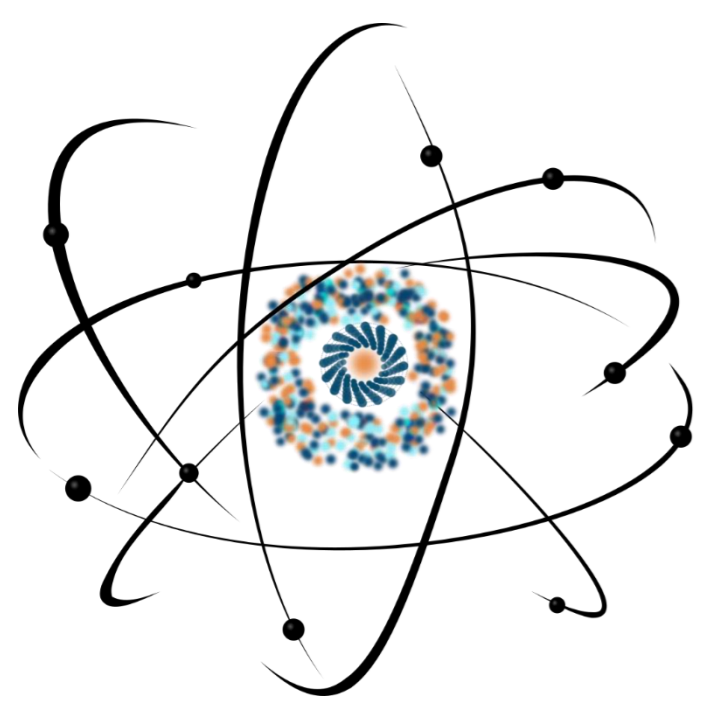


Analysis of evolution of free volumes in the BaGa₂O₄ ceramics doped with Eu³⁺ ions



H. Klym^{1*}, A. Ingram², Yu. Kostiv¹, A. Lucheckko³, I. Karbovnyk³

¹Lviv Polytechnic National University, Lviv, Ukraine

*halyna.i.klym@lpnu.ua, klymha@yahoo.com

²Opole University of Technology, Opole, Poland

³Ivan Franko National University of Lviv, Lviv, Ukraine

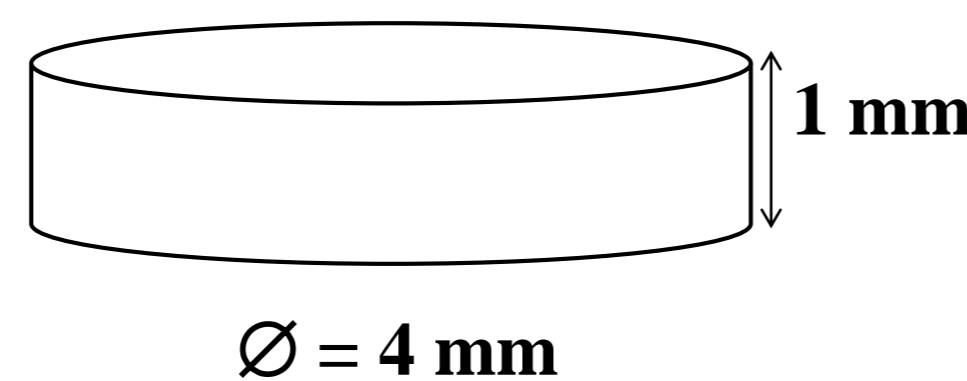


Introduction

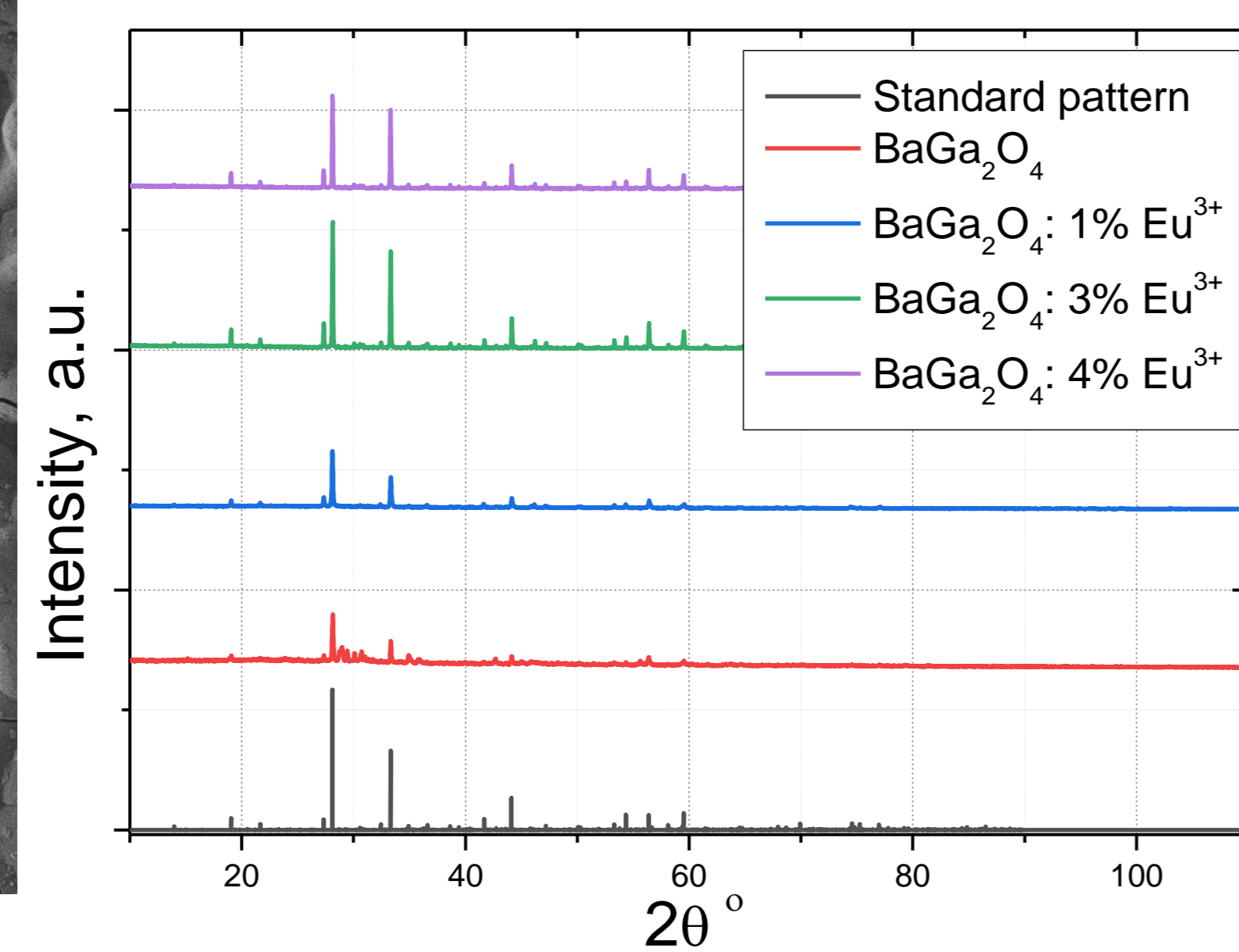
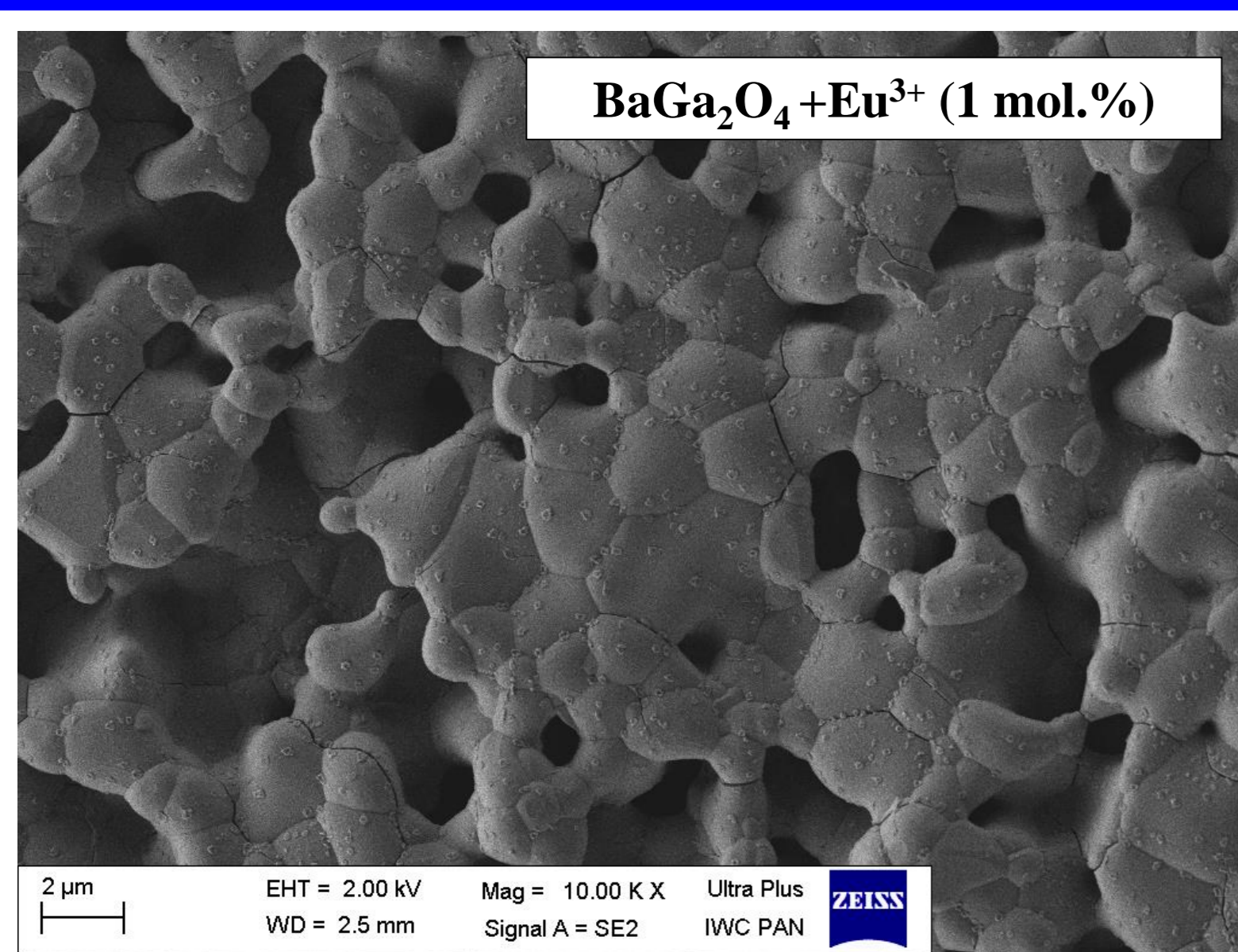
The BaGa₂O₄ ceramics doped with Eu³⁺ ions (1,3 and 4 mol%) synthesis were obtained by solid-phase sintering. The phase composition and microstructural features of ceramics were investigated using X-ray diffraction and scanning electron microscopy in comparison with energy dispersive methods. It is shown that undoped and Eu³⁺-doped BaGa₂O₄ ceramics are characterized by a developed structure of grains, grain boundaries and pores. Additional phases are mainly localized near grain boundaries creating of additional defects. The evolution of defect-related free volumes in the BaGa₂O₄ ceramics due to the increase of the content of Eu³⁺ ions has been studied using positron annihilation lifetime spectroscopy technique. It is established that the increase in the number of Eu³⁺ ions in the basic BaGa₂O₄ matrix leads to the agglomeration of free-volume defects with their subsequent fragmentation. The presence of Eu³⁺ ions result in the expansion of nanosized pores and increase in their number with their future fragmentation.

SAMPLE PREPARATION

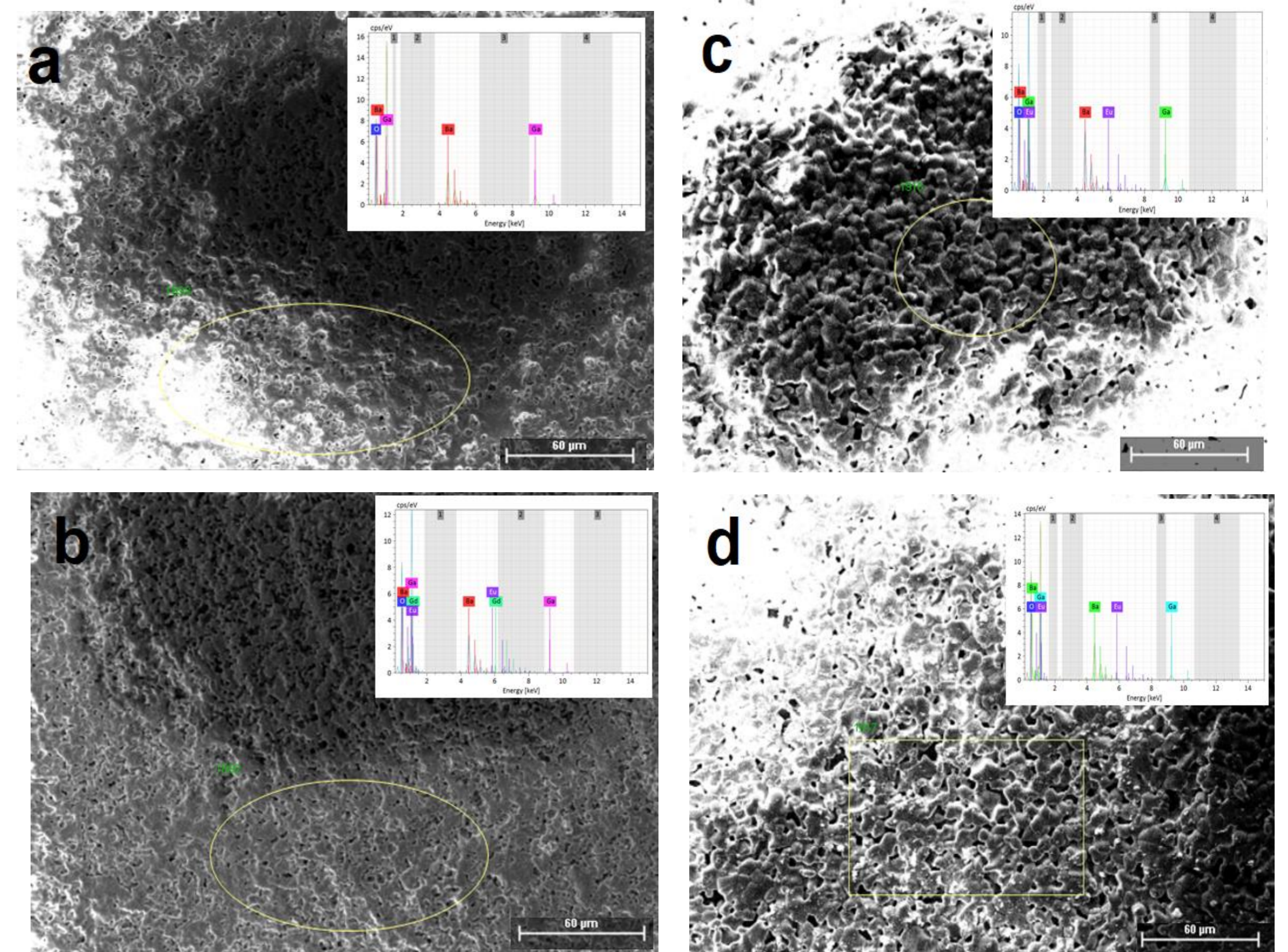
The polycrystalline BaGa₂O₄ samples were prepared by solid-state reaction method. As starting materials BaCO₃ and Ga₂O₃ with purity 99.99% were used. Powders of stoichiometric composition with 0, 1, 3 and 4 mol.% of Eu₂O₃ (99.99%) were mixed in an agate mortar for 6 h with further pressing in a steel mold. Obtained pellets were annealed at 1200 °C for 12 h in air. After that, the annealing of ceramic samples was carried out at 1300 °C for 4h. The obtained polycrystalline ceramic samples were 4 mm in diameter and 1 mm in thickness.



MICROSTRUCTURE and XRD DATA OF CERAMICS

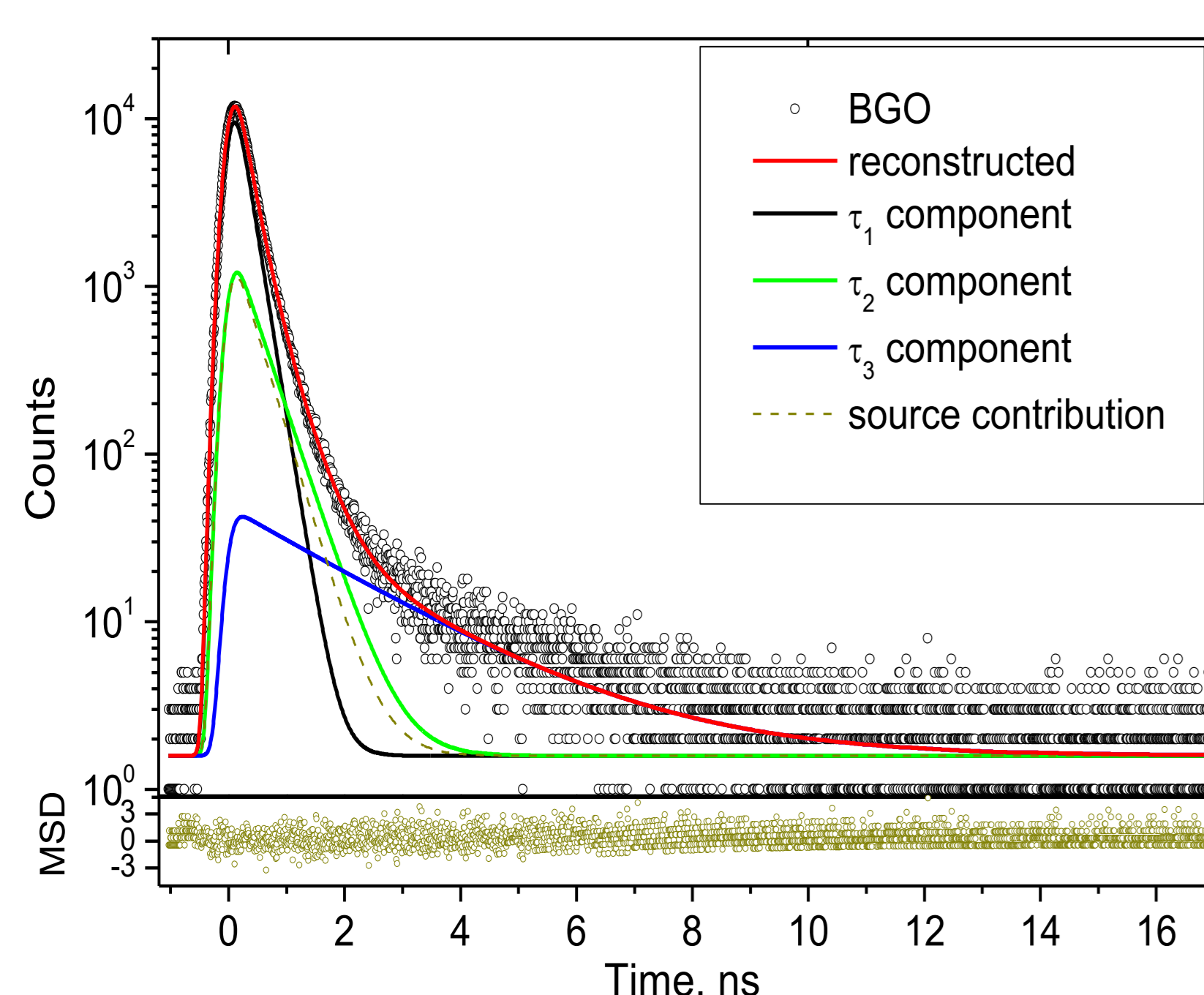


SEM and EDX results



Microstructure of the selected area and elemental composition of the undoped BaGa₂O₄ ceramics (a) and doped with 1 mol% (b), 3 mol% (c) and 4 mol% of Eu³⁺ ions

RESULTS: PAL characteristics



Sample	τ_1 , ns	I_1 , %	τ_2 , ns	I_2 , %	τ_3 , ns	I_3 , %
BaGa ₂ O ₃	0.200	83.3	0.424	14.9	2.196	1.8
BaGa ₂ O ₃ +1 mol% Eu ³⁺	0.206	85.1	0.450	13.2	2.289	1.7
BaGa ₂ O ₃ +3 mol% Eu ³⁺	0.212	89.9	0.550	7.9	2.390	2.2
BaGa ₂ O ₃ +4 mol% Eu ³⁺	0.201	83.3	0.411	14.4	2.157	2.4

Sample	τ_{av} , ns	τ_b , ns	κ_d , ns ⁻¹	$\tau_2 - \tau_b$, ns	τ_2/τ_b	R_3 , nm
BaGa ₂ O ₃	0.234	0.218	0.40	0.21	1.95	0.306
BaGa ₂ O ₃ +1 mol% Eu ³⁺	0.239	0.222	0.35	0.23	2.02	0.314
BaGa ₂ O ₃ +3 mol% Eu ³⁺	0.240	0.223	0.23	0.33	2.46	0.322
BaGa ₂ O ₃ +4 mol% Eu ³⁺	0.232	0.218	0.37	0.19	1.89	0.302

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}$$

Mean positron lifetime:
reflects cumulative defect
environment prevailing in sample

Lifetime τ_b :
associated with the positron trapping
in defect-free bulk

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}$$

$$\kappa_d = \frac{I_2}{I_1} \left(\frac{1}{\tau_b} - \frac{1}{\tau_2} \right)$$

Positron trapping rate
in defects

Size measure of extended defects
where positrons are trapped

Represents the nature of defects

$$\tau_2/\tau_b$$

Diagram explaining the evolution of defect-related voids in BaGa₂O₄ ceramics caused by Eu³⁺ doping

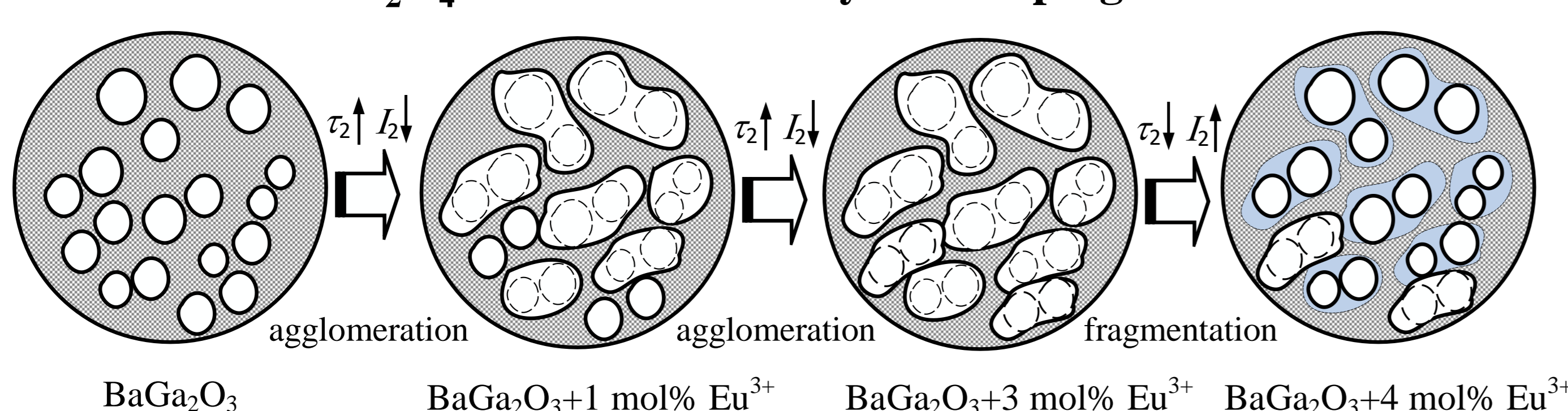
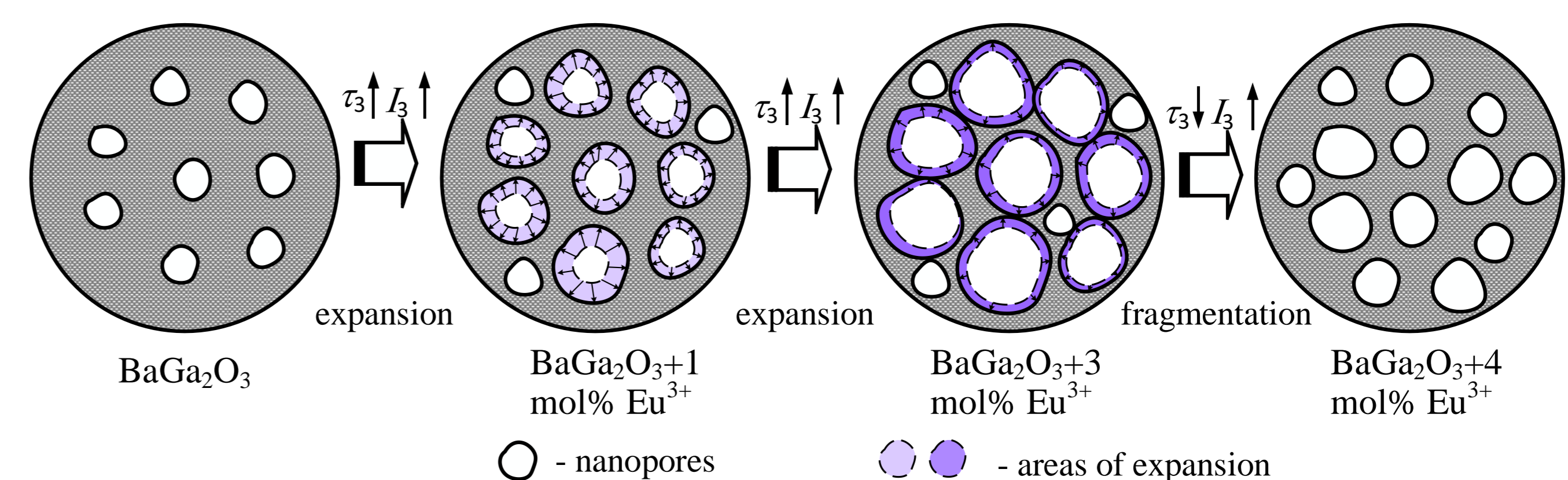


Diagram explaining the evolution of nanopores in BaGa₂O₄ ceramics caused by Eu³⁺ doping



Conclusion

The structural features and evolution of free-volume defects in the BaGa₂O₄ ceramics obtained by solid-phase synthesis from the initial BaCO₃ and Ga₂O₃ components with the addition of different amount of Eu₂O₃ content (1, 3 and 4 mol%) were investigated. The structural features of ceramics were studied using XRD as well as SEM with EDX elemental analysis. It is established that in accordance with the quantitative analysis of the elemental composition, samples of the undoped BaGa₂O₄ ceramics have the largest deviations from the stoichiometric composition, they are three-phases. Such processes are apparently caused by the evaporation of the constituent synthesis powders during the annealing process at high temperatures. The detected signs correlate with the XRD data. Additional phases in ceramics are mainly localized near the grain boundaries and create defective centers for positron capture studied by PAL spectroscopy. Analyzing the second component of PAL spectra for the undoped and Eu³⁺-doped BaGa₂O₄ ceramics, it was shown that an increase of Eu³⁺ content from 1 to 3 mol% leads to agglomeration of free-volume defects near grain boundaries of ceramics. At the same time, nanopores in ceramics expand and their number increases. Further increase in the content of Eu³⁺ ions are accompanied with fragmentation of both free-volume defects and nanopores.