       | --   | --    |
| 129             | 5.55   | 1760                        | --  | (a)      | --   | --    |
| <u>Group II</u> |  |                             |   |          |      |       |
| 134             | 5.53   | 1760                        | (a)   | --       | (a)  | (a)   |
| 135             | 5.40   | 1760                        | 5.34  | --       | 5.34 | 5.34  |
| 136             | 5.54   | 1760                        | (a)   | --       | (a)  | (a)   |
| 137             | 5.540  | 1760                        | 5.34  | --       | 5.34 | 5.34  |
| --              | 5.365  | --                          | --  | --       | --   | --    |
| 154             | 5.56   | 1760                        | (a)   | --       | (a)  | (a)   |
| 155             | 5.54   | 1760                        | 5.50  | --       | (a)  | (a)   |
| 156             | 5.40   | 1760                        | 5.34  | --       | 5.34 | 5.34  |
| 157             | 5.38   | 1760                        | 5.32  | --       | 5.34 | 5.34  |
| 64              | 5.63   | 1650                        | 5.57  | --       | --   | 5.56  |
| --              | 5.59   | --                          | 5.59  | --       | --   | 5.59  |
| 89              | 5.63   | 1650                        | --  | --       | --   | --    |
| --              | 5.59   | --                          | --  | --       | --   | --    |
| 93              | 5.63   | 1650                        | --  | --       | --   | --    |
| --              | 5.59   | --                          | --  | --       | --   | --    |

(a) Transformed to a rhombohedral structure upon oxidation.

TABLE 4. ANALYZED COMPOSITIONS OF TERNARY SOLID SOLUTIONS BEFORE AND AFTER AIR OXIDATION FOR 20 HR AT 1760 C

| Sample                       | Intended Composition,<br>mole per cent |       | Composition After Sintering,<br>mole per cent |         | Analyzed Composition<br>After Air Oxidation,<br>mole per cent |                        |
|------------------------------|--|-------|---|---------|---|------------------------|
|                              | R <sub>2</sub> O <sub>3</sub>          | RO    | R <sub>2</sub> O <sub>3</sub>                 | RO      | R <sub>2</sub> O <sub>3</sub>                                 | RO                     |
| <u>Group I<sup>(a)</sup></u> |  |       |   |         |   |                        |
| 63                           | 20 La                                  | 20 Ca | --  | --      | --  | --                     |
| 86                           | 30 La                                  | 5 Ca  | --  | --      | --  | --                     |
| 87                           | 30 La                                  | 10 Ca | --  | --      | --  | --                     |
| 88                           | 40 La                                  | 5 Ca  | --  | --      | --  | --                     |
| 90                           | 25 Y                                   | 15 Ca | --  | --      | --  | --                     |
| 91                           | 20 Y                                   | 20 Ca | --  | --      | --  | --                     |
| 92                           | 30 Y                                   | 10 Ca | --  | --      | --  | --                     |
| 125                          | 20 La                                  | 20 Ca | 20 La   | 8.5 Ca  | --  | --                     |
| 126                          | 30 La                                  | 5 Ca  | 30 La   | 3.0 Ca  | --  | --                     |
| 128                          | 30 La                                  | 10 Ca | --  | --      | --  | --                     |
| 129                          | 40 La                                  | 5 Ca  | 40 La   | 1.0 Ca  | --  | --                     |
| <u>Group II</u>              |  |       |   |         |   |                        |
| 134                          | 20 La                                  | 20 Ca | 22.1 La                                       | 17.9 Ca | 22.7 La   | 14.4 Ca                |
| 135                          | 25 Y                                   | 25 Ca | 19.0 Y  | 20.0 Ca | 20.0 Y  | 17.2 Ca <sup>(b)</sup> |
| 136                          | 25 La                                  | 25 Ca | 26.1 La                                       | 22.6 Ca | 27.3 La   | 19.3 Ca                |
| 137                          | 20 Y                                   | 20 Ca | 20.3 Y  | 20.3 Ca | 20.3 Y  | 17.6 Ca                |
| 154                          | 25 La                                  | 25 Ca | 25.6 La                                       | 19.9 Ca | 25.2 La   | 20.4 Ca                |
| 155                          | 20 La                                  | 20 Ca | 20.0 La                                       | 16.9 Ca | 21.6 La   | 16.0 Ca                |
| 156                          | 20 Y                                   | 20 Ca | 20.3 Y  | 17.9 Ca | 20.6 Y  | 16.4 Ca                |
| 157                          | 25 Y                                   | 25 Ca | 25.5 Y  | 22.1 Ca | 24.4 Y  | 19.8 Ca                |
| 64                           | 30 La                                  | 50 Th | 21.8 La                                       | 61.5 Th | 22.3 La   | 59.4 Th                |
| 89                           | 30 La                                  | 50 Th | --  | --      | --  | --                     |
| 93                           | 30 La                                  | 50 Th | --  | --      | --  | --                     |

(a) The initial chemical analyses of Group I samples are probably in error due to difficulties in separating calcium from lanthanum by the techniques used. The composition of Sample 63 is similar to that of the Group II samples.

(b) Apparently prepared as 20 Y<sub>2</sub>O<sub>3</sub>-20 CaO.

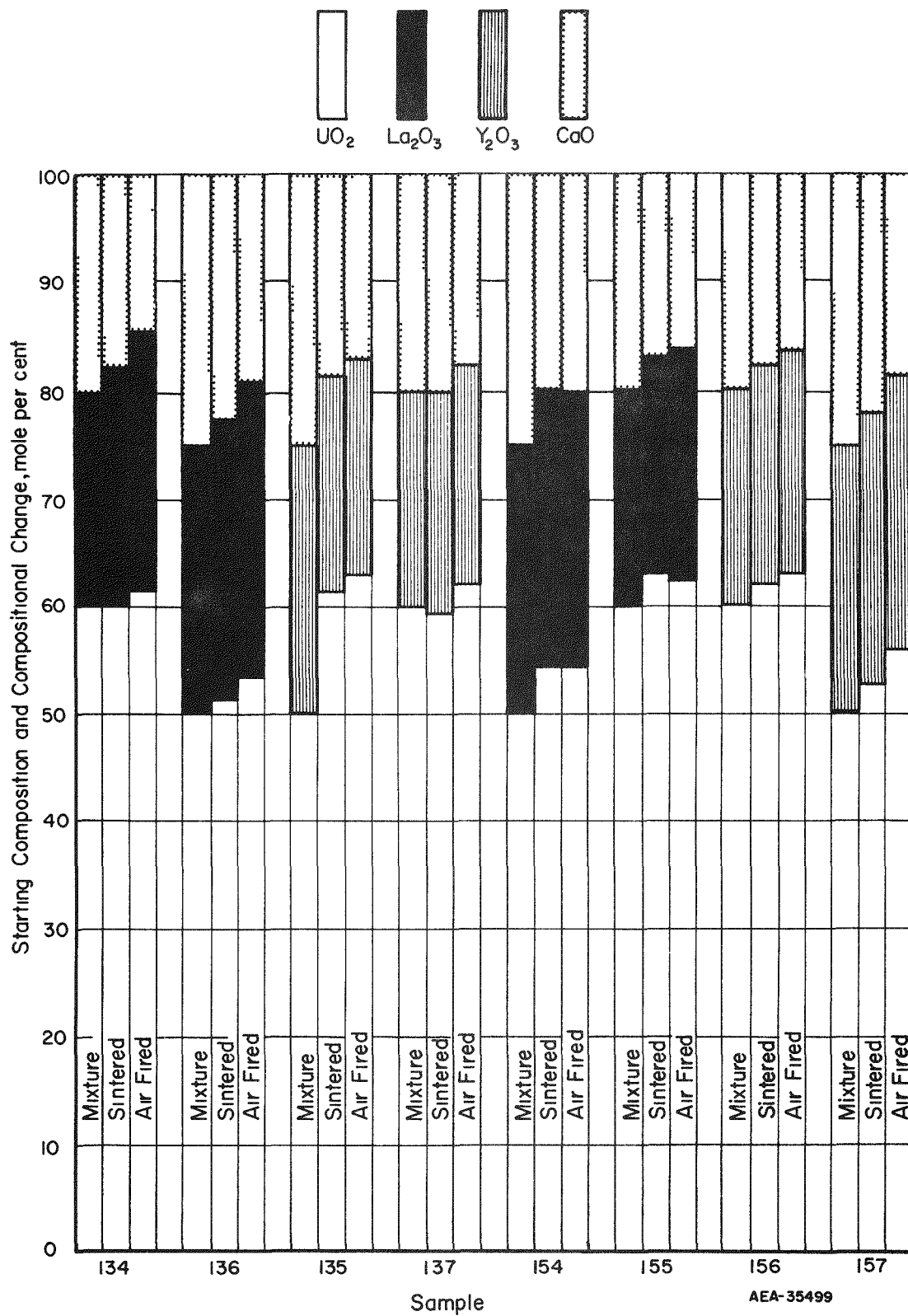


FIGURE 1. COMPOSITIONAL CHANGES OF TERNARY CERAMIC OXIDE BODIES AFTER VACUUM SINTERING AT 1650 C AND AIR FIRING AT 1760 C

The lattice-parameter studies were used in the present instances to detect any disruptive phase changes that might occur upon oxidation as well as to determine that solid solutions were obtained. Precision lattice-parameter determinations were not undertaken in the present work since no greater accuracy in the parameter determination is warranted than the knowledge of chemical composition, including variable oxygen content, permits. In addition, the observed X-ray patterns of the oxides were somewhat diffuse, making parameter measurements uncertain. This was also observed to be the case in the binary studies.

The solid solutions upon oxidation exhibited differing behavior depending upon composition. The  $\text{UO}_2\text{-Y}_2\text{O}_3\text{-CaO}$  materials maintained their fluorite structure with the lattice parameter decreasing with oxidation. This behavior also occurs for the binary  $\text{UO}_2\text{-La}_2\text{O}_3$  and  $\text{UO}_2\text{-Y}_2\text{O}_3$  systems, and is believed to occur as the result of the decrease in the uranium-ion size with oxidation.

The  $\text{UO}_2\text{-La}_2\text{O}_3\text{-CaO}$  materials transformed, upon oxidation, to a structure which is apparently rhombohedral, and isostructural to the  $\text{Ca}(\text{UO}_2)\text{O}_2$  structure reported by Zachariassen<sup>(5)</sup>. In the present instance, however,  $\text{La}_2\text{O}_3$  is in solid solution, producing shifts of the observed "d" values and unit-cell constants dependent upon composition. Although a transformation from a fluorite structure to a rhombohedral structure occurred for the  $\text{UO}_2\text{-La}_2\text{O}_3\text{-CaO}$  materials, it did not appear to be disruptive to the compacts in any way, in contrast to the transformation of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$  upon oxidation. It is probable that the transformation from the fluorite structure to the rhombohedral structure can occur without disrupting the body because of the similarity between the two structures.

The analyses of the weight losses which occurred upon air firing (Table 2) at 1760 C for periods to 20 hr indicate that stable materials can be produced when CaO is partially substituted for  $\text{La}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . The weight changes, which followed the same behavior previously observed with the binaries, are an initial weight gain due to oxidation, followed by a loss due to transpiration.

If the weight losses for the 20-hr period in Table 2 are rearranged in order of decreasing stability and correlated with the additive content it can be shown that the materials containing the most additive exhibited the most satisfactory stability. This rearrangement is given in Table 2. In order to assess the total additive content in which both CaO and  $\text{La}_2\text{O}_3$  or  $\text{Y}_2\text{O}_3$  are present simultaneously, an "average valence" for the solid solutions may be calculated by use of the following relation:

$$\bar{R} = \frac{\sum_{A_1}^{A_n} \text{Mole Per Cent } A_i \times \text{Valence } R_{A_i} \times \text{Atoms per Molecule } A_i}{\sum_{A_1}^{A_n} \text{Mole Per Cent } A_i \times \text{Atoms per Molecule } A_i}$$

The average valence,  $\bar{R}$ , calculated on the basis of the analyzed composition of the materials is given in Table 5, which shows that the more stable compositions are those associated with higher additive content.

The intended compositions and the compositional changes of cation content occurring before and after air oxidation are shown graphically in Figure 1. From this it may be seen that a trend toward a preferential loss of CaO is evident during sintering and upon air oxidation. Thus, the weight losses given in Tables 1 and 2 in part reflect this preferential loss.

TABLE 5. COMPARISON OF RELATIVE STABILITY VERSUS ADDITIVE CONTENT OF THE TERNARY SOLID SOLUTIONS FIRED FOR 20 HR AT 1760 C

| Sample | Observed Weight Change, per cent | Analyzed Composition, mole per cent |                      | Total Additive, mole per cent | Average Valence, $\bar{R}$ |
|--------|----------------------------------|-------------------------------------|----------------------|-------------------------------|----------------------------|
|        |                                  | R <sub>2</sub> O <sub>3</sub>       | RO                   |                               |                            |
| 63     | +1.71                            | 22 La                               | 22 Ca <sup>(a)</sup> | 44 ?                          | ?                          |
| 88     | +1.50                            | 40 La                               | 5 Ca <sup>(a)</sup>  | 45 ?                          | 4.14                       |
| 154    | +0.59                            | 25 La                               | 20 Ca                | 45                            | 4.16                       |
| 157    | +0.10                            | 25 La                               | 19 Ca                | 44                            | 4.23                       |
| 136    | -0.26                            | 27 La                               | 19 Ca                | 46                            | 4.13                       |
| 137    | -3.37                            | 20 Y                                | 17 Ca                | 37                            | 4.44                       |
| 135    | -3.41                            | 20 Y                                | 17 Ca                | 37                            | 4.44                       |
| 87     | -3.90                            | 30 La                               | 10 Ca <sup>(a)</sup> | <<40                          | >>4.30                     |
| 156    | -3.95                            | 20 La                               | 16 Ca                | 36                            | 4.47                       |
| 155    | -5.90                            | 21 La                               | 16 Ca                | 37                            | 4.38                       |
| 86     | -9.30                            | 30 La                               | 5 Ca <sup>(a)</sup>  | <<35                          | >>4.46                     |

(a) These are Group I samples which were not analyzed. With the possible exception of Sample 63 they probably contain less additive than the composition indicates.

The attempt to produce solid solutions of stabilized UO<sub>2</sub> (UO<sub>2</sub>-60 mole per cent La<sub>2</sub>O<sub>3</sub>) with ThO<sub>2</sub> indicated that the ThO<sub>2</sub> remained inert with respect to the UO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> solid solution. Air oxidation of these materials resulted in the UO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> oxidizing, resulting in a lattice-parameter decrease. In most instances the compacts decomposed to powder, but the weight loss of the materials was not excessive. The lattice parameter of the ThO<sub>2</sub> as fired in vacuum or upon air oxidation remained essentially unchanged.

Limited study of the electrical characteristics of the compositions of Samples 154 through 157 was made for comparison with the results obtained from study of the UO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> solid solutions. The electrical properties were quite similar to those obtained earlier. The resistance of each of the ternaries was quite high (slightly less than 10<sup>6</sup> ohm-cm) as fabricated after sintering in vacuum. By heating the samples in air concomitant with making the resistance measurements, a rapid decrease in resistivity occurred as it does in the binary systems. Additional temperature cycling increased the oxidation, and served to progressively lower the resistivity to values of the order of 10<sup>2</sup> ohm-cm, depending upon oxidation. Thus, as was reported earlier for the binary solid solutions, the resistivity of the ternaries is apparently dependent upon the degree of oxidation. Since it is not known whether complete oxidation of the solid solutions had occurred, the ultimate value for the resistivity is indeterminate.

The study of the thermoelectric power of the binary solid solutions of UO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> showed that p-type conductivity occurred for all samples with La<sub>2</sub>O<sub>3</sub> content of less than 50 mole per cent. At 50 mole per cent and beyond a change to n-type conductivity occurred. The same observation has recently been made on the "oxidized" solid solutions prepared by direct sintering of U<sub>3</sub>O<sub>8</sub>-La<sub>2</sub>O<sub>3</sub>. That is, the sign of the thermoelectric power was p-type for La<sub>2</sub>O<sub>3</sub> content less than 50 mole per cent, and n-type for La<sub>2</sub>O<sub>3</sub> content greater than 50 mole per cent. The interpretation has been made that at the 50 mole per cent La<sub>2</sub>O<sub>3</sub> content the Fermi level in the oxide remains constant with this variable oxygen content in accord with the Kroger and Vink hypothesis.<sup>(4)</sup>

The solid solutions Samples 155 through 157, exhibited p-type conductivity, which became n-type at variable temperatures ranging from 100 to 400 C. It is believed for this reason that all of the ternary solid solutions were understabilized because of the preferential loss of CaO. This conclusion is based upon the corresponding studies of the binaries where additions in excess of 50 mole per cent were observed to be the most stable. Thus, by comparison with the binaries and also by consideration of the additive content in Table 5 more stable ternary compositions may be possible than are described here, by increasing the additive content slightly.

## DISCUSSION

Recent studies of the binary solid solution of  $\text{UO}_2$  containing  $\text{La}_2\text{O}_3$  have attempted to correlate the results of the uranium oxide volatility, as determined by weight-loss measurements, with the results obtained from vapor-pressure studies. That is, it was of interest to determine if the weight losses of compacts of  $\text{UO}_2$ - $\text{La}_2\text{O}_3$ , fired in air at elevated temperatures, were comparable to predicted behavior based upon studies of the uranium oxide vapor pressure as determined by transpiration measurements of finely subdivided (-325 mesh) powders.

The early results suggested that the weight losses exhibited by compacts of  $\text{UO}_2$ -50 mole per cent  $\text{La}_2\text{O}_3$  were markedly less than expected on the basis of vapor-pressure measurements from the powdered specimens. From this it was tentatively postulated that the loss of uranium oxide from the solid solution was partially diffusion controlled, such that the surface of the compact became depleted of uranium, thus limiting further uranium loss to the rate at which the uranium diffused to the surface. The same conclusion, relative to diffusion as the rate-controlling factor, has been noted by Iida<sup>(6)</sup> for the  $\text{NiO}$ - $\text{Li}_2\text{O}$  system, in which the  $\text{Li}_2\text{O}$  is the volatile oxide that is preferentially lost.

Since the diffusion of uranium would appear to be markedly dependent on the stoichiometry of the solid solutions, it was of interest to determine whether the unusual stability, which occurs near the 50 mole per cent  $\text{La}_2\text{O}_3$  (or  $\text{Y}_2\text{O}_3$ ) was related to the stoichiometry.

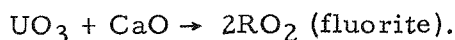
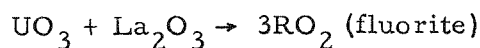
Later results have shown<sup>(2)</sup>, however, that both the vapor-pressure measurements and the measurement of volatility by weight loss of compacts are in general agreement, showing that diffusion and/or "surface passivation" are not necessarily required to explain the stability of the material. They remain, however, as factors which may be involved to an undetermined extent.

Chemical analyses of the 1760 C air-fired binary solid solutions have shown that the uranium exhibits variable oxidation as a function of  $\text{La}_2\text{O}_3$  content, showing for instance, an ultimate composition of  $\text{UO}_{2.48}$  at the 50 mole per cent  $\text{La}_2\text{O}_3$  content. Thus, these materials are not stoichiometric, in contrast to an earlier hypothesis, and the stoichiometry does not appear to contribute to the lowering of the vapor pressure of the uranium oxide which occurs at 50 mole per cent  $\text{La}_2\text{O}_3$  or  $\text{Y}_2\text{O}_3$ .

In the present feasibility study of the ternary oxides an attempt was made to achieve near stoichiometry by employing appropriate amounts of trivalent and divalent



additives, as indicated by the following reaction, written as fully oxidized:



In view of the results obtained from study of the binaries, it is probable that the equivalent of the above reactions is not actually obtained, and the solid solutions are almost certainly partially dissociated at very high temperatures to a lower oxygen/uranium ratio, equivalent to that obtained with the binaries.

There apparently exists at the present time no satisfactory explanation for the anomalous lowering of the vapor pressure of the uranium oxide which occurs at the 50 mole per cent composition for additives such as  $\text{Y}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$ . The only physical parameter relatable to such compositions is the p-to-n transition observed during work with the binaries. It is interesting to note that the same transition was observed to occur for the ternaries by employing the valence-compensation hypothesis, and in general, the weight losses from these compositions were suggestive of the same lowering of the uranium oxide vapor pressure as was observed to occur with the binaries.

#### CONCLUSION

The present work was conducted as a feasibility study to determine whether the additive content required to obtain a stable high-temperature nuclear fuel could be reduced and also to determine whether additives having cross sections lower than that of  $\text{Y}_2\text{O}_3$  could be substituted. The results appear sufficiently promising to suggest that a  $\text{UO}_2$ - $\text{Y}_2\text{O}_3$ - $\text{CaO}$  material may be competitively stable to  $\text{UO}_2$  containing 60 mole per cent  $\text{Y}_2\text{O}_3$ .

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