

Microwave dielectric permittivity and photoluminescence of Eu_2O_3 doped laser heated pedestal growth Ta_2O_5 fibers

C. P. L. Rubinger,¹ L. C. Costa,^{1,a)} M. Macatrão,¹ M. Peres,¹ T. Monteiro,¹ F. M. Costa,¹ N. Franco,² E. Alves,² B. Z. Saggiaro,³ M. R. B. Andreeta,³ and A. C. Hernandez³

¹Departamento de Física e I3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal

²Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal

³Instituto de Física de São Carlos, Universidade de São Paulo (USP), C.P. 369, CEP 13560-970, São Carlos, São Paulo, Brazil

(Received 24 April 2008; accepted 6 June 2008; published online 25 June 2008)

We report the microwave dielectric properties and photoluminescence of undoped and europium oxide doped Ta_2O_5 fibers, grown by laser heated pedestal growth technique. The effects of Eu_2O_3 doping (1–3 mol %) on the structural, optical, and dielectric properties were investigated. At a frequency of 5 GHz, the undoped material exhibits a dielectric permittivity of 21 and for Eu_2O_3 doped Ta_2O_5 samples it increases, reaching up to 36 for the highest doping concentration. Nevertheless, the dielectric losses maintain a very low value. For this wide band gap oxide, Eu^{3+} optical activation was achieved and the emission is observed up to room temperature. Thus, the transparency and high permittivity make this material promising for electronic devices and microwave applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.2952284]

In recent years, the doping of wide band gap transparent oxides with lanthanide ions has been performed mainly with the purpose of tuning desirable optical properties for optical and electro-optical applications.¹ The demand for materials with high luminescence efficiency provided by the intra- $4f^n$ transitions has been a driving force for the exploitation of the spectroscopic properties in several oxide hosts.²⁻⁴ Besides the interest in laser optical materials,⁵ oxide systems have been also widely investigated due to its interesting dielectric properties for dynamic random access memories and tunable microwave device applications.⁶⁻⁹ For instance, it is well known that high dielectric constant materials allow a high degree of miniaturization of the components used in many wireless communication systems.¹⁰ The claim for materials with high dielectric constant and low dielectric losses is one of the motivations of new material development.

In this letter, we report on the structural, optical, and microwave dielectric properties of Eu doped Ta_2O_5 grown by laser heated pedestal growth (LHPG) technique. The Ta_2O_5 was grown as transparent cylindrical fibers with 1 mm of diameter and 50 mm of length and have been intentionally doped with Eu_2O_3 from 0 (i.e., undoped) to 3 mol % of concentration. With an ~ 3.8 eV bandgap at room temperature (RT),¹¹ the tantalum pentoxide crystalline fiber is a suitable host for the incorporation of lanthanide ions. Undoped and 1 mol % doped was found to have a monoclinic crystalline structure, but increasing doping (between 2 and 3 mol %), the appearance of a triclinic phase is promoted.¹¹ The achievement of optically activated Eu^{3+} was observed for all the doped samples as shown by photoluminescence (PL) and photoexcitation luminescence data.¹¹ Figure 1 shows the temperature dependent PL spectra for the $\text{Ta}_2\text{O}_5:\text{Eu}$ (3 mol %) fiber carried out with above band gap excitation (325 nm cw He–Cd laser and an excitation power density less than 0.6 W cm^{-2}). The intra- $4f^6$ transitions of Eu^{3+} in the oxide matrix also sensitize the crystalline phase transfor-

mation as observed from the presence of three ${}^5D_0 \rightarrow {}^7F_0$ transitions.¹¹ Two of the lines (576.5 and 578 nm, measured at 14 K) correspond to Eu^{3+} related centers in the monoclinic phase while the third line observed at 581 nm was ascribed to Eu^{3+} in the triclinic phase.¹¹ The PL was measured between 14 K and RT using a closed cycle helium cryostat and collected in 90° geometry. The luminescence was dispersed by a Spex 1704 monochromator and detected by a cooled Hamamatsu R928 photomultiplier. As observed, the fingerprint ${}^5D_0 \rightarrow {}^7F_{J(J=0-4)}$ lines of Eu^{3+} are observed in the orange, red, and near infrared spectral regions. Even knowing that an overlap of the mentioned Eu -related optical centers occur, for this sample the dominant transitions correspond to

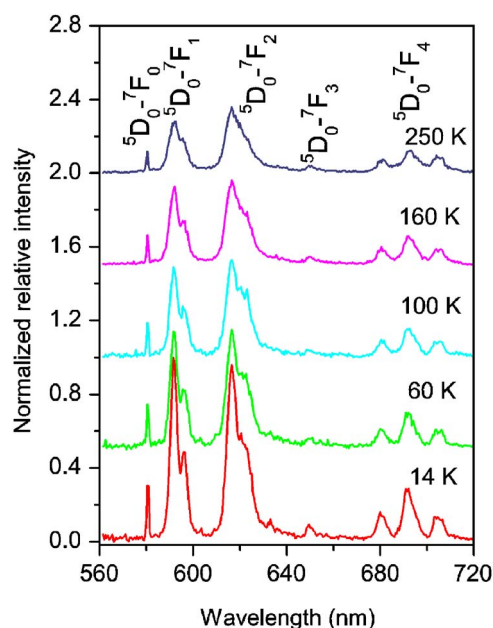


FIG. 1. (Color online) Temperature dependent PL spectra obtained with above band gap excitation (325 nm line of a He–Cd laser) for the $\text{Ta}_2\text{O}_5:\text{Eu}$ (3 mol %) fiber. The spectra were shifted vertically for clarity.

^{a)}Electronic mail: kady@ua.pt.

the Eu^{3+} emission in the triclinic crystal phase. Taking this into account, for the $\text{Ta}_2\text{O}_5:\text{Eu}$ (3 mol %) fiber the overall observed PL at 250 K corresponds to 47% of its initial value at 14 K.

It has been reported that the use of additives in polycrystalline ceramics of Ta_2O_5 such as TiO_2 ,¹² ZrO_2 ,¹³ SiO_2 ,¹⁴ and Al_2O_3 (Ref. 15) leads to increased ϵ' , reaching up to 138, 52, 46, and 42, respectively, at 1 MHz. Furthermore, the enhancement of dielectric constant has been associated with the phase transition of the oxide matrix. The moderate europium doping levels (1%–3%) in our Ta_2O_5 LHPG grown fibers were enough to promote the appearance of a new crystalline phase.

To measure the complex permittivity of the material, $\epsilon^* = \epsilon' - i\epsilon''$, a cavity perturbation method was used, in a rectangular cavity, operating in $\text{TE}_{1,0,11}$ mode at about 5 GHz.¹⁶ In the center of the cavity, where the electrical field is maximal, the sample is inserted, provoking the perturbation of the field. As a consequence, the transmission of the cavity changes.

According to the small perturbation theory,¹⁶ a linear relationship exists between the frequency shift Δf caused by the insertion of a sample in the cavity and the real part of the complex permittivity of the material ϵ' . The same behavior is observed in the change in the inverse of the quality factor of the cavity, $\Delta(1/Q)$, related to the imaginary part, ϵ'' . When we consider only the first order perturbation in the electric field caused by the sample, the expressions are simplified,¹⁷ that is,

$$\epsilon' = K \frac{\Delta f V}{f_0 v} + 1, \quad (1)$$

$$\epsilon'' = \frac{K}{2} \Delta \left(\frac{1}{Q} \right) \frac{V}{v}, \quad (2)$$

where K is a constant related to the depolarization factor, which depends on the geometric parameters, f_0 is the resonance frequency of the cavity, v is the volume of the sample, and V is the volume of the cavity. Using a sample of known dielectric constant, we can determinate the constant K . In our case we used Teflon® Polytetrafluorethylene. The cavity transmission had been measured by an HP 8753D network analyzer.

In Fig. 2, we present the transmission coefficient for the empty cavity and for $\text{Ta}_2\text{O}_5:\text{Eu}$ with different molar fractions. A frequency decreasing shift is observed, which increases with europium concentration, indicating that the dielectric constant increases. Also the broadening of the curves with doping concentration indicates that the dielectric losses increase.

The calculated value of $\epsilon' = 21$ at 5 GHz for our undoped Ta_2O_5 sample, being lower than the previously reported as $\epsilon' = 27$,⁹ indicates that our growth procedure leads to a material with less intrinsic defects and/or unintentional doping. For europium concentrations of 1%, 2%, and 3% we calculated ϵ' as 24, 32, and 36, respectively. The resolution and sensibility of the system do not permit us to calculate the exact absolute values of ϵ'' , but it ensures that they are lower than 5×10^{-3} . This enhancement of the dielectric constant with europium concentration is due to the appearance of a

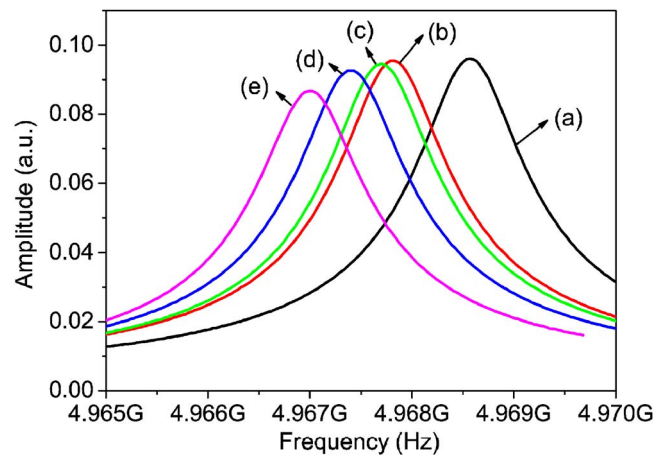


FIG. 2. (Color online) Transmission of the 5.0 GHz resonant cavity for (a) empty, (b) Ta_2O_5 , (c) $\text{Ta}_2\text{O}_5:\text{Eu}$ 1 mol %, (d) $\text{Ta}_2\text{O}_5:\text{Eu}$ 2 mol %, and (e) $\text{Ta}_2\text{O}_5:\text{Eu}$ 3 mol %.

triclinic phase and also to the specific atomic polarizability properties of the Eu_2O_3 coordination polyhedra.

For these crystalline samples, it was possible to obtain an increase of about 15 in ϵ' , with a doping concentration of 3%. The works of Refs. 13–15 obtained a similar variation, but for the lower frequency of 1 MHz and with the doping level up to 10%. Our results are an important achievement in the doping of the Ta_2O_5 . In summary, we produced a fiber with dielectric constant of 36 at 5 GHz, without degrading it by the dielectric losses, which is a promising material for microwave device applications.

M.P. and C.P.L.R. (BPD 34868/2007) thank UA and FCT for their grants. This work was funded by Fundação para a Ciência e Tecnologia (PTDC/FIS/66262/06 and PTDC/CTM/66195/2006) and supported by FEDER.

¹A. Goux, T. Pauporte, and D. Lincot, *J. Electroanal. Chem.* **587**, 193 (2006).

²T. Monteiro, A. J. Neves, M. J. Soares, M. C. Carmo, M. Peres, E. Alves, and E. Rita, *Appl. Phys. Lett.* **87**, 192108 (2005).

³A. S. S. de Camargo, C. R. Ferrari, R. A. Silva, L. A. O. Nunes, A. C. Hernandez, and J. P. Andreetta, *J. Lumin.* **128**, 223 (2008).

⁴A. T. de Figueiredo, V. M. Longo, S. de Lazaro, V. R. Mastelaro, F. S. De Vicente, A. C. Hernandez, M. S. Li, J. A. Varela, and E. Longo, *J. Lumin.* **126**, 403 (2007).

⁵A. J. Kenyon, *Prog. Quantum Electron.* **26**, 225 (2002).

⁶P. S. Dobal, R. S. Katiyar, Y. Jiang, R. Guo, and A. S. Bhalla, *J. Phys. Chem. Solids* **61**, 1805 (2000).

⁷H. Fujikawa and Y. Taga, *J. Appl. Phys.* **75**, 2538 (1994).

⁸F. C. Chiu, J. J. Wang, J. Y. M. Lee, and S. C. Wu, *J. Appl. Phys.* **81**, 6911 (1997).

⁹T. Lacrevez, B. Flechet, A. Farcy, J. Torres, M. Gros-Jean, C. Bermond, O. Cueto, B. Blampy, G. Angenieux, J. Piquet, and F. de Crecy, *Microelectron. Eng.* **82**, 548 (2005).

¹⁰R. J. Cava, *J. Mater. Chem.* **11**, 54 (2001).

¹¹M. Macatrão, M. Peres, F. M. Costa, T. Monteiro, N. Franco, E. Alves, B. Z. Saggiaro, M. R. B. Andreetta, and A. C. Hernandez, *J. Phys.: Condens. Matter* (unpublished).

¹²Y. Wang and Y. J. Jiang, *Mater. Sci. Eng., B* **99**, 221 (2003).

¹³R. J. Cava and J. J. Krajewski, *J. Appl. Phys.* **83**, 1613 (1998).

¹⁴R. J. Cava, J. J. Krajewski, J. W. F. Peck, and G. L. Roberts, *J. Appl. Phys.* **80**, 2346 (1996).

¹⁵R. J. Cava, J. W. F. Peck, J. J. Krajewski, G. L. Roberts, B. P. Barber, H. M. O' Bryan, and P. L. Gammel, *Appl. Phys. Lett.* **70**, 1396 (1997).

¹⁶C. P. L. Rubinger and L. C. Costa, *Microwave Opt. Technol. Lett.* **49**, 1687 (2007).

¹⁷F. Henry and A. Berteud, *J. Microwave Power* **15**, 65 (1980).