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THERMAL AND X-RAY CHARACTERIZATION OF K₂U₄O₁₃-Rb₂U₄O₁₃ SOLID SOLUTIONS

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Abstract

The preparation, characterization and thermal behavior of (K₁₋ₓRbx)₂U₄O₁₃ solid solutions have been studied in the range of 0<x<1. The solid solutions were prepared by heating K₂U₄O₁₃ and Rb₂U₄O₁₃ in required stoichiometry at about 600-700 ºC. The XRD patterns suggest formation of the solid solutions in full range of concentrations. The thermal patterns of the solid solutions in helium atmosphere indicates that these solid solutions are reduced to K₂U₄O₁₂ and Rb₂U₄O₁₂ on heating in inert atmosphere.

Introduction

Alkali metals are present in a nuclear reactor either as a fission product of nuclear fuel or coolant. Alkali metal uranates may be formed by fission product – fuel or fuel – coolant interactions either in operating or transient conditions. These uranates have less density as compared to nuclear fuel and these can cause swelling of the irradiated fuel and may result in rupture of the fuel cladding. Because of this reason the preparation, characterization and other properties of alkali metal uranates have been reported by different workers from time to time. Earlier, we had prepared mixed valent uranates K₂U₄O₁₂ and Rb₂U₄O₁₂ by heating the corresponding U(VI) uranates i.e. K₂U₄O₁₃ and Rb₂U₄O₁₃ in inert atmosphere [1]. Though K₂U₄O₁₃ and Rb₂U₄O₁₃ are isostructural [2-4] the corresponding mixed valent uranates K₂U₄O₁₂ and Rb₂U₄O₁₂ are not isostructural [1]. In this paper, we have studied the formation of solid solutions of K₂U₄O₁₃ and Rb₂U₄O₁₃ and their reduction in inert atmosphere.

Experimental

K₂CO₃ and Rb₂CO₃ used for preparations were of AR grade. Due to hygroscopic nature of Rb₂CO₃ it was handled in a dry box. Stoichiometric quantities of Rb₂CO₃ or K₂CO₃ and UO₂ required for preparations of Rb₂U₄O₁₃ and K₂U₄O₁₃ were taken in pestle mortar and mixed well with little acetone, to form a paste. The resultant powder obtained by heating this paste under an IR lamp, was carefully transferred to alumina boats. These boats were heated in a furnace at 600 ºC to prepare corresponding U(VI) uranates Rb₂U₄O₁₃ and K₂U₄O₁₃. The progress of the reaction was monitored by recording the XRD patterns of the products on a STOE X-ray diffractometer, using Cu Kα radiation (1.5405 Å).
Rb$_2$U$_4$O$_{13}$ and K$_2$U$_4$O$_{13}$ were mixed in different ratios and heated to at 700 °C for 48 hours to form the solid solutions of the corresponding compositions as shown in Table 1. The formation of the solid solutions was ascertained from their XRD patterns. These solid solutions were heated in a Mettler-Toledo thermal analyzer in alumina cups up to 1000ºC at a heating rate of 10ºC/min. in flowing helium gas.

Results and Discussion

K$_2$U$_4$O$_{13}$ and Rb$_2$U$_4$O$_{13}$ are reported in literature [2-4]. These compounds are isostructural and have hexagonal lattice and are expected to form solid solutions. However, the corresponding lower valent uranates K$_2$U$_4$O$_{12}$ and Rb$_2$U$_4$O$_{12}$ [3] are not isostructural and the probability of formation of solid solutions of these uranates, is uncertain. The XRD patterns of the solid products formed by heating K$_2$U$_4$O$_{13}$ and Rb$_2$U$_4$O$_{13}$ in different ratios at 700°C could be indexed on the basis of cell parameters of K$_2$U$_4$O$_{13}$ and Rb$_2$U$_4$O$_{13}$. There is a systematic change in Bragg angles of different hkl planes of these solid solutions. A part of the X-ray diffraction pattern of these solid solutions is shown in Fig. 1. As the concentration of K$^+$ ions increases in the solid solution lattice, the cell parameter “a” decreases up to a certain stage, after which it shows no appreciable change. The cell parameters “c” and cell volume systematically decrease with increase of K$^+$ concentration in the solid solution lattice. A plot of cell volume with atomic ratio of K in Rb+K is shown in Fig. 2. This indicates that (K$_{1-x}$Rb$_x$)$_2$U$_4$O$_{13}$ solid solutions are formed in complete concentration range. The TGA and DTA plots of the compounds K$_2$U$_4$O$_{13}$ and Rb$_2$U$_4$O$_{13}$ in inert atmosphere show that they start losing oxygen molecule at about

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Composition of the Solid solution formed</th>
<th>Crystal System</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Cell Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>K$_2$U$<em>4$O$</em>{13}$</td>
<td>Hexagonal</td>
<td>14.302</td>
<td>14.026</td>
<td>2485</td>
</tr>
<tr>
<td>2.</td>
<td>(K$<em>{0.66}$Rb$</em>{0.34}$)$_2$U$<em>4$O$</em>{13}$</td>
<td>Hexagonal</td>
<td>14.302</td>
<td>14.042</td>
<td>2487</td>
</tr>
<tr>
<td>3.</td>
<td>(K$<em>{0.24}$Rb$</em>{0.76}$)$_2$U$<em>4$O$</em>{13}$</td>
<td>Hexagonal</td>
<td>14.400</td>
<td>14.063</td>
<td>2490</td>
</tr>
<tr>
<td>4.</td>
<td>(K$<em>{0.12}$Rb$</em>{0.88}$)$_2$U$<em>4$O$</em>{13}$</td>
<td>Hexagonal</td>
<td>14.302</td>
<td>14.157</td>
<td>2508</td>
</tr>
<tr>
<td>5.</td>
<td>(K$<em>{0.08}$Rb$</em>{0.92}$)$_2$U$<em>4$O$</em>{13}$</td>
<td>Hexagonal</td>
<td>14.310</td>
<td>14.231</td>
<td>2524</td>
</tr>
<tr>
<td>6.</td>
<td>(K$<em>{0.08}$Rb$</em>{0.92}$)$_2$U$<em>4$O$</em>{13}$</td>
<td>Hexagonal</td>
<td>14.334</td>
<td>14.304</td>
<td>2539</td>
</tr>
<tr>
<td>7.</td>
<td>Rb$_2$U$<em>4$O$</em>{13}$</td>
<td>Hexagonal</td>
<td>14.340</td>
<td>14.304</td>
<td>2547</td>
</tr>
</tbody>
</table>
825°C and 780°C respectively, to form either $K_2U_4O_{12}$ or $Rb_2U_4O_{12}$. However, the solid solutions of these compounds lose oxygen at comparatively lower temperature. The XRD pattern of the residue obtained after complete reduction of these solid solutions, indicate that, these are mixtures of $K_2U_4O_{12}$ and $Rb_2U_4O_{12}$. The lower temperature of reduction of solid solutions $(K_{1-x}Rb_x)_2U_4O_{13}$ as compared to $K_2U_4O_{12}$ and $Rb_2U_4O_{13}$, may be due to comparatively unstable lattice of $K_2Rb_xU_{4-x}O_{13}$. Also, as the $K_2U_4O_{12}$ and $Rb_2U_4O_{12}$ are not iso-structural, formation of any one of these breaks the solid solution lattice and starts a mass loss. The TGA plots of a representative solid solution $(K_{0.52}Rb_{0.48})_2U_4O_{13}$ have been compared with that of $K_2U_4O_{12}$ or $Rb_2U_4O_{12}$ as seen in Fig. 3.

**Conclusion**

The $(K_{1-x}Rb_x)_2U_4O_{13}$ solid solutions are formed in complete range. The indexing of the XRD pattern of the solid solutions indicate that decrease in cell volume with increasing amount of K in the solid solution lattice. These solid solutions are reduced to lower valent uranates $K_2U_4O_{12}$ and $Rb_2U_4O_{12}$ at comparatively lower temperature to that of $K_2U_4O_{13}$ and $Rb_2U_4O_{13}$.

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**References**

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