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Thermal expansion studies on $UMoO_5$, $UMoO_6$, $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$

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ABSTRACT

In the present work, thermal expansion behavior of lower valent sodium uranium molybdates, i.e., $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ were studied under vacuum in the temperature range of 298–873 K using high temperature X-ray diffractometry (HTXRD). Expansion behaviors of $UMoO_5$ and $UMoO_6$ were also studied in vacuum from 298 to 873 K and 773 K, respectively. $UMoO_5$ was synthesized by reacting UO_2 with MoO_3 in equi-molar proportion in evacuated sealed quartz ampoule at 1173 K for 14 h. $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ were prepared by reacting $UMoO_5$ and MoO_3 with 1 and 2 moles of Na_2MoO_4, respectively, at 873 K in evacuated sealed quartz ampoule. XRD data of $UMoO_5$ and $UMoO_6$ were indexed on orthorhombic and monoclinic systems, respectively, whereas, the data of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ were indexed on tetragonal system. The lattice parameters and cell volume of all the four compounds, fit into polynomial expression with respect to temperature, showed positive thermal expansion (PTE) up to 873 K.

1. Introduction

The extraordinary heat transfer properties and the high melting points of liquid metals make them attractive reactor coolants for both thermal and fast reactors. Liquid sodium and eutectic mixtures of sodium and potassium have been used extensively as coolant in nuclear reactors. $(U,Pu)O_2$ is recommended as a fuel for fast breeder reactors (FBR)s which use liquid sodium as coolant. The behavior of solid fission products in irradiated oxide fuel has a strong effect on the availability of oxygen that influences fuel swelling and thermal properties such as melting point, thermal conductivity, thermal expansion, etc. [1,2]. Among a number of solid fission products, molybdenum of over 20% fission yield, exists in both the elemental and oxygen compounds form. However, almost half of all the molybdenum exists in the form of mixed oxides with uranium, the fuel element, as both the elements have similar electronic properties [3]. Also, the operation of defective uranium–plutonium oxide pins in the reactors may results in chemical reactions between the fuel – coolant and fuel – fission products. After pin failure, under favorable oxygen potential and temperature the oxide fuel along with high yield fission molybdenum can come in contact and interact with coolant to form ternary and polynary uranium compounds. The formation of Na_3UO_4 or $Na_3(U,Pu)O_4$ one of the dominant products has unfavorable mechanical, thermal and chemical properties as this compound has low density leads to increase in fuel volume and results in expansion of fuel pin defects [2]. Also such type of reactions are oxygen consuming reactions and can led to change the O/M of the fuel and ultimately the behavior of the fuel. Thus study of the formation and thermal stability of different sodium or potassium actinide molybdates becomes mandatory.

The synthesis, characterization and structural properties of various compounds in the alkali metal–actinide–molybdenum–oxygen system have been studied by many investigators [4–11]. Na–Mo–O [12–14], Na–U–O [15] and Na–U(VI)–Mo–O [16] systems are well characterized by many workers by studying the mechanical, thermal and chemical properties of various compounds in these systems. The thermal expansion behavior of Na_2MoO_4, $Na_2Mo_2O_7$ and $Na_2Mo_4O_{13}$ was investigated by Singh et al. [14] using differential thermal analysis and high temperature X-ray diffraction techniques. Dahale et al. [17,18] have reported structural and thermodynamic studies on the sodium–actinide–molybdenum–oxygen system with general formula $Na_2X(MoO_4)_3$ and $Na_4X(MoO_4)_4$, i.e. (X = U, Th and Pu), using X-ray powder diffraction and thermal analysis techniques. Recently, thermal expansion data of $Th(MoO_4)_2$, $Na_2Th(MoO_4)_3$ and $Na_4Th(MoO_4)_4$ compounds have been reported by Meera Keskar et al. [19], where all the three compounds showed positive thermal expansion from room temperature to 1123 K.

As no information is available on the thermal expansion behavior of the compounds in Na–U(IV)–Mo–O system, which may form during the operation of defective oxide fuel pins, the present work on the thermal expansion studies of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ have been undertaken by means of high temperature X-ray diffractometry, in the temperature range from ambient to 873 K under vacuum.

Though magnetic susceptibility measurement, calorimetric studies, enthalpy measurement, phase diagram and structural studies of $UMoO_5$ have already reported [3,20–23] information

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on the thermal expansion data of the same is not available in the literature. Hence, along with $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ we report here the thermal expansion data of $UMoO_5$ and $UMoO_6$, the oxidized product phase obtained by heating $UMoO_5$ in air at 1173 K, using HTXRD in the temperature range from ambient to 873 and 773 K, respectively.

2. Experimental

2.1. Sample preparation

$UO_{2.00}$ (Reactor grade) and MoO_3 (Analytical Reagent grade) were used as starting materials for the preparation of $UMoO_5$. $UO_{2.00}$ was prepared by reducing uranium oxide in Ar-7% H_2 atmosphere at 1123 K for 4–5 h. $UMoO_5$ was synthesized by reacting $UO_{2.00}$ and MoO_3 in equi-molar ratio in evacuated sealed quartz ampoule at 1173 K for 14 h. $UMoO_6$ was obtained by heating a mixture of UO_2 and MoO_3 in equi-molar proportion in a platinum boat, at 1073 K, for 40 h. $UMoO_5$ when heated in air at 1173 K for 8–10 h also confirmed the formation of $UMoO_6$. Synthesis of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ is explained in detail in the earlier work [17,18]. Formation of all the product phases was confirmed by the comparison of their X-ray powder diffraction patterns, with those reported in the literature [23,24,18].

2.2. Instrumental analysis

Instrumental techniques regarding characterization of various compounds using XRD and high temperature XRD (HTXRD) for thermal expansion measurements are similar to the earlier work reported by Singh et al. [14,19]. Before collecting the high temperature data, to check the thermal stability of $UMoO_5$ and $UMoO_6$, thermograms of both the compounds were recorded on a Mettler thermoanalyzer, recording both Thermogravimetric (TG) and differential thermal analysis (DTA) curves simultaneously. The samples were heated in alumina cups at the heating rate of 10 K/min up to 1173 K in a flowing stream of dry air and as well as in helium atmosphere. Thermal stabilities of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ in air as well as in helium atmosphere have been studied and reported in the previous work [18]. The refined lattice parameters, obtained within an accuracy of ±0.0005 nm, were calculated by the method of least squares using a computer program by Wadhawan [25].

3. Results and discussion

3.1. Thermal studies of $UMoO_5$ and $UMoO_6$

Since information on the thermal stability of $UMoO_5$ is not available, the same was studied in helium atmosphere as well as in air by heating the sample in a thermoanalyser.

$UMoO_5$, when heated in helium atmosphere up to 1173 K, did not show either weight change in the TG curve or any peak in the DTA curve, indicating the thermal stability of the compound. XRD patterns of the compound at room temperature and after heating at 1173 K were identical, confirming the stability of the compound in inert atmosphere.

When heated in air, TG curve of $UMoO_5$ showed the weight gain in two equal steps at 693–923 K and 923–1173 K, accompanied with corresponding exothermic peaks at 893 and 973 K, respectively. To characterize the intermediate phase formed during the oxidation of $UMoO_5$, further work needs to be carried out. The end product formed at 1173 K was identified as $UMoO_6$, the formation of which was confirmed by XRD and weight gain calculation. TG and DTA curves obtained during the heating of $UMoO_5$ in air are shown in Fig. 1.

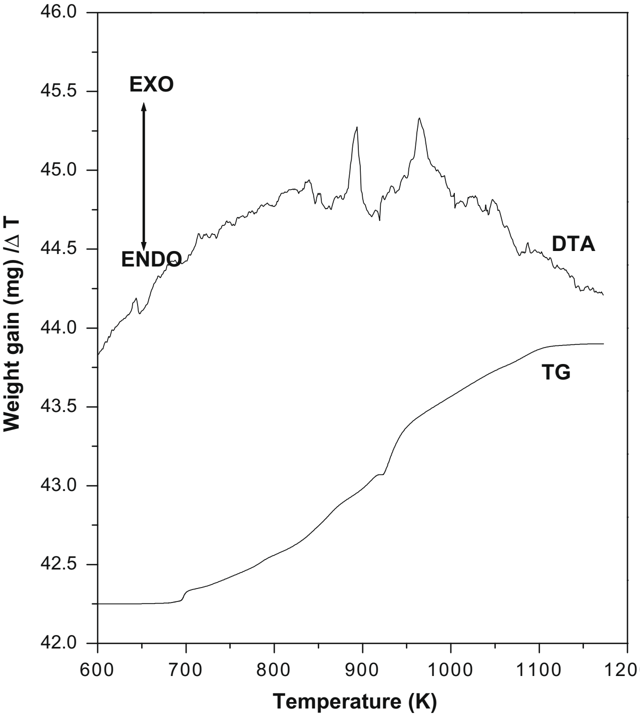

Fig. 1. TG and DTA curves for $UMoO_5$, heated in air atmosphere.

$UMoO_6$, when heated in helium atmosphere showed the thermal stability of compound up to 1073 K whereas when heated in air, started decomposing above 1123 K, indicating slow weight loss above 1123 K.

3.2. Thermal expansion studies of $UMoO_5$ and $UMoO_6$

Room temperature XRD data of $UMoO_5$ was indexed on the orthorhombic system with the refined lattice parameters $a = 0.7352(1)$ nm, $b = 1.2756(3)$ nm and $c = 0.4126(1)$ nm, which are comparable with the reported cell parameters [22]. The observed density determined by a pyknometric method using carbon tetrachloride as solvent ($\rho_{(obs)} = 7.03$ g/cm^3), was in agreement with the X-ray density ($\rho_{(cal)} = 7.08$ g/cm^3). The room temperature XRD data of $UMoO_6$ was indexed on the monoclinic system with the lattice parameters $a = 0.7193(4)$ nm, $b = 0.5467(3)$ nm, $c = 1.3610(13)$ nm and $\beta = 104.7(2)$ which are comparable with those reported in literature [24].

$UMoO_5$ was heated up to 1173 K in vacuum in high temperature chamber. It was observed that above 873 K, apart from the shift in the X-ray line positions to lower 2θ, XRD pattern started showing additional lines of UO_2 indicating the slow decomposition of the compound. Thus to calculate the thermal expansion coefficient of $UMoO_5$, HTXRD data of the compound was collected from ambient to 873 K. Similarly, $UMoO_6$ also when heated in vacuum started showing the additional lines above 773 K and thus thermal expansion data was collected up to 773 K only.

The variation of lattice parameters a, b and c and volume as a function of temperature from 298 to 873 and 773 K for $UMoO_5$ and $UMoO_6$, respectively, are shown in Figs. 2 and 3. As seen from Figs. 2 and 3, both the compounds show increase of lattice parameters and cell volume with increase in temperature through out. Percentage expansion of lattice parameters and cell volume was calculated using the formula

$$\text{Expansion}(\%) = \frac{a_t - a_{298}}{a_{298}} \times 100$$

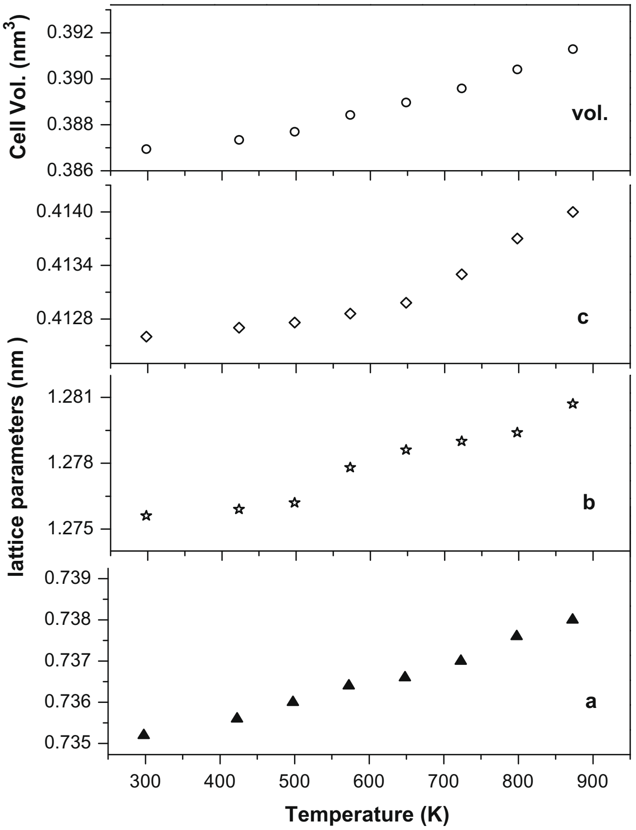

Fig. 2. Variation of lattice parameters and cell volume with temperature for $UMoO_5$.

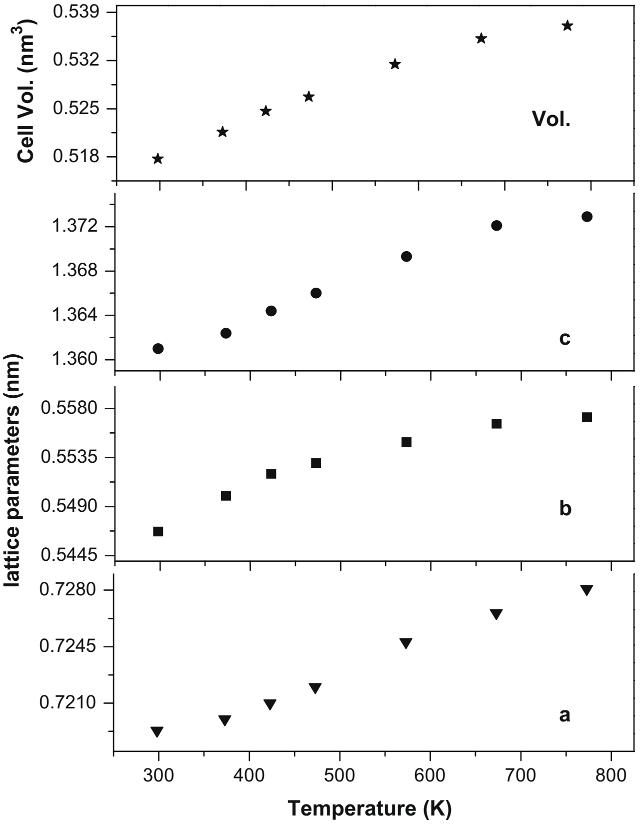

Fig. 3. Variation of lattice parameters and cell volume with temperature for $UMoO_6$.

where a_t represents the lattice parameter or volume at any temperature T and a_{298}, at room temperature.

The percentage expansion values of variation of lattice parameters a, b and c of $UMoO_5$ and $UMoO_6$ were fitted to third order polynomial equations of the form $A + B_1T + B_2T^2 + B_3T^3$, where A, B_1, B_2 and B_3 are constants and T denotes the absolute temperature. The equations for a, b, c and cell volumes for $UMoO_5$ and $UMoO_6$ are given below:

$UMoO_5$:

$$a\,(\mathrm{nm}) = 0.7340 + 4.1947 \times 10^{-6}T - 2.0857 \times 10^{-9}T^2 + 2.8607 \times 10^{-12}T^3 \quad (1)$$

$$b\,(\mathrm{nm}) = 1.2795 - 2.9325 \times 10^{-5}T + 6.4020 \times 10^{-8}T^2 - 3.3365 \times 10^{-11}T^3 \quad (2)$$

$$c\,(\mathrm{nm}) = 0.4125 + 6.3890 \times 10^{-7}T - 2.7197 \times 10^{-9}T^2 + 4.5235 \times 10^{-12}T^3 \quad (3)$$

$$\mathrm{Vol.}\,(\mathrm{nm})^3 = 0.3876 - 6.8524 \times 10^{-6}T + 1.6941 \times 10^{-8}T^2 - 4.8965 \times 10^{-12}T^3 \quad (4)$$

$UMoO_6$:

$$a\,(\mathrm{nm}) = 0.7284 - 7.6591 \times 10^{-5}T + 1.8952 \times 10^{-7}T^2 - 1.177 \times 10^{-10}T^3 \quad (5)$$

$$b\,(\mathrm{nm}) = 0.5223 + 1.1976 \times 10^{-4}T - 1.4497 \times 10^{-7}T^2 + 6.2894 \times 10^{-11}T^3 \quad (6)$$

$$c\,(\mathrm{nm}) = 1.3692 - 8.7230 \times 10^{-5}T + 2.4942 \times 10^{-7}T^2 - 1.6877 \times 10^{-10}T^3 \quad (7)$$

$$\mathrm{Vol.}\,(\mathrm{nm})^3 = 0.5052 + 2.4113 \times 10^{-5}T + 8.3952 \times 10^{-8}T^2 - 7.9834 \times 10^{-11}T^3 \quad (8)$$

The thermal expansion coefficient of a, i.e., α_a was obtained by using the relation

$$\alpha_a = \frac{\delta a_T}{\delta_T} \times \frac{1}{a_{298}} \quad (9)$$

where $(\delta a_T/\delta_T)$ is the temperature derivative of the lattice parameter a and a_{298} is room temperature lattice parameter. Similarly, α_b, α_c and volume expansion coefficient α_v were calculated by differentiating respective equations using the formula given in Eq. (9). The values of average coefficients of thermal expansion of lattice parameters and cell volume of $UMoO_5$ and $UMoO_6$ in the temperature range 298–873 and 298–773 K, respectively, are given in Table 1.

3.3. Thermal expansion studies of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$

Thermogravimetric studies of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ in helium atmosphere reveled both the compounds are thermally stable up to 1023 K [18]. But, when both the compounds were heated in vacuum up to 1023 K, XRD patterns showed additional lines above 873 K and thus high temperature data was collected from room temperature to 873 K. Room temperature XRD data of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ was indexed on tetragonal system with refined lattice parameters $a = 0.5276$ nm, $c = 1.155(8)$ nm and $a = 1.1320$ (1) nm and 1.1861(11) nm, respectively.

The variations of lattice parameters and cell volume of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ with temperature in the range of 298–873 K are shown in Figs. 4 and 5, respectively. As observed in both the figures the lattice parameters as well as cell volume of the compounds showed increase with increase in temperature. The lattice parameters and cell volume of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ were fitted to third order polynomial expressions which are given below:

Table 1
The coefficient of average linear and volume thermal expansion of $UMoO_5$, $UMoO_6$, $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$.

Compound	Temperature range (K)	Average thermal expansion coefficient linear	
		Linear (10^{-6} K^{-1})	Volume (10^{-6} K^{-1})
$UMoO_5$	298–873	$\alpha_a = 5.726$, $\alpha_b = 5.201$, $\alpha_c = 3.432$	$\alpha_v = 15.35$
$UMoO_6$	298–773	$\alpha_a = 22.326$, $\alpha_b = 54.453$, $\alpha_c = 19.501$	$\alpha_v = 95.70$
$Na_2U(MoO_4)_3$	298–873	$\alpha_a = 7.783$, $\alpha_c = 14.423$	$\alpha_v = 30.08$
$Na_4U(MoO_4)_4$	298–873	$\alpha_a = 14.631$, $\alpha_c = 20.345$	$\alpha_v = 51.51$

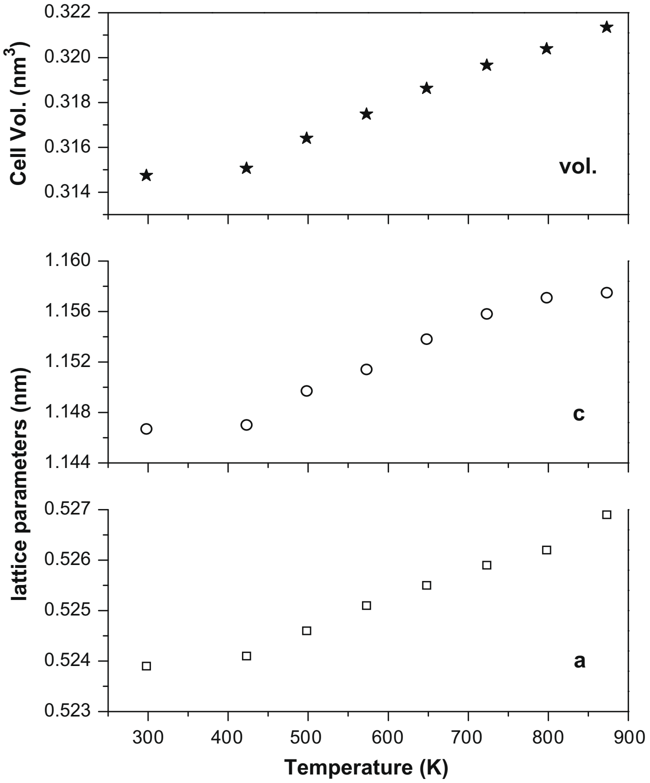

Fig. 4. Variation of lattice parameters and cell volume with temperature for $Na_2U(MoO_4)_3$.

$Na_2U(MoO_4)_3$:

$$a\,(\text{nm}) = 0.5243 - 5.7193 \times 10^{-6}T + 1.6515 \times 10^{-8}T^2 - 7.6084 \times 10^{-12}T^3 \quad (10)$$

$$c\,(\text{nm}) = 1.1651 - 1.2986 \times 10^{-4}T + 2.7350 \times 10^{-7}T^2 - 1.5445 \times 10^{-10}T^3 \quad (11)$$

$$\text{Vol.}\,(\text{nm})^3 = 0.3204 - 4.3194 \times 10^{-5}T + 9.6041 \times 10^{-8}T^2 - 5.2062 \times 10^{-11}T^3 \quad (12)$$

$Na_4U(MoO_4)_4$:

$$a\,(\text{nm}) = 1.1311 - 7.3695 \times 10^{-6}T + 4.1047 \times 10^{-8}T^2 - 2.0842 \times 10^{-13}T^3 \quad (13)$$

$$c\,(\text{nm}) = 1.1776 + 2.5460 \times 10^{-5}T + 1.1436 \times 10^{-8}T^2 - 1.2208 \times 10^{-12}T^3 \quad (14)$$

$$\text{Vol.}\,(\text{nm})^3 = 1.5161 - 4.1848 \times 10^{-5}T + 2.2572 \times 10^{-8}T^2 - 1.2975 \times 10^{-11}T^3 \quad (15)$$

The average thermal expansion coefficients of lattice parameters and cell volume for $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ were calculated and are included in Table 1.

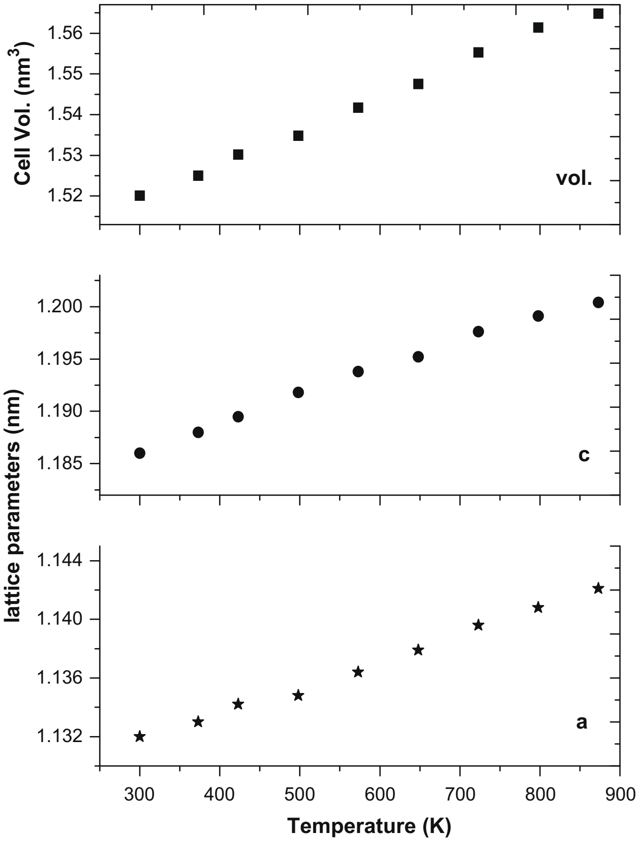

Fig. 5. Variation of lattice parameters and cell volume with temperature for $Na_4U(MoO_4)_4$.

4. Conclusions

$UMoO_5$, when heated in thermoanalyser in helium atmosphere indicated the thermal stability of the compound up to 1173 K, where as in air, it oxidized between 693 and 1173 K to form $UMoO_6$, which was confirmed by weight gain calculation and XRD. Lattice parameters and cell volume of $UMoO_5$ and $UMoO_6$, increased with increase in temperature from ambient to 873 and 773 K, respectively. The average volume expansion coefficient of $UMoO_5$ and $UMoO_6$ were found to be 15.35×10^{-6} K^{-1} and 95.70×10^{-6} K^{-1}, respectively. Similarly, the lattice parameters and cell volume of $Na_2U(MoO_4)_3$ and $Na_4U(MoO_4)_4$ increased progressively with increase in temperature from 298 to 873 K giving average volume expansion coefficient 30.08×10^{-6} K^{-1} and 51.51×10^{-6} K^{-1}, respectively.

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