Thermolysis and magnetism of $Tb_xH_{2-3x}Sb_2O_6{\cdot}nH_2O$ (x = 0.33, 0.67) pyrochlores

Maxim Ulyanov, Konstantin Ageev, Dmitry Zakharyevich

Chelyabinsk State University, Chelyabinsk, Russia.

In recent years, the idea of using magnetic cooling based on the magnetocaloric effect as an alternative to vapor–gas cooling in liquefaction technology has attracted increasing attention from researchers due to its energy efficiency. The aim of the present research was the synthesis of hydrated terbium antimonate promising for magnetic cooling technology by hydrolysis and mechanochemical activation, and complex analysis of the in fluence of modifying elements on the physicochemical, magnetic and magneticaloric properties and structure of polyantimonic acid. As a result of studies, the methodology for the synthesis of hydrated terbium antimonate has been developed and it has been demonstrated that the phase formation in the fully substituted compound of $Tb_xH_{2-3x}Sb_2O_6{\cdot}nH_2O$ (x = 0.33, 0.67) composition occurs after grinding and calcination at 200°C as a result of ion-exchange reaction.

Keywords: polyantimonic acid; magnetic cooling; hydrogen energy; hydrogen liquefaction; caloric materials

1. Introduction

Today, polyantimonic acid (PAA) ($Sb_2O_5{\bullet}nH_2O$, where 2<n<6) and compounds based on it are promising ion-exchange proton-conducting materials. Most often, PAA has a pyrochlore-type structure [1], but there are also antimony acids with an ilmenite-type structure or a cubic $KSbO_3$-type structure [2]. The high conductivity of antimonic acids with a pyrochlore-type structure is associated with its features, which consist of the presence of channels penetrating the framework of the compound. The channels are filled with oxonium ions and water molecules. Removal of the latter leads to the formation of anhydrous forms containing only OH groups or relatively isolated protons. A significant increase in conductivity (more than 3 orders of magnitude) is observed [3] with an increase in the number of water molecules per molar unit of Sb_2O_5. The ion-exchange and magnetic properties, thermolysis of PAA were studied in detail in [4-7].

2. Results and discussion

In this investigation, we present the results of studies of magnetic properties, the composition and structure of phases formed during the thermolysis of $Tb_xH_{2-3x}Sb_2O_6{\cdot}nH_2O$ terbium hydroantimonates, and determination of the temperature ranges of their stability.

Thermal studies of $Tb_xH_{2-3x}Sb_2O_6{\cdot}nH_2O$ were carried out using a Netzsch STA 449F5 Jupiter synchronous thermal analyzer with recording of the change in sample mass and the rate of its change during heating at a rate of 10 deg/min in the temperature range of 30-700°C. It is shown that a monotonic decrease in the mass of the substance occurs with an increase in temperature from 30 to 700°C for the $Tb_{0.67}Sb_2O_6{\cdot}nH_2O$ compound. The mass loss associated with the removal of gaseous products was 18.28%. A 3-stage thermal transformation is observed when heated to 700°C: up to 260°C (stage 1), 260-430°C (stage 2), 430-700°C (stage 3). Equations for the reactions of thermal transformations were proposed based on the analysis of gaseous products obtained using mass spectroscopy, and the composition of the chemical phases at each stage of thermolysis was determined, assuming that the number of antimony atoms does not change during thermal transformations, and thermal transformations with an increase in temperature to 700°C in $Tb_{0.67}Sb_2O_6{\cdot}nH_2O$ occur in a pyrochlore-type structure [7].

It is shown that the change magnetic entropy ΔS_m in $Tb_{0.67}Sb_2O_6{\cdot}nH_2O$ at T = 3 K are 2.2 $Jkg^{-1}K^{-1}$, 4.7 $Jkg^{-1}K^{-1}$ and 6.2 $Jkg^{-1}K^{-1}$ for μ_0H = 1 T, 3 T and 7 T, respectively. The corresponding RC values are about 8.4 Jkg^{-1} and 89 Jkg^{-1} for μ_0H = 1 T and 7 T, respectively. The estimated maximum values of $-\Delta S_m$ are ∼1.05, 3.26, and 3.94 $Jkg^{-1}K^{-1}$ and RC are about 4.2, 20.9, and 41.8 Jkg^{-1} for μ_0H = 1, 3, and 5 T, respectively in $Tb_{0.33}HSb_2O_6{\cdot}nH_2O$.

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