

## #01458 Volumetric defect analysis in functional ceramic materials with positron annihilation lifetime spectroscopy

U. Defect-induced effects in low-dimensional and novel materials

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### Abstract

In this study, we present the application of positron annihilation lifetime spectroscopy (PALS) method to investigate extended free-volume defects in functional ceramic materials. Specifically, we examine technologically modified  $\text{MgAl}_2\text{O}_4$  and  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics in both bulk and thick-film forms, as well as  $\text{Eu}^{3+}$ -doped  $\text{BaGa}_2\text{O}_4$  ceramics.

For PALS measurements, we utilized the ORTEC system with a positron source of  $^{22}\text{Na}$  isotope [1]. The acquired PALS spectra were analyzed using the LT software, employing two, three, or four-component fitting procedures based on the structural characteristics of the ceramics. Our findings reveal that two PALS channels are active in functional ceramic materials: positron trapping and ortho-positronium (o-Ps) decay. In the investigated ceramics, the first component primarily reflects the microstructural features of spinels, such as characteristic vacant cation sites in octahedral and tetrahedral positions. The second component of the spectra represents positron trapping in free-volume defects in technologically modified  $\text{MgAl}_2\text{O}_4$  ceramics, while the decay process of o-Ps is described by single or multiple components, depending on the level of porosity and experimental setup. In the case of  $\text{MgAl}_2\text{O}_4$  ceramics, three or four components are the most appropriate fit when employing positron annihilation lifetime spectroscopy. Analysis of the second component demonstrates that increasing the sintering temperature during technological modification results in volume reduction and a decrease in the number of defect-related voids. This process is accompanied by a decrease in the size of nanopores (third component), while the overall number of nanopores remains unaffected.

Examining the second component of PALS spectra using three and four-component analysis for undoped and  $\text{Eu}^{3+}$ -doped  $\text{BaGa}_2\text{O}_4$  ceramics, we observe that increasing the  $\text{Eu}^{3+}$  content from 1 to 3 mol% leads to the agglomeration of free-volume defects near grain boundaries. Simultaneously, the nanopores in the ceramics expand, and their number increases. Further increase in the  $\text{Eu}^{3+}$  ion content causes fragmentation of both free-volume defects and nanopores. By utilizing a three-component fitting procedure, the PALS measurements provide insights into the transformation of inner free-volume defects in  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics induced by monolithization processes and varying content of additional NiO phase. We observe that the fragmentation of voids occurs with increasing NiO phase from 1 to 8%, followed by void agglomeration during the monolithization of ceramics. Prolonging this process leads to limited fragmentation in ceramics with a 12% NiO content. The introduction of the NiO phase creates new positron-trapping sites in the ceramics (with a small amount of NiO) and reduces the size of free-volume defects formed by the NiO phase, indicating the monolithization process in ceramics.

## #01407 Defect-related effects in functional $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics

U. Defect-induced effects in low-dimensional and novel materials

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### Abstract

The  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  spinels have significant potential for various applications, such as negative temperature coefficient thermistors, precise temperature sensors, and in-rush current limiters. Modifying these materials through technological processes, as well as changes in microstructure, can lead to transformations in their internal free-volume defects. Therefore, advancing in this direction requires the development of new methods for studying material structures beyond traditional approaches. One such method is positron annihilation lifetime spectroscopy (PALS). The objective of this study is to examine defect-related free volumes in the  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics spinels using PALS tools.

PALS measurements were conducted using an ORTEC spectrometer, where a  $^{22}\text{Na}$  source was positioned between two sandwiched ceramic samples with varying amounts of additional NiO phase or thick-film structures. The obtained data were analyzed using the LT computer program, with the most accurate results achieved through two-component fitting procedures.

Applying a two-state positron trapping model, the first spectral component was associated with the main spinel structure in spinel-type ceramic materials, while the second component was linked to extended defects located near grain boundaries in proximity to the extracted additional phases. The intensity of the first component corresponded to the quantity of the main spinel phase, while the intensity of the second component reflected the amount of the additional NiO phase near grain boundaries. For ceramics with 1% addition of NiO phase, the intensity of the second component was 18%. This additional phase was localized near grain boundaries and partially filled pores. In samples with 8% NiO, the intensity of the second component increased to 21%. In ceramics with 10% NiO, a grain-pore structure did not develop due to the monolithization process accompanied by the surface extraction of additional NiO phase. Similar tendencies were observed for ceramics with 12% addition of NiO phase. These transformations aligned well with the positron trapping parameters.

The lifetime values of the first and second components in  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics were typical for spinel-structured materials, measuring 0.37 ns and 0.20 ns, respectively. The lower value of the second component in ceramics with 8% NiO phase (0.17 ns) correlated well with the Ni content in different crystallographic positions. It was demonstrated that the process of positron trapping in these ceramics with higher amounts of additional phases was more pronounced (the positron trapping rate of defects increased from 0.48 to 0.62 ns<sup>-1</sup>). The results of the PALS measurements confirmed the occurrence of interphase mass-transfer processes in mixed transition-metal manganite ceramics, resulting from monolithization processes during technological modification and the optimal content of additional NiO phase.

## #01399 Positron annihilation study of free-volume defects in doped BaTiO<sub>3</sub> ceramics

U. Defect-induced effects in low-dimensional and novel materials

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### Abstract

This study focused on investigating the microstructure and inner free-volume defects in both undoped and Ca-doped BaTiO<sub>3</sub> ceramics using a combination of methods. The ceramics were prepared by sintering undoped BaTiO<sub>3</sub> and BaTiO<sub>3</sub> doped with 5, 10, and 15 mol% of Ca at a temperature of 1250°C. Positron annihilation lifetime measurements were conducted using an ORTEC spectrometer, and a <sup>22</sup>Na source was positioned between two sandwiched ceramic samples. The obtained data were analyzed using the LT computer program, with the most accurate results obtained through two-component fitting procedures.

In parallel with the positron annihilation measurements, scanning electron microscopy (SEM) was employed to examine the microstructure of the ceramic samples. The typical samples exhibited a grain-porous microstructure with clusters of fractional grains. Adopting a two-state positron trapping model, the short lifetime ( $\tau_1 \approx 0.15$  ns) observed in polycrystalline ceramic materials is generally attributed to the unrestricted annihilation of positrons, a value that aligns closely with the theoretically calculated lifetime for free positrons in BaTiO<sub>3</sub>. This observed value is similar to that of BaTiO<sub>3</sub> single crystals. The second lifetime ( $\tau_2$ ) corresponds to the annihilation of positrons at defect sites, specifically vacancy complexes formed by oxygen vacancies and metal ion vacancies. The present study determined  $\tau_2$  to be approximately 0.32 ns. It is noteworthy that  $\tau_2$  increases as the Ca content in BaTiO<sub>3</sub> ceramics rises from 5 to 10 mol%, while it decreases in samples with 15 mol% of Ca. The intensity ( $I_2$ ) associated with  $\tau_2$  decreases from 22% to 16% in the 5 and 10 mol% Ca-doped samples, but then increases to 25% in samples with 15 mol% of Ca. These findings suggest that the addition of Ca to BaTiO<sub>3</sub> ceramics results in an enlargement of free-volume defects and a reduction in their quantity. Thus, the process of defect agglomeration occurs when Ca is added at concentrations of 5 and 10 mol%. However, further increasing the Ca content to 15 mol% leads to the fragmentation of free-volume defects.

## #01637 Synchrotron study of luminescence spectra of Eu-doped BaGa<sub>2</sub>O<sub>4</sub> ceramics

R. Neutron and synchrotron x-ray methods and applications in engineering materials and processes

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### **Abstract**

Eu-doped BaGa<sub>2</sub>O<sub>4</sub> holds significant practical importance due to its luminescent properties. The incorporation of europium dopants into the BaGa<sub>2</sub>O<sub>4</sub> host offers the potential for efficient light emission and tailored optical characteristics. Europium impurities act as luminescent centers, introducing characteristic emission peaks in the visible range. The ability to control the concentration of Eu dopants enables some fine-tuning options. Additionally, high melting point and resisting chemical reactions with various substances make it suitable for use in harsh operating conditions. In this effort, luminescence and luminescence excitation spectra of pure and Eu-doped (1, 2, 3 and 4% Eu) BaGa<sub>2</sub>O<sub>4</sub> are investigated in detail. Excitation characteristics of BaGa<sub>2</sub>O<sub>4</sub> and its europium-doped counterpart are examined to understand their optical properties and potential for efficient light emission. The luminescence excitation spectra were recorded within 220 to 550 nm excitation wavelengths range while monitoring the emission responses at 390, 594 and 616 nm. A comparison between the excitation spectra of pure BaGa<sub>2</sub>O<sub>4</sub> and Eu-doped BaGa<sub>2</sub>O<sub>4</sub> provides insights into the influence of europium dopants on the properties of the host material. The excitation spectra provide valuable information about the absorption and energy transfer mechanisms, enabling a deeper understanding of the luminescent behavior in BaGa<sub>2</sub>O<sub>4</sub>. This investigation contributes to the knowledge of luminescence excitation in BaGa<sub>2</sub>O<sub>4</sub> and Eu-doped BaGa<sub>2</sub>O<sub>4</sub>, laying the foundation for further optimization and development of these materials for advanced applications in optoelectronics.

## #01463 Exploring the impact of irradiation on the structural and electrical properties of PEDOT:PSS nanocomposites

I. Synthesis and characterization of functional nanocomposite materials

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### Abstract

Nanoscale fillers added to dielectric matrices, particularly polymers, create nanocomposites with remarkable mechanical, thermal, and electrical properties. In this study, we empirically investigate the structural characteristics and electrical behavior of PEDOT:PSS polymer layers containing high-purity single-walled (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) before and after exposure to irradiation.

All the samples analyzed exhibit the lowest impedance (highest conductivity) at room temperature, with electrical conductivity decreasing upon cooling. Generally, the real part of the impedance ( $\text{Re}(Z)$ ) shows a slight increase with frequency up to a certain threshold frequency, beyond which it drops rapidly. For pure PEDOT:PSS and PEDOT:PSS/SWCNTs samples, this threshold frequency is approximately 100 kHz, while it is slightly lower for composite layers with MWCNTs.

The temperature effect on the impedance of the fabricated polymer/CNTs composite layers is significant. The real part of the impedance ( $\text{Re}(Z)$ ) exhibits a drastic increase starting from a specific temperature, which varies depending on the sample composition. For pure polymer, this occurs at temperatures of 80-90 K, and below 60 K,  $\text{Re}(Z)$  is nearly beyond the measurable range. In layers reinforced with SWCNTs, the impedance increase is more gradual, and it is even more so for MWCNTs-reinforced composites. In the case of MWCNTs, reliable measurements can be conducted at temperatures as low as 40 K.

The presence of incorporated CNTs in the samples alters the conditions for residual water storage due to structural changes introduced by the specific nanofiller. As a result, the time required for complete water removal differs, and the process ultimately concludes at different temperatures. This assumption is further supported by the observation that samples with MWCNTs exhibit slower growth of real impedance with decreasing temperature and generally higher conductivity at the lowest measured temperatures.

It has been demonstrated that composites reinforced with nanostructures dispersed in a matrix containing Boron, Nitrogen, or Carbon elements can provide radiation shielding across a range of energies without generating harmful secondary particles. Conversely, polymers reinforced with carbon nanotubes display an electrical response that is highly dependent on the absorbed radiation dosage.

The conductivity of an un-irradiated plate depends on the doping level of CNTs. If the doping level exceeds a threshold, current flows across the plate, but this conductive path can be disrupted by a sufficiently high radiation dosage. Therefore, the presence of CNTs in the polymer creates a simple circuit breaker that immediately signals critical exposure when the protective layer can no longer block incoming radiation.

## **#01467 Enhanced thermo-physical properties of epoxy resin with carbon nanotube reinforcements**

I. Synthesis and characterization of functional nanocomposite materials

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### **Abstract**

Polymer nanocomposites are renowned for their exceptional thermo-physical properties. However, the successful mass production of carbon nanotube-reinforced polymer composites relies heavily on stringent technological processes. Consequently, it necessitates experimental methods to regulate manufacturing conditions, with particular emphasis on achieving uniform dispersion of the nanofillers. This study focuses on investigating the thermal conductivity of engineered polymer nanocomposites by incorporating varying amounts of single-walled and multi-walled carbon nanotubes (CNTs) into an epoxy matrix. The addition of a relatively small quantity of CNTs is known to induce significant modifications in the properties of the original epoxy host material. Here, we aim to uncover how increased loading levels and improved dispersion quality influence the overall thermosetting characteristics of the composite material. Cylindrical samples, measuring 17 mm in height and 7 mm in diameter, were prepared using commercially available epoxy resin and carbon nanotubes with an average outer diameter of approximately 2 nm and lengths ranging from 5 to 30 microns. The thermal behavior of the nanofiller-incorporated polymer matrix was examined through visual thermographic analysis and direct thermal response measurements. An experimental setup consisting of an NI USB-6009 DAQ unit, a 5V/1A electrical furnace with a flat heated surface, and a thermocouple for temperature measurement was employed. The acquired data, including temperature-time plots during heating and cooling cycles, were collected using the DAQ module with 14-bit resolution and a sample rate of 48 kS/s. The entire experiment was effectively controlled by custom-developed NI LabVIEW software. Additionally, FLIR TG series thermal cameras were utilized to gain visual insights into the heat flow processes occurring within the samples. The recorded thermal response data serve as the basis for discussing the underlying mechanisms responsible for the contrasting thermo-physical behaviors observed in single-walled and multi-walled carbon nanotube-reinforced epoxy composites.

