Materials Science and Engineering B 184 (2014) 14–17

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Short communication

Dielectric permittivity of some novel copper/cobalt and rare-earth metal tungstates

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ARTICLE INFO

Article history:
Received 10 September 2013
Received in revised form
15 December 2013
Accepted 5 January 2014
Available online 28 January 2014

Keywords:
Oxides
Chemical synthesis
Dielectric properties

ABSTRACT

Polycrystalline samples of new copper and samarium tungstates ($Cu_3Sm_2W_4O_{18}$ and $CuSm_2W_2O_{10}$) and cobalt and europium tungstate ($CoEu_4W_3O_{16}$) have been successfully synthesized by the solid state reaction of *d*-electron metal tungstates MWO_4 (M = Cu, Co) with corresponding rare-earth metal tungstate RE_2WO_6 (RE = Sm and Eu). Broadband dielectric spectroscopy provides experimental evidence that in tungstates under study both relative dielectric permittivity (ε_r) and loss tangent ($\tan\delta$) strongly depend on the temperature and frequencies. Maximal relative permittivity value $\varepsilon_r = 42$ for $CuSm_2W_2O_{10}$, $\varepsilon_r = 30$ for $Cu_3Sm_2W_4O_{18}$, and $\varepsilon_r = 63{,}000$ for $CoEu_4W_3O_{16}$ at low frequency ($\nu = 0.1$ Hz) and at 373 K indicates that only these ions which have the large number of unpaired and unscreened electrons on the unfilled shells are responsible for the colossal dielectric effect.

1. Introduction

Nowadays, lanthanide compounds in form of micro- and nanocrystals have received considerable attention owing to their variety of chemical, electronic, magnetic, and optical properties [1–13]. Numerous rare-earth metal tungstates and molybdates exhibit various crystal structures (e.g. wolframite, scheelite, perovskite), good mechanical strength, and excellent thermal as well as chemical stability. For these reasons, ceramic and nanocrystalline materials based on rare-earth tungstates or molybdates have shown great potential applications in display devices, optical fibers and scintillators, as well as in solid-state lasers [1–3,10,11,14–18]. Rare-earth tungstates and molybdates have been shown to be promising host matrixes for the luminescence of optically active lanthanide ions such as Nd^{3+}, Eu^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+}.

Our earlier studies have shown the existence of new *d*-electron and rare-earth metal tungstates described by the following chemical formulas: $MRE_4W_3O_{16}$ (M = Co or Zn, and RE = Y, Nd, Sm–Ho), $CuRE_2W_2O_{10}$ (RE = Sm–Gd), and $Cu_3RE_2W_4O_{18}$ (RE = Sm–Gd, or Dy–Er) [19–22]. They were prepared by a solid-state reaction according to the following reactions [19–22]:

$$MWO_{4(s)} + 2RE_2WO_{6(s)} = MRE_4W_3O_{16(s)} \quad (1)$$

$$CuWO_{4(s)} + RE_2WO_{6(s)} = CuRE_2W_2O_{10(s)} \quad (2)$$

$$3CuWO_{4(s)} + RE_2WO_{6(s)} = Cu_3RE_2W_4O_{18(s)} \quad (3)$$

In our previous papers we have found the most effective conditions of their synthesis and composition [19–22]. These compounds were also characterized by means of XRD, simultaneous DTA and TG, IR, SEM, TEM and EPR methods [19–24]. Our earlier studies have shown that a substitution of yttrium ions by trivalent europium ions in obtained by us for the first time zinc and yttrium tungstate, $ZnY_4W_3O_{16}$, leds to a novel promising red phosphor for white light emitting diodes (WLEDs) [23]. Additionally, it has been also demonstrated that at the Eu^{3+} concentration of 1 mol.% in $ZnY_4W_3O_{16}$ matrix the obtained $ZnY_4W_3O_{16}$:Eu^{3+} phosphor can emit light in the visible region [23]. Novel promising laser material for a nonlinear optics has been obtained by us, by a substitution of Nd^{3+} instead Y^{3+} in $ZnY_4W_3o_{16}$ tungstate [24]. Recently, the broadband dielectric spectroscopy measurements carried out on $MPr_2W_2O_{10}$ (M = Cd, Co, Mn) [25], $CdRE_2W_2O_{10}$ (RE = Y, Nd, Sm, Gd–Er) [26] as well as $CuEu_2W_2O_{10}$, and $Cu_3Eu_2W_4O_{18}$ [27] showed the significant value of dielectric constant dependent on presence of transition metal ions having the unfilled 3*d*-shells.

This paper reports on the dielectric properties of $CuSm_2W_2O_{10}$, $Cu_3Sm_2W_4O_{18}$, and $CoEu_4W_3O_{16}$ tungstates, which are important from the viewpoint of their potential dielectric and luminescence applications.

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http://dx.doi.org/10.1016/j.mseb.2014.01.006

2. Experimental

2.1. Sample preparation

Copper tungstate ($CuWO_4$), cobalt tungstate ($CoWO_4$), and rare-earth metal tungstates (RE_2WO_6, RE = Sm and Eu) were used as the starting materials. These compounds were separately synthesized by annealing in air stoichiometric mixtures of CuO (99.99%, Aldrich) with WO_3 (99.9%, Fluka), $CoSO_4 \cdot 7H_2O$ (99.9%, Aldrich) with WO_3 as well as RE_2O_3 (99.99%, Alfa Aesar) with WO_3 according to the procedure used by us in previous studies, and under thermal conditions reported earlier [19–28]. In order to obtain new copper and samarium tungstates, initial $CuWO_4/Sm_2WO_6$ mixtures were heated in air, in ceramic crucibles, with 12-h heating stages, and in the temperature range from 1023 to 1123 K. After each heating stage, the samples were gradually cooled to room temperature, weighted and ground in an agate mortar. Polycrystalline sample of $CoEu_4W_3O_{16}$ was prepared in an analogous manner. Stoichiometric mixture of starting tungstates ($CoWO_4/2Eu_2WO_6$) was heated in air, and in the temperature range of 1273–1423 K. Monitoring of solid-state synthesis of samples under study was carried out by using of powder XRD method.

2.2. Methods

Powder X-ray diffraction patterns of samples under study were collected within the range 12–80° 2Θ with a step 0.02° and counting time 10 s per step on a HZG-4 diffractometer with Co Kα radiation ($\lambda_{aver.}$ = 0.179021 nm). The indexing procedure of recorded powder X-ray diffraction patterns was made using POWDER program [29].

The density of tungstates under study was measured on an Ultrapycnometer 1000 Quantachrome Instruments (model Ultrapyc 1200e, USA) using nitrogen (99.99%) as a pycnometric gas.

Broadband dielectric spectroscopy measurements were carried out using pellets, polished and sputtered with (~80 nm) Ag electrodes in a frequency range from 10^{-1} to 10^6 Hz with use a Novocontrol Alpha Impedance Analyzer and in the temperature range 173–373 K. For dielectric measurements, the samples in a powder form were compacted to a pastille (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa and they were next sintered through 2 h at 873 K.

3. Results and discussion

3.1. X-ray diffraction studies

The room-temperature XRD patterns in the 15–45° range of $CuSm_2W_2O_{10}$, $Cu_3Sm_2W_4O_{18}$, and $CoEu_4W_3O_{16}$ are presented in Fig. 1. Sharp and very intense reflections recorded on the powder XRD patterns indicated the crystalline nature of samples under study. Furthermore, any diffraction lines characterized the used starting materials as well as other cobalt and europium tungstate, $Co_2Eu_2W_3O_{16}$, obtained by us as the product of heating of $CoWO_4$ with Eu_2WO_6 mixed at the molar ratio 2:1 [20], were not identified on the powder diffraction patterns of tungstates under study. All of the XRD peaks can be indexed as a single-phase monoclinic $CuSm_2W_2O_{10}$ (Fig. 1a), a triclinic $Cu_3Sm_2W_4O_{18}$ (Fig. 1b), and an orthorhombic $CoEu_4W_3O_{16}$. The calculated lattice parameters, the number of molecules per unit cell, and the value of experimental density for samples under study are presented in Table 1. These values are in good agreement with the data reported by us earlier [20,22].

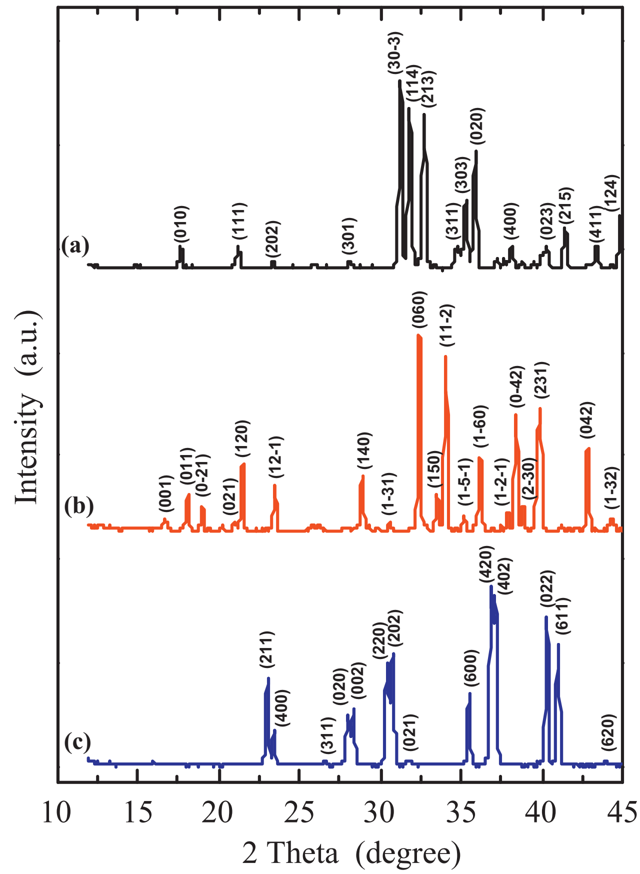

Fig. 1. XRD patterns of $CuSm_2W_2O_{10}$ (a); $Cu_3Sm_2W_4O_{18}$ (b); $CoEu_4W_3O_{16}$ (c) (Miller indices are given for the prominent diffraction lines).

3.2. Dielectric measurements

The results of broadband dielectric spectroscopy measurements of tungstates under study are depicted in Figs. 2–7. The relative dielectric constant (ε_r) increases with temperature from 38 to 42 for $CuSm_2W_2O_{10}$ (Fig. 2) and from 25 to 30 for $Cu_3Sm_2W_4O_{18}$ (Fig. 3) at 10^{-1} Hz as well as it decreases with the frequency. For

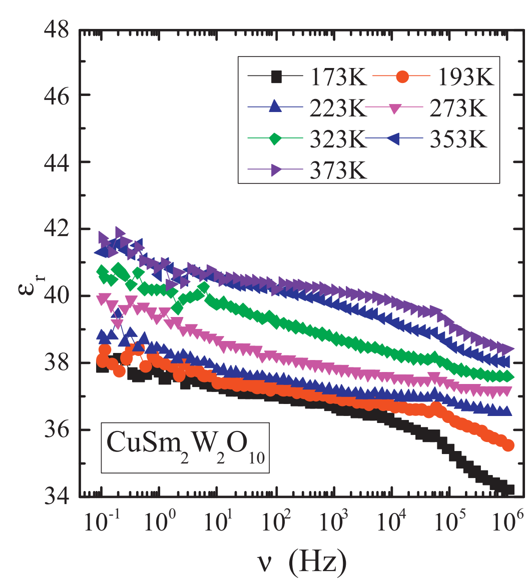

Fig. 2. Dielectric constant ε_r vs. frequency ν for $CuSm_2W_2O_{10}$.