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# High temperature phase transitions in rare-earth element niobates $R_3NbO_7$ [1]

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**Abstract**

Refractory compounds based on oxides of rare-earth metals (REMs) and niobium are promising materials for use in different areas of modern engineering. However, the body of published data on complex physicochemical studies of the aforementioned phases is extremely restricted, especially for the high temperature range. The purpose of the present study was to probe the thermophysical properties of $R_3NbO_7$ (R = Y, La–Lu) at $T \geq 298$ K and to identify the phase transitions that occur.

## EXPERIMENTAL

The polycrystalline REM niobates being investigated were synthesized ceramically with the use of $R_2O_3$ (>99.9%) and $Nb_2O_5$ (of high purity). To this end, compacted specimens of stoichiometric composition were sintered in air in two stages (stage I: 1400 K, 200 h; stage II: 1670 K, 50 h), the specimens being subjected to an intermediate grinding. The compounds produced were identified by X-ray phase analysis (XPA); this was performed on a Philips PW-1700 powder diffractometer (The Netherlands). We employed a high temperature accessory, which enabled us to investigate the crystal structure of the substances over the entire range of temperatures studied. The results obtained gave evidence of the synthesized REM niobates being homogeneous. A calculation of the unit cell parameters (Table 1) indicated that the niobates of Y and Dy–Lu possess a cubic crystal system (the crystal cell parameter for these compounds is doubled on the assumption that a type I Bravais lattice exists), whereas

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TABLE 1

Parameters $a$, $b$, $c$ (Å) and unit cell volumes $V$ (Å$^3$) for REM niobates $R_3NbO_7$

| REM | $a$ | $b$ | $c$ | $V$ |
|---|---|---|---|---|
| Y | 10.488 | | | 1153.66 |
| La | 11.166 | 7.624 | 7.752 | 659.95 |
| Pr | 10.995 | 7.508 | 7.660 | 632.33 |
| Nd | 10.904 | 7.516 | 7.626 | 624.99 |
| Sm | 10.723 | 7.534 | 7.615 | 615.23 |
| Eu | 10.663 | 7.513 | 7.578 | 607.08 |
| Gd | 10.655 | 7.507 | 7.550 | 603.90 |
| Tb | 10.535 | 7.522 | 7.574 | 600.24 |
| Dy | 10.548 | | | 1173.64 |
| Ho | 10.519 | | | 1163.95 |
| Er | 10.471 | | | 1148.00 |
| Tm | 10.420 | | | 1131.37 |
| Yb | 10.395 | | | 1123.38 |
| Lu | 10.354 | | | 1110.00 |

those of La–Tb had a rhombic crystal system. The values that we have obtained give a good fit to the data provided in ref. 1.

The $Nd_3NbO_7$ single crystals to be studied by X-ray structure analysis were produced by dissolution in the melt. For this purpose, a mixture of the starting oxides $Nd_2O_3$ and $Nb_2O_5$ was ground, and to this chemically pure $SrCO_3$ and $SrCl_2 \cdot 6H_2O$ were added. The blend thus prepared was heated to 1700 K in a platinum crucible and, after protracted (50 h) isothermal soaking, was cooled at a rate of 10 K h$^{-1}$. The synthesized crystals were washed in diluted chloric acid in order to remove the solvent.

An X-ray electron probe analysis showed the elemental composition of the synthesized crystals to correspond to the formation of the compound $Nd_3NbO_7$.

The crystal structure of $Nd_3NbO_7$ at room temperature and at elevated temperatures was identified with an Enraf-Nonius SAD-4 automatic diffractometer. All the requisite calculations were performed with a computer, using a package of SDP programs.

The heat capacity of $R_3NbO_7$ niobates was studied in air by the methods of continuous stepwise ($\Delta T = 5$ K) programming of temperature and mixing in DSK-111 and NT-1500 differential calorimeters (Setaram, France). Instrument calibration was performed by a reference measurement of the heat capacity and $(H_T^{\ominus} - H_{298.15}^{\ominus})$ of certified $\alpha$-$Al_2O_3$ under strictly identical conditions. In greater detail, the procedure of conducting thermochemical experiments and the statistical processing of results are described in refs. 2 and 3.

The thermal expansion of polycrystalline specimens of REM niobates

was investigated on a quartz dilatometer in a helium atmosphere at a heating rate of 30 K $min^{-1}$. Computer processing of experimental results according to a program developed by us, which executes the zero correction of dilatometric curves and allows for the intrinsic dilatometer trend for the heating rate chosen, permitted the value of the temperature coefficient of linear expansion (TCLE) to be determined with an error that did not exceed 1%.

## DISCUSSION

In Table 2 we report the coefficients of the polynomial dependences $C_p = f(T)$ for REM niobates. $R_3NbO_7$ (with R = La, Pr, Nd, Gd or Sm) exhibited regions where the heat capacities varied anomalously.

For La, Pr, Nd and Gd niobates the values of the excess phase transformation enthalpies did not exceed 0.6 kJ $mol^{-1}$ (see Fig. 1). The temperature dependences of the TCLE and relative elongation are given in Fig. 2 and Table 3. Dilatometric results confirmed the occurrence of phase transitions in the above niobates and indicated that the relative elongation in the niobates suffered no discontinuous change at the

TABLE 2

Coefficients of temperature dependences of heat capacity for REM niobates, $C_p = a + bT + cT^{-2}$ (J $mol^{-1}$ $K^{-1}$)

| R | $a$ | $b \times 10^3$ | $-c \times 10^{-5}$ | Error (%) | Interval (K) |
|---|---|---|---|---|---|
| Y | 252.88 | 34.98 | 34.19 | 0.5 | 298.15–1100 |
| La | 136.15 | 333.84 | | 0.3 | 298.15–368 |
| | 313.68 | −148.57 | | 0.2 | 368–400 |
| | 237.22 | 56.69 | 15.44 | 0.9 | 400–1800 |
| Pr | 154.60 | 320.69 | | 0.2 | 298.15–370 |
| | 509.81 | −639.33 | | 0.2 | 370–385 |
| | 250.14 | 60.51 | 14.47 | 0.5 | 385–1100 |
| Nd | 170.09 | 247.54 | | 0.4 | 298.15–442 |
| | 374.07 | −213.95 | | 0.3 | 441–488 |
| | 282.90 | 24.30 | 59.57 | 0.3 | 488–1100 |
| Sm | 273.73 | 45.32 | 41.94 | 0.5 | 298.15–1000 |
| Eu | 263.00 | 64.07 | 26.75 | 0.4 | 298.15–1100 |
| Gd | 109.71 | 428.57 | | 0.2 | 298.15–332 |
| | 537.78 | −860.77 | | 0.1 | 332–348 |
| | 262.34 | 22.12 | 38.11 | 0.9 | 348–1800 |
| Tb | 245.67 | 67.73 | 19.90 | 0.4 | 298.15–1100 |
| Dy | 261.21 | 40.33 | 19.01 | 0.5 | 298.15–1100 |
| Ho | 256.21 | 41.28 | 14.56 | 0.5 | 298.15–1100 |
| Er | 250.78 | 38.52 | 26.00 | 0.6 | 298.15–1100 |
| Tm | 262.19 | 36.53 | 24.50 | 0.5 | 298.15–1100 |
| Yb | 279.12 | 28.22 | 37.62 | 0.6 | 298.15–1100 |
| Lu | 262.59 | 29.31 | 45.50 | 0.4 | 298.15–800 |

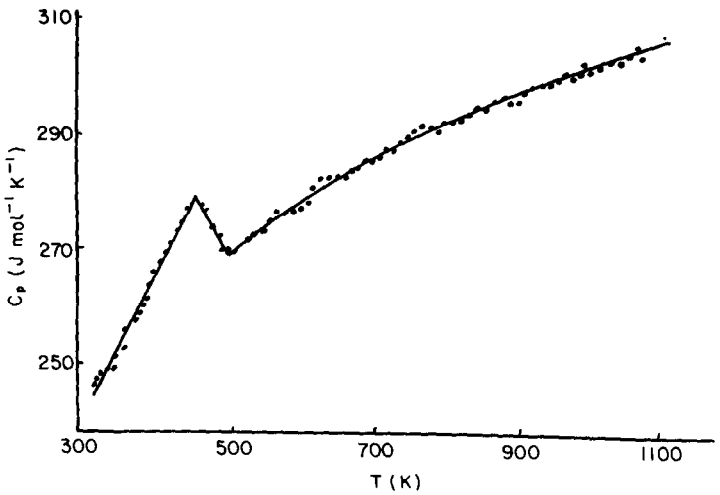


Fig. 1. Temperature dependence of the heat capacity of $Nb_3NbO_7$.

transformation temperatures. Thus, the character of variation of the geometric dimensions of $R_3NbO_7$ (R = La, Pr, Gd, Nd) specimens and the trend of the temperature dependences of $C_p$ indicate the presence of $\lambda$-type transformations in these compounds.

In Fig. 3 we show the temperature dependences of heat capacity and TCLE for $Sm_3NbO_7$ in the region of the phase transition. The results obtained suggest that the value for the transformation of this compound ($\approx$2.04 kJ mol$^{-1}$) greatly exceeds the above-cited values for other REM niobates. Besides, at the phase transition temperature—1048 K—the TCLE and the relative elongation of $Sm_3NbO_7$ undergo a sudden change.

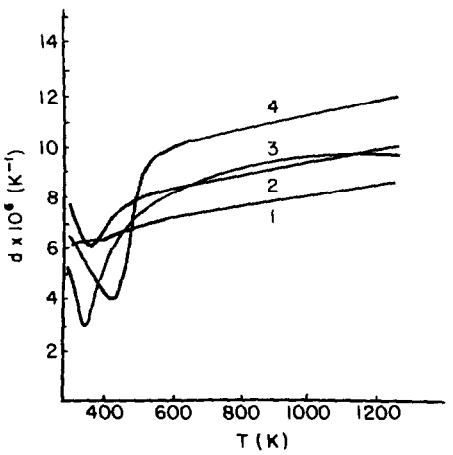


Fig. 2. Temperature dependence of the TCLE for REM niobates $R_3NbO_7$, where R = Pr Curve 1, La Curve 2, Gd Curve 3, Nd Curve 4.

TABLE 3

Values of polynomial coefficients $\Delta l/l = (A + B)(T - 273.15) + C(T - 273.15)^2$, describing the temperature dependence of relative elongation for $R_3NbO_7$ phases

| Compund | Relative density | $A \times 10^4$ | $B \times 10^6$ | $C \times 10^9$ | Interval (K) |
|---|---|---|---|---|---|
| $La_3NbO_7$ | 79.2 | 0.8940 | 6.9846 | 3.1744 | 293.15–1250 |
| $Pr_3NbO_7$ | 90.6 | 1.2694 | 6.3019 | 2.2471 | 293.15–1250 |
| $Nd_3NbO_7$ | 82.6 | 1.2526 | 6.4205 | −7.8741 | 293.15–573 |
| | | 9.9913 | 8.8367 | 1.4597 | 573–1250 |
| $Sm_3NbO_7$ | 79.6 | 1.9927 | 9.9338 | 1.4845 | 293.15–800 |
| $Gd_3NbO_7$ | 57.4 | 6.8590 | 9.7938 | 0.6519 | 373–1150 |
| $Tb_3NbO_7$ | 60.3 | 1.9100 | 9.5200 | 0.7700 | 293.15–1250 |
| $Dy_3NbO_7$ | 59.8 | 1.6532 | 8.2263 | 1.9809 | 293.15–1250 |
| $Ho_3NbO_7$ | 61.4 | 1.8200 | 9.0600 | 1.1900 | 293.15–1250 |
| $Er_3NbO_7$ | 56.2 | 2.0446 | 10.217 | 0.2917 | 293.15–1250 |
| $Yb_3NbO_7$ | 58.4 | 2.3700 | 9.9700 | 0.9500 | 293.15–1250 |

We carried out XPA of high and low temperature modifications of La, Pr, Nd, Gd and Sm niobates. For $R_3NbO_7$ (R = La, Pr, Nd, Gd), X-ray diffraction patterns indicated preservation of the crystal system and the absence of an appreciable variation of the crystal lattice parameters caused by the occurrence of phase transitions. This is a demonstration that the anomalies in the physicochemical properties of REM niobates arise possibly from the displacement of individual atoms in the crystal cells.

Table 4 summarizes the values of the parameters and unit cell volume

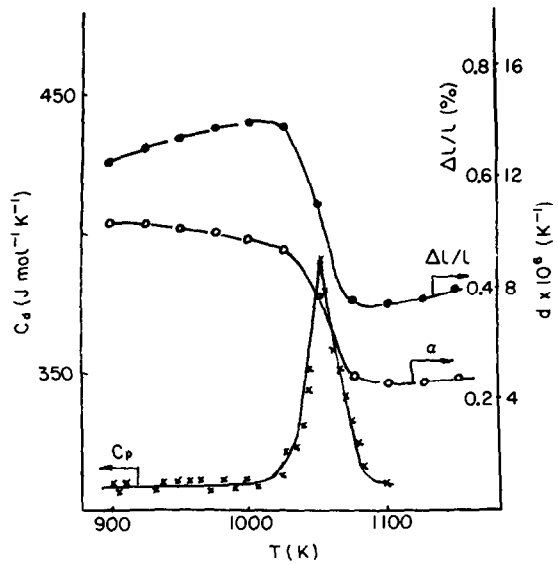


Fig. 3. Temperature dependence of the heat capacity, relative elongation and TCLE for $Sm_3NbO_7$ in the region of the phase transition.

TABLE 4

Values of the parameters $a, b, c$ (Å) and unit cell volume $V$ (Å$^3$) as a function of temperature

| $T$ (K) | $a$ | $b$ | $c$ | $V$ |
|---|---|---|---|---|
| 293 | 10.723 | 7.534 | 7.615 | 615.23 |
| 500 | 10.740 | 7.547 | 7.624 | 617.95 |
| 770 | 10.774 | 7.565 | 7.604 | 619.74 |
| 1020 | 10.780 | 7.589 | 7.649 | 625.76 |
| 1170 | 10.773 | 7.529 | 7.619 | 618.01 |
| 1270 | 10.807 | 7.521 | 7.620 | 619.36 |
| 1370 | 10.843 | 7.538 | 7.529 | 620.81 |

for $Sm_3NbO_7$ as a function of temperature; these values have been determined by the XPA method. The data obtained provide evidence that near the phase transition temperature the parameters $c$ and $b$ of the rhombic crystal cell undergo a change which leads to the cell decreasing in volume. The cubic dilatation results obtained for $SM_3NbO_7$ by the high temperature XPA method coincide with the dilatometric analysis data within the experimental error.

To ascertain crystallochemical features of the phase transformations in isostructural La, Pr, Nd and Gd niobates, we made, as an example, an X-ray structure analysis of $Nd_3NbO_7$ single crystals at 293 and 573 K.

TABLE 5

Positional parameters of atoms in the $Nd_3NbO_7$ single crystal at 293 K

| Atom | $X$ | $Y$ | $Z$ |
|---|---|---|---|
| $Nd_1$ | 0.000 | 0.000 | 0.000 |
| $Nd_2$ | 0.2268(2) | 0.2963(3) | 0.250 |
| Nb | 0.000 | 0.500 | 0.000 |
| $O_1$ | 0.127(3) | 0.317(4) | −0.041(4) |
| $O_2$ | 0.131(3) | 0.026(5) | 0.250 |
| $O_3$ | 0.000 | 0.427(8) | 0.250 |

TABLE 6

Interatomic distances $d$ (Å) in the crystal structure of $Nd_3NbO_7$ at 293 K

| Bond | $d$ | Bond | $d$ |
|---|---|---|---|
| $Nd_1$–$O_1$ | 4 × 2.78(3) | Nd–$O_2$ | 2.32(4) |
| Nd–$O_2$ | 4 × 2.39(2) | $Nd_2$–$O_3$ | 2.66(2) |
| Nd–$O_1$ | 2 × 2.47(3) | Nb–$O_1$ | 4 × 198(3) |
| | 2 × 2.41(3) | Nb–$O_3$ | 2 × 1.98(2) |
| $Nd_2$–$O_2$ | 2.29(4) | | |

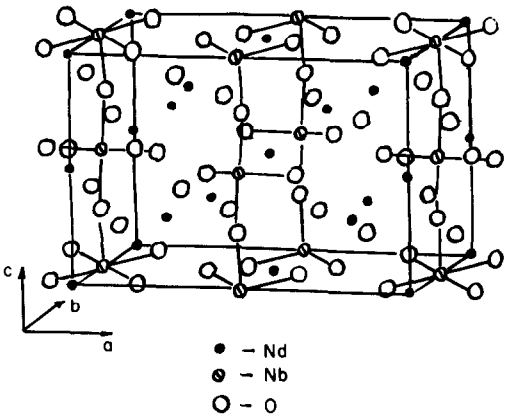


Fig. 4. Crystal structure of $Nd_3NbO_7$ at 293 K.

Table 5 gives positional parameters of the atoms in a $Nd_3NbO_7$ single crystal at 293 K; space group Cmcm, $d = 10.904(2)$; $b = 7.516(2)$; $c = 7.626(2)$ Å; $R = 0.08$. The interatomic distances are given in Table 6.

As can be seen from Fig. 4, the coordination polyhedra for the atoms are an octahedron for Nb, a tetragonal prism for $Nd_1$ and a heptahedron for $Nd_2$. Joining along the common edges, the $Nd_1$ polyhedra form chains along the $c$ axis, and these chains, in turn, are bound up with the Nb polyhedra into layers on the (011) plane. The layers formed by the coordination polyhedra of $Nd_1$ and Nb are bound into the common framework of the crystal structure through $Nd_2$ heptahedra. As X-ray structural investigations at 573 K showed, the type of crystal structure did not change as a result of the phase transition ($a = 10.926(2)$; $b = 7.535(2)$; $c = 7.650(2)$ Å, $R = 0.07$). An insignificant variation of the distances was observed in the coordination polyhedra of Nd and Nb, and was caused by the distortion of these polyhedra.

## CONCLUSIONS

By invoking methods of high temperature ceramic synthesis from the solution in the melt, we have produced polycrystalline and single-crystalline single-phase niobate specimens of composition $R_3NbO_7$ (R = Y, La–Lu). Using XPA data, we have defined more exactly the unit cell parameters for these niobates. A study has been made of the heat capacity and thermal dilatation at high temperatures. Some niobates have been found to exhibit phase transformations. To define more exactly the nature of the transitions that occur, we have made X-ray analyses of the crystal structure of these compounds at different temperatures.

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