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Positron Trapping Processes in Temperature-Sensitive Thick- film Structures

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Positron trapping processes in so-called "free" thick-film structures based on spinel-type $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics are studied. The observed positron trapping can be fully defined within the two-state positron trapping model. The defect-related component in the fit of the experimentally measured positron lifetime spectra for thick films and bulk ceramics testifies to similarity of positron trapping processes in spinel-based materials. It is shown that in some cases the size of free-volume entities in thick films can rise due to redistribute space of their inner structure at addition glasses and other compounds. But positrons are trapped more strongly in bulk ceramics due to more ramified their grain/pores structure.

Keywords: Spinel, Thick film, Ceramics, Positron trapping, Fitting parameters.

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1. INTRODUCTION

Spinel-structured ceramics are known to be widely used in industrial electronics and engineering for temperature measurement and control (temperature sensing arrangements), in-rush current limiting flow rate monitoring and indication, etc. [1]. Some time ago, by introducing a number of principally new selection guidelines for advanced manganite ceramics possessing NTC (negative temperature coefficient) thermistor effect inside quaternary Cu-Ni-Co-Mn oxyspinel system, we confirmed the principal possibility to produce a wide range of NTC thermistors within abovementioned quaternary system in bulk performance [2]. But their sensing functionality is significantly restricted because of bulk performance allowing, as a rule, no more than one kind of application.

Because of significant complications in the structure of spinel-type $(Mn,Cu,Ni,Co)_3O_4$ ceramic materials revealed at the levels of individual grains, grain boundaries and pores, the further progress in this field is dependent to a great extent on the development of new characterization techniques, which can be used in addition to traditional ones (X-ray diffraction, Raman scattering spectroscopy, etc.) [3].

This idea can be successfully realized due to unique possibilities of positron annihilation technique in the variant of PAL spectroscopy – one of the most powerful experimental methods for studying of structurally intrinsic voids/pores in solids, which was effectively used earlier for investigation of vacancy-like defects and some of their extended modifications (clusters, agglomerates, micro- and nano-voids, etc.) in "traditional" single-crystal semiconductors and insulators [4]. Early we successful used this method for the characterization of bulk spinel-type ceramics [5]. However, until now no attempts was done with respect to the research of structural peculiarities of thick-film elements. Basic difficulties were related to the thick-film elements obtained on Al_2O_3 substrate (not as the so-called "free" film) that makes the study of this material separately from substrate impossible. In this work, we will try to study of free-volume features of so-called "free" thick-film structures based on transition-metal manganite $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics using PAL spectroscopy.

2. EXPERIMANTAL

Base bulk $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ (Co-enriched) ceramics were prepared by a conventional ceramic processing route [2]. The pellets were sintered in a special regime for 2 hours at 1040 °C. Temperature-sensitive pastes were prepared by mixing powders of basic ceramics with glass powder (without PbO) and organic components). The prepared pastes were printed as multilayered structure (in the form of 3 and 4 layers) on alumina substrates (Rubalit 710) using a manual screen-printing device equipped with a steel screen [6]. Then thick films were sintered in furnace PEO-601-084. During finishing stage the multilayered thick films was separated from substrate using special thermo-procedure.

The conventional PAL spectroscopy technique uses fast-positron beams obtained owing to the well-known β^+-decay reactions of ^{22}Na radioactive isotope [4]. Since the total duration of the above β^+-decay reaction is nearly a few picoseconds (~3.7 ps), it can be accepted that 1.275 MeV γ-quantum is emitted simultaneously with the positron and it can be used as a starting point in the following PAL measurements. Penetrating the sample body, the positron energy is decreased rapidly to the level of thermal energies. Then this thermalized positron diffuses in a sample body. Finally, it is captured by some trapping sites (vacancy-type defects, dislocations, grain boundaries, etc.), two 0.511 MeV γ-quanta being mostly eliminated. In this a sequence, the single positron-related event, revealed itself as the mass-energy transformation of electron-positron pair, is realized [4].

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Table 1 – PAL characteristics of $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ (Co-enriched) bulk ceramics with combine 3- and 4-layered thick films mathematically treatment within two-component fitting procedure

Sample	Fitting parameters				Positron trapping modes				
	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_{av}, ns	τ_b, ns	κ_d, ns^{-1}	$\tau_2 - \tau_b$, ns	τ_2/τ_b
Based Co-enriched ceramics	0.15	0.84	0.33	0.16	0.18	0.16	0.60	0.17	2.04
3-layered thick film and ceramics	0.17	0.83	0.36	0.16	0.20	0.19	0.50	0.17	1.92
4-layered thick film and ceramics	0.15	0.84	0.34	0.16	0.18	0.17	0.57	0.17	2.01

The total duration of this event or, in other words, the positron lifetime τ is determined by time difference between start (E = 1.275 MeV) and one of annihilation or stop (E = 0.511 MeV) γ-quanta within the same β^+-decay reaction.

The PAL spectra were recorded with fast coincidence system (ORTEC) at the temperature T = 22 °C and relative humidity RH = 35 %, provided by special climatic installation. Each spectrum was measured with a channel width of 6.15 ps and contained ~10^6 coincidences in total, which can be considered as normal measurement statistics. Isotope ^{22}Na (activity ~50 kBq) was used as a source of positrons, which was sandwiched between two identical samples. In our case we used the following sample configurations: bulk ceramics, 3-layered thick films and based ceramics; and 4-layered thick films and based ceramics. Such approach was used due to necessity of experimental samples with thickness over 1 mm.

The measured PAL spectra were processed with standard LT 9.0 computer program [7], the obtained curve being fitted by two components with τ_1, τ_2 lifetimes and I_1, I_2 intensities. Therefore, the positron trapping modes in the studied materials, e.g. average positron lifetimes $\tau_{av.}$, positron lifetime in defect-free bulk τ_b and positron trapping rate in defects κ_d were calculated using a formalism of two-states trapping model [4]. The (τ_2–τ_b) difference was accepted as a size measure for extended free-volume defects where positrons are trapped, as well as the τ_2/τ_b ratio was taken in a direct correlation to the nature of these defects [8].

3. RESULTS AND DISCUSSION

Best-fit parameters for the experimental PAL spectra of $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ (Co-enriched) spinel ceramics and thick films based on these ceramics are given in Table 1. By accepting two-state positron trapping model [4,8], for spinel ceramic materials the first shortest lifetime component spectra with lifetime τ_1 and intensity I_1 was corresponded to the main spinel structure reflected microstructure specificity with characteristic octahedral and tetrahedral cation vacancies and the second one – free-volume entities and extended defects located near grain boundaries.

It is shown (see Table 1) that the values of lifetime τ_1 and intensity I_1 corresponds to the amount of the main spinel phase are identical for bulk ceramics and thick film structures. It is obvious, as the same spinel-type phase is formed in based Co-enriched ceramics and at preparation of thick-film structures.

The lifetime τ_2 is directly related to a size of free-volume entity (trapping center) and the intensity I_2 is proportional to the number of such "defects" [8] and addition phases located near grain boundaries [9]. In our case these values are practically identical for bulk ceramics and thick-film structures based on these ceramics. In some cases, the lifetime τ_2 of the second component is higher in thick films. It can be related with increasing of a size of free-volume defects near grain boundaries due to redistribute space of inner structure of thick films at addition glass and other compound.

The other parameters of two-state positron trapping model such as average lifetimes $\tau_{av.}$, bulk lifetime τ_b can be considered near after the values for bulk ceramics and thick films.

Since the amount of grain/pores in the thick films was smaller, the process of positron trapping in these materials can be less intensive (the positron trapping rate of defects κ_d increased from 0.60 to 0.50 ns^{-1}).

Nevertheless, there were no significant changes in τ_2/τ_b and (τ_2–τ_b) parameters. In all cases, the same type of positron trapping centre is formed in bulk and thick films. The character size of these extended positron traps near grain boundaries estimated due to (τ_2–τ_b) difference is close to single-double atomic vacancies [6].

4. CONCLUSION

Experimental PAL spectra, measured for the $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ (Co-enriched) bulk ceramics and thick films, are decomposed into two discrete components (τ_1, I_1) and (τ_2, I_2). The observed components can be fully defined within the two-state positron trapping model. Positrons are trapped more strongly in bulk ceramics due to more ramified their grain/pores structure. The size of free-volume entities in thick film can rise due to redistribute space of their inner structure at addition glasses and other compounds.

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