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THERMAL EXPANSION STUDIES ON SOME RARE-EARTH PYROHAFNATES BY HIGH TEMPERATURE X-RAY POWDER DIFFRACTOMETRY

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ABSTRACT

Pyrohafnates of rare-earth elements have potential applications as neutron absorber materials in nuclear technology. These compounds have the general formula $R_2Hf_2O_7$, where R represents the rare-earth element. The percentage thermal expansion of lanthanum, europium and gadolinium pyrohafnates has been measured from room temperature to 1473 K by X-ray powder diffractometry.

INTRODUCTION

Rare-earth elements and hafnium find extensive applications as neutron absorber materials in nuclear technology. Rare-earth pyrohafnates of the general formula $R_2Hf_2O_7$ (where R is a rare-earth element) are being considered for control rod applications in nuclear reactors. Spink and Schemel [1] have discussed the feasibility of using these compounds as power reactor control rod materials. In this context it is important to study the thermophysical properties, such as thermal conductivity and thermal expansion, of these compounds. Recently, the thermal diffusivity and conductivity of lanthanum, europium and gadolinium pyrohafnates have been reported from our laboratory [2]. This paper describes the thermal expansion behaviour of the above three compounds in the temperature range 298–1473 K.

The crystal structure of the $R_2Hf_2O_7$ compound could be of the pyrochlore or the closely related fluorite type, depending on the ionic radius (r) of the rare-earth element [3]. From La through Gd the structure is pyrochlore, and it is stated empirically that the pyrochlore type phase can be formed only if the ratio $r(Hf^{4+}):r(R^{3+})$ is greater than 1.22. The unit cell of

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the pyrochlore structure is face-centred cubic, like the fluorite structure, but with exactly double the cell size of the fluorite [4].

Identification of systems containing the pyrochlore type phase is often difficult, owing to the similarity of the pyrochlore and fluorite structures. The cation sub-lattices of the two structures are identical except for the order present in the pyrochlore. Super-lattice lines due to this ordering can be detected in the X-ray diffraction pattern only when the atomic numbers of the two types of cation are significantly different, as in the case of the light lanthanide elements and hafnium. The differences between the anion sub-arrays of fluorite and pyrochlore are that, in pyrochlore, one-eighth of the anion sites of the fluorite are vacant and six-sevenths of the remaining anions are shifted from their ideal fluorite sites in an orderly manner such that the Hf^{4+} ions are six-coordinated and the R^{3+} ions are eight-coordinated. It is this order present in the cation and anion sub-lattices of the pyrochlore structure that makes its unit cell edge double that of the fluorite cell. In most of these systems, the contribution from the anion sub-lattice to the X-ray diffraction pattern would be small, and the pyrochlore anion array is not greatly different from the fluorite anion sub-array. Unequivocal identification of the type of phase is further complicated by the fact that some pyrochlores are incompletely ordered. Klee and Weitz [5] have found a continuous transition from the ordered pyrochlore to the disordered fluorite structure in the case of the rare earth pyrohafnates in a study using X-ray diffraction and IR spectroscopic techniques. Also, the transition temperature to the disordered state is found to decrease with increasing atomic number of the rare-earth element [3]. Since the solid state reactions involving HfO_2 and R_2O_3 require high temperatures, of the order of 1800 K, the pyrohafnates of heavier rare-earth elements (Eu and Gd, as against La) prepared by this route would form only the partially ordered pyrochlore phase.

EXPERIMENTAL

The pyrohafnates were prepared by heating stoichiometric mixtures of the respective rare-earth sesquioxide and hafnium dioxide at 1773 K for 6 h in a Superkanthal furnace.

A high temperature attachment (HDK1, Rich. Seifert) mounted on an X-ray powder diffractometer (D500, Siemens) was employed in the study. The diffractometer was provided with a diffracted beam monochromator made of a curved graphite crystal. The experimental set-up, its calibration, measurements on standard materials and initial studies using the system have been reported elsewhere [6]. In the high temperature chamber, the sample is mounted as a thin layer on a tungsten strip which can be resistively heated at programmed rates. The temperature of the sample is measured by a Pt–Rh (type S) thermocouple spot welded at the rear of the sample strip. Heating was carried out in flowing argon or helium at low pressure.

Lattice parameters at different temperatures were calculated using the high angle reflections with Cu $K\alpha_1$ in the case of the lanthanum compound and with the weighted average of the $K\alpha$ radiation in the case of the other two compounds. Selected diffraction angles were determined accurately by scanning slowly across the peaks. The approximate lattice parameters calculated from the Miller indices and reflection angles were refined by the method of least squares by using the computer program of Werner [7]. The estimated error in the lattice parameter is of the order of ± 0.0005 Å.

RESULTS AND DISCUSSION

In the X-ray pattern of $La_2Hf_2O_7$, which corresponds to the pyrochlore phase, the background was low and the high angle reflections were well resolved into peaks due to the $K\alpha_1$ and $K\alpha_2$ components of the radiation. In the case of $Eu_2Hf_2O_7$ and $Gd_2Hf_2O_7$, although almost all lines of the pyrochlore phase including the super-lattice reflections were observed, the background level was high and the high angle lines were broad and poorly resolved with respect to the $K\alpha_1$ and $K\alpha_2$ components. This can be considered as the manifestation of the partial disorder expected in the pyrochlore lattice of the europium and gadolinium pyrohafnates synthesised at temperatures around 1800 K [3]. At lower temperatures, prolonged heating for hundreds of hours may be required for refractory compounds like hafnium oxide to react.

The lattice parameter of $La_2Hf_2O_7$ at all temperatures was calculated using the well resolved $K\alpha_1$ reflections from the (12 4 0), (10 6 6) and (12 4 4) planes in the 2θ range 128°–142°. In the case of the other two compounds, the unresolved $K\alpha$ reflections in a lower 2θ region (80°–100°) corresponding to the planes (8 4 0), (8 4 4) and (6 6 6) were used for calculating lattice parameters. Percentage expansion was calculated using the formula

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

where a_T represents the lattice parameter at any temperature T and a_{298} that at the room temperature. The room temperature lattice parameters observed for the compounds, viz., 10.7697 Å ($La_2Hf_2O_7$), 10.5310 Å ($Eu_2Hf_2O_7$) and 10.5162 Å ($Gd_2Hf_2O_7$), are in good agreement with the literature values [5].

The observed variation of percentage expansion of the rare earth pyrohafnates is presented in Fig. 1. The percentage expansion values have also

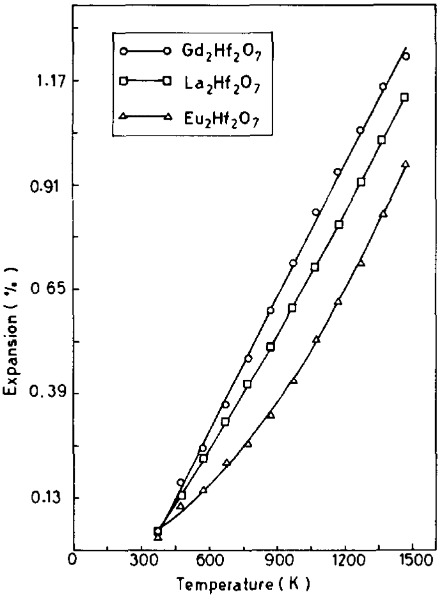

Fig. 1. Variation of the percentage thermal expansion of lanthanum, europium and gadolinium pyrohnafnates with temperature.

been fitted to equations of the form $a + bT + cT^2$, and they are shown below (temperature in K).

$La_2Hf_2O_7$: $-0.2609 + 0.7875 \times 10^{-3}\ T + 0.1064 \times 10^{-6}\ T^2$
$Eu_2Hf_2O_7$: $-0.0435 + 0.1059 \times 10^{-3}\ T + 0.3878 \times 10^{-6}\ T^2$
$Gd_2Hf_2O_7$: $-0.3976 + 1.1822 \times 10^{-3}\ T + 0.0444 \times 10^{-6}\ T^2$

The expansion behaviour of the above three compounds can be seen to be very similar. The expansion of $Eu_2Hf_2O_7$ is found to be the lowest of the three. The values for $La_2Hf_2O_7$ and $Gd_2Hf_2O_7$ are within 10% of each other at higher temperatures and better than 10% at lower temperatures. For any corrrelation to be made between percentage thermal expansion and parameters such as the atomic number or the ionic radius of the rare earth element, data on more compounds of the family are needed.

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