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Review

A review of the high temperature oxidation of uranium oxides in molten salts and in the solid state to form alkali metal uranates, and their composition and properties

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Abstract

An extensive review of the literature on the high temperature reactions (both in melts and in the solid state) of uranium oxides (UO_2, U_3O_8 and UO_3) resulting in the formation of insoluble alkali metal (Li to Cs) uranates is presented. Their uranate(VI) and uranate(V) compounds are examined, together with mixed and oxygen-deficient uranates. The reactions of uranium oxides with carbonates, oxides, per- and superoxides, chlorides, sulfates, nitrates and nitrites under both oxidising and non-oxidising conditions are critically examined and systematised, and the established compositions of a range of uranate(VI) and (V) compounds formed are discussed. Alkali metal uranates(VI) are examined in detail and their structural, physical, thermodynamic and spectroscopic properties considered. Chemical properties of alkali metal uranates(VI), including various methods for their reduction, are also reported. Errors in the current theoretical treatment of uranate(VI) spectra are identified and the need to develop routes for the preparation of single crystals is stressed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

A review of low temperature (below 400°C) oxidation of uranium dioxide appeared last year in this Journal [1], aimed at workers with this material in the nuclear industry. This review complements that work by focusing on the high temperature oxidation (above 500°C) of the various stable oxides of uranium and on the ultimate products of such oxidation, the various uranates that can be formed. It is therefore of interest to such workers as well as those interested in the chemistry of uranium, and fills a gap in the review literature. Cordfunke [2] in 1969 reviewed the earlier literature on uranium oxides and noted in passing some uranate(V) and uranate(VI) species, and that these systems had not been studied systematically. In the 30 yr since then a substantial amount of work on uranates has appeared in the literature but no reviews thereon, particularly the important areas of their properties and their formation from uranium oxides. We now present a systematic account of the high temperature chemistry of uranates. (We omit those polyuranates that can only be formed in aqueous solution.)

All reviews mentioning the uranium–oxygen system say that it is one of the most complex binary systems known: we concur and thus briefly note that the following uranium oxides have been described as individual thermodynamically stable compounds; UO_2, U_3O_7, U_3O_8, U_4O_9 and UO_3, together with several intermediate phases and UO, which has been claimed but probably only exists at very high temperatures. UO_2 has the fluorite structure and readily reacts with oxygen, which enters interstitial sites, the product being represented as UO_{2+x}. Initially 2:1:2 defect clusters are formed and as more oxygen enters the lattice these become 2:2:2 clusters when x in UO_{2+x} reaches ca. 0.1. The rate of oxidation of UO_2 is very temperature dependent, occurring

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barely perceptibly at room temperature but almost pyrophorically around 500°C. The overall oxidation to U_3O_8 proceeds via the route $UO_2 \rightarrow U_4O_9$ ($UO_{2.25}$) $\rightarrow U_3O_7$ ($UO_{2.33}$) $\rightarrow U_3O_8$ ($UO_{2.66}$) [3,4]. Charge compensation is believed to be achieved by forming U^{5+} and U^{6+} ions, but the extent to which U^{4+} loses electrons in UO_{2+x} has not been established. UO_3 is formed by the low temperature decomposition of uranyl salts since on further heating it loses oxygen and decomposes to U_3O_8.

Uranium was discovered just over 200 yr ago and yellow-orange uranates were prepared and investigated by Berzelius and others around 1820. They were originally prepared by heating U_3O_8 with alkali chlorides or with alkali carbonates. Today there are many routes to uranate(VI), viz., reacting uranium oxides with alkali metal oxides, peroxides, superoxides, nitrates, nitrites, sulfates, chlorides, chlorates and bromates in the presence of air or oxygen in the solid state or in a suitable molten salt. The latter includes melts based on chlorides, carbonates and nitrates, and mixtures thereof. Reactions yielding uranate(V) species are included in this account but discussed separately.

The exact composition of uranates has required careful analysis. The original workers were able to analyse their samples by gravimetric methods and determine accurately the weight composition of uranates obtained but the formulae they proposed were often in error due to incorrect values of valence used. Grandeau [5] in 1886, for example, gave the formula of potassium uranate as '$KO \cdot Ur_2O_3$' but from his analytical results it can now be easily calculated that he had actually prepared potassium monouranate, $K_2O \cdot UO_3$.

Of the various studies on the alkali metal uranates most attention has been focused on their lithium, sodium and potassium compounds, and this review will therefore reflect this.

The structure of uranates has been largely confined to X-ray powder diffraction studies. As a consequence there are disputes in the literature concerning crystal symmetry. Uranates are essentially insoluble in aqueous, non-aqueous and molten salt systems, and hence single crystal studies have been limited so far, and only few single crystal uranates have been prepared from molten salt media of sufficient size for investigation by modern X-ray spectrometers.

Spectroscopic studies of alkali metal uranates commenced in the 1960s with infrared spectra. No solution spectra have been reported, due to the above mentioned extreme solubility limitations and only two Raman investigations have been reported, in 1981 and 1998. Conventional laser Raman instruments cannot be used because of the intense fluorescence generated. Alkali metal uranates do not absorb above 600 nm at room temperature, and therefore excitation with a 647 nm Kr ion laser or a 780 nm diode laser is required for generating measurable Raman spectra. The excitation spectra of two lithium uranates, Li_2UO_4 and Li_4UO_5, have been reported [6] but the first comprehensive study of the electronic spectra of pure alkali metal uranates has just been published, recorded using diffuse reflectance spectroscopy [7].

We start this review by considering the composition of the various alkali metal uranates, focusing first on the species containing uranium in its highest oxidation state, +6. The high temperature reactions of uranium oxides (UO_2, U_3O_8 and UO_3), first with alkali metal carbonates and then oxides, peroxides, chlorides, sulfates, nitrates, nitrites, chlorates and bromates are next reviewed. This is followed by an account of the current understanding of their structures from mainly X-ray powder diffraction data. Since there is no solution chemistry of uranates, (their solubility even in molten salts at high temperatures has recently been determined as not more than a few 100 ppm [8]) this major aspect of the chemistry of most compounds does not here exist. They will react and thus dissolve chemically at room temperature in aqueous carbonate solutions and in acid media, and it is from the latter dissolution data that the thermodynamic data that we have collected have been obtained.

We do not include kinetics in this review because such measurements are exceedingly difficult, and it may even be impossible to measure quantitatively the kinetics of the oxidation of an insoluble powdered uranium oxide in a melt to an insoluble uranate, or in the solid phase, at temperatures well above 500°C. Factors such as particle size, porosity, and uniformity from surface to interior of the uranium oxides are a few of the items that would have to be known before meaningful kinetics could be obtained. Most workers have thus concerned themselves with the conditions and time required to obtain their end-products. Only our recent work [9] has reported the analysis of quenched samples at regular time intervals, to determine when the reactions were complete, and no kinetic data could be obtained because the oxidants were both reacting with the uranium oxides and decomposing at the same time at the temperature necessary to achieve oxidation.

We thus conclude with the major chemical and physical properties of uranates, including the recent diffuse reflectance findings and infrared and Raman spectra, the main techniques that can yield data from solids.

2. Compounds formed in M_2O–UO_3 systems, where $M = Li$, Na, K, Rb and Cs

Alkali metal uranate(VI) compounds obtained by high temperature synthesis are examined. These uranates are normally prepared in the presence of air, oxygen, or some other oxidising agent. Uranate(V) compounds are discussed later in Section 3.7.

2.1. Lithium uranates

Of all the alkali uranate systems lithium has been the most extensively studied. Several lithium uranates(VI) have been reported [10–12]. Their existence is now widely acknowledged but there is still some controversy concerning the composition of uranates with high uranium content (Li:U atomic ratio below 2).

Lithium monouranate, Li_2UO_4, is well characterised. It has been prepared by several independent workers [13–16] and characterised by infrared spectroscopy and X-ray powder diffraction analysis. Single crystals of Li_2UO_4 were obtained by Kovba et al. [17] (by fusing anhydrous LiCl with U_3O_8) and by Gerbert et al. [18] (by heating powdered monouranate in fused lithium chloride (1:200 mol) in air at 800–810°C for four days). The composition of the monouranate determined by chemical analysis corresponded closely to the expected formula Li_2UO_4 [15,19]. The monouranate, Li_2UO_4, was thermally stable up to 1300°C (heating in air for 60 h) and only the α-$Li_2UO_4 \rightarrow \beta$-$Li_2UO_4$ phase transformation (with the latter phase being hexagonal) occurred under these conditions [10].

Other normal lithium uranates, Li_4UO_5, '$Li_2U_2O_7$' and $Li_2U_3O_{10}$, were prepared by Efremova et al. [10,20] by heating various mixtures of Li_2CO_3 with U_3O_8. Lithium diuranate has been reported to be thermally stable up to and above 1300°C [21]. The exact composition, and existence, of lithium diuranate is still disputed and is considered at the end of this section.

The existence of basic Li_4UO_5 has been confirmed by Hoekstra and Siegel [22], who found that its formation from UO_3 and Li_2CO_3 occurred in three successive steps (see Section 3.1, reactions (5)–(7)). Scholder and Gläser [11] were the first to report a more basic uranate of composition Li_6UO_6.

Kovba [24] investigated polyuranates formed in the Li_2UO_4–U_3O_8–O_2 system at 750–900°C. Below 800°C the compounds with the following overall compositions were found: $Li_2O{\cdot}(1.60–1.64)UO_3$ ($=Li_{22}U_{18}O_{65}$), $Li_2O{\cdot}1.75UO_3$, $Li_2O{\cdot}3UO_3$ and $Li_2O{\cdot}6UO_3$. All attempts to prepare uranates having a higher uranium content resulted in the formation of mixtures of U_3O_8 and $Li_2O{\cdot}6UO_3$. Upon increasing the temperature to 850–900°C lithium triuranate decomposed, yielding $Li_2O{\cdot}(2.67–2.75)UO_{2.95}$ and $Li_2O{\cdot}6UO_3$ phases. Lithium diuranate was not obtained at temperatures up to 900°C and thus Kovba concluded that this uranate probably does not exist: sometime earlier he [24] had reported that so-called 'lithium diuranate' is a mixture of $Li_2O{\cdot}1.75UO_3$ and $Li_2U_3O_{10}$.

Hauck [12] has reviewed previous findings and reinvestigated the Li_2O–UO_3 system under an oxygen atmosphere ($P_{O_2} = 1$ atm). A summary of his findings is presented in Fig. 1. These appear to show that lithium diuranate cannot be formed but it must be noted that Hauck's lithium uranates were formed in pure oxygen (see later). At high uranium content (Li:O atomic ratio <2) and high temperatures some of the polyuranates decompose (shaded areas on the diagram) and at lower temperatures the formation of oxygen-deficient uranates occurs. At temperatures below 600°C equilibrium is not attained in this composition region.

The following lithium uranates(VI) do exist according to Hauck [12]: Li_6UO_6 (α and β forms), Li_4UO_5, Li_2UO_4, $LiU_{0.83}O_3$, $Li_2U_3O_{10}$ and $Li_2U_6O_{19}$. At temperatures below 540°C and above 850°C Li_6UO_6 decomposes into Li_4UO_5 and Li_2O. The $\alpha \rightarrow \beta$ phase transformation of Li_2UO_4, claimed by Efremova et al. [10,20], Hauck attributed to the formation of α-$LiU_{0.83}O_3$, which Kovba [24] had previously reported as $Li_2O{\cdot}(1.60–1.64)UO_3$. The high temperature β-form of $LiU_{0.83}O_3$ was assigned to Kovba's $Li_2O{\cdot}1.75UO_3$. Hauck confirmed the decomposition of $Li_2U_3O_{10}$ to $Li_2U_{2.7}O_9$ (Kovba's $Li_2O{\cdot}(2.67–2.75)UO_{2.95}$) above 910°C and reported the thermal decomposition of $Li_2U_6O_{19}$ to β-U_3O_8 and $Li_2U_{2.7}O_9$ at 990°C.

The existence of Li_6UO_6, first reported by Scholder and Gläser [11], was later confirmed by Wolf and Hoppe [25] who also discovered that this uranate is capable of cation exchange: heating α-Li_6UO_6 with M_2O ($M = Na$ or K) at 700–750°C for 12–20 days resulted in the formation of M_4UO_5 uranates [26]; and heating α-Li_6UO_6 with M_2O ($M = K$, Rb or Cs) at 680–700°C for 10–30 days produced uranates of composition $M_2Li_4[UO_6]$ [27].

Toussaint and Avogadro [15] however reported formation of both lithium mono- and diuranates in nitrate melts, with the structure of the diuranate very close to that obtained by Kovba [24] for $Li_2O{\cdot}1.6UO_3$, and confirmed their composition by chemical analysis.

Fujino et al. [13] reinvestigated uranates formed upon heating mixtures of Li_2CO_3 with U_3O_8 at 650–800°C in air. They obtained uranates with Li to U atomic ratios of 0.667, 1.205, 2 and 4, corresponding to $Li_2U_3O_{10}$, $Li_2O{\cdot}1.66UO_3$, Li_2UO_4 and Li_4UO_5 uranates, respectively. Lithium hexauranate, $Li_2U_6O_{19}$, could not be prepared this way and attempts to do so resulted in a mixture of α-U_3O_8 and $Li_2U_3O_{10}$. The X-ray powder diffraction pattern obtained for $Li_2O{\cdot}1.66UO_3$ agreed well with that reported by Toussaint and Avogadro [15] for $Li_2U_2O_7$ and could be indexed using the orthorhombic structure suggested by Kovba [24] for $Li_{22}U_{18}O_{65}$ ($Li_2O{\cdot}1.64UO_3$). The reported X-ray patterns of $Li_2U_2O_7$ [15] and $Li_{22}U_{18}O_{65}$ [23] are, however, different. Attempts to prepare Li_6UO_6 were not successful as the X-ray diffraction pattern obtained was identical to that measured for Li_4UO_5, but the explanation offered, of thermal decomposition of Li_6UO_6, could not have occurred because the preparative temperature, 650–800°C, is not high enough to cause decomposition, a minimum of 850°C being required [12], Fig. 1.

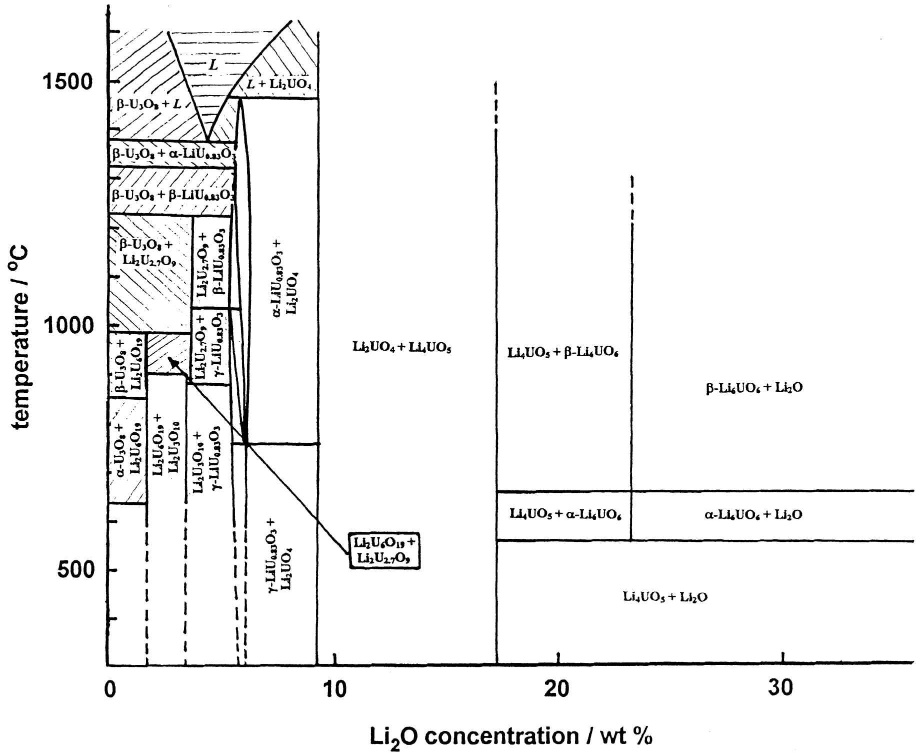

Fig. 1. Phase diagram of Li_2O–UO_3 system at 1 atm. O_2 (after Hauck [12]). Vertical lines separating adjacent two-component phases represent the compound common to both those phases. At high uranium content and high temperatures some uranates decompose, shown by shaded areas.

Another recent study on lithium uranates(VI), formed in the Li_2O–UO_3 system below 930°C at an oxygen pressure of 1 atm, was reported by Prins and Cordfunke [28]. They did not find any new uranates and generally confirmed the phase diagram reported by Hauck [12] (Fig. 1). They also confirmed the existence of Li_6UO_6, Li_4UO_5, Li_2UO_4, $Li_2O\cdot 1.6UO_3$, $Li_2O\cdot 1.75UO_3$ and $Li_2U_3O_{10}$. The uranate $Li_2O\cdot 1.64UO_3$, previously reported by Kovba [24] as the end member of the homogeneity region of $Li_2O\cdot(1.60–1.64)UO_3$, they found to be a mixture of $Li_2O\cdot 1.60UO_3$, and $Li_2O\cdot 1.75UO_3$. They further reported that no evidence for the existence of lithium diuranate was obtained. They also stated that their compound Li_6UO_6, identified as such by X-ray diffraction, upon detailed analysis was shown to have the formula $Li_{6.43}UO_{6.215}$.

However, we were able to report that lithium diuranate *does* exist as an individual phase, and its cell parameters and its electronic and vibrational spectra have been recently measured [8,29]. It was prepared by heating a stoichiometric mixture of Li_2CO_3 and U_3O_8 in air at 750°C for 48 h. It must therefore be concluded that lithium diuranate can indeed be prepared, and is stable up to and above 1300°C [21], provided that it is prepared by heating in air. We therefore propose that in pure oxygen it decomposes to $LiU_{0.83}O_3$ and U_3O_8. In addition to the diuranate, at least ten other lithium uranates(VI) have thus currently been established.

2.2. Sodium uranates

Sodium uranates have been intensively investigated, particularly Na_4UO_5, Na_2UO_4 and $Na_2U_2O_7$, [14,23,30]. Chemical analysis of the prepared mono- and diuranates showed that their compositions are in agreement with those expected from the formula $Na_2O\cdot xUO_3$, where $x = 1$ or 2, respectively [15,19,31]. Sodium monouranate exists in two modifications, α and β, the transformation from α to β occurring at around 900–925°C [10,31].

Carnall et al. [32] investigated sodium polyuranates prepared by high temperature solid phase synthesis and reported the formation of the polyuranates, $Na_2O\cdot xUO_3$, with x ranging between 2.1 and 2.5, and 6 and 13. The former group members have a structure close to that of $Na_2U_2O_7$ but the latter polyuranate phase has not been fully characterised, and its structure was said to be related to α-UO_3 and α-U_3O_8 [32].

Cordfunke and Loopstra [31] prepared Na_4UO_5, α- and β-Na_2UO_4 and $Na_2U_2O_7$ uranate species. The result of all their attempts to prepare more acidic uranates, i.e., with higher uranium content than diuranate, was limited to the formation of mixtures of $Na_6U_7O_{24}$ ($Na_2O{\cdot}2.33UO_3$) and U_3O_8. They also reported that Na_2UO_4 starts to decompose into $Na_2U_2O_7$ above 750°C and after several days of heating β-Na_2UO_4 at 950°C the monouranate had completely disappeared. However, Spitsyn et al. [21] had previously reported that β-Na_2UO_4 only started to decompose into the diuranate at 1300°C. According to Cordfunke and Loopstra [31], even $Na_2U_2O_7$ begins to decompose at this high temperature. Hence we can conclude that Spitsyn et al. [21] had missed the slow decomposition of β-Na_2UO_4 at 950°C to diuranate. $Na_6U_7O_{24}$ will also decompose into diuranate and U_3O_8 when heated in air above 900°C. Heating sodium diuranate in air at 850°C for 220 h resulted in the formation of $Na_{1.85}U_2O_{6.93}$, which contained only uranate(VI) [33].

As with lithium, sodium does not form many polyuranates, and apart from the diuranate only one has been well established, $Na_6U_7O_{24}$, but some others have been claimed [32]. Basic uranates of lithium and sodium are limited to two and one, respectively.

2.3. Potassium uranates

Apart from the usual mono-, di- and triuranates, K_2UO_4, $K_2U_2O_7$ and $K_2U_3O_{10}$, potassium tetra- and hexauranates, $K_2U_4O_{13}$ and $K_2U_6O_{19}$, can be prepared by reacting triuranate with U_3O_8. Efremova et al. [10] additionally claimed the preparation of K_4UO_5 but Hoekstra and Siegel [22], and Van Egmond and Cordfunke [34], were unable to prepare this uranate.

Thermal decomposition of potassium triuranate occurs at 1100–1200°C, forming a non-homogeneous mixture of the diuranate and U_3O_8 [4]

$$3K_2U_3O_{10} \Longleftrightarrow 3K_2U_2O_7 + U_3O_8 + \frac{1}{2}O_2. \quad (1)$$

The reaction can be reversed upon slowly cooling the mixture or by heating an appropriate stoichiometric mixture of $K_2U_2O_7$ and U_3O_8 in air at 800–900°C. Chawla and Misra [35] reported a similar reversible thermal decomposition of the tetrauranate occurring under an inert atmosphere

$$K_2U_4O_{13} \Longleftrightarrow K_2U_4O_{12} + \frac{1}{2}O_2. \quad (2)$$

Anderson [33] reinvestigated the K_2O–UO_3 system, focusing on the composition of the polyuranates, $K_2O{\cdot}xUO_3$ with $x = 2$–8. In an earlier work [36] he had reported that potassium di-, tetra- and hexauranates exist as distinct compounds. A pentauranate, $K_2U_5O_{16}$, was interpreted as a mixture of the above phases. However, more detailed structural investigation [33] has questioned the existence of the tetra- and hexauranates and it was concluded that only two polyuranate phases exist in the range of compositions studied. These two were given a preliminary assignment to a ‘triuranate’, the exact composition of which could not be expressed by the simple formula $K_2U_3O_{10}$, and to a polyuranate $K_2U_8O_{25}$ but with x now probably >8.

However, Van Egmond and Cordfunke [34] subsequently found the following uranates in the potassium uranate system: K_2UO_4, $K_2U_2O_7$ $K_2U_4O_{13}$ and $K_2U_7O_{22}$. There was no indication of the formation of octa-, hexa- or triuranates. Kovba [24] had earlier reported a uranate with composition $K_8U_{16}O_{52}$.

At this time six, mainly poly-, potassium uranates have thus been established. This lower number can be attributed to the (apparent) inability of potassium to form basic uranates. Some have been claimed, e.g., K_4UO_5, but have not been reproduced or authenticated. This is in contrast to lithium and sodium that can form basic uranates but do not form many polyuranate species.

2.4. Rubidium and caesium uranates

Compared with lithium, sodium and potassium, considerably less work has been done on uranates containing the heavier alkali metals, rubidium and caesium. Normal mono- and diuranates of these elements are well established orange–yellow compounds [21,37,38]. They are usually prepared by reacting stoichiometric mixtures of α-U_3O_8 or γ-UO_3 and the corresponding alkali metal carbonate or chloride in air or oxygen at ca. 600°C [10,36,39–41]. Rubidium monouranate loses alkali metal oxide at ca. 1000–1200°C, producing the corresponding diuranate, $Rb_2U_2O_7$ [10,21,42]. In contrast, caesium monouranate, when heated above 900°C, loses not only caesium oxide but also oxygen, producing, together with $Cs_2U_2O_7$, the black oxygen-deficient tetrauranate, $Cs_2U_4O_{13-x}$ [42]. Rubidium diuranate is thermally stable, but caesium diuranate, $Cs_2U_2O_7$, when heated above 600°C in an inert atmosphere, also loses oxygen yielding $Cs_2U_4O_{12}$ [43]. This reaction is somewhat similar to the decomposition of potassium tetrauranate, reaction (2).

Of the basic uranates, only Rb_4UO_5 has been reported, prepared by reaction between Rb_2CO_3 and γ-UO_3 at 600–650°C [39]. Both rubidium and caesium form a variety of polyuranates. Tetra-, hexa- and heptauranates ($M_2U_4O_{13}$, $M_2U_6O_{19}$ and $M_2U_7O_{22}$, M = Rb or Cs), as well as caesium uranates(VI) containing three and sixteen uranium atoms ($Cs_2U_3O_{10}$ and $Cs_2U_{16}O_{49}$, respectively), have all been prepared, usually by reacting the corresponding alkali metal carbonates with α-U_3O_8 or γ-UO_3 at ca. 600°C [39,40,42–44]. The most complex polyuranates (tetra-, hexa-, etc.) are thus formed only by the heavier alkali metals (K, Rb and Cs). Here the large uranium-containing polyanions are stable due to the small polarising power of the associated alkali metal cations. It also has been claimed that all caesium polyuranates can be converted above 600°C into $Cs_2U_4O_{12}$ [43,45].

2.5. Mixed and oxygen-deficient uranates

Sometimes in the literature there are occasional remarks about some unusual and unidentified compounds formed during the reactions of uranium oxides with various alkali metal compounds. Toussaint and Avogadro [15] reported the formation of weak solid solutions of lithium, potassium and caesium diuranates in $Na_2U_2O_7$ during the reaction of uranium dioxide with mixed alkali metal nitrate melts but they may be better viewed as $Na_2U_2O_7$ doped with these alkali metal cations.

More often, however, oxygen-deficient species are encountered. For the alkali earth metals formation of uranates containing less oxygen than is stoichiometrically required (e.g., MUO_{4-x}) is more often the rule than the exception [46]. Fujino et al. [13] noted that formation of uranates during the reaction of U_3O_8 with lithium or sodium carbonates proceeded in two stages, first by formation of oxygen-deficient species and then by complete oxidation of the uranates formed. Anderson [33] has noted that sodium diuranate can produce a series of oxygen-deficient compounds, $Na_2U_2O_{7-x}$ ($x < 0.5$), that still have the $Na_2U_2O_7$ structure. An unusual lithium uranate has been reported [47] upon oxidation of UO_2 in molten (Li–K)NO_3 eutectic: it was neither identifiable as the di- or monouranate species. X-ray powder diffraction analysis showed that its pattern was not due to a mixture of mono- or diuranate species. It was said not to correspond with any known uranate species but unfortunately (as in other similar cases) its X-ray diffraction pattern was not published or discussed in sufficient detail to enable any comparison to be made. Recently [48] we encountered an unusual product formed upon the oxidation of UO_2 in carbonate melts containing added sodium chloride and our investigations allowed us to conclude that this compound was an oxygen-deficient sodium uranate, $Na_2O{\cdot}xUO_{3-y}$ ($1 < x < 2$).

3. High temperature reactions leading to the formation of alkali metal uranates

In this section we consider the high temperature behaviour of uranium oxides (UO_2, U_3O_8 and UO_3), first with alkali metal carbonates, and then oxides, peroxides, chlorides, sulfates, nitrates, nitrites, chlorates and bromates to form uranates. Reactions producing uranates, containing uranium in oxidation state <6 are all grouped in Section 3.7.

3.1. Reactions with alkali metal carbonates

The solid state reaction of Li_2CO_3 with U_3O_8 at 750–800°C in air leads to the formation of a variety of lithium uranates, depending on the Li:U ratio in the mixture: these are Li_4UO_5, Li_2UO_4, $Li_2U_2O_7$, $Li_2U_3O_{10}$ and $Li_2U_6O_{19}$ [10,13,14,20,49–52]. Uranium trioxide reacts similarly [14,20,52,53] and the following equations represent the general reactions that occur:

$$\frac{y}{3}U_3O_8 + xM_2CO_3 + \frac{y}{6}O_2 \rightarrow (M_2O)_x(UO_3)_y + xCO_2 \tag{3}$$

$$yUO_3 + xM_2CO_3 \rightarrow (M_2O)_x(UO_3)_y + xCO_2, \tag{4}$$

where M is an alkali metal and $(M_2O)_x(UO_3)_y$ represents the general composition of a normal alkali metal uranate(VI).

Noticeable interaction between U_3O_8 and Na_2CO_3 begins at 400°C and the reaction rate increases with increasing temperature. It has been shown that the process is at first controlled by the chemical reaction rate and then by the rate of Na_2CO_3 diffusion through the surface layer of $Na_2U_2O_7$ to the unreacted U_3O_8 [54]. Sodium diuranate was always the first product formed upon the reaction of U_3O_8 with Na_2CO_3, and is independent of the Na:U ratio in the mixture [10,55]. As the temperature is increased, and if an excess of Na_2CO_3 is present, the diuranate then reacts with this carbonate above 700°C to yield Na_2UO_4 or Na_4UO_5, now depending on the Na:U ratio [10,22,31,56–58]:

$$2UO_3 + M_2CO_3 \rightarrow M_2U_2O_7 + CO_2 \tag{5}$$

$$M_2U_2O_7 + M_2CO_3 \rightarrow 2M_2UO_4 + CO_2 \tag{6}$$

$$M_2UO_4 + M_2CO_3 \rightarrow M_4UO_5 + CO_2. \tag{7}$$

On the other hand, if the Na:U ratio is <1, polyuranate species, such as $Na_6U_7O_{24}$, can be formed [31]. Initial formation of $Na_2U_2O_7$ at 546°C upon heating UO_3–Na_2CO_3 mixtures, followed by formation of Na_2UO_4 at 680°C, was confirmed by Kryukova et al. [59] using differential thermal analysis (DTA). They, however, reported that only sodium mono- and diuranates were formed in the temperature range 20–1000°C.

Fujino et al. [13] studied the reaction of U_3O_8 with Li_2CO_3 and Na_2CO_3 and concluded that it occurs in two stages: (i) initial formation of oxygen-deficient uranates and (ii) the oxidation of the uranates formed to yield uranate(VI) compounds. The reaction rate of stage (i) was high at low alkali metal-to-uranium atomic ratio (ca. 0.5) but decreased as the ratio increased towards unity, when process (i) became the rate-determining step.

Potassium carbonate reacts with U_3O_8 in a similar manner to Na_2CO_3 and regardless of the initial K:U ratio the first product formed is $K_2U_2O_7$, which on further temperature increase reacts with an excess of K_2CO_3 to form K_4UO_5 and K_2UO_4 or with an excess of U_3O_8 to produce a range of polyuranates: $K_2U_3O_{10}$, $K_2U_4O_{13}$, $K_2U_6O_{19}$ and $K_2U_7O_{22}$ [10,14,24,52,60–63]. The preparation of $K_9U_6O_{22.5}$ by reaction of U_3O_8 with excess K_2CO_3 in a Nb_2O_5 melt has been reported by Saine et al. [64]. The scheme in Fig. 2 outlines the possible reactions occurring in the K_2CO_3–UO_x system, where $x = 2$, 2.67 and 3.

The reaction of uranium dioxide with alkali metal carbonates in the presence of oxygen is similar to that of U_3O_8. Rüdorff and Leutner [65] have reported the preparation of lithium, sodium and potassium monouranates upon heating UO_2 with the corresponding carbonate up to 800°C in an oxygen atmosphere

$$UO_2 + M_2CO_3 + \frac{1}{2}O_2 \rightarrow M_2UO_4 + CO_2 \qquad (8)$$

Heating UO_2 with K_2CO_3 (K:U mole ratio = 0.5) in air at 900°C results in the formation of potassium tetrauranate, $K_2U_4O_{13}$, but reaction under an inert atmosphere yields KUO_3 [66].

The first studies of the reaction of UO_2 with molten carbonates were in 1990 by Kryukova et al. [67]. They examined the kinetics of the oxidation of UO_2 in the ternary carbonate melt, Li_2CO_3–Na_2CO_3–K_2CO_3 (1:1:1) between 410°C and 500°C in an argon atmosphere with and without added oxygen. Formation of non-specified diuranates was observed and the yield of diuranates increased upon increasing the partial pressure of oxygen in the atmosphere above the melt: the mechanism of oxidation was not studied. The degree of conversion of UO_2 into the diuranates was 16–18%, under an inert atmosphere, and reached 28% in the presence of O_2 (Ar:O_2 = 1:1.5 mol). The formation of diuranates in the absence of oxygen occurred upon use of non-stoichiometric uranium dioxide, UO_{2+x}, where x was 0.16 ± 0.01.

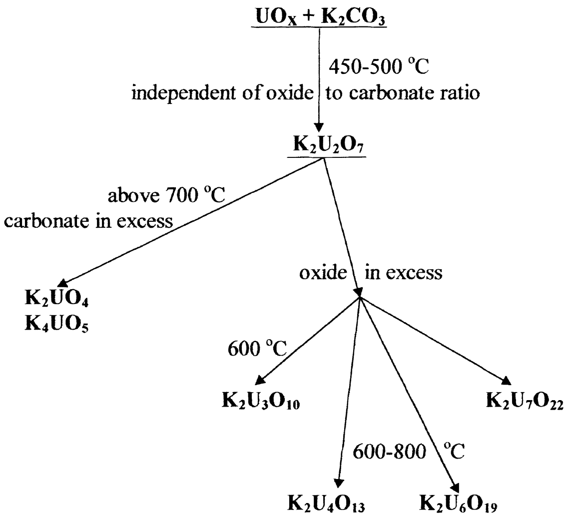

Fig. 2. High temperature reactions of potassium carbonate with uranium oxides UO_x, $x = 2$, 2.67 and 3, in air.

We recently carried out an extensive study of the reaction of uranium dioxide with molten alkali metal carbonate mixtures between 450 and 900°C [9,48,68]. We found that UO_2 oxidation proceeded *via* initial formation of an insoluble layer of alkali metal uranate(VI) species on the surface of UO_2 particles, and then was controlled by mass transfer of the oxidising species inwards through this layer. When oxygen was in the atmosphere above the melt, the oxidising species were peroxide and superoxide ions, formed upon the dissolution of oxygen in the carbonate melt. The extent of UO_2 oxidation was thus controlled by oxygen solubility in the melt and could be increased by the addition of alkali metal chlorides or sulfates [48]. Which alkali metal uranates were formed upon UO_2 oxidation depended on which cations were present in the melt, with monouranates predominating above 550–600°C, and diuranates at lower temperatures.

The only study of the reaction of uranium trioxide with the ternary carbonate eutectic is that of Habboush et al. [69] who reported the formation of an unspecified monouranate. The reaction was said to start in the solid state at 80°C, reach its maximum rate just below the melting point of the mixture, and continue more slowly in the liquid state.

3.2. Reactions with alkali oxides and peroxides

The reaction of uranium oxides with alkali metal oxide species has been used for the preparation of various uranates, mainly lithium and sodium. Prins and Cordfunke [28] reported that the use of Li_2O instead of Li_2CO_3 resulted in a much faster conversion of uranium oxide into uranates, and a greater yield.

Keller et al. [56] have investigated the reactions of lithium and sodium oxides with the actinide dioxides, UO_2, NpO_2, PuO_2 and AmO_2 under an oxygen atmosphere. Fig. 3 summarises their findings for the UO_2/PuO_2–Li_2O and PuO_2–Na_2O systems. Fusion with sodium peroxide was also used to achieve dissolution of PuO_2 [70]. Complete conversion of PuO_2 into soluble plutonates took ca. 10 min at 400–420°C, using a PuO_2:Na_2O_2 mass ratio of 1:5.

Findley et al. [71] have reported the formation of polybasic sodium uranate, Na_4UO_5, upon heating uranium dioxide with sodium oxide or peroxide, and Tso et al. [30] performed a detailed study of the reactions of UO_2 with Na_2O_2 that resulted in the formation of the sodium uranates(VI), Na_4UO_5, Na_2UO_4 and $Na_2U_2O_7$. They heated mixtures of UO_2 and Na_2O_2 under vacuum or in argon, argon–oxygen and oxygen atmospheres at

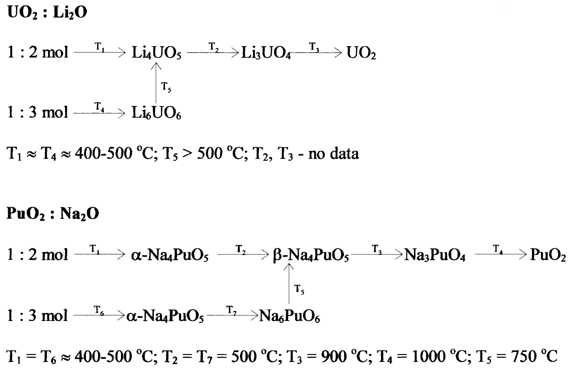

Fig. 3. Formation of uranates and plutonates upon the reaction of uranium dioxide with lithium oxide and plutonium dioxide with sodium oxide (after Keller et al. [56]).

360–800°C for 36–120 h. The following reactions were proposed:

$$UO_2 + 2Na_2O_2 \rightarrow Na_4UO_5 + \frac{1}{2}O_2 \ (360°C) \qquad (9)$$

$$2UO_2 + Na_2O_2 + \frac{1}{2}O_2 \rightarrow Na_2U_2O_7 \qquad (10)$$

$$3Na_2O_2 + Na_2U_2O_7 \rightarrow 2Na_4UO_5 + \frac{3}{2}O_2 \qquad (11)$$

$$Na_4UO_5 + Na_2U_2O_7 \rightarrow 3Na_2UO_4. \qquad (12)$$

Heating U_3O_8 with sodium peroxide in air at 700–900°C generally resulted in the formation of sodium monouranate [31,52–55,72,73]:

$$3Na_2O_2 + U_3O_8 \rightarrow 3Na_2UO_4 + O_2. \qquad (13)$$

Sodium diuranate and higher polyuranates, $Na_2O{\cdot}xUO_3$ where $x = 2$–5, were prepared by heating Na_2O or Na_2O_2 with uranium trioxide at 800–900°C [32,54].

Sodium oxide or peroxide dissolved in the ternary carbonate eutectic melt, $(Li–Na–K)_2CO_3$, reacted with UO_2 to form the same products obtained upon heating the oxides together [9]. In both cases sodium monouranate was formed upon oxidation at 450–600°C:

$$Na_2O + UO_2 + \frac{1}{2}O_2 \rightarrow Na_2UO_4 \qquad (14)$$

$$Na_2O_2 + UO_2 \rightarrow Na_2UO_4. \qquad (15)$$

The reaction of uranium oxides with alkali metal superoxides has been little studied. No information about the direct reaction was published and only one account examined the reaction of uranium dioxide with physically dissolved potassium superoxide or chemically generated superoxide species in $(Li–Na–K)_2CO_3$ melt at 450°C [48]. Potassium diuranate is formed thereby

$$4KO_2 + 6UO_2 + K_2CO_3 \rightarrow 3K_2U_2O_7 + CO_2. \qquad (16)$$

3.3. Reactions with alkali metal chlorides

The possible application of alkali metal chloride melts in oxide nuclear fuel processing and reprocessing has meant that the published data has concentrated on cathodic deposition or anodic dissolution of uranium oxides, UO_2 and U_3O_8 [74–76]. Two species, UO_3Cl^- and UO_2^{2+}, were reported present in solution, and the following mechanism was proposed for the electrochemical deposition of oxide phases:

$$UO_2^{2+} + 2UO_3Cl^- + 2e^- \rightarrow U_3O_8 + 2Cl^-. \qquad (17)$$

The preparation of mono- [77] and polyuranates [78,79] by reacting alkali chlorides with uranium oxides in air was reported over 100 yr ago. This reaction can proceed by either direct oxidation (e.g., (18)) or by pyrohydrolysis (e.g., (19)):

$$4U_3O_8 + 12KCl + 5O_2 \rightarrow 6K_2U_2O_7 + 6Cl_2 \qquad (18)$$

$$4U_3O_8 + 12KCl + 6H_2O + 2O_2 \rightarrow 6K_2U_2O_7 + 12HCl. \qquad (19)$$

Upon comparison with alkali carbonates, where initially formed diuranates can be converted to monouranates by reaction with an excess of carbonate, the diuranate was the usual final product formed upon the reaction of uranium oxides in air with an excess of sodium or potassium chlorides [80]. However, this oxidation reaction with an excess of LiCl yielded only lithium monouranate [36,80]. The possibility of the preparation of Na_2UO_4 and K_2UO_4 by fusing the corresponding diuranates or uranium oxides in air with a large excess of alkali metal chloride was, however, reported in the early literature [58,77,78,81] but few experimental conditions were given.

Anderson [33] and Allpress et al. [36] have studied the reactions of U_3O_8 and UO_3 mixed with excess alkali metal chloride MCl (M = K, Rb, Cs). They found that diuranates were formed at low temperatures (ca. 500°C) by a solid state reaction. Using infrared spectroscopy, X-ray powder diffraction and chemical analysis of the intermediate products formed they proposed the following reaction mechanism:

$$U_3O_8 + 3xMCl + \frac{1}{2}O_2 \rightarrow 3M_xUO_3Cl_x \ (T > 500°C) \qquad (20)$$

$$5M_xUO_3Cl_x + \frac{1}{2}O_2 \rightarrow M_4U_5O_{16}Cl_2 + (5x - 4)MCl + Cl_2 \ (T > 300°C) \qquad (21)$$

$$5M_xUO_3Cl_x + H_2O \rightarrow M_4U_5O_{16}Cl_2 + (5x-4)MCl + 2HCl\ (T > 300°C) \quad (22)$$

$$2M_4U_5O_{16}Cl_2 + 2MCl + \frac{3}{2}O_2 \rightarrow 5M_2U_2O_7 + 3Cl_2\ (T > 300°C) \quad (23)$$

$$2M_4U_5O_{16}Cl_2 + 2MCl + 3H_2O \rightarrow 5M_2U_2O_7 + 6HCl\ (T > 300°C), \quad (24)$$

where M = alkali metal and $x \approx 0.6$–1. Reactions (21)–(24), proceed simultaneously. Formation of $Cs_4U_5O_{16}Cl_2$ was not observed during the reaction of U_3O_8 with CsCl and the reaction must have occurred via

$$Cs_xUO_3Cl_x + \frac{1}{2}O_2 + (2-2x)CsCl \rightarrow Cs_2U_2O_7 + Cl_2\ (T > 300°C). \quad (25)$$

Several years earlier Vidavskii et al. [82] had reported similar results for the reaction of U_3O_8 mixed with NaCl in air. The reaction started at 500°C and yielded uranyl chloride, chloro-uranate ($NaUO_3Cl$–$Na_2U_2O_7$) and sodium diuranate. The uranyl chloride reacted with NaCl as the temperature was increased, yielding $Na_2U_2O_7$, also formed as the product of thermal decomposition of the chloro-uranate.

Aloy [83,84] has reported, in 1901, that heating uranium dioxide (in a bunsen flame) with potassium chloride and in a current of chlorine produced UO_2Cl_2, which upon temperature increase reacted with KCl to yield potassium tetrachlorouranate, $K_2UO_2Cl_4$.

Uranium dioxide can be dissolved in chloride melts containing aluminium chloride under an inert atmosphere [85]. Uranium tetrachloride and aluminium oxide or oxychloride were thus formed in the absence of oxygen:

$$3UO_2 + 4AlCl_4^- + 2Cl^- \rightarrow 2Al_2O_3 + 3UCl_6^{2-} \quad (26)$$

$$UO_2 + 2AlCl_4^- \rightarrow 2AlOCl + UCl_6^{2-}. \quad (27)$$

Later, Dai et al. [86] recorded the absorption spectra of the dissolution of UO_2 in an $AlCl_3$ melt (under inert conditions in a sealed cell) and concluded that a binary complex between UCl_4 and $AlCl_3$ was formed. A process has also been developed for expediting dissolution of UO_2 and U_3O_8 in chloride melts, including NaCl–KCl, LiCl–NaCl and LiCl–KCl, in the presence of chlorine or phosgene by the addition of catalytic amounts of thallium(I) or iron(II) chlorides [87].

It is not possible to carry out the reaction of UO_2 with aluminium chloride in carbonate melt media due to the expected reaction between $AlCl_3$ and carbonates [48]. An oxidation reaction between UO_2 and tetrachloroaluminate however did occur and yielded monouranate, via intermediate formation of uranium oxide-chloro species:

$$2UO_2 + 2KAlCl_4 + O_2 + 2KCl \rightarrow 2K_2UO_2Cl_4 + 2AlOCl \quad (28)$$

$$2K_2UO_2Cl_4 + 2K_2CO_3 \rightarrow K_2(U_2O_5O)Cl_2 + 6KCl + 2CO_2 \quad (29)$$

$$K_2(U_2O_5O)Cl_2 + 2K_2CO_3 \rightarrow 2K_2UO_4 + 2KCl + 2CO_2. \quad (30)$$

3.4. Reactions with alkali metal and ammonium sulfates

No information about the reaction of uranium dioxide with pure alkali metal sulfates is available and only Vidavskii et al. [88] have reported the reaction of U_3O_8 with M_2SO_4 (M = Na or K). They found that reaction began at 500°C and resulted in initial formation of uranyl sulfate, UO_2SO_4, which subsequently reacted with sodium or potassium sulfate to produce the corresponding diuranate at 1000°C. Reaction of uranyl phosphate with excess of potassium sulfate at 800–1000°C resulted in the formation of potassium monouranate [5].

We recently reported results of UO_2 oxidation in carbonate melts containing added sodium sulfate [48]. No potential intermediate uranyl sulfate complexes were detected, and the reaction resulted in the formation of sodium uranate, $Na_2O(UO_{3-y})_x$ ($1 < x < 2$; $y < 0.02$).

Brambilla and Facchini [89] studied the dissolution of uranium and plutonium dioxides (at concentrations up to 25 wt%) in molten alkali metal sulfates and sulfate eutectics at 550–600°C with addition of 100% H_2SO_4:

$$2M_2SO_4 + 2H_2SO_4 \rightarrow 4MHSO_4 \quad (31)$$

$$UO_2 + 4MHSO_4 \rightarrow UO_2SO_4 + 2M_2SO_4 + SO_2 + 2H_2O \quad (32)$$

$$PuO_2 + 4MHSO_4 \rightarrow Pu(SO_4)_2 + 2M_2SO_4 + 2H_2O, \quad (33)$$

where M = Li, Na, K. They investigated the dissolution of both UO_2 powder and sintered ceramic pellets, and reported that the pellets did not disintegrate in the molten salt but were directly dissolved. The rate of dissolution of UO_2 powder was around 4 times greater than that of the ceramic pellets under identical conditions but the available surface area of the samples was not specified or discussed. Uranium and plutonium dioxides could subsequently be recovered from the melts by electrolysis.

Initial dissolution of uranium dioxide in potassium pyrosulfate melts at 700–800°C has been suggested as a possible 'head-end' process in the reprocessing oxide nuclear fuels [90]. Dissolution of 25 wt% of UO_2 in this melt took around 2.5 h after which the temperature of the melt was lowered to 600°C and alkali metal uranates were precipitated upon addition of solid NaOH. Fusion with NH_4HSO_4 was recommended for dissolution of PuO_2 or PuO_2–UO_2 samples [91,92]. Complete dissolution (at a mass ratio of the dioxides to NH_4HSO_4 of 1:200) took ca. 2–4 h at 500–520°C.

Solid state reactions at 250°C of uranium oxides, UO_2 or UO_3, with $(NH_4)_2SO_4$ in the absence of oxygen resulted in the formation of $(NH_4)_4U(SO_4)_4$ or $(NH_4)_2UO_2(SO_4)_2$, respectively, which on further temperature increase produced at 350°C $(NH_4)_2U(SO_4)_3$ or $(NH_4)_2(UO_2)_2(SO_4)_3$, thus retaining the oxidation state of uranium in the starting oxide [93]. Mixed valence uranium oxides, i.e., $UO_{2.17}$, U_4O_9, U_3O_7 and U_3O_8, form mixtures of the above sulfate salts having uranium in both +4 and +6 oxidation states, depending upon the composition of the initial oxides. No salts containing uranium in the +5 oxidation state were reported.

3.5. *Reactions with alkali metal nitrates and nitrites*

The oxidation of uranium dioxide using alkali metal nitrates has been previously extensively investigated in view of the possible application of nitrate melts for pyrochemical reprocessing of oxide nuclear fuels [13,15,47].

Toussaint and Avogadro [15] have studied the reaction of UO_2 with (Na–K)NO_3, (Na–Li)NO_3 and (Na–Cs)NO_3 melts containing from 5 to 95 mol% of sodium nitrate at 450–490°C. The reaction was generally carried out for about 4 h at an initial UO_2 to nitrate mass ratio of 1:10. The results obtained under these conditions showed that mixed uranates of general formula $Na_{2-x}M_xU_2O_7$ (M = Li, K, Cs) were formed. The lithium species was obtained for the (Na,Li)NO_3 melt when the concentration of sodium was >60 mol%; the potassium species and the caesium species were obtained when the Na mol% was >30 and >5 in (Na,K)NO_3 and (Na,Cs)NO_3 melts, respectively. The limits of solubility of Li, K or Cs ions in $Na_2U_2O_7$ were determined: the maximum solubility of these cations was around 0.8, 2.6 and 0.1 wt%, respectively. From (Na–K)NO_3 melts containing 80 mol% of KNO_3 potassium di- and triuranates were formed, and X-ray studies revealed the expected presence of a small concentration of sodium ions replacing some of the potassium ions in the diuranate. The following reactions were suggested in these systems:

$$UO_2 + MNO_3 \rightarrow UO_3 + MNO_2 \quad (34)$$

$$xUO_3 + 2MNO_3 \rightarrow M_2O \cdot UO_3 + 2NO_2 + \frac{1}{2}O_2. \quad (35)$$

Morgan et al. [47] investigated the behaviour of UO_2 powder in molten (Li–K)NO_3 eutectic (42.2 mol% $LiNO_3$), (Na–K)NO_3 mixture (50 mol% $NaNO_3$) and $NaNO_3$ at 420–500°C, and that of PuO_2 in the (Na–K)NO_3 melt at 525°C at a mass ratio of the dioxides to nitrates of 1:100. They reported that the reaction required around 2.5 h for completion at 500°C in the (Li–K)NO_3 eutectic or at 420°C in the (Na–K)NO_3 melt. No reaction with PuO_2 was observed at temperatures up to 525°C. The alkali metal uranates formed could be then dissolved by passing HNO_3 vapour through the melt at 200–275°C. Increasing the temperature above 300°C caused decomposition of the soluble uranium species with precipitation of unidentified solid particles and gas evolution. Analysis of the uranates formed upon the UO_2 oxidation in the above melts (at UO_2 to nitrates mole ratio of 1:20) showed the formation of insoluble diuranate species in $NaNO_3$ and (Na–K)NO_3 melts: sodium diuranate in the former and mixed sodium-potassium diuranate (<10% of potassium) in the latter. The product obtained in the (Li–K)NO_3 eutectic melt was neither identifiable as the di- or monouranate species, nor as a mixture of these, and was said not to correspond with any known uranate species.

According to Morgan et al. [47] the following reactions are the only valid oxidation reactions possible in nitrate melts (M = alkali metal):

$$2UO_2 + 4MNO_3 \rightarrow M_2U_2O_7 + 2MNO_2 + 2NO_2 + \frac{1}{2}O_2 \quad (36)$$

$$2UO_2 + 3MNO_3 \rightarrow M_2U_2O_7 + MNO_2 + 2NO_2 \quad (37)$$

$$2UO_2 + 2MNO_3 \rightarrow M_2U_2O_7 + NO + NO_2 \quad (38)$$

$$2UO_2 + 4MNO_3 \rightarrow M_2U_2O_7 + 4NO_2 + M_2O. \quad (39)$$

Fujino et al. [13] have studied the reactions of UO_2 powder with $LiNO_3$ and $NaNO_3$ and of ceramic UO_2 with $NaNO_3$ upon heating mixtures of UO_2 and nitrate in a stream of oxygen at 450–600°C. When the $LiNO_3$:UO_2 mole ratio was <0.667 the products formed consisted of a mixture of U_3O_8 and lithium uranates: above this ratio only uranates were produced, with no U_3O_8 formation. Depending on the Li:U ratio in the starting mixture a variety of lithium uranates, $Li_2O \cdot xUO_3$, was produced, having x values of 3, 1.65, 1, 0.5 and 0.167. Similar results were obtained with $NaNO_3$ but uranates free from U_3O_8 were obtained only in mixtures with $NaNO_3$ to UO_2 molar ratios above 0.8 (reaction time 3 h). Sodium mono- and diuranates were the products formed in this system. Unlike Morgan et al. [47] Fujino and co-workers did not analyse for the formation of nitrite or Na_2O. Nor did they observe evolution of the brown NO_2 in their oxygen stream. When pieces of sintered ceramic UO_2 pellets were heated with the appropriate amount of $NaNO_3$ in a stream of oxygen (600–700°C, 3 h) a uniform powder consisting of the expected uranate species was obtained. It was therefore assumed that the ceramic readily disintegrated during this reaction. Thus the behaviour of ceramic UO_2 in nitrate melts was different from that in sulfate melts. No differences between the reactions with pellets or powder were reported but the authors did not make it clear if the absence of any differences applied only to the products formed upon the oxidation or, more importantly, also to the physical parameters of the reaction.

The kinetics of UO_2 oxidation in the ternary carbonate melts, $(Li–Na–K)_2CO_3$, containing 5–15 mol% $NaNO_3$ or $NaNO_2$ under an argon atmosphere, have been examined by Kryukova et al. [67] at 410–500°C. A diuranate was reported but its associated cation or cations were not specified. This product was formed in both nitrate- and nitrite-containing melts, and the yield of the diuranate increased with increasing concentration of the oxidising agent and temperature. From three variable parameters (initial $NaNO_3$ concentration, temperature and time) the first was found to be the principal factor controlling UO_2 conversion into diuranate.

Recently we found [9] that reaction of uranium dioxide with alkali metal nitrates dissolved in carbonate melts proceeded to a greater extent than that with pure nitrate melts [47]. When the reaction was carried out in the ternary carbonate melt, $(Li–Na–K)_2CO_3$, at 450°C the product formed upon oxidation depended on which alkali melt nitrate was added: $Na_2U_2O_7$ in the melt with added $NaNO_3$; $K_2U_2O_7$ with added KNO_3; and a complicated mixture of uranates with $LiNO_3$. We can now conclude that Kryukova et al. [67] had precipitated largely (>95%) sodium diuranate. The first stage of the oxidation is described by reaction (34) and then the following reactions occur:

$$3KNO_2 + KNO_3 + 3UO_2 \rightarrow 3UO_3 + 2K_2O + 4NO \quad (40)$$

$$K_2O + 2UO_3 \rightarrow K_2U_2O_7 \quad (41)$$

$$K_2CO_3 + 2UO_3 \rightarrow K_2U_2O_7 + CO_2. \quad (42)$$

The overall reaction is thus

$$4KNO_3 + 6UO_2 + K_2CO_3 \rightarrow 3K_2U_2O_7 + 4NO + CO_2. \quad (43)$$

We however found [9] that, depending on the UO_2 to nitrate mole ratio, another reaction can also occur

$$4KNO_3 + 10UO_2 + 3K_2CO_3 \rightarrow 5K_2U_2O_7 + 2N_2 + 3CO_2 \quad (44)$$

but the exact mechanism of the reaction is much more complicated and also depends on the order of adding the reactants to the melt [34–36].

Similar reactions occur in the carbonate melt containing added potassium nitrite:

$$2KNO_2 + 3UO_2 \rightarrow K_2O + 3UO_3 + N_2 \quad (45)$$

$$2KNO_2 + UO_2 \rightarrow K_2O + UO_3 + NO \quad (46)$$

and potassium diuranate is ultimately formed according to reactions (41) and (42) [9].

Vidavskii et al. [94] have reported that the reaction between U_3O_8 and $NaNO_3$ commenced at 410°C and that with KNO_3 at 390°C and produced the corresponding diuranates. Sodium diuranate reacted with the products of decomposition of $NaNO_3$ to give α-Na_2UO_4 at 1000°C but potassium diuranate did not react further. Ohwada [16] has used the reaction of U_3O_8 or UO_3 with $LiNO_3$ (800°C) and $NaNO_3$ (900°C) to obtain lithium and β-sodium monouranates, respectively.

3.6. Reactions with alkali metal chlorates and bromates

The oxidation of uranium dioxide with alkali metal chlorates has been little studied and only few reports exist on the reaction of other uranium oxides with alkali chlorates. Drenkmann [78] had in 1861 reported that U_3O_8 reacted with $KClO_3$ and that when he repeatedly treated the quenched melt with boiling water he obtained, not unnaturally, hydrated uranium trioxide, $UO_3 \cdot 2H_2O$. α-U_3O_8 and γ-UO_3 were reported to react on heating with $KClO_3$, liberating chlorine and some oxygen [95,96]. Fowler and Grant [95] some 30 yr after Drenkmann reported that U_3O_8 started to react with $KClO_3$ (at mass ratios of 1:2 and 2:1) at 300°C and that the reaction led to the formation of a reddish-yellow residue of potassium monouranate at 390°C. The formation of potassium monouranate upon the reaction of uranium trioxide with $KClO_3$ was confirmed five years later by Brunck [97], who, however, reported only chlorine formation and no oxygen evolution. Although the reaction of uranium oxides with alkali chlorates has been known since the middle of the 19th century, Ditte [77,81] was the first to study this reaction in detail between 1882 and 1884. He found that K_2UO_4 was produced on heating U_3O_8 with $KClO_3$, and that Na_2UO_4 was formed with $NaClO_3$. Simple heating of U_3O_8 with $NaClO_3$ produced a brisk reaction with the appearance of flame but addition of sodium carbonate moderated the reaction. Gradual addition of $NaClO_3$ to molten NaCl containing U_3O_8 produced a very slow but complete reaction. Ditte gave no equations but the following equations would account for the observed phenomena:

$$U_3O_8 + 6KClO_3 \rightarrow 3K_2UO_4 + 7O_2 + 3Cl_2 \quad (47)$$

$$2UO_3 + 4KClO_3 \rightarrow 2K_2UO_4 + 5O_2 + 2Cl_2. \quad (48)$$

All the above earlier workers studied the reactions of uranium oxides in mixtures with relatively high concentrations of chlorate and this can possibly explain the formation of chlorine. Unfortunately when Ditte [81] studied the reaction of U_3O_8 with sodium chlorate in the presence of carbonate he did not specify if any chlorine was formed. It is obvious that the accuracy of the early work was limited and the methods used for the characterisation of the reaction products, e.g., uranates, were also not elaborate.

No further work was done on the reaction of uranium oxides with alkali metal chlorates in the following 100 yr until recently, when we reported a study on UO_2 oxidation by potassium chlorate in the $(Li–Na–K)_2CO_3$ melt between 450°C and 550°C [98]. The following reaction occurred:

$$3UO_2 + KClO_3 + 3K_2CO_3 \rightarrow 3K_2UO_4 + KCl + 3CO_2. \qquad (49)$$

The reason why potassium uranate was precipitated is probably the same for why addition of KNO_3 leads to precipitation of $K_2U_2O_7$ from carbonate melts (Section 3.5).

Carnall et al. [99] observed that addition of solid sodium bromate, $NaBrO_3$, to solutions of UO_2^{2+} in molten $LiNO_3–NaNO_3$ at 210–270°C resulted in a mixture of diuranates containing predominantly $Na_2U_2O_7$. In this case the nitrate melt served only as an inert solvent and did not participate in the reaction. The reaction proposed was

$$10UO_2^{2+} + 4BrO_3^- \rightarrow 10UO_3 + 2Br_2 + O_2 \qquad (50)$$

with $UO_2(BrO_3)^+$ as intermediate. However they did not put forward any evidence for any intermediate.

3.7. Reactions producing uranates(V)

Conversion of uranium oxides into alkali metal uranates, containing uranium in oxidation state less than +6, requires an inert atmosphere and sometimes a reducing agent. Of the lower oxidation state uranates, dark violet lithium uranate(V), $LiUO_3$, has been prepared by reacting UO_2 with Li_2CO_3 under vacuum or dry argon at 740–800°C for from 38 to 180 h [50,100]:

$$Li_2CO_3 + 2UO_2 \rightarrow 2LiUO_3 + CO. \qquad (51)$$

Similarly, lower oxidation state sodium uranates have been prepared by heating UO_2 with Na_2CO_3 in an argon atmosphere for various time periods: $Na_{11}U_5O_{16}$ and $NaUO_3$ at 700°C (160 h) or at 1000°C (16 h) [101,102]; and Na_3UO_4 at 1100°C (48 h) [103].

A variety of uranate(V) compounds (i.e., $NaUO_3$, Na_3UO_4, Li_3UO_4 and Li_7UO_6) has been prepared by heating uranium dioxide with lithium or sodium oxides or sodium peroxide under vacuum at 500–800°C for various times [11,65,104–107], for example

$$UO_2 + 2Na_2O \rightarrow Na_3UO_4 + Na\ (600–800°C,\ 8–12\ h). \qquad (52)$$

Uranium dioxide acts in this case as a reducing agent. Scholder and Gläser [11] reported that addition of metallic sodium to a starting $UO_2–Na_2O$ mixture increased the rate of reaction (52); we presume that this is due to the initial formation of a liquid phase involving liquid sodium.

Liquid sodium acts as a reducing agent with uranium oxides above 600°C, yielding brown sodium uranates(V) [107]:

$$3Na + 2UO_3 \rightarrow Na_3UO_4 + UO_2 \qquad (53)$$

$$3Na + U_3O_8 \rightarrow Na_3UO_4 + 2UO_2. \qquad (54)$$

Below 400°C sodium reduces uranium oxides to UO_2 but if the temperature is increased then it reacts with the sodium oxide formed:

$$2Na + UO_3 \rightarrow Na_2O + UO_2 \qquad (55)$$

$$2Na_2O + UO_2 \rightarrow Na_3UO_4 + Na. \qquad (56)$$

In the presence of sodium uranate(VI) the following reaction was reported [11]:

$$2Na_2O + UO_2 + Na_2UO_4 \rightarrow 2Na_3UO_4. \qquad (57)$$

Chippindale et al. [108] observed that the reaction of uranium trioxide with sodium carbonate yielded a salmon-pink sodium uranate of composition $(Na_2O)_{1.281}UO_3$, which can further react with uranium dioxide to produce a chocolate-brown, stable in air, sodium uranate(V):

$$1.281Na_2CO_3 + \alpha\text{-}UO_3 \rightarrow (Na_2O)_{1.281}UO_3 + 1.281CO_2 \qquad (58)$$

$$(Na_2O)_{1.281}UO_3 + 1.562UO_{2.18} \rightarrow 2.562NaUO_3. \qquad (59)$$

A brown potassium uranate(V) was prepared by Rüdorff et al. [106] and Kemmler-Sack and Rüdorff [109] by heating UO_2 and K_2UO_4 at 800°C in an inert atmosphere

$$UO_2 + K_2UO_4 \rightarrow 2\,KUO_3. \qquad (60)$$

This uranate can be also prepared by thermal decomposition of $K_2U_2O_7$ in an inert atmosphere at 850–900°C, but the reaction is very slow [34]. Recently Dickens and Powell [110] reported the preparation of this uranate in two successive steps: (i), synthesis of $(K_2O)_{1.281}UO_3$ by heating the stoichiometric mixture of α-UO_3 and K_2CO_3 at 800°C for two days and (ii), reduction of $(K_2O)_{1.281}UO_3$ by reaction with the stoichiometric amount of $UO_{2.18}$ at 800°C for four days under an argon atmosphere.

Apart from oxygen-deficient caesium tetrauranate (Section 2.4), few rubidium and caesium uranates containing uranium in oxidation state <6 have been prepared. However, reaction of rubidium monouranate with uranium dioxide will yield the light-brown rubidium uranate(V)

$$Rb_2UO_4 + UO_2 \rightarrow 2\,RbUO_3. \qquad (61)$$

The reaction occurs at 650°C [111] or at 400–500°C under vacuum [106,112]. Reaction of Rb_2UO_4 with hydrogen apparently results in the formation of the rubidium uranate(IV), Rb_2UO_3 [112].

Computer simulation studies of the structure of alkali metal uranates(V), MUO_3, have been undertaken by Ball [113]. Their crystal structures and lattice properties were evaluated using lattice simulations and defect calculations. It now remains for others to compare Ball's tabulations with experimental data as single crystals of uranates these are prepared.

4. Some structural aspects of alkali metal uranates

The ability of oxygen to form bonds with other atoms is remarkably high. Often oxygen forms stable chemical species or groups with other atoms that remain unaltered from compound to compound. Oxygen donor properties play an important role when oxygen bonds with an element with accessible d- or f-orbitals. In this case oxygen p_π-orbitals overlap metal d- or f-orbitals, producing molecular π-orbitals, and a stable complex ion is formed. This overlapping can increase as the symmetry of the complex ion formed decreases [114]. The formation of the stable uranyl ion (UO_2^{2+}) is an example of this process [115]. A somewhat modified uranyl group is a structural feature of uranates (mono- and di-), where additional oxygen atoms are co-ordinated to the UO_2^{2+} oxycation in an equatorial (*x,y*) plane. Structural studies of uranate compounds showed no discrete uranate ions but identified the existence of a 'modified' uranyl group within the uranate ion to which two of the oxygen atoms were bound more strongly than the remainder [31,19]. Fig. 4(A) shows the arrangement of the oxygen atoms around uranium in monouranate: 'uranyl' oxygen atoms (designated as primary or O_I) have a short U–O bond length (ca. 1.8 Å) and 'equatorial' (secondary or O_{II}) a U–O bond length of ca. 2.2 Å. The primary U–O bond is around twice as strong as the secondary. The crystal lattice of the monouranates consists therefore of somewhat flattened uranium–oxygen octahedra, joined by sharing four secondary oxygen atoms. Such octahedra can be connected in two ways, forming either infinite layers (Fig. 4(B)) or chains (Fig. 4(C)). The former situation is realised in Li_2UO_4, β-Na_2UO_4 and K_2UO_4, and the latter in α-Na_2UO_4. The alkali metal ions hold the sheets or chains together. The monouranate ion (UO_4^{2-}) must therefore be considered as $[(UO_2)O_2]^{2-}$. Similarly, the diuranate ion ($U_2O_7^{2-}$) is more correctly represented as $[(UO_2)O_{1.5}]_2^{2-}$ or $[(UO_{1.5})O_2]_2^{2-}$.

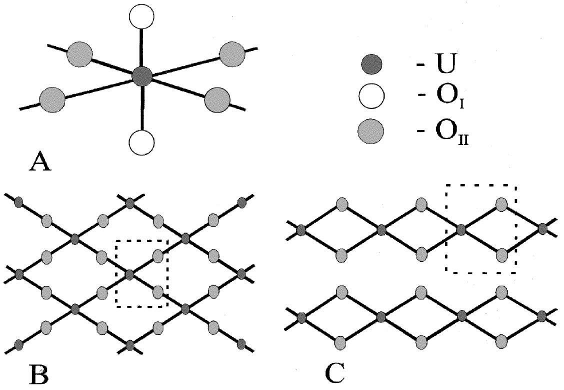

Fig. 4. Structure of monouranates: (A) arrangement of oxygen atoms around a uranium atom; (B) structure of the infinite uranium–oxygen layer viewed along the *z*-axis; (C) structure of infinite uranium–oxygen chains viewed along the *z*-axis. O_I – primary and O_{II} – secondary oxygen atoms.

Numerous investigations have been performed on the determination of the structure of alkali metal uranates, mainly by X-ray powder diffraction but with some single crystal and neutron diffraction studies. A summary of the main findings for mono- and diuranates is presented in Table 1. Single crystal studies have been obtained for Li_2UO_4 [18], β-Na_2UO_4 [18,116], $Na_2U_2O_7$ [66] and $K_2U_2O_7$ [117]. Crystals of the lithium and β-sodium monouranates were grown from a MCl–M_2UO_4 melt (M = Li or Na), and those of sodium and potassium diuranates from melts comprising the corresponding alkali metal carbonate, U_3O_8 and Nb_2O_5. The symmetry of the arrangement of the oxygen atoms around uranium can be deduced from the description of the structure of the corresponding uranate (see, for example, Krol [6]) and this information can be subsequently used when performing the analysis of the absorption spectra of alkali uranates. A detailed consideration of the structural properties of alkali metal uranates was not within the scope of this review. However, Table 2 contains the reported structural data for some of the less common uranates(VI) and Table 3 comprises information on the uranates(V).

X-ray powder diffraction has been the major analytical tool for identifying and characterising alkali metal uranate compounds and recently has been supplemented by neutron diffraction studies. Structural data on many uranate compounds have been reported in the literature [10,13,15,17,18,22,24,28,29,31–34,36,51,61,66, 99,108,112,117,119,124,134,135]. In most of these accounts only indexing parameters of the X-ray patterns measured were given. In recent studies there is complete agreement concerning the symmetry of the monouranate compounds; orthorhombic for lithium and α-sodium, and tetragonal for the potassium species. As Tables 1 and 2 show, for several polyuranate compounds there is

Table 1
Structural assignments of alkali metal mono- and diuranates

Compounds	Crystal class	Space group	Symmetry point group	Refs.
Li_2UO_4	Orthorhombic	F_{mmm} or P_{nma}	D_{2h}	[16–18,29,53,112,118–121]
	Hexagonal			[118]
α-Na_2UO_4	Orthorhombic	C_{mmm}	D_{2h}	[29,31,112,118–122]
β-Na_2UO_4	Orthorhombic	F_{mmm}	D_{2h}	[16,17,19,31,116,118–120]
K_2UO_4	Cubic			[118]
	Tetragonal	$I4/_{mmm}$	D_{4h}	[17,19,29,34,53,112,118–120]
	Orthorhombic		D_{2h}	[118]
Rb_2UO_4	Tetragonal	$I4/_{mmm}$		[34,44,53,112]
Cs_2UO_4	Tetragonal			[10,17,41,53,123]
$Li_2U_2O_7$	Orthorhombic			[15,29]
$(Li,Na)_2U_2O_7$ [a]	Rhombohedral	R3m	D_{3d}	[99,118]
$Na_2U_2O_7$	Rhombohedral	R3m	D_{3d}	[19,66,112]
	Orthorhombic			[29,119]
	Monoclinic		C_{2h}	[31,118]
$K_2U_2O_7$	Rhombohedral	R3m	D_{3d}	[19,112,117,118]
	Orthorhombic		D_{2h}	[29,33,118,119]
	Monoclinic	$P2_1/m$ or	C_2	[34]
		$P2_1$	C_2	[61]
$Rb_2U_2O_7$	Rhombohedral			[33]
	Hexagonal			[44]
	Monoclinic	$P2_1/m$		[34]
$Cs_2U_2O_7$	Hexagonal			[123]
	Monoclinic			[41]

[a] The exact composition has not been reported [99]; but up to 0.8% of Li could be introduced into the $Na_2U_2O_7$ lattice [15].

Table 2
Structural assignments reported for less common alkali metal uranates

Compounds	Crystal class	Space group	Symmetry point group	Refs.
Li_4UO_5	Tetragonal	I4/m	C_{4h}	[6,22]
	Rhombohedral			[10]
Na_4UO_5	Tetragonal	I4/m	C_{4h}	[22]
	Rhombohedral			[10]
K_4UO_5	Rhombohedral			[10]
Rb_4UO_5	Tetragonal			[39]
$Li_{22}U_{18}O_{65}$ ($= Li_2O.1.60$–$1.64UO_3$)	Orthorhombic			[51]
$Li_2U_3O_{10}$	Tetragonal		C_{2h}	[20]
	Monoclinic	$P2_1/c$ or		[118]
		$P2_1/b$		[124]
$K_2U_4O_{13}$	Hexagonal	$P6_3/m$		[34]
$Rb_2U_4O_{13}$	Hexagonal	$P6_3/m$		[34]
$K_2U_7O_{22}$	Orthorhombic	Pbam		[34]
$Rb_2U_7O_{22}$	Orthorhombic	Pbam		[34]

still some controversy about the symmetry groups to which they are belong: patterns for sodium diuranate, for example, have been indexed using monoclinic [31], hexagonal [112], rhombohedral [15,66] and orthorhombic [32,33,90] systems.

5. Properties of uranate compounds

Important physical and thermodynamic properties of alkali metal uranates, predominantly the lighter, Li to K, mono- and diuranate species, are now discussed, together with their readiness to undergo reduction.

5.1. Physical properties

Although the properties of alkali metal uranates have been studied for more than a century, some published data are still not consistent. One simple example concerns the reported colours of solid uranates. Table 4 summarises the variety of reported data, beginning from the time of Berzelius [136]. The uranates of rubidium

Table 3
Crystal classes assigned to some alkali metal uranates(V)

Compounds	Crystal class	Refs.
$LiUO_3$	Trigonal	[50,100,125,126]
	Rhombohedral	[111]
	Hexagonal	[125,126]
$NaUO_3$	Rhombohedral	[31,102,106,108,109,111]
	Monoclinic	[127,128]
KUO_3	Cubic	[109,111,112,129,130]
$RbUO_3$	Cubic	[106,111,112,131]
Li_3UO_4	Tetragonal	[49,100,132]
Na_3UO_4	Cubic	[11,103,104,107,133]

and caesium are not included because they were not reported until the middle of this century, by which time reliable analytical techniques were available, (and the colours of some of them have not been stated, but all are expected to be in the orange–yellow range). An account of colour studies performed on several alkali metal uranates, including their thermochromic properties, has been recently published [7].

The thermal stability of mono- and diuranates decreases in each species with increasing radius of the alkali metal cations and the volatility of the oxides [21,42]. In air lithium monouranate is thermally stable and does not change its composition after 60 h heating at 1300°C [10]. Under vacuum, however, lithium monouranate decomposes

$$Li_2UO_4 \rightarrow LiUO_3 \rightarrow (Li,U)O_{2\pm x} \qquad (62)$$

ultimately forming solid solutions of lithium and uranium oxides [127]. Sodium and potassium monouranates are less stable and decompose in air at 1200–1300°C, yielding diuranates. Pure diuranates are reported stable up to 1300°C [10], the maximum temperature so far investigated. However, a subsequent investigation suggested that decomposition temperatures of mono- and diuranates might be somewhat lower [31].

In the earliest investigations Ditte reported in the 1880s that uranates do not melt at 'light red heat' [77,81] and later Kovba et al. [17] even suggested that alkali metal uranates do not melt or sublime without decomposition. However, melting temperatures have been reported for sodium and potassium monouranates: 1635 ± 10°C for Na_2UO_4 and 1620 ± 10°C for K_2UO_4 (in air) [144], and Li_2UO_4 was said to melt above 1600°C [12], thus making the problem of the limits of thermal stability of uranates still unresolved.

Alkali uranate compounds do not physically dissolve in water [77,81] or any other readily available solvent but are easily soluble in dilute acids or carbonate solutions, forming uranyl salts or uranyl carbonate

Table 4
Colours of alkali metal uranates M_2UO_4 and $M_2U_2O_7$ (M = Li, Na and K)

Compounds	Colour	First author, year and reference
Li_2UO_4	Yellow–orange	Toussaint (1974) [15]
	Orange–yellow	Guiter (1939) [14]; Efremova (1961) [20]; Spitsyn (1961) [53]; Prigent (1965) [52]
	Orange	Weigel (1986) [119]
$Li_2U_2O_7$	Yellow	Toussaint (1974) [15]
Na_2UO_4	Yellow	Drenckmann (1861) [78]; Lange (1967) [137]
	Golden yellow	Ditte (1882, 1884) [77,81]
	Reddish yellow	Michel (1890) [138]
	Greenish yellow	Ditte (1882, 1884) [77,81]
	Green–yellow	Lide (1992) [139]
	Orange–yellow	Viltange (1954, 1960) [72,73]; Ippolitova (1961) [55]; Spitsyn (1961) [53]; Prigent (1965) [52]; Efremova (1969) [54]
	Orange	Cordfunke (1971) [31]; Weigel (1986) [119]
	Red	Lide (1992) [139]
$Na_2U_2O_7$	Yellow	Patera (1849, 1853, 1854, 1856) [140]; Frondel (1956) [141]
	Orange–yellow	Zimmermann (1881, 1882) [79,142]; Cordfunke (1971) [31]; Fujino (1983) [13]
	Orange	Gasperin (1986) [66]; Weigel (1986) [119]
	Light brown	Toussaint (1974) [15]
K_2UO_4	Greenish yellow	Ditte (1882, 1884) [77,81]
	Orange–yellow	Grandeau (1882, 1885) [143]; Montignee (1947) [62]; Martin (1951) [63]; Efremova (1961) [60]; Spitsyn (1961) [53]; Prigent (1965) [52]; Lange (1967) [137]; Keller (1972) [57]; Lide (1992) [139]
	Orange	Weigel (1986) [119]
$K_2U_2O_7$	Orange–yellow	Zimmermann (1881, 1882) [79,142]
	Orange	Allpress (1968) [36]; Jove (1988) [117]
	Brick red	Berzelius (1824) [136]

complexes, respectively [77,79,81,142,145,146]. The exact mechanism of the carbonate dissolution of uranates is not yet fully understood, and more data are needed to allow modelling of the geochemical behaviour of nuclear waste, but a data base has been assembled for the Swedish nuclear waste management program [147]. The solubility of uranates in molten salts has been characterised only qualitatively in chloride melts as 'extremely small' [17]. Recently we measured the solubilities of lithium, sodium and potassium mono- and diuranates in a range of carbonate melts as a function of temperature, melt basicity and oxygen partial pressure in the atmosphere, and found that the uranate solubility did not exceed 200 mol ppm [8]. Similarly, as with other oxide species in molten salts of oxoacids (carbonates, sulfates, etc.), alkali metal uranates undergo either acidic or basic dissolution in carbonate melts, depending on the melt and the atmosphere composition [8].

It is generally agreed that polyuranate compounds are stable towards hydrolysis while the reaction of monouranates with water yields di- or higher polyuranates [80,145]:

$$xM_2UO_4 + (x-1)H_2O \rightarrow M_2O(UO_3)_x + (2x-2)MOH. \quad (63)$$

Pechurova et al. [145] reported that the value of x increases with increasing radius of the alkali metal cation being used. After several hours of treatment of the monouranates with water x was found to be 1.94 for Li, 2.13 for Na, 3.80 for Rb and 3.63 for Cs, respectively. No data for the potassium cation is available. Diuranates and lithium monouranate can be safely handled in air [19]. Hoekstra [19] has reported that sodium and potassium monouranates are 'extremely hygroscopic' but Cordfunke and Loopstra [31] have described sodium monouranate only as 'more or less hygroscopic'. The hygroscopic nature of Na_2UO_4 was also noted by O'Hare and Hoekstra [148].

We used diffuse reflectance spectroscopy to study the hydrolysis of three (Li, Na and K) monouranates [7] and found that their tendency towards hydrolysis was $K_2UO_4 > Na_2UO_4 > Li_2UO_4$. The nature of the hydrolysis reaction of K_2UO_4 was dependent on the humidity level in the atmosphere, and analysis of the spectra of the final products showed that a mixture of di- and tri- (or higher) uranates was formed. Studies of the hydrolysis of Na_2UO_4 revealed that (layer) β-Na_2UO_4 hydrolyses much faster than the (chain) α-form, which is essentially stable to hydrolysis. We were therefore able to conclude that the Na_2UO_4 used by the earlier workers [19,31,148] contained different proportions of the β-form.

5.2. Thermodynamic properties

Little thermodynamic data has been reported for the alkali metal uranates. Measurements have been made mainly by three groups of workers, at Reactor Centrum Nederland, the Argonne National Laboratory and the AERE, Harwell [30,148–157]. They obtained standard enthalpies of formation of some alkali metal uranates(VI) and (V) and these are given in Table 5. It is not possible at present to deduce clear trends but generally ΔH_f^0 for uranates decreases (in absolute value) only with increasing radius of the smaller alkali metal cations (Li to K). However, for each alkali metal ΔH_f^0 is lowest for the monouranate and increases with increasing basicity or acidity of the uranate.

5.3. Reduction of uranates

Direct conversion of uranates(VI) into compounds containing uranium in a lower oxidation state, and ultimately into UO_2, is of practical interest if the uranate species are to be intermediates in the processing or reprocessing of oxide nuclear fuels.

Alkali metal uranates(VI) can be reduced to uranates(V) by reaction with uranium dioxide under vacuum or under an inert atmosphere. Heating lithium monouranate with UO_2 in vacuum at 650–750°C results in the formation of dark-violet $LiUO_3$ [50,52,65]

$$Li_2UO_4 + UO_2 \rightarrow 2\,LiUO_3. \quad (64)$$

Similar reactions were reported for sodium and potassium uranates [11,65,104,106,109,151]. Li_3UO_4 and Li_7UO_6 can be similarly prepared [11].

The reduction of uranate(VI) compounds with hydrogen results either in formation of uranates(V) or uranium dioxide. The first examples of hydrogen reduction of diuranates to UO_2 were reported by Zimmermann over a 100 yr ago [79,142]. More recent investigations showed that uranate(V) species are formed upon the reduction of mono- and diuranates at intermediate temperatures (450–600°C) [11,107,128,158–160]. Carrying out this reaction at much higher temperature, 800–1000°C, for several hours yields UO_2 [158,160]. Galkin et al. [159] have studied the reduction of $Na_2U_2O_7$ by hydrogen at 550°C and reported the formation of a mixture of $NaUO_3$ and UO_2 after 1 h, and complete reduction to UO_2 in 4 h. They thus concluded that the reaction proceeds in two stages via the intermediate formation of sodium uranate(V):

$$Na_2U_2O_7 + H_2 \rightarrow 2NaUO_3 + H_2O \quad (65)$$

$$2NaUO_3 + H_2 \rightarrow 2UO_2 + 2NaOH. \quad (66)$$

Reduction of lithium uranates by H_2 in the presence of Li_2CO_3 or Li_2O at 750–900°C gives exclusively lithium uranates(V), i.e., Li_3UO_4 and Li_7UO_6 [11,49,100]. Formation of Na_3UO_4 has also been observed but this was by the reduction of $Na_2U_2O_7$ with metallic sodium at 600°C [107].

Table 5
Standard enthalpies of formation of alkali metal uranates (25°C)

Uranate	ΔH_f^0, kJ mol^{-1}	Refs.	Uranate	ΔH_f^0, kJ mol^{-1}	Refs.
Li_4UO_5	$-(2639.7 \pm 3.7)$	[150]	$Na_2U_2O_7$	$-(3203.8 \pm 2.8)$	[30]
Na_4UO_5	$-(2457.3 \pm 2.8)$	[30]		$-(3194.8 \pm 1.8)$	[156]
Li_2UO_4	$-(1938.54 \pm 3.56)$	[149]	$Rb_2U_2O_7$	$-(3138 \pm 25)$ [a]	[152]
	$-(1967.5 \pm 2.0)$	[150]	$Cs_2U_2O_7$	$-(3156.1 \pm 6.7)$	[152]
α-Na_2UO_4	$-(1901.3 \pm 2.3)$	[30]		$-(3220.2 \pm 1.8)$	[155]
	$-(1864.27 \pm 3.56)$	[148]	$Li_2U_3O_{10}$	$-(4437.6 \pm 3.6)$	[150]
	$-(1897.3 \pm 1.1)$	[156]			
β-Na_2UO_4	$-(1889.0 \pm 2.3)$	[30]	$LiUO_3$	$-(1522.1 \pm 1.7)$	[151]
	$-(1850.42 \pm 3.56)$	[154]	$NaUO_3$	$-(1494.6 \pm 1.6)$	[151]
K_2UO_4	$-(1888.66 \pm 3.47)$	[149]		$-(1495.8 \pm 3.3)$	[157]
Rb_2UO_4	$-(1891.21 \pm 3.56)$	[149]	KUO_3	$-(1522.9 \pm 1.6)$	[151]
Cs_2UO_4	$-(1897.32 \pm 3.56)$	[157]	$RbUO_3$	$-(1520.9 \pm 1.7)$	[151]
	$-(1928.15 \pm 1.0)$	[152]	Na_3UO_4	$-(1998.7 \pm 3.8)$	[153]

[a] Estimated value.

Note: Where data have been converted from kcal mol^{-1} to kJ mol^{-1} the original reported accuracy is preserved.

Around the turn of this century other methods of pyrochemical reduction of uranates to UO_2 were explored, e.g., by sulfur and ammonium chloride [161] or by molten $MgCl_2$ [162]. The former method is efficient but no chemical reason for the latter to work is apparent.

Gray and Kerrigan [163] used DTA to investigate the reduction of three sodium uranates, Na_2UO_4, $Na_2U_2O_7$ and $Na_6U_7O_{24}$, with aluminium. Reaction with $Na_2U_2O_7$ and $Na_6U_7O_{24}$ starts in the solid state (below 660°C). Depending on temperature and mixture composition the reduction reaction results in the formation of U_3O_8, UO_2, U, UAl_2 or UAl_3, and the following reactions were proposed:

$$9Na_2U_2O_7 + 4Al \rightarrow 9Na_2O + 2Al_2O_3 + 6U_3O_8 \ (250^\circ C) \tag{67}$$

$$3U_3O_8 + 4Al \rightarrow 2Al_2O_3 + 9UO_2 \ (6000\text{–}640^\circ C) \tag{68}$$

$$Na_2U_2O_7 + 4Al \rightarrow Na_2O + 2Al_2O_3 + 2U \ (> 900^\circ C) \tag{69}$$

$$Na_2U_2O_7 + 8Al \rightarrow Na_2O + 2Al_2O_3 + 2UAl_2 \ (> 900^\circ C) \tag{70}$$

$$Na_2U_2O_7 + 10Al \rightarrow Na_2O + 2Al_2O_3 + 2UAl_3 \ (> 900^\circ C). \tag{71}$$

Our calculations however show that reaction (67) is not thermodynamically favourable. Unfortunately there is no reliable data on the entropy of formation ΔS_f for sodium diuranate. However, the overall free energy of reaction (67), ΔG, will be positive if the entropy of formation ΔS_f of $Na_2U_2O_7$ is greater than 262 J mol^{-1} K^{-1}. The values of ΔH_f available for diuranates, including $Na_2U_2O_7$, are close to that of α-U_3O_8 (−3574.8 kJ mol^{-1}). We therefore consider that their ΔS_f values are also similar. Since ΔS_f for α-U_3O_8 is 282.6 J mol^{-1} K^{-1} we suggest that a similar value is expected for $Na_2U_2O_7$. This thus means that the overall free energy ΔG of reaction (67) is close to zero and hence this reaction is not expected to proceed. Gray and Kerrigan [163] introduced reaction (67) on the basis of a peak in their thermograms which must now be re-considered. In reactions (69)–(71) the possible future reaction of Na_2O and Al_2O_3 to form aluminate has not been considered. The authors based their proposals mainly upon their interpretation of DTA curves and micrographic analysis of solidified samples, and future work would be useful here.

An industrial plant has recently been described for recycling potassium diuranate (formed during the production of UF_6) into uranium metal at a cost of ca. 15% of the cost of refining the uranium [164].

6. Spectroscopic studies of uranate(VI) compounds

The first spectra of uranium compounds (U(III), U(IV) and U(VI)) in fused salts were reported almost 40 years ago by Gruen and McBeth [165]. They found that these three oxidation states of uranium could be stabilised in (Li–K)Cl eutectic, but only U(VI) in (Li–K)NO_3 eutectic melt. Subsequently, a number of researchers studied the spectra of uranium species in other molten salts, mainly halides [166–172], and later room temperature melts were employed [173]. The earliest work has been reviewed by Smith [174] and Gruen [175], and all the spectra reported until recently for hexavalent uranium in molten salts have been those of the uranyl ion.

Since uranate(VI) species are essentially insoluble in water and other non-aqueous solvents, this makes direct measurement and comparison of their absorption spectra impossible. However, we have recorded spectra during the oxidation of uranium dioxide in alkali metal chloride melts and observed the formation of alkali metal uranate species [8]. We also obtained spectra during and after the dissolution of alkali metal mono- and diuranates in LiCl–KCl eutectic melt. Solid monouranates (e.g., Na_2UO_4) continued to dissolve in the melt for more than four hours but the final concentration of uranium in the saturated melt at 450°C was ca. 38 mol ppm. Diuranates, after initial dissolution, reacted with this chloride melt to form monouranates

$$M_2U_2O_7 + 2\,MCl + \frac{1}{2}O_2 \rightarrow 2\,M_2UO_4 + Cl_2 \qquad (72)$$

The spectral profiles of alkali metal uranates obtained in this way suffered somewhat from high temperature broadening and the low solubility of uranates in these media.

Two approaches are generally used to overcome these problems and obtain better absorption spectra, viz., measuring the diffuse reflectance spectra of powdered solids at low temperatures and recording the spectra of crystals doped with compounds of interest. The first method provides more accurate information if in the second the uranate units in the uranium-doped crystals have a different symmetry (corresponding to the symmetry of the matrix) from that of the pure uranate.

Single crystals of alkaline earth molybdates and tungstates (with the scheelite structure) doped with uranium(VI) have been used for measuring excitation and absorption spectra [176,177]. The symmetry of the uranate ion (UO_4^{2-}) in these matrixes has been described as tetrahedral (T_d) [176] and also as monoclinic (C_2) [177]. Blijenberg [178] has measured the excitation spectra of the octahedral uranate group (UO_6^{6-}) in a U_3O_8-doped single crystal of NaF as well as in samples of M_2MgWO_6, where M = Ba or Sr. Seemann et al. [179–183], and Krol and Blasse [184], have measured the diffuse reflectance spectra of the octahedral uranate group in compounds having the ordered perovskite-type structure, e.g., A_2BUO_6, where A and B = Ba, Sr, Ca, Mg or Pb(II). Three groups of bands can be distinguished in the spectra: a strong absorbance region below 400 nm; medium strong bands (approximately 75% of the intensity of the first group) between 500 and 400 nm; and low intensity bands above ca. 500 nm.

More recently Allen et al. [46] recorded the diffuse reflectance spectra of some alkaline earth uranates, including the normal monouranates of Mg, Ca, Sr and Ba, and some diuranates. They found several absorption bands above 360 nm but at higher energies the absorption was essentially constant and attributed to the overlap of several broad bands. This region has been described as the 'very intense structureless continuum' [108]. Between 360 and 625 nm Allen et al. [46] divided the observed absorption bands into three groups, similar to the regions where transitions are observed for uranyl compounds [185,186]: 360–385, 420–455 and 480–530 nm. They attempted (tentatively) to explain the number of observed transitions using symmetry group analysis for the uranate ion, based on the substantial correlation between the spectra of uranyl ion and its symmetry within various complexes that had been previously established [186].

Krol [6] has measured the excitation spectra of several uranates, including two alkali metal species, Li_4UO_5 and Li_2UO_4, and he attributed the site symmetry of the uranate ion in these alkali uranates to C_{4h} and C_S, respectively. Recently, diffuse reflectance spectra of lithium, sodium and potassium mono- and diuranates and lithium triuranate were reported over a wide temperature range (up to 700° for potassium compounds) [7] but no analysis of the spectra was conducted. As a typical example of the electronic spectrum of alkali metal uranates the diffuse reflectance spectrum of sodium diuranate recorded at −196°C is presented in Fig. 5(A).

The theory of the spectra of uranate(VI) compounds is yet to be developed. Analysis of the charge transfer transitions within the octahedral uranate group, UO_6^{6-} [178], has been performed on the basis of the calculations of the electronic structure of uranium hexafluoride, UF_6, which is isoelectronic with UO_6^{6-} and has been studied in detail [187–189]. In total, from 18 to 20 charge transfer transitions have been theoretically predicted in the electronic spectrum of UF_6 below 410 nm [187,188], but only six were experimentally observed [187]. In the octahedral UO_6^{6-} group the first electric dipole allowed transition occurs higher than that of the first allowed magnetic dipole by around 10 000 cm^{-1} and therefore only magnetic dipole allowed transitions should be observed in the visible region of the spectra of the uranates. In practice, the symmetry of the monouranate ion is not octahedral, and lowering its symmetry leads to lifting the degeneracy of its orbitals. This feature was recognised by Krol [6] when he attempted to analyse the excitation spectra of several uranates, in particular Li_4UO_5 and Li_2UO_4.

Starostin [190] used a somewhat different approach when he analysed the absorption spectra of crystals of the scheelite type MXO_4 (M = Ca, Sr or Ba and X = W or Mo) doped with uranium. He considered an individual uranate unit, UO_4^{2-}, to have D_{2d} symmetry and predicted three transitions from the highest occupied level to unoccupied non-bonding uranium 5f- and 6d-orbitals. This scheme satisfactorily accounted for the experimental results obtained by Morozov et al. [176]. Recently Holliday and Manson [177] have suggested that the magnitude of distortion of the uranate group within the structure of molybdate or tungstate crystals might be greater than previously anticipated, thereby lowering the symmetry to S_4 or even C_2.

Two molecular orbital energy level diagrams have been constructed, based on the electronic structure of

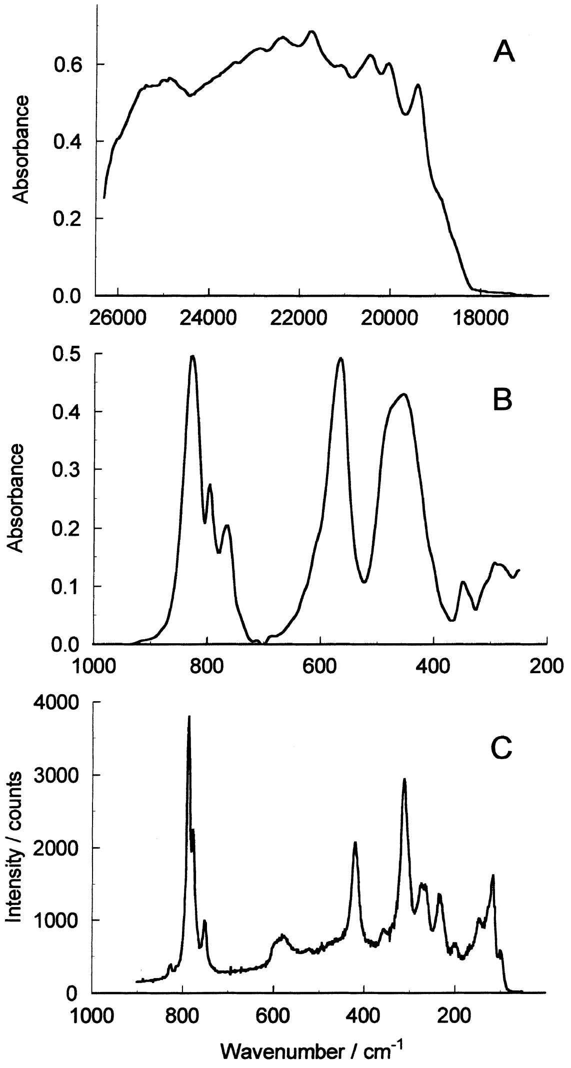

Fig. 5. Electronic and vibrational spectra of solid sodium diuranate: (A) diffuse reflectance spectrum recorded at −196°C [7]; (B) infrared and (C) Raman spectra [29].

UF_6 [178] and on the model used by Starostin [190]. However, some orbitals in both approaches are not considered because, without any explanation, only four and not six electrons from each oxygen atom were included. Thus the conclusions drawn in references [6,178,190] should be viewed with caution. It is possible that the 'missing' electrons are located in low energy levels, and therefore do not participate in transitions in the visible and near uv regions and hence their conclusions could be valid. More theoretical work is therefore required before the electronic spectra of uranates can be fully understood and successfully interpreted.

Measurements of the infrared spectra of alkali metal (Li, Na and K) uranates, using KBr disks and Nujol mulls, have been performed by several researchers (mostly for the identification and analysis of uranate species) and the spectra of the following common uranates(VI) were reported: Li_2UO_4 [6,12,16,19,29], $Li_2U_2O_7$ [19,29], $Li_2U_3O_{10}$ [17,19,29], Na_2UO_4 (α- and β-phases) [16,19,29,191], $Na_2U_2O_7$ [19,29,31,32,99], K_2UO_4 [19,29,192] and $K_2U_2O_7$ [19,29,33,36]. Carnall et al. [99] reported that the disk technique gives spectra with sharper bands then those obtained using Nujol mulls. Information on the infrared spectra of $Li_2O{\cdot}1.6UO_3$ and $Li_2O{\cdot}1.75UO_3$ has also been reported [12] and recently the actual spectra were published [29]. In addition, the infrared spectra of some rubidium and caesium uranates were measured: Rb_2UO_4 and Cs_2UO_4 [19,192], $Rb_2U_2O_7$ [19] and $Cs_2U_2O_7$ [41]. The infrared spectra of a great variety of other uranates have also been reported, including the spectra of sodium [31,32] and potassium [33] polyuranates.

Some of this spectral data has been analysed in terms of reported crystal structures. Only Ohwada [16,191,192] performed a normal co-ordinate analysis of the optically active uranium-oxygen lattice vibrations on lithium, sodium (α and β) and potassium monouranates, whilst the other workers restricted their analysis to the assignment of the observed bands arising from the bending and stretching of uranium–oxygen bonds. Ohwada's approach considered the infinite $[(UO_2)O_2]^{2-}$ layer structure of lithium, β-sodium and potassium monouranates, and the similar infinite chain structure of α-Na_2UO_4, adopting the space group D_{2h} for Li_2UO_4, α- and β-Na_2UO_4, and D_{4h} for K_2UO_4.

Later Krol [6] recorded vibrational (infrared and Raman) spectra of Li_2UO_4 and Volkovich et al. [29] those of lithium, α-sodium and potassium monouranates, and found more vibrations than allowed by the layer-structure model proposed by Ohwada [16,191,192].

Only these two reports of the Raman spectra of alkali metal uranates(VI) so far exist. This is because orange–yellow uranates absorb up to 600 nm and a laser with a longer excitation wavelength is required. Only two lasers are currently suitable, the krypton ion laser and the recent 780 nm diode laser. The Raman spectra reported by Krol [6] were obtained using a Kr^+ laser, for Li_2UO_4 and Li_4UO_5, and the spectra reported by us [29] for lithium, sodium and potassium mono- and diuranates, and $Li_2U_3O_{10}$, $Li_2O{\cdot}1.6UO_3$ and $Li_2O{\cdot}1.75UO_3$, employed the diode laser. Typical examples of vibrational (infrared and Raman) spectra of $Na_2U_2O_7$ are given in Fig. 5(B) and (C). A comparative analysis of the Raman and infrared spectra of alkali metal uranates, carried out in terms of uranate group site symmetries, allowed the following assignments: C_{2h} for Li_2UO_4 and $K_2U_2O_7$, D_{2h} for α-Na_2UO_4, D_{4h} for K_2UO_4, and D_2 for $Na_2U_2O_7$ [29].

It must be noted that in investigating uranate compounds, as well as other complex inorganic molecules, several independent techniques should be used. These should include structural studies by X-ray or neutron diffraction, electronic and vibrational spectroscopy, together with theoretical calculations and computer simulations. Techniques also need to be developed to obtain the many uranates as single crystals. Only then it will be possible to draw reliable conclusions concerning the symmetry and structure of intrinsic uranate moieties.

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