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Stability of Dy_6UO_{12} under high pressure and high temperature

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ABSTRACT

In this paper, results obtained from high pressure-high temperature X-ray diffraction study of Dy_6UO_{12} are reported. X-ray diffraction (XRD) studies at ambient temperature on Dy_6UO_{12} reveals that the rhombohedral structure is stable up to 21.6 GPa. Beyond 21.6 GPa the peaks broaden out substantially indicating emergence of disorder in the system. Bulk modulus and its pressure derivative is 144 GPa and 7.0 respectively. High Pressure and High Temperature (HP-HT) XRD studies up to ~ 11 GPa and ~673 K was carried out using novel combination of membrane cell DAC coupled to a high flux micro-focus X-ray generator. At ambient pressure, thermal expansion coefficient comes out to be $14.5 \times 10^{-6}\ K^{-1}$ at 400 K. Further, at 1 GPa and 2.6 GPa the thermal expansion coefficients are $21.4 \times 10^{-6}\ K^{-1}$ and $32 \times 10^{-6}\ K^{-1}$ respectively, in the temperature range ~293–673 K. The thermal expansion coefficient shows an increasing trend with pressure.

1. Introduction

Uranate compounds are ternary oxides, where the element uranium is in any one of the following oxidation states-+4, +5 or +6. Typical chemical formula of uranate is $R_xU_yO_z$, where R represents a cation. Rare earth uranates-RE_6UO_{12} (RE = Rare earth) type of compounds exist in rhombohedral structure at ambient temperature and are studied because of their importance to nuclear industry. Uranates are compounds that are likely to be formed during fuel irradiation in nuclear reactors, wherein U or U–Pu oxides are used as fuels because UO_2 shows substantial solubility with the rare earth oxides due to their similar ionic radii. Some of these uranate compounds act as neutron poison which is useful to control nuclear reactivity [1]. Due to the interest in these systems many RE_6UO_{12} type compounds are synthesized and their crystal structures are determined [2–5]. Their high temperature properties have already been reported in the literature [4,5]. High temperature x-ray diffraction (XRD) studies show positive thermal expansion coefficient for all RE_6UO_{12} (RE: La, Gd, Nd, Sm, Tb and Dy). La_6UO_{12} shows the largest thermal expansion as compared to other RE_6UO_{12} compounds. The lattice thermal expansion coefficients increase with increasing temperature and expansion is more along the *a*-axis compared to the *c*-axis which is attributed to lesser density of atoms along the *a*-axis. Also, it is reported that the heat capacity increases with increasing temperature [5–8].

There are very few reports of HP-HT studies with laboratory based X-ray source. Earlier, HP-HT study with Paris–Edinburg type DAC has been reported [9]. In the present paper we report *in-situ* high pressure & high pressure-high temperature (HP-HT) structural stability studies on Dy_6UO_{12}.

2. Experimental methods

2.1. Preparation of materials

The sample was prepared by using urea–combustion method [3,4]. In this method, nitrate solutions of dysprosium (Dy) and uranium(U) were mixed in stoichiometric proportion (U: Dy:: 1:6). The solution was heated on a hot plate (~1000 °C) and urea crystals were added to hot solution slowly. Higher than the stoichiometric amount of urea was added to the solution to enhance the reaction rate. The uranyl-nitrate urea gel burned with flame/smouldered leading to the formation of a floppy mass on heating. The details of the synthesis of Dy_6UO_{12} are reported elsewhere [4]. Dy_6UO_{12} was confirmed to have formed in single phase with rhombohedral structure having a = 9.9806 Å and c = 9.4403 Å which is in

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agreement with the literature values [3].

2.2. High pressure study at ambient temperature

High Pressure X-ray Diffraction (HPXRD) experiment on the polycrystalline sample of Dy_6UO_{12} was carried out using a Mao-Bell type Diamond Anvil Cell (DAC). The diamond anvils are having culet diameter of ~500 μm. Stainless steel gasket of thickness 60 μm (indented region) and hole size of dia~250 μm was used in the high pressure experiment. The experiments were carried out at synchrotron x-ray source at BL-11, Indus-2, RRCAT, Indore. XRD patterns were collected for 30 min, at each pressure, in transmission geometry. The diffraction data was collected using mar345 IP detector and the 2D data obtained was analysed using Fit2D software [10]. AIDS83 software was used to get the lattice parameters at various pressures. The operating parameters of the beamline were 2.5 GeV and 150 mA. A wavelength of 0.6202 Å was selected for high pressure experiments. Powder sample was first pelletized and a chip of dia. ~100 μm of Dy_6UO_{12} was cut. This chip was loaded into a stainless steel (SS) gasket hole. Silver was used as a pressure calibrant as its peaks do not overlap with sample peaks. Methanol: Ethanol: Water mixture in the ratio of 16:3:1 was used to obtain hydrostatic pressure environment inside the sample chamber of DAC. Dy_6UO_{12} was pressurized in steps up to 28 GPa to study the compressibility behaviour at ambient temperature. Pressure was dropped slowly in steps and diffraction patterns were taken after relaxation time of 30 min at each step (reverse cycle).

2.3. High pressure at 373–673 K

Diacell HeliosDAC (of M/s Almax-Easy Lab, UK) was used for generating simultaneously high pressure and high temperature. It is designed to achieve HP-HT conditions of 25 GPa and 1273 K simultaneously. Resistive heating method was employed for heating the sample. Heater in circular form was placed inside DAC around the diamond anvils. Temperature is estimated using thermocouple placed in contact with cylinder diamond. As sample and the thermocouple were spatially separated, we had calibrated the temperature reading of thermocouple with equation of state of NaCl and KCl. This was further verified by measuring the melting point of NH_4Cl and AgCl [11].

We had carried out High Pressure-High Temperature (HP-HT) X-ray diffraction studies using novel custom designed-combination of membrane cell DAC coupled to a high flux micro-focus X-ray machine (of M/s XENOCS, France) [11]. Molybdenum target was used which results in X-ray of wavelength 0.711 Å. The X-ray multi-layered mirror optics focuses intense monochromatic beam at the focal spot. The FWHM of the focused beam is~ 130 μm and the flux is ~15.5×10^6 photon/sec at 50 kV and 1 mA.

For HP-HT XRD experiments powdered sample was pelletized and a small chip of dia ~150 μm was cut from the pellet. The sample along with NaCl was loaded in 70 μm thick SS gasket, having 250 μm through hole which was mounted on the cylinder of the DAC. The culet diameter of the diamonds was 600 μm. Since NaCl has high compressibility it functions as pressure transmitting medium. Also, NaCl functions as pressure calibrant and pressure was estimated using EOS of NaCl. The equation of state and thermal expansion behaviour of NaCl at HP-HT is discussed extensively in the literature [12–14]. To increase pressure in membrane DAC, helium gas was supplied to the membrane of the DAC in a controlled fashion using a pressure controller. During the heating of the sample, gas mixture of argon (inert) and 2% hydrogen (reducing) was passed at a very low flow rate of ~15–18 sccm in order to avoid graphitization of the diamond as well as tarnishing of the interior surface of DAC. Mica sheet was fixed on both the sides of DAC, along the X-ray path to create insulation of the hot zone.

HP-HT experiments were carried out up to ~11 GPa and ~673 K in the temperature interval of ~100 K. XRD patterns were collected for 30 min with a relaxation time of 30 min between successive temperature intervals. Finally, data obtained from mar345 IP detector was analysed using Fit2D image processing software. Least square analysis using AIDS83 were carried out to estimate lattice parameters at various pressures and temperatures.

3. Results and discussion

3.1. High pressure study at ambient temperature

High pressure x-ray diffraction pattern on Dy_6UO_{12} up to 28 GPa is shown in Fig. 1. The diffraction peaks do not show any noticeable change apart from continuous decrease in the volume of the unit cell with pressure. The HPXRD data up to 21.6 GPa, were fitted to the rhombohedral structure (Space Group: R-3) and lattice parameter values were obtained using AIDS83 program. Lattice parameters *a* and *c*, decrease in a linear fashion with increasing pressure and these are shown in Fig. 2. The *c* axis compresses more readily under these conditions and as a consequence the ratio *c*/*a* decreases by 0.75% over the pressure range of 21.6 GPa. This indicates that *a* axis is more rigid as compared to *c* axis. Crystal structure of Dy_6UO_{12} can be visualized using polyhedra representation wherein, two UO_6 polyhedra are separated by two DyO_6 polyhedra along the *c* axis. The two DyO_6 polyhedra share edges, whereas, UO_6 and DyO_6 polyhedra are linked at one corner [Fig. 3]. Corner sharing is considered to be more stable as compared to the edge sharing by Pauling's rule for ionic structures [15]. Hence, the compression along the edge sharing DyO_6 polyhedra is more at high pressures, leading to the observed trends in the lattice parameter variation as a function of pressure.

Variation of lattice parameter and volume as a function of pressure is given in Table 1. Pressure-volume data up to 21.6 GPa, fitted to Birch–Murnaghan equation of state, yields bulk modulus and its pressure derivative to be 144 (10) GPa and 7.0 (1.8) respectively (Fig. 4) [16]. Beyond 21.6 GPa, peaks broaden significantly with reduction in intensity. Also, several sample peaks such as- (003)/(211), (300), (122)/(113) merge, due to which peak positions at these pressures could not be determined. The broadening

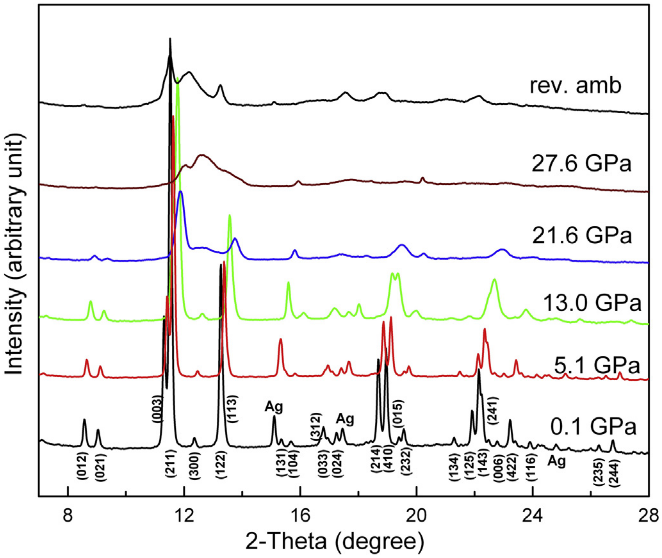

Fig. 1. High pressure x-ray diffraction patterns at ambient temperature.