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Structural features and magnetic behavior of nanocrystalline powders of terbium oxide prepared by the thermal decomposition of terbium acetate in air

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ABSTRACT

Nanostructured powders of terbium oxides were prepared by the thermal decomposition of terbium acetate at different temperatures. The powders were investigated by means of XRD, HRTEM, magnetic measurements, and IR spectroscopy. It has been found that the most likely composition of the oxides is Tb_4O_7, and the powders containing more than one crystalline phase. At low temperatures the prepared oxides exhibit antiferromagnetic ordering with the Weiss constants ranging from −14 to −22 K. At 2 K the effective value of total angular momentum per one Tb ion in the paramagnetic state $J = 2.5 \pm 0.1$. The effects of the calcination temperature on the crystal structure, microstructure and magnetic behaviors of the samples are discussed in terms of that surface impurities presented in the nanocrystalline powders of Tb oxides influence the cation Tb^{4+}/Tb^{3+} ratio in their crystal lattice.

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1. Introduction

Terbium oxides find their wide use in many diverse scientific and technological applications [1–4], such as optical, ceramic, and chemical ones. In optics these compounds have been utilized, for example, by TV manufacturers because Tb^{3+} ions are among the most common CRT phosphors [5]. Like other rare earth oxides terbium oxides can serve as materials for various ceramics: from clay bowls to advanced electronics. Terbia based materials can be made electrically conductive finding electrochemical applications as components for the cathodes of solid oxide fuel cells. In chemical industry these compounds can be used in oxygen generation systems. Also they have already been successfully used as catalysts in reactions involving oxygen. For example, a ceria–terbia mixed oxide manifests good redox behavior [6,7] and catalytic activity for the storage and release of oxygen and in the oxidation of carbon monoxide [6].

It has been known that in the binary Tb oxides the lanthanide cations can exist in two states: Tb^{3+} and Tb^{4+}. As a result, in addition to the sesquioxide that features all the lanthanides, and the dioxide that does only Tb, Ce, and Pr, the phase diagram “Tb oxide – oxygen” exhibits several regions that correspond to crystalline oxygen-deficient fluorite-related phases TbO_x, where $1.5 < x < 2.0$ [8]. These, stable at room temperature, crystalline phases are also referred to as intermediate terbium oxides. In some of these phases with definite stoichiometry oxygen vacancies are ordered within the crystal lattice, and such phases have been found to belong to the so-called homologous series. A generic chemical formula Tb_nO_{2n-2m} has been proposed for them, with n and m being nonzero integers peculiar to Tb oxides (see, e.g., [9]).

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A common thermolysis of Tb salts in air generally yields oxygen-deficient fluorite-related terbium oxides TbO_x with the composition of $x \approx 1.75$ [8]. Mostly in earlier literature, these oxides have been mistaken for a single-phased intermediate Tb_4O_7, however, in fact, there is no such a crystalline phase at all, and the oxides $TbO_{1.75}$ having been appeared to represent two-phase mixtures of the fluorite-related Tb_7O_{12} and $Tb_{11}O_{20}$ [9–11]. The crystal structures of both these intermediate oxides have been determined [12]. Nanocrystalline microstructure in the intermediate Tb oxides is of particular interest, since one may expect that when the crystallite size decreases down to nanometer scale, the ratio of surface to bulk atoms increases substantially to endow materials based on these oxides with novel features [13,14].

Other interesting phenomena usually observed in the intermediate Tb oxides are originated from the paramagnetic nature of both Tb^{3+} and Tb^{4+} cations affected by the crystal field in these solids. Although the magnetic behaviors of almost all the crystalline phases in the Tb–O system, including those related to the composition Tb_4O_7, have been investigated in detail with respect to the magnetic susceptibilities (χ) measured at room temperatures and the temperature dependences of χ, low-temperature magnetic measurements of these solids have received much less attention from researchers.

In the present study we aimed at obtaining powdered terbium oxides by the thermal decomposition in air of terbium acetate under conditions that favor the formation of nanocrystalline microstructure in these materials such as relatively low calcination temperatures and short times of the air-calcining. In these cases it is obvious that the phase composition of the powders and their microstructural properties can not be predicted and require careful investigations. For this purpose we used X-ray diffractometry, high-resolution transmission electron microscopy and magnetic measurements, including, in particular, those performed at liquid helium temperatures. A special attention was put on surface impurities that can be present in fine powders of rare earth oxides. In order to learn about how the amount of these impurities can influence the magnetic behavior and microstructural properties of the samples under study elemental analysis, thermogravimetry, and IR spectroscopy were used.

2. Material and methods

Nanocrystalline powders of terbium oxide were synthesized via the acetate route as follows. 2 g of commercially obtained 99.99% purity terbium oxide were added to 15 ml of nitric acid, 63.2% and 15 ml of acetic acid, 70%, stirred until completely dissolved, and evaporated dry in air. The obtained precipitate was air-calcined for 1 h at three different temperatures: 500, 600 and 700 °C (samples 1, 2 and 3, respectively).

The samples were additionally examined for purity by X-ray fluorescent analysis on a COMITA X-Art M energy dispersive spectrometer. The spectrometer was equipped with a silver anode X-ray tube as the source of exciting radiation and with a lithium drifted silicon, Si(Li), detector. To attribute the observed peaks to the corresponding characteristic X-ray transitions we referred to X-ray spectroscopy handbooks [15,16]. The X-ray fluorescence spectrum of the sample 3 of terbium oxide synthesized via the acetate route (Fig. 1) indicates that, except for terbium, the mass content of metals with atomic number more or equal than that of magnesium is no more than 0.1% for every element. The synthesis procedures described above for the samples of terbium oxide suggest that the X-ray fluorescence data obtained for the sample 3 are applicable to all the others.

Elemental C, H (by combustion method), and O (by pyrolysis method) analysis was conducted with the use of an Elementar CHNS/O Vario Micro cube analyzer. IR spectra were recorded in the range of wavelengths 4000–675 cm^{-1} on a Perkin–Elmer Spectrum 100 spectrometer with UATR accessory.

The field dependence of magnetization at room temperature (21 °C) was measured in a magnetic field range of 0–10 kOe using a vibrating sample (VSM) M4500 EG&G PARC magnetometer, while the temperature dependence of magnetization was measured on a MPMS 5XL Quantum Design SQUID magnetometer at $T = 2$–300 K and in a magnetic field H of 1 kOe. The latter device was also used to record the field dependencies of magnetization at $T = 2$ K.

X-ray diffraction patterns were obtained at room temperature using a powder DRON ADP-1 and a θ–θ Bragg–Brentano ARL X'TRA diffractometers with Cu radiation. The latter diffractometer was equipped with a solid-state X-ray Peltier detector enabling substantially increased peak-to-background ratio and optimized angular and energy resolution without using β-filters and monochromators.

3. Results

It has been known (see, e.g., [18]) that the color of powders of intermediate Tb oxides varies from brown to dark-brown, while TbO_2, C–Tb_2O_3, and B–Tb_2O_3 have dark-red, white and gray colors, respectively. In our case all the three samples had dark-brown appearance under natural indirect sunny daylight.

3.1. IR spectroscopy and elemental analysis

A typical IR spectrum of the samples of terbium oxide (sample 2, in this particular case) prepared via the acetate route is shown in Fig. 2 (black curve). Most intense absorption bands (AB) in the spectrum are those at around 3400, 1500, 1400, 1070 and 850 cm^{-1}. A broad AB centered at about 3400 cm^{-1} is attributed to adsorbed water molecules. ABs at 1400 and 850 cm^{-1} arise due to the stretching and out-of-plane bending vibrations of anions $[CO_3]^{2-}$, which are bound to the RE metal ions on the surface of terbium oxides in a monodentate manner. An absorption band at 1500 cm^{-1} can be attributed to the anions $[CO_3]^{2-}$ coordinated in a more complex manner [19]. Though the origin of $[CO_3]^{2-}$ ions can be different, they appear on the surface of terbium oxides mostly because of the efficient sorption of atmospheric carbon dioxide and water vapors in a process $CO_2 + H_2O = H_2CO_3$ with the following reaction of the acid with the surface of the oxides [20]. A broad and weak AB at about 1070 cm^{-1} is attributed to the totally symmetric ν(CO) vibration that becomes IR-active due to the loss of the D_{3h} symmetry [21] that features only free carbonate ions. Weak ABs at 2920 and 2860 cm^{-1} are resulted from hydrocarbon impurities on the surface of terbium oxide.

The IR ABs of terbium oxides prepared at different temperatures differ in intensities, mainly in the wavenumber region related to the vibrations of carbonate species. The higher the calcination temperature, the less intense ABs at 1500 and 1400 cm−1 are (cf. black and red curves in Fig. 2). Elemental CH/O analyses give, for example, values of 0.8 mass %, 0.4 mass % and 5.9 mass % for the content of C, H, and O, respectively, in the sample 1, and also show a decrease of the content of C and H in the samples prepared at higher calcination temperatures. It is noteworthy that the pyrolysis method used for the elemental analysis on oxygen requires a sample to be heated up to about 900 °C. On heating the samples of terbium oxide, the oxygen releases not only due to the decomposition of impurities chemisorbed on the powder surface, but also from the crystal lattice of the oxides. This means that the amount of oxygen in the samples related only to the surface impurities cannot be measured, in contrast to the case of RE sesquioxides, for example Ho_2O_3 [22], where oxygen does not evolve from the crystal lattice of the oxide at those temperatures.

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