Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 8027–8031

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Thermal properties of Er:Li_2TiGeO_5 ferroelastic ceramics

A. Sieradzki[a,*], D. Szewczyk[b], A. Gągor[b], R. Poprawski[a], A. Jeżowski[b]

[a]*Institute of Physics, Wrocław University of Technology, Wybrzeże St. Wyspiańskiego 27, 50-370 Wrocław, Poland*
[b]*Institute of Low Temperature and Structure Research, Polish Academy of Sciences in Wrocław, ulica Okólna 2, 50-422 Wroclaw, Poland*

Received 10 December 2013; received in revised form 27 December 2013; accepted 30 December 2013
Available online 9 January 2014

Abstract

Micron-grained (2–11 μm), erbium-doped, polycrystalline lithium titanium germinate ceramics were fabricated out of the heat-treated of the presintered samples at a temperature of 970 °C. X-ray diffraction showed a high crystallinity of the synthesized ceramics and confirmed formation of the *natisite* type structure with the P4/nmm symmetry. FE-SEM analysis revealed that the microstructure of obtained ceramics depends on dopant concentration. The number of pores increases with increasing the dopant dose. The specific heat measurements showed that the temperature of the ferroelastic phase transition was significantly reduced for Li_2TiGeO_5 ceramics (222 K) compared to the bulk (233.5 K). The investigations of the thermal conductivity showed its untypical behavior, proportional to the square of temperature, for a dielectric at low temperatures which could be explained by the microstructure of the samples.

Keywords: C. Thermal conductivity; Ferroelastic ceramics; Rare-earth doping; DSC

1. Introduction

Optoelectronic devices which can be reversibly modified by application of an external stimulus such as light, heat or stress, have recently attracted attention due to their wide applications [1]. One of the most attractive features is the ferroelastic switching, since the conversion between the dielectric properties has succeeded in new photo-electronic conversion [2]. The ferroelastics may be also efficiently utilized in acoustooptics [3]. The lattice instability in proper ferroelastics associated with the structural phase transition with respect to the specific acoustic phonons leads to extremely high values of elastic compliances, low values of acoustic wave velocities. Consequently, this leads to an increase in the efficiency of elastooptic interactions [4]. Among many advantages, the investigated ferroelastic possessing the low thermal expansion and relatively high thermal conductivity may be used as templates for rare-earth dopants and become a candidate material for solid-state lasers [5]. These parameters are essentially coupled with the thermal properties of a material. Thus, the problem of searching for new optoelectronic materials is closely linked with studies of the phase transitions, which are accompanied by the thermal phenomena.

The ferroelastic ceramics delimited by the grain size are almost unrestricted in the attainable degrees of orientations. The realizable values of orientations are bounded by a random distribution and a perfect single-crystal texture. In contrast to ceramic textures which are limited by the crystallographic symmetry and the deformation processes are constrained to a twin-like crystallographic reorientations. Thus, the domain switching in the ferroelastic ceramics can yield a maximum degree of orientations that corresponds to the maximum number of possible directions of structural distortions. In turn, the easy structural switching can modify the optical properties [6].

Lithium titanium germinate Li_2TiGeO_5 (LTGO) belongs to the class of materials with a general formula of A_2TiMO_5 (where A = Li, Na; and M = Si, Ge) named *natisites* [7,8]. This compound exhibits interesting physical properties such as a giant ionic conductivity and structural phase transitions of ferroelastic nature [9], which are related to its layered structure. The LTGO crystal has a tetragonal structure with the space group *P4/nmm* with the unit cell parameters $a = 6.66110(8)$ Å and $c = 4.4372(6)$ Å at room temperature [10]. The titanium

*Corresponding author. Tel.: +48 71 3202955; fax: +48 71 3283696.
E-mail address: adam.sieradzki@pwr.wroc.pl (A. Sieradzki).

0272-8842/$ - see front matter © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.12.155

sites are surrounded by five oxygen ions whereas the germanium ions are in tetragonal positions. The crystal structure is built from the infinite sheets ($TiOGeO_4$) of corner-shared GeO_4 tetrahedra and TiO_5 square pyramids separated by layers of alkali lithium ions. Small displacements of this group give rise to spontaneous strains in the crystal and explain the appearance of the domain structure below T_c [11]. At room temperature, the only free positional parameters are the z-coordinates of the TiO_5 group with two distinct oxygen sites: the apical O(1) atom and O(2). In the low-temperature phase described by orthorhombic Pmmn, instead of O(2) there are two non-equivalent oxygen sites O(2) and O(3). Several thermal and optical measurements for Li_2TiGeO_5 have revealed a ferroelastic phase transition at 233.5 K [12–14].

The optical studies of Li_2TiGeO_5 crystal showed that the introduction of Cr^{4+} ions as dopants led to the appearance of the broad fluorescent band at 1100–1600 nm with the maximum of 1200 nm in the optical spectrum [11]. This material is selected as a potential matrix for lasing due to a lack of the octahedral positions in the structure, its nearly congruent melting point and high melting temperature (1143 °C). For this reasons, it seems to be interesting to investigate an influence of the rare-earth dopant (erbium) in *natisite* materials on their physical properties. In the laser construction one of the important factors are the thermal properties, which may strongly affect its stability (especially for the high power lasers).

This work aims synthesis and a thermal characterization of erbium doped Li_2TiGeO_5 ceramics. We synthesized the polycrystalline ceramics for the following reasons: a simple manufacture, an unrestricted attainable degree of grain orientations, bounded by a random distribution, and an ideal single-crystal structure. The freedom of the grain orientation may affect the elastic properties of the investigated material which in turn may perturb its thermal properties. In addition, the structure changes itself due to a dopant which can also affect the heat transport in the material. All the undesirable thermal changes may strongly influence the laser action.

2. Experimental

The starting mixtures for the synthesis of erbium doped Li_2TiGeO_5 ceramics were prepared from Li_2CO_3, TiO_2, and GeO_2. The Er_2O_3 contents in the initial charge were as follows: 1%, 1.5% and 2% (wt). These reagents were thoroughly mixed in stoichiometric proportions, ground together in an agate mortar and synthesized in three steps. Powdered mixtures were initially formed into disc shape pellets, sintered at 800 °C in air for 12 h, then cooled down to the room temperature. The next step was to grind the samples in an agate ball-mill for 2 h and again to form the powder into discs. Finally, the samples were sintered at 970 °C for 12 h and slowly (40 mK/min) cooled down to ensure a good condition for crystallization sintering. The X-ray diffractograms were taken for all sintered samples to verify the synthesis process. Powder diffraction data (XRD) were collected at X′Pert PRO X-ray diffraction system equipped with PIXcel ultra-fast line detector, divergence slits and Soller slits for Cu Kα radiation. Measurements were done in a reflection mode in the Bragg–Brentano geometry.

Morphology of the samples was examined by the Field Emission Scanning Electron Microscopy (FE-SEM) using a FEI Nova NanoSEM 230 microscope. The samples were mounted in a hole drilled in a disc made of conducting resin and then were polished using 500–4000 grit papers, washed with distilled water and finally dried at room temperature. Due to charge built up on samples surfaces during analysis the SEM images were acquired in the low vacuum mode (60 Pa H_2O) using LVD (low vacuum detector) working in SE (secondary electrons) mode. 3 kV primary electron beam acceleration voltage was applied.

The heat capacity was measured using a Mettler Toledo DSC-1 calorimeter with heat-flux resolution of 0.1 μW. Sample mass was chosen to be around 20 mg to ensure a good signal, and at the same time a constant temperature across the sample. Samples were slightly crushed to ensure a good thermal contact and laid on the bottom of a pan in two tightly arranged layers. All the measurements were done with the calorimeter purged with nitrogen to prevent water absorption. The temperature change rate was chosen to be 2 K/min and kept constant in all measurements to ensure the same thermal dynamics for all samples. The DSC thermograms for different samples for cooling and heating cycles were taken. The excess heat capacity associated with the phase transitions was calculated by subtraction from the data the baseline representing variations of lattice heat in the absence of the phase transitions.

The thermal conductivity was measured by the axial stationary heat flux method over the temperature range 5–300 K. One end of the sample was anchored onto a thick copper panel, mounted on the heat key of the cryostat, in order to keep the sample cold. The temperature of the chamber was stabilized at ± 3 mK and measured by germanium and platinum thermometers. But the sample temperature was measured by the constantan–manganin thermocouple. The temperature gradient along the sample was determined by means of the differential thermocouple and its typical value was 0.2–0.3 K. Experiment was performed under a high vacuum and to reduce the heat loses four shields were used. The measurement error was kept below $\pm 2\%$.

3. Results and discussion

A quality of the obtained samples was checked by the X-ray diffraction. The X-ray diffractograms for erbium doped Li_2TiGeO_5 samples are shown in Fig. 1. The positions of diffraction peaks indicate the formation of *natisite* tetragonal type structure with the symmetry P4/nmm. The intensive and sharp diffraction patterns indicate the high crystallinity of the samples. In the case of 1% samples minor impurities of TiO_2 were detected, 1.5% is a single phase, whereas in 2% sample traces of TiO_2 may be noted.

The surface morphology was investigated by the Field Emission Scanning Electron Microscopy measurements at room temperature for three samples. The results are shown