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And

Wroclaw University of Economics and Business

Dissertation Summary

„SYNTHESIS AND STRUCTURAL AND OPTICAL PROPERTIES OF ALKALI-YTTRIUM DOUBLE TUNGSTATE NANOCRYSTALS DOPED WITH RARE EARTH IONS”

mgr inż. Paulina Ropuszyńska-Robak

Doctoral thesis performed under the direction of dr hab. Lucyny Macalik

Nano-sized materials form a group of compounds with many interesting physical properties. The grain size, surface structure as well as intermolecular interactions allow obtaining unique properties of nanomaterials. The rare-earth double alkaline tungstates studied in this doctoral thesis are expressed by $M^I\text{RE}^{III}(\text{WO}_4)_2$ formula where M^I is deemed as alkali metal ion that yields lanthanide or Y^{3+} ion having nanometric size which constitute a large group of compounds with favourable magnetic to luminescent properties that defines their applicative nature. Double tungstates containing rare earth ions are attractive laser materials due to the long life time of the excited level, low excitation threshold and generation of very efficient stimulated emission. The above mentioned alkaline tungstates have also excellent chemical and thermal stability. Despite many years of research undertaken to

explain the nature of their properties and mechanisms of accompanying phenomena, they are still being actively examined by scientists. The only change that has been made in this examination relates to focusing more on nanocrystalline materials rather than on monocrystalline ones. Because of that, the subject of the doctoral dissertation was focused on the study of the luminescent properties of nanosize materials. Double tungstates with yttrium matrix co-doped with trivalent ions of erbium and thulium as well as holmium and ytterbium were selected for the research.

In the first stage, a relatively easy and fast synthesis of nanocrystals was developed, resulting in a very good material in terms of optic investigation. The site of the alkali metal ion was replaced with Li^+ , Na^+ , K^+ and Rb^+ ions respectively. Both the hydrothermal method and the Pechini method were characterized, along with a description of the influence of the selection of factors such as temperature, pressure, type of reaction medium or precursor heating time on the crystal structure of the obtained materials. Based on the optimization applied to all parameters, it was possible to obtain a more precise design of luminescent materials for further research.

In the next stages of the research work, the physicochemical properties of the obtained compounds were investigated using a number of different research techniques. The morphology, particle size and shape as well as the phase purity of the obtained materials were examined using X-ray diffraction (XRD), Rietveld's method and by applying transmission electron microscopy (TEM) together with the scanning electron microscopy (SEM) methods. The vibrational spectra (IR and Raman), measured at room temperature, provided information on the phonon properties of the tested materials. The examination of spectroscopic characteristics of the tested materials that were optically activated with specific lanthanide ions (Ho^{3+} and Er^{3+} as well as Tm^{3+} and Yb^{3+} pairs) was based on the measurements of absorption spectra, luminescence excitation spectra, emission spectra as well as the luminescence decay kinetics of excited states. The analysis of the emission spectra obtained at different excitation values and the research on the luminescence decay curves allowed to determine the changes applied in the dynamics and relaxation of the excited states that take part in the luminescence phenomena. The analysis of energy transfer between Er^{3+} and Tm^{3+} ions in double tungstate showed that this material is interesting in terms of application for phosphors and optical amplifiers operating in the range of about 2 μm .

The theses of this doctoral dissertation carried out by examining the properties of double alkali-yttrium tungstates doped with rare earth ions fall into the main area of basic research. The results of the research were included in three papers published in journals from the Philadelphia list with an international scope. The obtained results complement and broaden the knowledge of changes occurring in the structure and phonon properties of the tungstate nanocrystalline matrix under the influence of changing alkali ion and grain size, as well as the mechanisms of energy transfer between active ions in the tungstate matrix, which can be helpful in the construction of solid-state lasers.