Analysis of the impurity composition of zirconia ceramics by photoluminescence spectroscopy

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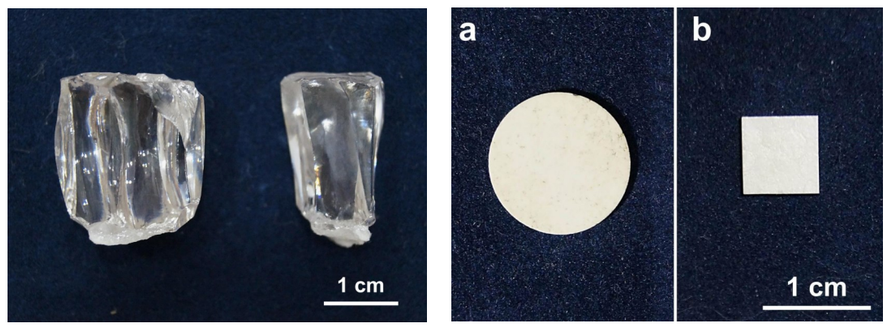
Motivation

Ceramic materials based on stabilized zirconia combine a number of unique properties. Due to this, they have a wide range of applications in many fields of science and technology [1-3]. For example, the high oxygen-ionic conductivity at elevated temperatures of these materials makes them suitable as oxygen sensors in gaseous media and as electrolytic membranes in solid oxide fuel cells (SOFCs) etc. [3-5]. As is known, the electrical conductivity and thermomechanical properties of ceramic solid electrolytes depend on the technology of their preparation, as well as on the characteristics and methods of synthesis of the initial powders. Differences in the structure of the material and the content of impurities in it may be associated with this. The presence of uncontrolled impurities in stabilizing zirconia ceramics can be investigated by a wide range of physical-chemical methods. However, the photoluminescence spectroscopic methods, which have higher sensitivity compared to other spectrophotometric methods, are the most promising in the study of ceramic electrolyte plates. It also has a non-destructive effect on the structure of the materials under investigation.

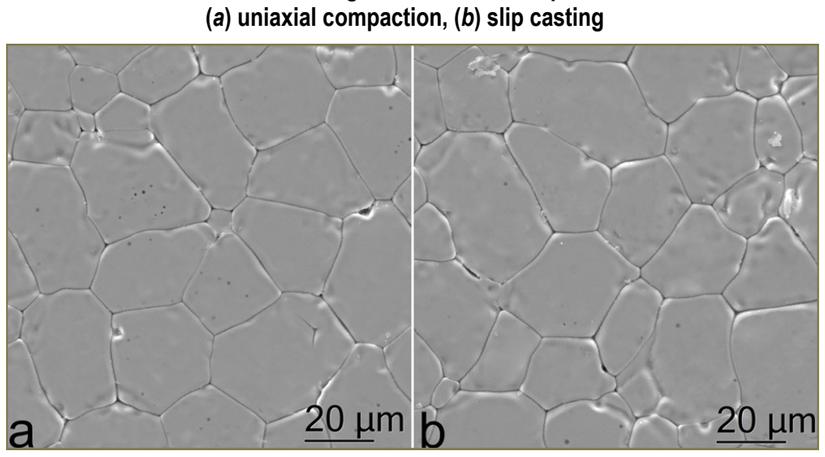
Materials and Methods

- The $(ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}$ ceramic specimens synthesized from crushed single crystals of similar composition using (*a*) uniaxial compaction and (*b*) slip casting. The specimens were air heat treated at 1680 °C for 2 h.
- The test single crystals were grown using directional melt crystallization [6]. The charge was prepared from zirconium oxide (ZrO_2), yttrium oxide (Y_2O_3) and europium oxide (Eu_2O_3) with a purity of min. 99.96 wt.%.
- The surface morphology and elemental composition of the ceramic specimens were studied using scanning electron microscopy and energy dispersion spectroscopy.
- The phase composition of the ceramic was analyzed using X-ray diffraction and Raman spectroscopy.
- The local structure and impurity composition of ceramics was studied by photoluminescence spectroscopy using Eu^{3+} ions as a spectroscopic probe.

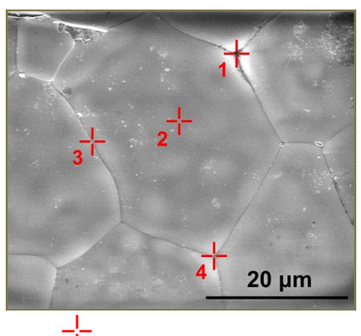


Microstructure and impurity composition

Microstructure images of the ceramic specimens: (*a*) uniaxial compaction, (*b*) slip casting



Elemental analysis data for ceramics synthesized using slip casting



Spectrum Recording Area / Oxide	Concentration, mol.%		
	ZrO_2	Y_2O_3	Al_2O_3
1	87.1	9.6	3.3
2	89.5	9.9	0.6
3	89.2	10.0	0.8
4	89.2	9.9	0.9

The ⊹ symbols show areas in which the ZrO_2, Y_2O_3 and Al_2O_3 oxide concentrations were measured

Conclusions

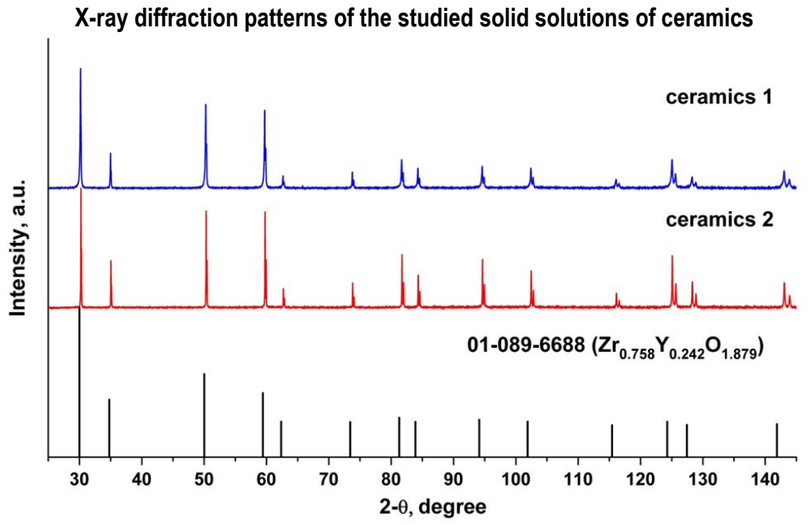
- **In the $(ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}$ ceramic compacts studied, the presence of uncontrolled impurity as a Cr_2O_3-Al_2O_3 solid solution was revealed.**
- **Photoluminescence spectroscopy and confocal microscopy methods have shown that this impurity localizes to the surface of the ceramic as individual inclusions.**
- **The X-ray diffraction results indicate that the compacts prepared using various methods are single-phase and consist of cubic ZrO_2 with close values of the crystal lattice parameters. Other phases were not found. According to Raman spectroscopy, the study ceramics have a t"-phase structure, which is close to the fluorite structure.**
- **The local crystalline environment of Eu^{3+} ions in $(ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}$ ceramics, formed with the participation of oxygen vacancies, has been found to be identical to the local environment of Eu^{3+} ions in crystals of the same composition.**

References

[1] Y.W. Chen, J. Moussi, J.L. Drury, et al., Expert Rev. Med. Devices. V. **13**, 945 (2016);
[2] U. Peuchert, Y. Okano, Y. Menke, et al., J. Eur. Ceram. Soc. V. **29**. 283 (2009);
[3] N. Mahato, A. Banerjee, A. Gupta, et al., Prog. Mater. Sci. V. **72**. 141 (2015);
[4] Y. Mansilla, M. Arce, C. Gonzalez Oliver, et al., Mater. Today: Proc. V. **14**. 92 (2019);
[5] J.W. Fergus, J. Power Sources. V. **162**. 30 (2006);
[6] V.V. Osiko, M.A. Borik, E.E. Lomonova. Synthesis of refractory materials by skull melting technique. Springer Handbook of Crystal Growth. Berlin: Springer; p. 433-477, 2010;
[7] D.A. Agarkov, M.A. Borik, T.V. Volkova, et al., J. Lumin. V. **222**. 117170 (2020);
[8] C. Guguschev, J. Götze, M. Göbbels, American Mineralogist. V. **95**. 449 (2010);
[9] J. Dexpert-Ghys, M. Faucher, P. Caro, J. Solid State Chem. V. **54**. 179 (1984).

Phase composition

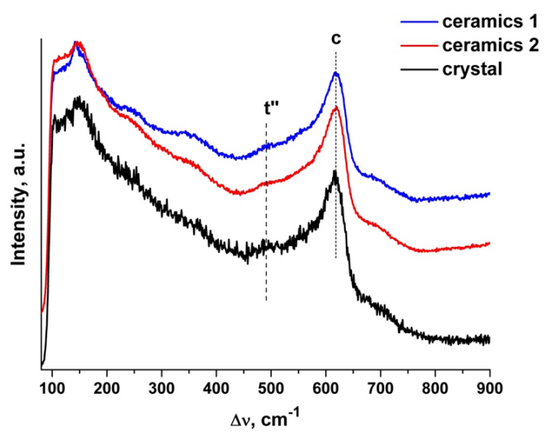
X-ray diffraction patterns of the studied solid solutions of ceramics



$(ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}$ Solid Solution	Phase Composition*	Space Group	Unit Cell Parameters a, Å
Single Crystal	c – ZrO_2	Fm3m	5.141(1) [7]
Ceramic №1 (Uniaxial Compaction)	c – ZrO_2	Fm3m	5.1381(3)
Ceramic №2 (Slip Casting)	c – ZrO_2	Fm3m	5.1368(3)

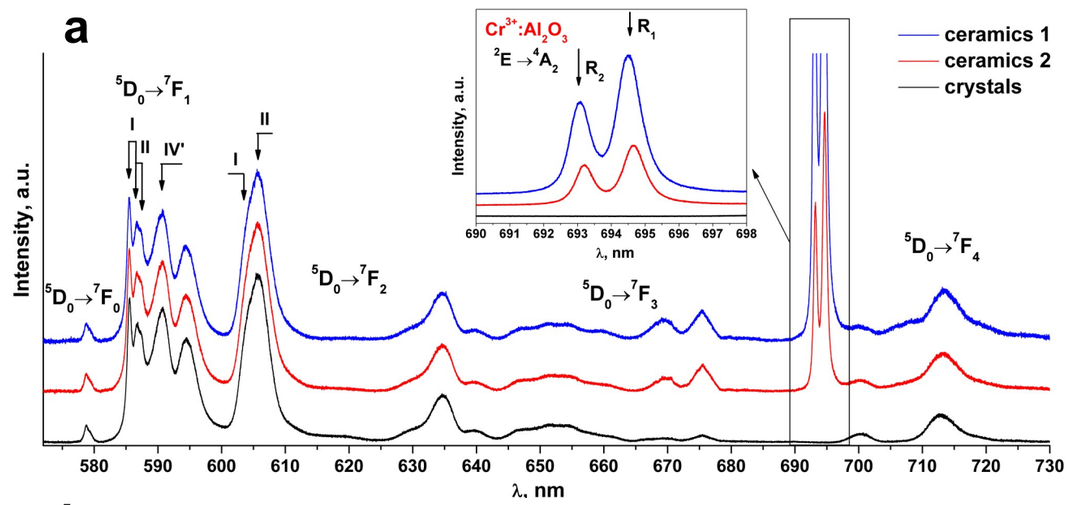
*c is cubic ZrO_2 modification

Raman spectra of single crystal and ceramic solid solutions ($\lambda_{exc.}$ = 632.8 nm, T = 300 K)

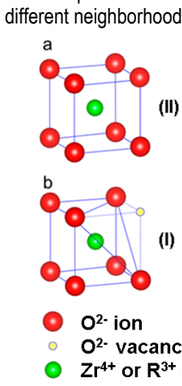


Spectral-luminescent properties

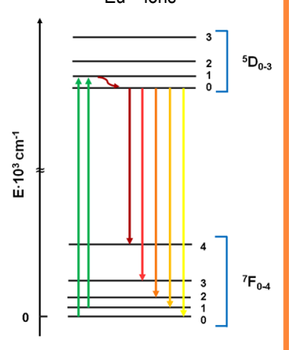
Luminescence spectra of single crystal and ceramic solid solutions: (1) uniaxial compaction; (2) slip casting. $\lambda_{exc.}$ = 532 nm (*a*); 527 nm (*b*), T = 300 K. *Inset:* luminescence bands (R_1 and R_2) of Cr^{3+} ions in Al_2O_3 for the $^2E \rightarrow {}^4A_2$ transition [8].



The Eu^{3+} optical centers with different neighborhood [9]

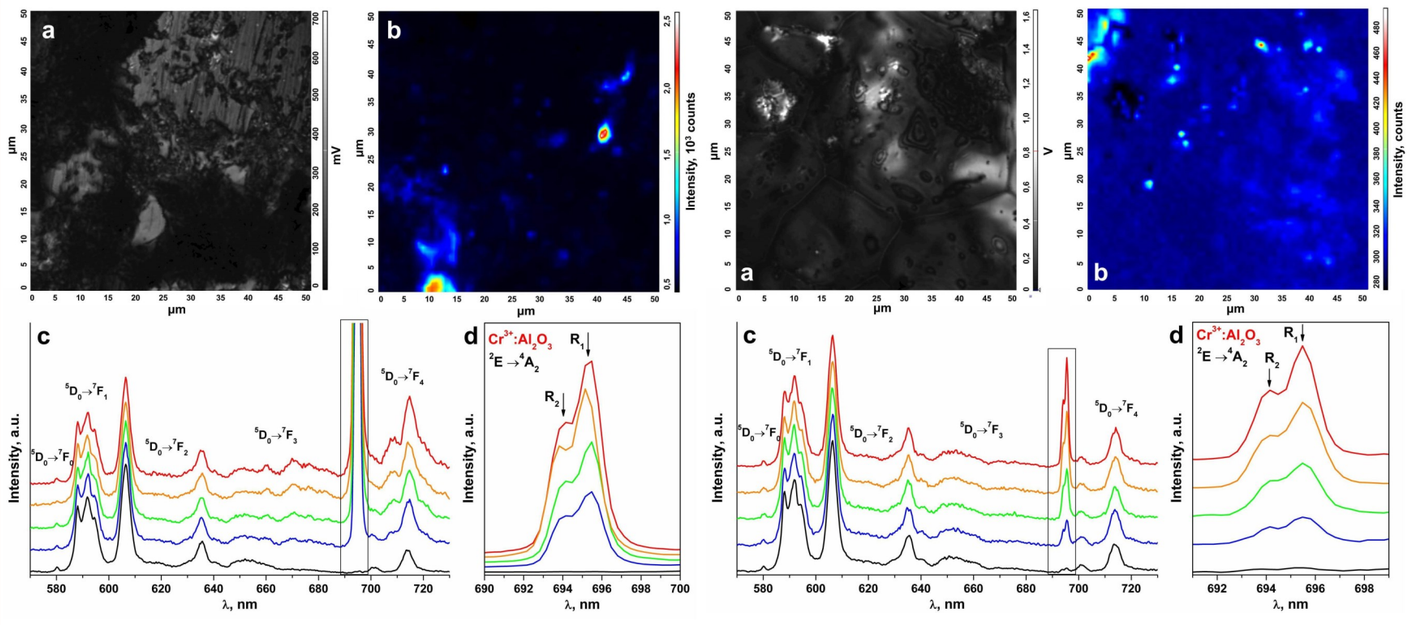


Energy structure of levels of Eu^{3+} ions



Impurity distribution

Ceramics №1 (uniaxial compaction) **Ceramics №2 (slip casting)**



(*a*) – Surface image of ceramic samples; (*b*) – R_1 and R_2 luminescence band intensity distribution map for the Cr^{3+} ions in Al_2O_3 in the surface area shown in fig. (a); (*c*) – luminescence spectra of the ceramic samples excited with a λ = 473 nm laser, T = 300 K, corresponding to the intensity scale in fig. (b); (*d*) – R_1 and R_2 luminescence bands of the Cr^{3+} ions in Al_2O_3 for the $^2E \rightarrow {}^4A_2$ transition.

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