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# Thermal conductivity of strontium uranates

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**Abstract**

The thermal conductivity of $Sr_3UO_6$, $Sr_2UO_5$, $Sr_3U_2O_9$, $SrUO_4$, $Sr_2U_3O_{11}$ and $SrU_4O_{12.8}$ uranates has been measured in the temperature range 300–1100 K using an axial heat flow comparative set up. The measured conductivity values of all these oxides are of the order of 3–1 $W K^{-1} m^{-1}$ and are much less than that of $UO_2$ over the entire temperature range of measurements. An increase of thermal conductivity with $SrO/UO_3$ ratio is observed in these systems. The temperature dependence of the observed values of the thermal conductivity is explained using the mechanism for phonon mode of heat conduction.


## 1. Introduction

The ternary oxides composed of uranium oxide mixed with divalent metal oxides are quite complex and are characterized by the formation of uranates, in which the hexavalency of uranium is stabilized. Six uranates, viz, $Sr_3UO_6$, $Sr_2UO_5$, $Sr_3U_2O_9$, $SrUO_4$, $Sr_2U_3O_{11}$ and $SrU_4O_{12.8}$ are known to exist in the strontium–uranium–oxygen system [1–3]. These uranates have been studied extensively with respect to their preparation, characterization, crystallographic, thermodynamic, thermal expansion and electrical transport properties [1–10]. However, attention has not been given so far to their thermal transport properties. In an earlier study, Srirama Murti and Krishnaia [11] showed that the thermal conductivity of $SrUO_4$ is much less than that of $UO_2$. Since there is no thermal conductivity data available for these uranates, we have carried out a systematic study of the thermal conductivity of different uranates in the temperature range of 300–1100 K and the results have been analyzed to identify the mode of heat conduction in them.

## 2. Experimental

The strontium uranates were prepared using strontium nitrate (E. Merck AG, G.R. grade) and nuclear pure $U_3O_8$ by solid-state synthesis. Appropriate quantities of the carefully ground mixtures of $Sr(NO_3)_2$ and $U_3O_8$ to give the desired mol% of SrO and $UO_3$ were heated at 1223 K initially for 12 h. The powder was again ground thoroughly and heated at 1273 K for a further period of 12 h. Cylindrical samples of 2.5 cm in diameter and 1.5–2 cm in height required for the thermal conductivity measurements were prepared by uniaxial cold compaction of the powder followed by sintering in air over the temperature range of 1400–1523 K for 24 h and cooled thereafter. The bulk density of these pellets was found to be in the range of 85–89% of the theoretical value. These uranates were characterized by X-ray diffraction analysis. The patterns were obtained by Ni filtered CuK$\alpha$ radiation and a computer controlled X-ray diffractometer model Philips PW 1710.

The thermal conductivity has been measured in air in the temperature range 300–1100 K by a steady-state axial heat flow comparative apparatus. In this, the sample is inserted between two identical reference materials (Pyroceram-9606 certified against NBS, USA) having the same diameter as that of the sample. An axial heat flow is established through this three-element stack

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by sandwiching it between a heat source and a heat sink and inserting the stack in a guard furnace consisting of four separate heaters. The thermal resistance at the finely polished interfaces of the sample and the reference material is minimized by inserting thin platinum foil between them. This also helps to avoid any reaction between the contacting faces of the sample and the reference. The thermal conductivity of the sample is determined from the thermal conductivity of the reference material and the measured temperature gradients along the sample and reference when steady state is achieved. The accuracy of the measurements has been found to be within ±3%. More details of the experimental apparatus have been described elsewhere [12].

## 3. Results and discussion

In order to get an idea about the nature of the porosity of the samples, their microstructure has been examined by scanning electron microscopy. This examination suggests that the pores are largely spherical in shape and randomly distributed. Therefore, the measured thermal conductivity values are corrected for porosity, using the following simplified equation [13]

$$\lambda = \lambda_0(1 - P)^{3/2}, \tag{1}$$

where $\lambda$ is the measured thermal conductivity, $P$ is the fractional porosity and $\lambda_0$ is the conductivity corresponding to zero porosity. The corrected thermal conductivity is plotted as a function of temperature in Fig. 1. The porosity-corrected thermal conductivity of $UO_2$ and $U_3O_8$ is also included in the figure for comparison. The present measurements show that the conductivities of all these uranates decrease monotonically with increasing temperature in the investigated range. It is noted that the thermal conductivities of all these uranates are lower than that of $UO_2$ in the temperature range up to 1100 K [14]. Among these uranates $Sr_3UO_6$ shows the maximum thermal conductivity value and $SrU_4O_{12.8}$ the minimum. It is interesting to note in this context that the reported variation of the thermal conductivity for $Na_3UO_4$ [15,16] closely matches with that for $SrU_4O_{12.8}$ in the same temperature range. Fig. 2 gives the variation of conductivity of strontium uranates as a function of mol% of SrO content on the SrO–$UO_3$ tie line at three different temperatures. In all these cases it is observed that the conductivity increases with increase of

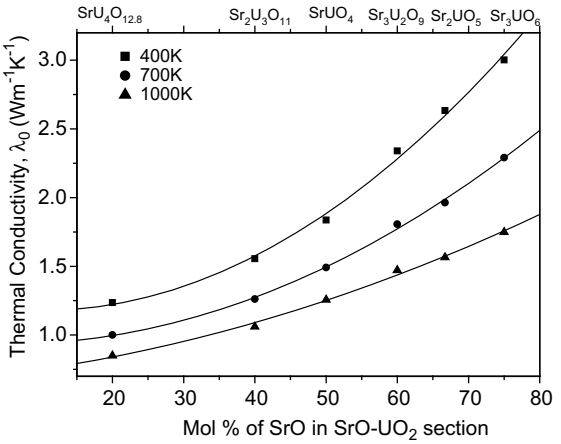


Fig. 2. Variation of the thermal conductivity of strontium uranates versus mol% of strontia content in the SrO–$UO_3$ section at three different temperatures.

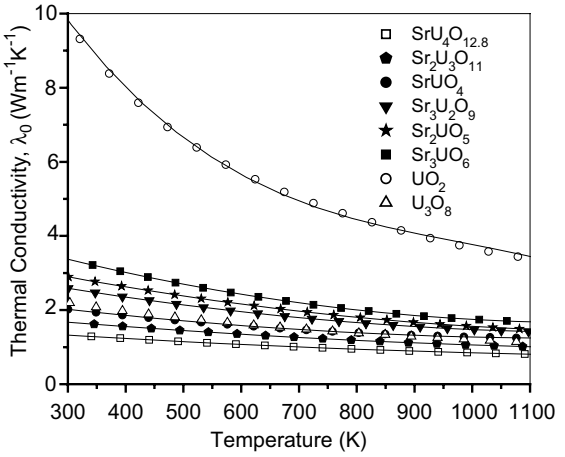


Fig. 1. Thermal conductivity corrected to 100% theoretical density of strontium uranates along with $UO_2$ [14] and $U_3O_8$ [18] as a function of temperature.

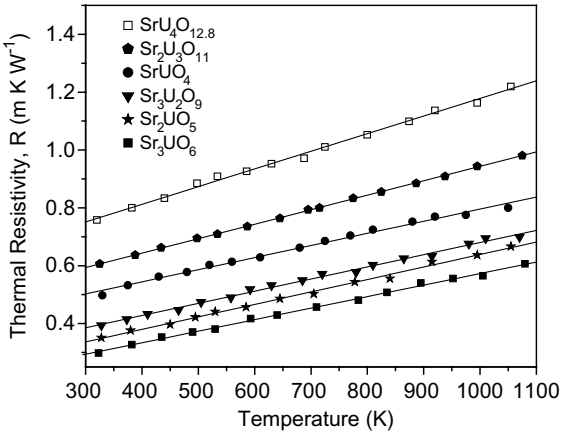


Fig. 3. Thermal resistivity of strontium uranates as a function of temperature. The solid line is determined by fitting the thermal conductivity data to the relation $R = 1/\lambda = A + BT$ using the least-squares method.

Table 1
Composition and observed $A$ and $B$ values of strontium uranates along with those of $U_3O_8$ and $UO_2$

| Compound | Composition (mol%) | | $A$ (m K W$^{-1}$) $\times 10^{-1}$ | $B$ (m W$^{-4}$) $\times 10^{-4}$ | Crystal structure | Ref. |
|---|---|---|---|---|---|---|
| | SrO | $UO_3$ | | | | |
| $SrU_4O_{12.8}$ | 20 | 80 | 5.68 | 6.10 | Monoclinic | [1] |
| $Sr_2U_3O_{11}$ | 40 | 60 | 4.43 | 5.00 | Triclinic | [1] |
| $SrUO_4$ | 50 | 50 | 3.77 | 4.19 | Orthorhombic | [3] |
| $Sr_3U_2O_9$ | 60 | 40 | 2.59 | 4.21 | Orthorhombic | [3] |
| $Sr_2UO_5$ | 66.7 | 33.3 | 2.07 | 4.32 | Monoclinic | [7] |
| $Sr_3UO_6$ | 75 | 25 | 1.74 | 3.98 | Monoclinic | [6] |
| $U_3O_8$ | | | 2.93 | 5.39 | Orthorhombic | [18] |
| $UO_2$ | | | 0.29 | 2.414 | Cubic | [14] |

strontium and the difference is higher at lower temperatures.

As in the case of typical ceramic oxides, the temperature dependence of the thermal resistivity ($R$), which is the reciprocal of the thermal conductivity ($\lambda$), of these uranates can be described by the following equation:

$$R = 1/\lambda = A + BT, \tag{2}$$

where $T$ is the absolute temperature and $A$ and $B$ are constants, which can be obtained from the least-squares fitting of the experimental data. The linear variation of resistivity with temperature of these uranates is shown in Fig. 3. The fitted values of $A$ and $B$ are given in Table 1 along with mol% of strontium oxide in the SrO–$UO_3$ section and their structure along with that of $U_3O_8$ and $UO_2$ for comparison.

The observed linear variation of the thermal resistivity with temperature reveals that, in the temperature range under investigation, the heat conduction is predominantly due to phonon scattering [17]. Accordingly, $A$, the first term in Eq. (2), represents the defect thermal resistivity. This results from the phonon interactions with lattice imperfections, impurities, isotopic or other mass differences as well as bulk defects such as grain boundaries in the samples. The second term namely $BT$, represents the intrinsic lattice thermal resistivity caused by phonon–phonon scattering interactions. It is evident from Fig. 1 that the thermal conductivity of these uranates increases with strontium concentration. In the case of $UO_2$ the values of $A$ and $B$ are found to be $2.97\times10^{-2}$ m K W$^{-1}$ and $2.414\times10^{-4}$ m W$^{-1}$, respectively [14]. The crystal structure of $UO_2$ is fcc whereas the strontium uranates are monoclinic, triclinic or orthorhombic making it difficult to compare the thermal conductivity behavior on the basis of structural differences. However, $SrUO_4$ and $Sr_3U_2O_9$ are orthorhombic and a comparison of $A$ and $B$ values reveals that the $B$ term resulting from the intrinsic phonon–phonon interaction process is almost the same. It is to be noted that a similar type of thermal conductivity behavior has been observed in the case of orthorhombic $\alpha$-$U_3O_8$ with $A = 2.93 \times 10^{-1}$ m K W$^{-1}$ and $B = 5.39 \times 10^{-4}$ m W$^{-1}$ [18]. However, a generalization of numerical values of these constants for a given crystal system is not possible since these constants depend on various factors like atomic volume in the crystal cell, Debye temperature, phonon velocity, the number of atoms in the unit cell, sum of the cross sections of all the phonon-defect scattering centers etc. [19,20].

## 4. Conclusions

The thermal conductivity of these oxides is found decrease with increasing of temperature in the entire range of measurement. The thermal conductivity values are found to increase with increasing value of SrO/$UO_3$ ratio. The thermal conductivity of strontium uranates is 2–3 times lower than that of $UO_2$ and their values are comparable to $U_3O_8$ and $Na_3UO_4$ in the measured temperature range. The observed behavior of the thermal conductivity of these uranates is due to the phonon mode of heat conduction.

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