Optical Materials xxx (2017) 1–6

Contents lists available at ScienceDirect

Optical Materials

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

Luminescence of Mn^{4+} ions in $CaTiO_3$ and $MgTiO_3$ perovskites: Relationship of experimental spectroscopic data and crystal field calculations

Vesna Đorđević [a, *], Mikhail G. Brik [b, c, d, **], Alok M. Srivastava [e], Mina Medić [a], Predrag Vulić [f], Estelle Glais [g, h], Bruno Viana [g], Miroslav D. Dramićanin [a]

[a] University of Belgrade, Vinča Institute of Nuclear Sciences, PO Box 522, 11001 Belgrade, Serbia
[b] College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing 400065, China
[c] Institute of Physics, University of Tartu, W. Ostwald Str. 1, Tartu 50411, Estonia
[d] Institute of Physics, Jan Dlugosz University, Al. Armii Krajowej 13/15, Czestochowa PL-42200, Poland
[e] GE Global Research, One Research Circle, Niskayuna, NY 12309, United States
[f] University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia
[g] PSL Research University, Chimie Paristech-CNRS UMR 8247, Institut de Recherche de Chimie Paris, 11 rue Pierre et Marie Curie, 75005 Paris, France
[h] Sorbonne Universités, UPMC Univ. Paris 6, CNRS UMR7574, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 4 place Jussieu, 75005 Paris, France

ARTICLE INFO

Article history:
Received 27 January 2017
Received in revised form
13 March 2017
Accepted 14 March 2017
Available online xxx

Keywords:
Red luminescence
Mn^{4+}
Perovskite
Crystal field
LED

ABSTRACT

Herein, the synthesis, structural and crystal field analysis and optical spectroscopy of Mn^{4+} doped metal titanates $ATiO_3$ (A = Ca, Mg) are presented. Materials of desired phase were prepared by molten salt assisted sol-gel method in the powder form. Crystallographic data of samples were obtained by refinement of X-ray diffraction measurements. From experimental excitation and emission spectra and structural data, crystal field parameters and energy levels of Mn^{4+} in $CaTiO_3$ and $MgTiO_3$ were calculated by the exchange charge model of crystal-field theory. It is found that crystalline field strength is lower (Dq = 1831 cm^{-1}) in the rhombohedral Ilmenite $MgTiO_3$ structure due to the relatively longer average Mn^{4+}–O^{2-} bond distance (2.059 Å), and higher (Dq = 2017 cm^{-1}) in orthorhombic $CaTiO_3$ which possess shorter average Mn^{4+}–O^{2-} bond distance (1.956 Å). Spectral positions of the Mn^{4+} $^2E_g \rightarrow {}^4A_{2g}$ transition maxima is 709 nm in $MgTiO_3$ and 717 nm in $CaTiO_3$ respectively in good agreement with calculated values.

1. Introduction

The discovery of efficient phosphor based on the red luminescence of Mn^{4+} ($3d^3$ electron configuration; isoelectronic with the Cr^{3+} ion) is an important goal of the current research in LED phosphors. The best known Mn^{4+} activated material that has found practical application is the magnesium fluorogermanate (MFG) phosphor. This phosphor has been applied as a color correcting phosphor in High Pressure Mercury Vapor Lamps and in fluorescent lamps for providing light for plant growth [1]. So far, Mn^{4+} has been successfully incorporated in several host material structures, such as: oxides [2,3], titanates [4–8], aluminates [9–12], fluorides [13–15], zirconates [16], stannates [8,17], niobates [18,19], and tellurites [20].

Of fundamental interest is the ability to tune the wavelength of Mn^{4+} emission ($^2E_g \rightarrow {}^4A_{2g}$ transition) by changing the fraction of covalence in the "Mn^{4+}-ligand" bonding which is host lattice dependent. A major challenge in the spectroscopy of Mn^{4+} is to identify the parameters that cause the variations in the energy level of Mn^{4+} ^2E state. The knowledge of the variation in the emission versus host composition, local coordination and chemical bonding would help scientists to identify and develop materials that satisfy the requirements of new lighting devices. In the spirit of this approach we have undertaken the evaluation of Mn^{4+} in two titanates; $CaTiO_3$ that crystallizes in the orthorhombic perovskite structure and $MgTiO_3$ which crystallizes in the rhombohedral Ilmenite structure.

* Corresponding author.
** Corresponding author. College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing 400065, China.
E-mail addresses: vesipka@vinca.rs (V. Đorđević), mikhail.brik@ut.ee (M.G. Brik).

http://dx.doi.org/10.1016/j.optmat.2017.03.021
0925-3467/

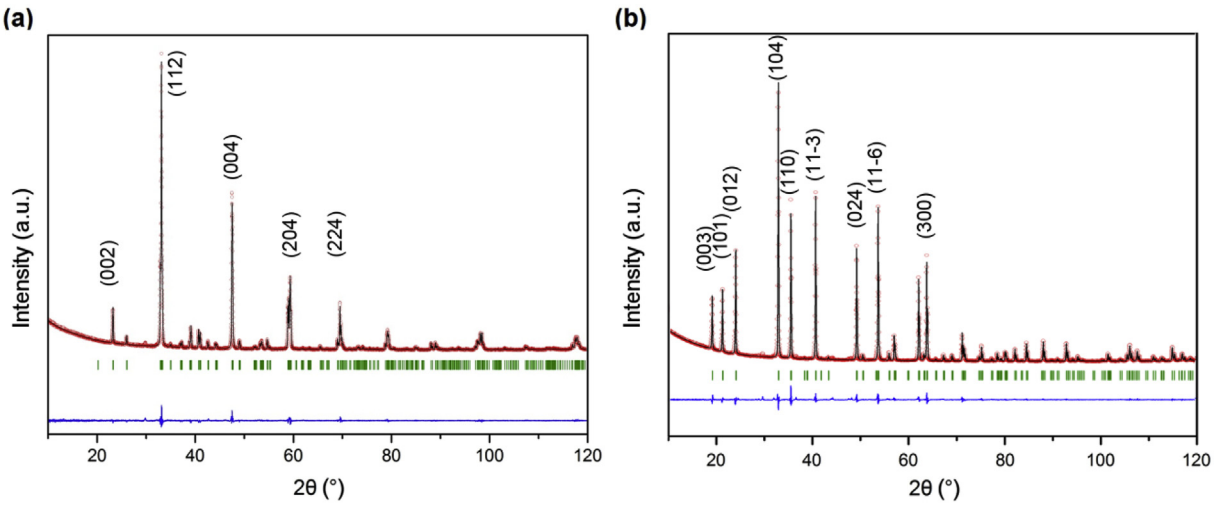

Fig. 1. Observed (dotted red line), calculated (solid black line), and difference (solid blue line at the bottom) XRD patterns of (a) $CaTiO_3$:Mn^{4+}, and (b) $MgTiO_3$:Mn^{4+} powder samples. Main diffractions peaks were indexed by ICDD: 01-081-0561 for $CaTiO_3$, and ICDD: 01-073-7748 for $MgTiO_3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Crystallographic data obtained from refined structural parameters for $CaTiO_3$:Mn^{4+} and $MgTiO_3$:Mn^{4+} samples.

$CaTiO_3$: Mn^{4+} – Orthorhombic					
Space group			*Pbnm* (62)		
Unit Cell Parameters	a = 5.37935(4) Å		b = 5.44028(4) Å	c = 7.63877(4) Å	
Atom	**x**	**y**	**z**	B_{iso}	**Wyckoff Position**
Ca1	0.99365(24)	0.03524(10)	0.25	0.636(14)	4*c*
Ti1	0	0.5	0	0.232(11)	4*b*
O1	0.07082(45)	0.48427(37)	0.25	0.871(60)	4*c*
O2	0.71058(28)	0.28880(27)	0.03846(24)	0.680(39)	8*d*
		R_{wp}: 5.64	R_p: 4.04		
$MgTiO_3$: Mn^{4+} – Rhombohedral					
Space group			$R\bar{3}$ (148)		
Unit Cell Parameters		a = 5.05 Å		c = 13.89 Å	
Atom	**x**	**y**	**z**	B_{iso}	**Wyckoff Position**
Mg1	0	0	0.35633	0.636(14)	6c
Ti1	0	0	0.14536	0.232(11)	6c
O1	0.31501	0.01904	0.24836	0.871(60)	18f
		R_{wp}: 6.02	R_p: 4.24		

There are several synthesis methods to prepare the perovskites $CaTiO_3$ and $MgTiO_3$ materials in powder form, such as sol-gel [21–27], polymer precursor [28–30], precipitation [31], solid state [25,30,32,33] and hydrothermal method [30]. The sol-gel method is a relatively easy method of synthesis, very good in preparing doped samples, using lower temperatures treatments, that facilitate the formation of nanopowder materials. Nevertheless, some of the reported sol-gel methods use long time or temperatures higher than 750 °C [21,23,26], and the products are often synthesized along with other titanate-structured byproducts [21,22,27].

To obtain pure phase of well crystallized Mn^{4+} doped $CaTiO_3$ and $MgTiO_3$ nanoparticles, we used molten salt assisted sol-gel method [34]. By Rietveld refinement of XRD measurements, we determined structural features of obtained materials. Structural data were further used for calculation of crystal field parameters for Mn^{4+} ions in two different perovskite materials, and evaluation of their energy levels. Results of calculations are validated by comparison with experimentally determined luminescence spectra.

2. Materials and methods

For the synthesis of Mn^{4+}-doped $MgTiO_3$ and $CaTiO_3$ perovskites, the combination of wet chemical sol-gel method with annealing in molten salts was used (so-called Molten salt assisted sol-gel method). In both materials doped with manganese, Mn^{4+} ion is stabilized in the structure by isoionic exchange with Ti^{4+} ion in 2% quantity, giving $MgTi_{0.98}Mn_{0.02}O_3$ and $CaTi_{0.98}Mn_{0.02}O_3$ compositions. Both materials were prepared in the same way except for addition of either calcium or magnesium ions source.

In the first step, the gel was prepared by typical sol-gel method using acetic acid (CH_3COOH, HPLC, Fisher), ethanol (C_2H_5OH, Absol. HPLC, Fisher), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \times 6H_2O$, 98%, Alfa Aesar) or calcium nitrate tetrahydrate ($Ca(NO_3)_2 \times 4H_2O$, 99%, Alfa Aesar), titanium(IV) *n*-butoxide ($Ti(OC_4H_9)_4$, 98%, Acros Organics), and manganese(II) nitrate hexahydrate ($Mn(NO_3)_2 \times 6H_2O$, 98+%, Alfa Aesar), mixed in the molar ratio of 3:16:1:0.98:0.02, respectively. $Ti(OC_4H_9)_4$ was added dropwise to CH_3COOH and C_2H_5OH solution mixture at

Please cite this article in press as: V. Đorđević, et al., Luminescence of Mn^{4+} ions in $CaTiO_3$ and $MgTiO_3$ perovskites: Relationship of experimental spectroscopic data and crystal field calculations, Optical Materials (2017), http://dx.doi.org/10.1016/j.optmat.2017.03.021