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Thermochemical properties of $MnNb_2O_6$

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Abstract Homogeneous manganocolumbite ($MnNb_2O_6$) was synthesized from Nb_2O_5 and MnO oxides. Powder sample was orthorhombic with unit cell parameters: $\alpha = 0.5766$ nm, $b = 1.4439$ nm, $c = 0.5085$ nm and $V = 0.4234$ nm^3. Heat capacity over the temperature range of 313–1253 K was measured in an inert atmosphere with combined thermogravimetry and calorimetry using NETZSCH STA 449C Jupiter thermoanalyzer. Melting point was 1767 ± 3 K, enthalpy of melting was 144 ± 4 kJ mol^{-1}. Experimental heat capacity of $MnNb_2O_6$ is fitted to polynomial $C_{pm} = 221.46 + 3.03 \cdot 10^{-3}\ T + -39.79 \cdot 10^{5}\ T^{-2} + 40.59 \cdot 10^{-6}\ T^2$.

Keywords Heat capacity · Heat of melting · Manganese niobate

Introduction

Thermodynamic modeling of high temperature processes with participation of niobate of trasition metals is difficult due to the absence of information about thermochemical properties in data bases [1–3]. There is only limited information about thermochemical data for $CaNb_2O_6$ [4], $MgNb_2O_6$ [5], $SrNb_2O_6$ [6], and $BeNb_2O_6$ [7]. The compound of $MnNb_2O_6$ has not been sufficiently studied, and data about its thermochemical properties have not been found.

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The purpose of the study was to measure the heat capacity of $MnNb_2O_6$, its temperatures, and heat of phase transformations.

Materials and methods

The synthesis of $MnNb_2O_6$ from Nb_2O_5 and MnO oxides has been conducted by heating (1373 K) pressed mixture within 4 h in a helium flow. The X-ray analysis has been executed by XRD7000C diffractometer (Cu-K_α radiation). Experiments have been carried out using NETZSCH STA 449C Jupiter thermoanalyzer and a special DSC-C_p sensor. Behavior of $MnNb_2O_6$ at a heating rate of 20 K min^{-1} up to 1823 K is studied with the purpose of determination of temperatures and enthalpy of phase transformations. Experiments have been carried out in platinum crucibles with alundum substrates and lids. Each lid has a hole. The weight of $MnNb_2O_6$ sample is 18.63 mg. Measurements of heat capacity of the sample are carried out in a dynamic mode with rate of 10 K min^{-1} in the temperature range of 313–1253 K. Single crystal of synthetic sapphire of the National Bureau of Standards (NBS) is used as the reference sample. The heat capacity of $MnNb_2O_6$ is defined by a comparison method. The weight of sapphire is equal to 55.80 mg, the height is equal to 0.5 mm and the diameter is 6.0 mm. The weight of $MnNb_2O_6$ powdery sample is 88.70 mg. Calculation of the specific heat capacity (C_{ps}) of the studied material is performed by the formula:

$$C_{ps} = (m_{sap}/m_{sam}) \cdot \left((DSC_{sam} - DSC_{bl})/(DSC_{sap} - DSC_{bl})\right) \cdot C_{ps,sap}, \quad (1)$$

where m_{sap} is the weight of sapphire (mg), m_{sam} is the weight of sample (mg), DSC_{sap} is the DSC signal of sapphire (μV), DSC_{sam} is the DSC-signal of the sample (μV), DSC_{bl} is the

DSC-signal of a base line (μV), and $C_{ps,sap}$ is the heat capacity of a sapphire (J g^{-1} K^{-1}).

Results and discussion

The phase purity of the sample was checked by comparing their XRD pattern with (00-033-899) pattern in the Powder diffraction file—PDF2 database (ICDD, USA, release 2008). From the results of the X-ray analysis, the received sample was found to be of single-phase (Fig. 1). The manganese niobate had a crystal lattice of orthorhombic symmetry with space group *Pcan* (60) with the unit cell parameters: $\alpha = 0.5766$ nm, $b = 1.4439$ nm, $c = 0.5085$ nm and $V = 0.4234$ nm^3.

Heating of $MnNb_2O_6$ up to 1767 K at the rate of 20 K min^{-1} showed its stability and the absence of phase transformations (Fig. 2). The effect of melting at 1767 ± 3 K had been revealed with heat of melting equal to 144 ± 4 kJ mol^{-1}.

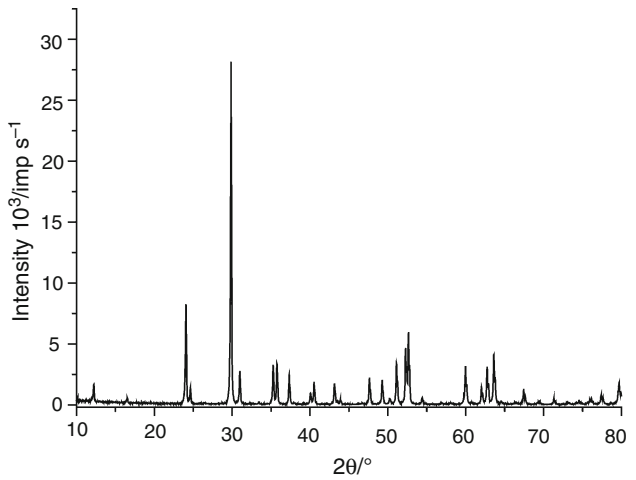

Fig. 1 X-ray powder diffraction pattern of $MnNb_2O_6$, Cu-K_α radiation

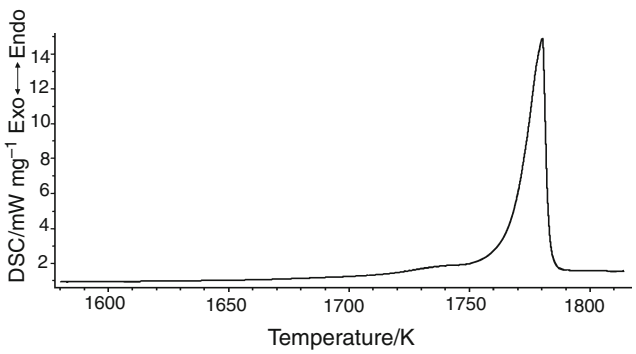

Fig. 2 DSC curve of $MnNb_2O_6$ at a heating rate of 20 K min^{-1} in an atmosphere of argon flow

Series of experiments by determination of the heat capacity of sapphire (Fig. 3) had been carried out with the purpose of measuring error estimation of heat capacity. Proceeding from the received results, the measurement error of heat capacity of sapphire reached the maximum value of ±3% at temperatures above 800 K.

The results of measurement of the heat capacity of $MnNb_2O_6$ are given in the Fig. 4 in the investigated temperatures interval. The temperature dependencies of the values of $MnNb_2O_6$ heat capacity are described by the expression:

$$C_{pm} = 221.46 + 3.03 \cdot 10^{-3} T + -39.79 \cdot 10^{5} T^{-2} + 40.59 \cdot 10^{-6} T^{2}. \quad (2)$$

The calculated value C_{pm} ($MnNb_2O_6$, 298.15 K) is 181.2 ± 5.4 J mol^{-1} K^{-1}.

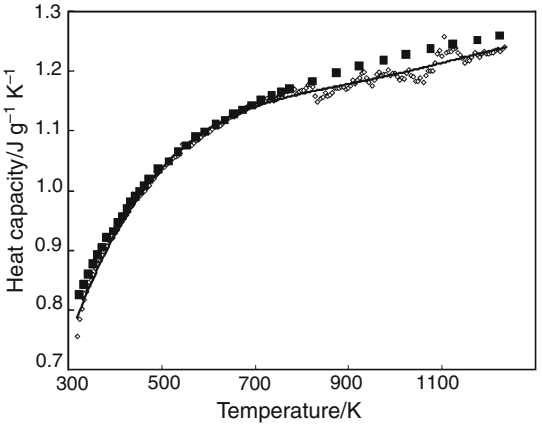

Fig. 3 Heat capacity of sapphire (*filled square* NBS data, *open circle* experimental data, - fitting polynomial)

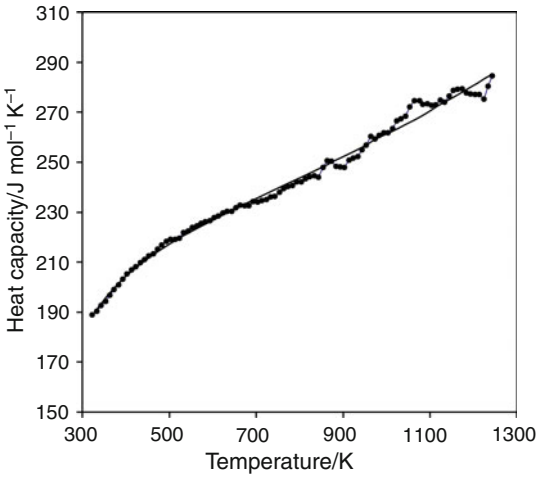

Fig. 4 Heat capacity of $MnNb_2O_6$ (*filled circle* experimental data, - fitting polynomial)

Conclusions

Thus, the stability of the weight and the absence of the phase transformations at heating of $MnNb_2O_6$ up to temperature of melting have been established. The temperature of melting is equal to 1767 K, and heat of melting − 144 kJ mol^{-1}. Heat capacity of $MnNb_2O_6$ in the temperature interval of 313–1253 K has been measured. Results of experiments are taken on the basis of calculations of the thermochemical properties of $MnNb_2O_6$. The obtained experimental and calculation data supplement the absence of the thermodynamic properties values of $MnNb_2O_6$, and they can be used at modeling of processes.

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