Temperature dependence of density and thermal expansion of oxides of praseodymium and dysprosium in the temperature range 300 to 1000 K

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Abstract: In this communication the variation of density and thermal expansion of oxides of praseodymium and dysprosium with temperature is studied and reported. The gamma ray attenuation technique is employed to carry out the study with a gamma ray densitometer fitted with high temperature furnace designed in our laboratory. The temperature dependent quantities such as linear gamma ray attenuation ($\mu$), density ($\rho$) and the coefficient of linear thermal expansion ($\alpha$) of Pr$_6$O$_{11}$ and Dy$_2$O$_3$ have been fit to a second degree polynomial equation.

Key words: rare earth oxides, thermal expansion, gamma ray attenuation.

1. Introduction
The measurement of thermal expansion of the oxides of rare-earth elements is important for using these oxides as refractory materials. These oxides are used as refractory materials because of high melting temperature and also chemical stability at high temperatures. Application of materials at high temperature needs the data of thermal expansion. On the other hand, the change in physical size of material on heating gives the thermal expansion which enable us to determine the ability of materials to withstand thermal shock. There are various methods for measuring the thermal expansion such as high temperature electrostatic levitation, method of sessile drop, pycnometric method, electromagnetic levitation method, X-ray diffraction, interferometry method and gamma ray attenuation method [1-5]. To study the thermo-physical properties at high temperature the gamma ray attenuation method is advantageous over the other methods because there is no thermal contact of gamma radiation with sample which leads to reducing the thermal losses and eliminates sample and probe compatibility problem. Using the gammaray densitometer thermo physical properties of some alloys and alkali halides were studied in our laboratory [6-15].The results on rare earth oxides by x-ray diffraction method were reported by Stecura and Campbell [16].Thermal expansion of the oxides of Yttrium, Cerium, Samarium, Europium and Dysprosium have been reported [17] from Interferometric method. The objective of this work is to report thermo-physical properties such as linear gamma ray attenuation ($\mu$), density ($\rho$) and the coefficient of linear thermal expansion ($\alpha$) of Pr$_6$O$_{11}$ and Dy$_2$O$_3$.
2. Experimental

A gamma ray densitometer was fabricated in our laboratory as per the design proposed by Drotning [19] to carry out measurements on oxides of praseodymium and dysprosium. The design is shown in fig.1. The gamma ray densitometer coupled with a programmable temperature controlled furnace (PTC) having type K thermocouple was used for making measurements in the range 300–1000 K. To detect the gamma radiation a NaI thallium activated detector was used along a PMT. The pre-amplified signal is fed to a multi-channel analyzer (MCA) for analyzing the required spectrum.

The pellets of oxides of praseodymium and dysprosium powders were prepared by a die set using the hydraulic press. The pellets were mounted firmly on the sample holder and inserted into an air tight quartz tube as shown in fig.2. To measure the exact temperature of the sample a thermo-couple sensor is connected at the site of the sample. This assembly is firmly inserted into the PTC furnace and whole operation is monitored with help of electric panel.

![Fig 1 Gamma ray densitometer](image1)

![Fig 2 Sample holder](image2)

The temperature is programmed in such a way that it is increased by 50 K in every step from 300 K and stabilizes there for a certain length of time. The average value of the gamma ray counts are considered and recorded at every step of temperature before and after the sample in the furnace. The cooling rate varied between 10 K/min from 1000 – 800 K, 6 K/min from 800 – 500 K, 4 K/min from 500 – 400 K, and 2 K/min thereafter up to 300 K. In the present work, all the measurements have been made in the solid phase only. This procedure was repeated until the entire temperature range 1000 – 300 K was covered for the samples. All the measurements of Pr$_6$O$_{11}$ and Dy$_2$O$_3$ are taken in solid phase only.

3. Analysis of data

The fundamental equation for attenuation given by

$$I(T) = I_0(T) \exp[- \mu_m \rho(T) l(T)]$$

(1)

is used in gamma ray attenuation method.

Where $I_0$ and $l$ are the intensities of mono energetic $\gamma$-ray before and after passing through the sample material, $\mu_m$ the mass attenuation coefficient of the sample, $\rho$ the density of the sample and $l$ the thickness of the sample along the beam direction.

From Eq(1) it is clear that any change in the temperature is accompanied by change in density of the material further ensuring the change in intensity. The method suggested by Drotning [19] is employed to study the density and thermal expansion of the materials.

The temperature dependent density to calculate at different temperatures is expressed as

$$\rho(T) = \left[ \frac{1}{\mu_m} \right] \ln \left[ \frac{I_0(T)}{I(T)} \right]$$

(2)

The mean volumetric and linear thermal expansion over a temperature interval $\Delta T = T_2 - T_1$ are
\[ \alpha_\rho = \frac{(\rho_2 - \rho_1)}{\rho_1 \Delta T} \]  \hspace{1cm} (3)

\[ \alpha_l = \frac{(l_2 - l_1)}{l_1 \Delta T} \]  \hspace{1cm} (4)

Where \( \rho_1 = \rho_1(T_1) \), \( \rho_2 = \rho_2(T_2) \), \( l_1 = l(T_1) \), \( l_2 = l(T_2) \)

By multiplying Eq. (3) and (4), we obtain

\[ \Delta T^2 \alpha_\rho \alpha_l = \frac{1}{\rho_1 l_1} (\rho_2 - \rho_1)(l_2 - l_1) \]

\[ \left[ \frac{\rho_2 l_2}{\rho_1 l_1} - 1 \right] - \left[ \frac{\rho_2 - \rho_1}{\rho_1} \right] - [l_2 - l_1] \]  \hspace{1cm} (5)

Here let us express

\[ \left( \frac{\rho_2 l_2}{\rho_1 l_1} \right) - 1 = Z \]  \hspace{1cm} (6)

From Eqs (3), (4), (5) and (6) we have

\[ \Delta T^2 \alpha_\rho \alpha_l = Z - (\Delta T)\alpha_l - (\Delta T)\alpha_\rho \]  \hspace{1cm} (7)

The \( Z \) value can be obtained from measured intensities at different temperatures from

\[ Z = \left( \frac{\rho_2 l_2}{\rho_1 l_1} \right) - 1 = \left\{ \ln \left[ \frac{I_0(T_2)}{I(T_2)} \right] \right\} - 1 \]  \hspace{1cm} (8)

The relation between volumetric thermal expansion and linear thermal expansion for isotropic materials is

\[ \alpha_\rho = -3\alpha_l (1 - 2\alpha_l \Delta T) \]  \hspace{1cm} (9)

From Eq. (7) and Eq. (9)

\[ -3\Delta T^2 \alpha_l^2 (1 - 2\alpha_l \Delta T) = Z - \Delta T\alpha_l (1 - 2\alpha_l \Delta T) \]

Taking \( X = \frac{\Delta l}{l} = \alpha_l \Delta T \)

The above equation becomes

\[ 6X^3 + 3X^2 - 2X - Z = 0 \]  \hspace{1cm} (10)

By substituting the value of \( Z \) in the cubic equation (10), \( X \) may be determined and hence thermal expansion is obtained.

For linear attenuation at different temperatures the following expression is used

\[ \mu_i(T) = \mu_m \rho(T) \]  \hspace{1cm} (11)

The intensities of gamma radiation without sample \( (I_0) \) and with sample \( (I) \) are recorded at every temperature. At temperature \( T_1 \), thickness of the sample \( (l_1) \) is measured and \( \mu_m \) is determined.

Measurements of \( (I) \) and \( (I_0) \) at different temperatures enable the determination of \( Z \) through Eq.(8) and hence \( X \) can be found from the solution of Eq.(10). From the value of \( X \) mean linear thermal expansion (\( \alpha_l \)) can be determined as a function of temperature. All the measurements are
confined to solid phase and the experimental data obtained in the present work have been fit to a least-squares quadratic polynomial of the form

$$\rho(T) = a + bT + cT^2$$

(12)

In this experiment, the intensities \(I_0\) and \(I\) have been obtained for the same time and under the same experimental conditions. Estimated error in these measurements is about 2%.

4. Results and Discussion

The results obtained for the temperature dependence of the linear attenuation coefficient (\(\mu_l\)), density (\(\rho\)), and the coefficient of linear thermal expansion (\(\alpha\)) of Pr\(_6\)O\(_{11}\) and Dy\(_2\)O\(_3\) are summarized in Table 1. The values obtained for coefficient of linear thermal expansion by other workers [16,17] from other methods are also included in Table 1 for comparison.

Table 1: Data of linear gamma ray attenuation coefficient, density and coefficient of linear thermal expansion at various temperatures

| Sample | Present work | Previous work | Present work | Previous work |
|--------|--------------|---------------|--------------|---------------|
|        | Pr\(_6\)O\(_{11}\) | Stecura and Campbell [16] X-ray diffraction | Dy\(_2\)O\(_3\) | Stecura and Campbell [16] X-ray diffraction |
|        | \(\mu_l\) (m\(^{-1}\)) | \(\rho\) (kg m\(^{-3}\)) | \(\alpha\) (x 10\(^{-6}\) K\(^{-1}\)) | \(\mu_l\) (m\(^{-1}\)) | \(\rho\) (kg m\(^{-3}\)) | \(\alpha\) (x 10\(^{-6}\) K\(^{-1}\)) | \(\mu_l\) (m\(^{-1}\)) | \(\rho\) (kg m\(^{-3}\)) | \(\alpha\) (x 10\(^{-6}\) K\(^{-1}\)) |
| T (K)  |                |                | T (K)        |                |                |
| 300    | 53.007         | 6500           | -            | 67.22          | 7800           | -            | 300    | 6.6            |
| 350    | 52.59          | 6449           | 11.1         | 298            | 7762           | 6.85         | 366    | 7              | 371    | 6.84          |
| 400    | 52.54          | 6443           | 11           | 374            | 7756           | 7.01         | 393    | 6.6            |
| 450    | 52.48          | 6435           | 11.06        | 479            | 7750           | 7.15         | 458    | 7.5            | 472    | 7.18          |
| 500    | 52.41          | 6427           | 11.21        | 481            | 7743           | 7.28         | 492    | 7.5            |
| 550    | 52.35          | 6419           | 11.36        | 66.74          | 7736           | 7.4          | 528    | 7.4            | 577    | 7.39          |
| 600    | 52.27          | 6409           | 11.68        | 66.62          | 7730           | 7.5          | 625    | 7.6            |
| 650    | 52.18          | 6399           | 12.05        | 66.56          | 7723           | 7.6          | 699    | 7.6            | 673    | 7.53          |
| 700    | 52.10          | 6388           | 12.38        | 699            | 7715           | 7.78         |
| 750    | 51.99          | 6375           | 12.92        | 66.45          | 7710           | 7.74         | 749    | 7.5            | 775    | 7.65          |
| 800    | 51.88          | 6362           | 13.41        | 793            | 7703           | 7.8          | 819    | 7.8            |
| 850    | 51.76          | 6347           | 14.1         | 66.34          | 7697           | 7.84         | 870    | 7.8            | 873    | 7.76          |
| 900    | 51.63          | 6331           | 14.66        | 898            | 7690           | 7.86         |
| 950    | 51.47          | 6311           | 15.61        | 66.22          | 7683           | 7.92         | 920    | 7.9            | 972    | 7.86          |
| 1000   | 51.31          | 6292           | 16.38        | 999            | 7677           | 7.94         | 1003   | 8              |

The variation of linear attenuation coefficient with temperature, the temperature dependence of density and the temperature dependence of coefficient of linear thermal expansion of Pr\(_6\)O\(_{11}\) and Dy\(_2\)O\(_3\) have been shown in Figs. 3 and 4 respectively.
The linear attenuation coefficient ($\mu_l$) of $\text{Pr}_6\text{O}_{11}$ decreases from a value of $53.007 \text{ m}^{-1}$ at $300 \text{ K}$ to a value of $51.315 \text{ m}^{-1}$. This variation of linear attenuation coefficient with temperature is represented by a non-linear second degree polynomial equation

$$\mu_l(T) = 53.22 + (-1.198 \times 10^{-3})T + (-6.447 \times 10^{-7})T^2$$

The coefficient of temperature dependence of linear attenuation coefficient is $-0.001198 \text{ m}^{-1} \text{ K}^{-1}$.

The density of $\text{Pr}_6\text{O}_{11}$ decreases from a value of $6500 \text{ kg m}^{-3}$ at $300 \text{ K}$ to a value of $6292 \text{ kg m}^{-3}$ at $1000 \text{ K}$, a decrease of about $3.20 \%$. The temperature dependence is a negative non-linear function of temperature and it is represented by non-linear second degree polynomial equation

$$\rho(T) = 6526 + (-0.1469)T + (-7.906 \times 10^{-5})T^2$$

The coefficient of temperature dependence of density is $-0.1469 \text{ kg m}^{-3} \text{ K}^{-1}$.

The thermal expansion increases with temperature and is represented by the equation

$$\Delta l / l(T) = (2.707 \times 10^{-3}) + (-0.002483 \times 10^{-3})T + (1.5925 \times 10^{-8})T^2$$

The coefficient of linear thermal expansion increases with temperature and the results on thermal expansion in the temperature range from $300 – 1000 \text{ K}$ have been analyzed and is represented by a non-linear second degree polynomial equation

$$\alpha(T) = 12.88 + (-10.26 \times 10^{-5})T + (1.3731 \times 10^{-8})T^2$$

The linear attenuation coefficient ($\mu_l$) of $\text{Dy}_2\text{O}_3$ decreases from a value of $67.22 \text{ m}^{-1}$ at $300 \text{ K}$ to a value of $66.17 \text{ m}^{-1}$. This variation of linear attenuation coefficient with temperature is represented by a non-linear second degree polynomial equation

$$\mu_l(T) = 67.70 + (-2.287 \times 10^{-3})T + (-7.851 \times 10^{-7})T^2$$

The coefficient of temperature dependence of linear attenuation coefficient is $-0.002287 \text{ m}^{-1} \text{ K}^{-1}$.

The density of $\text{Dy}_2\text{O}_3$ decreases from a value of $7800 \text{ kg m}^{-3}$ at $300 \text{ K}$ to a value of $7677 \text{ kg m}^{-3}$ at $1000 \text{ K}$, a decrease of about $1.57 \%$. The temperature dependence is a negative non-linear function of temperature and it is represented by non-linear second degree polynomial equation
\[ \rho(T) = 7855 + (-2.653 \times 10^{-1})T + (9.1091 \times 10^{-5})T^2 \]

The coefficient of temperature dependence of density is \(-0.2653 \text{ kg m}^{-3} \text{ K}^{-1}\).

The thermal expansion increases with temperature and is represented by the equation
\[ \Delta l/l(T) = (-5.931 \times 10^{-4}) + (8.48 \times 10^{-6})T + (6.21 \times 10^{-11})T^2 \]

The coefficient of linear thermal expansion increases with temperature and is represented by a non-linear second degree polynomial equation
\[ \alpha(T) = 5.245 + (54.73 \times 10^{-4})T + (-2.8103 \times 10^{-6})T^2 \]

5. Conclusions
Praseodymium and Dysprosium oxide pellets have been prepared. The gamma ray attenuation measurements have been made on these pellets using a gamma ray densitometer fabricated in our laboratory as per the design suggested by Drotning [19]. The results on the temperature dependence of linear attenuation coefficient, density and coefficient of linear thermal expansion of \(\text{Pr}_6\text{O}_{11}\) and \(\text{Dy}_2\text{O}_3\) have been reported and these variations have been fit to second degree polynomial equations. For praseodymium oxide the decrease of density with increasing temperature in the range 300 – 1000 K is about 3.20 % where as it is 1.57 % in the case of dysprosium oxide. The temperature variation of density, thermal expansion and linear gamma ray attenuation coefficient for \(\text{Pr}_6\text{O}_{11}\) and \(\text{Dy}_2\text{O}_3\) are being reported for the first time using the gamma ray attenuation technique.

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