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Structure and Spectral Luminescence Properties of (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ Ceramics Synthesized by Uniaxial Compaction and Slip Casting

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Abstract: The structure, phase composition and spectral luminescence properties of single crystal and ceramic specimens of (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ solid solutions synthesized using uniaxial compaction and slip casting techniques have been compared. The ceramic specimens have been synthesized from crushed single crystal specimens of similar composition. It has been shown that the crystalline structures of the ceramic and single crystal specimens are identical and cubic. The ceramic specimens synthesized using different methods prove to have close microstructure patterns. The spectral luminescence properties of Eu$^{3+}$ ions in the (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ ceramic specimens are similar to those of the single crystals with similar composition. The (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ ceramic specimens prove to have uncontrolled Cr$^{3+}$:Al$_2$O$_3$ impurities due to the synthesis conditions.

Keywords: zirconia; ceramic; single crystal; structure; luminescence spectra

1. Introduction

Zirconia-based materials exhibit a wide range of physicochemical properties that provide the possibility of their use in various applications [1–3]. For example, the high oxygen-ionic conductivity of these materials makes them suitable as solid-state electrolytes in solid oxide fuel cells, oxygen gages, oxygen pumps, etc. [3–5].

Zirconia-based solid state electrolytes are most typically synthesized using various ceramic technologies [6–11]. The synthesis method and conditions greatly affect the structural, physical, mechanical and transport properties of the ceramics. The structure, phase composition and density of the ceramic electrolytes depend largely on the precursor particle synthesis method. Ceramic material parameters such as grain size, porosity and component distribution homogeneity in the bulk and at the grain boundaries may dramatically change the electrophysical parameters of solid state electrolyte materials.

Precursor particles for ZrO$_2$–Y$_2$O$_3$ ceramics are produced using solid state synthesis, laser ablation, hydrothermal techniques, sol–gel technologies, combustion, co-deposition of metal hydroxides, co-crystallization of salts, etc. The most widely used methods are solid state synthesis [12] and various modifications of sol–gel synthesis [13–15].
It was of interest within the scope of this work to implement zirconia ceramic synthesis from molten powder obtained by crushing of ZrO$_2$-Y$_2$O$_3$ single crystals. The (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ composition of the source single crystals was chosen because our earlier studies of the transport properties of ZrO$_2$-Y$_2$O$_3$ crystals showed that crystals containing 9 mol.% Y$_2$O$_3$ stabilizing oxide have the highest ionic conductivity [16]. Eu$^{3+}$ ions were introduced in the ZrO$_2$-Y$_2$O$_3$ single crystals as a spectroscopic probe for studying the local neighborhood of the stabilizing oxide ions [17–22].

Thus, the aim of this work was to synthesize (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ ceramics from crushed single crystals of similar composition by uniaxial compaction and slip casting, to study its structure, phase composition and the local neighborhood of the Eu$^{3+}$ and Y$^{3+}$ ions in this ceramic and to compare these parameters with those of single crystal specimens with similar composition.

2. Materials and Methods

The test (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ solid solution single crystals were grown using directional melt crystallization at a 10 mm/h rate in a 130 mm diameter water-cooled crucible with direct high-frequency heating on a Kristall-407 plant (frequency 5.28 MHz, power 60 kW) (Moscow, Russia) [23,24]. The charge was prepared from zirconium oxide (ZrO$_2$), yttrium oxide (Y$_2$O$_3$) and europium oxide (Eu$_2$O$_3$) with a purity of min. 99.96 wt.%.

Some of the as-synthesized (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ solid solution single crystals were mechanically crushed to powder less than 1 mm in size, which was used for the synthesis of ceramic specimens. The preliminarily crushed (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ powder was ground with oleic acid addition in a drum with lining and grinding bodies made from stabilized zirconium dioxide (Y$_2$O$_3$ stabilizer) («Fritsch», Idar-Oberstein, Germany). The final powder had a grain size of ~40 µm and a specific surface area of ~8000 cm$^2$/g.

The ceramic specimens were synthesized using two methods, i.e., uniaxial compaction and slip casting of thin films on a moving substrate.

Casting powders were prepared for the uniaxial compaction of ceramic specimens. Granulated powder was compacted in the form of discs (radius ~15 mm, thickness ~0.48 mm) at a 15 kN pressure. The specimens were air heat treated at 1680 °C for 2 h in furnaces with lanthanum chromite heaters and VK-97 closed corundum ceramic crucibles («Nabertherm», Lilienthal, Germany). The density of the specimens was ~5.85 g/cm$^3$, i.e., 98% of the density of single crystals with similar composition (~5.98 g/cm$^3$). The ceramic specimens synthesized by uniaxial compaction are shown in Figure 1a.

Figure 1. (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ ceramic specimens synthesized from crushed single crystals of similar composition using (a) uniaxial compaction and (b) slip casting.
Slip casting of films on a moving ribbon (substrate) was implemented using a special plant designed by JSC «ECON» (JSC «ECON», Obninsk, Russia). The 7 mm × 7 mm × 0.3 mm pieces were placed on porous aluminum oxide kiln furniture and air heat treated at 1680 °C for 2 h. The density of the specimens was ~5.86 g/cm², i.e., 98% of the density of single crystals with similar composition (~5.98 g/cm²). The ceramic specimens synthesized by slip casting are shown in Figure 1b.

The density of the (ZrO₂)₀.909(Y₂O₃)₀.09(Eu₂O₃)₀.001 single crystal and ceramic specimens was measured by hydrostatic weighing on a Sartogosm CE224-C balance (St. Petersburg, Russia).

The surface morphology and elemental composition of the ceramic specimens were studied using scanning electron microscopy (SEM) and energy dispersion spectroscopy under a Quanta TM 3D 200i scanning electron microscope equipped with a microanalysis system (EDS) (FEI Company, Hillsboro, OR, USA). The SEM images were taken at a 20 kV accelerating voltage under high vacuum conditions (~10⁻³ Pa).

The phase composition of the ceramic specimens was studied using X-ray diffraction on an Empyrean diffractometer from PANalytical B.V. Co. (CuKα radiation, λ = 1.5414 Å) with a vertical goniometer and a PIXcel 3D detector (PANalytical B.V. Co, Almelo, Netherlands). The diffraction patterns were identified using the JSPDS PDF 2 1911 database.

The phase composition was also studied using Raman spectroscopy on a NTEGRA SPECTRA instrument from NT-MDT Co. with a 632.8 nm He-Ne laser as the excitation source (NT-MDT Co., Zelenograd, Russia). The Raman spectra were recorded in the reflection scheme with a resolution of 0.8 cm⁻¹.

The local neighborhood of the stabilizing oxide ions was studied using optical spectroscopy with Eu³⁺ ions being used as a spectroscopic probe. The T = 300 K luminescence spectra were recorded using an FHR 1000 spectrophotometer from Horiba Co. (Horiba Co., Kyoto, Japan) and a Hamamatsu R928B photomultiplier («Hamamatsu Photonics», Naka Ward, Japan) was used as a radiation detector. The excitation sources were YVO₄:Nd (λexc = 532 nm) and LiYF₄:Nd (λexc = 527 nm) lasers.

The 473 nm luminescence spectra were recorded for different areas of the ceramic specimen on a NTEGRA SPECTRA instrument from NT-MDT Co. (NT-MDT Co., Zelenograd, Russia) at room temperature. Confocal microscopic images were taken from 50 × 50 µm areas of the specimens.

The excitation spectra were recorded on a RF-5301PC spectrofluorometer from Shimadzu Co. (Shimadzu Co., Kyoto, Japan) with a 150 W xenon lamp used as an excitation source and a R212-14 photomultiplier used as a radiation detector.

3. Results

X-ray phase analysis data for the test (ZrO₂)₀.909(Y₂O₃)₀.09(Eu₂O₃)₀.001 ceramic specimens (Figure 2) suggest that the material is single-phase and has a fluorite-type cubic structure.

The test ceramic specimens synthesized using different methods (uniaxial compaction and slip casting) from crushed single crystals have close unit cell parameters, as summarized in Table 1. The lattice parameter of the (ZrO₂)₀.909(Y₂O₃)₀.09(Eu₂O₃)₀.001 ceramics is somewhat smaller than that of the single crystal material with similar composition.

The Raman spectra of the (ZrO₂)₀.909(Y₂O₃)₀.09(Eu₂O₃)₀.001 ceramics synthesized using different methods are shown in Figure 3. For comparison, the Raman spectrum of single crystals with similar composition is also shown.

The shape and positions of the bands in the Raman spectra of the ceramic specimens are close to those in the Raman spectra of the single crystals with similar composition. The Raman spectra of both the single crystal and ceramic specimens contain, along with the band typical of the cubic phase (c), a band near ~483 cm⁻¹ that is typical of the t° phase [25–27]. The structure of the t° phase is close to cubic except for a small shift of the oxygen ions along a certain direction relative to their positions in the fluorite structure.

Figure 4 shows the surface SEM images of the test (ZrO₂)₀.909(Y₂O₃)₀.09(Eu₂O₃)₀.001 ceramic specimens.
Figure 2. Fragments of the X-ray diffraction patterns of \((\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.09}(\text{Eu}_2\text{O}_3)_{0.001}\) ceramic solid solutions synthesized using different methods from crushed single crystals: (1) uniaxial compaction; (2) slip casting.

Table 1. Phase composition and lattice parameters of \((\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.09}(\text{Eu}_2\text{O}_3)_{0.001}\) single crystals and ceramics synthesized using different methods from crushed single crystals.

| (\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.09}(\text{Eu}_2\text{O}_3)_{0.001} | Solid Solution | Phase Composition $^1$ | Space Group | Unit Cell Parameters $a$, Å |
|-------------------------------------------------|----------------|-------------------------|-------------|-----------------------------|
| Single Crystal                                   | c-ZrO$_2$      | Fm3m                    | 5.141(1) [17]|                             |
| Ceramic #1 (Uniaxial Compaction)                 | c-ZrO$_2$      | Fm3m                    | 5.1381(3)   |                             |
| Ceramic #2 (Slip Casting)                        | c-ZrO$_2$      | Fm3m                    | 5.1368(3)   |                             |

$^1$ c is cubic ZrO$_2$ modification.

Figure 3. Raman spectra of \((\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.09}(\text{Eu}_2\text{O}_3)_{0.001}\) single crystal and ceramic solid solutions synthesized using different methods from crushed single crystals: (1) uniaxial compaction; (2) slip casting. $\lambda_{\text{exc.}} = 632.8$ nm, $T = 300$ K.
The SEM data suggest that the microstructures of the ceramic specimens synthesized using different methods slightly differ. The ceramic specimens synthesized using uniaxial compaction (Figure 4a) have a rough surface. The grain sizes could only be determined after specimen polishing. On the contrary, the ceramic specimens synthesized using slip casting on a ribbon had a smoother surface and their microstructure could be visualized under optical or electron microscope without preliminary polishing. The grain size was approx. 10 to 40 μm for the specimens synthesized using different methods.

Energy dispersion elemental analysis of the ceramic materials suggests that their chemical composition is identical to that of the single crystal specimens except for the presence of aluminum on the specimen surfaces.

The presence and distribution of the uncontrolled aluminum oxide impurity was studied for different ceramic specimen areas. The content of europium oxide in the material is commensurable with the energy dispersion method error and therefore was not measured. Figure 5 shows the grain structure of the ceramic specimen synthesized using slip casting. Table 2 shows experimentally measured concentrations of ZrO₂, Y₂O₃ and Al₂O₃ oxides in this ceramic specimen for the areas shown in Figure 5.

Table 2 suggests that the Al₂O₃ concentration at the ceramic grain surfaces was 0.6 mol.%. The oxide distribution along the grain boundaries was local (the Al₂O₃ concentration being within 1–3 mol.%). In the area corresponding to the intergrain volume (area 1 in Figure 5) between three ceramic grains, the Al₂O₃ concentration was 3.3 mol.%.

It can be hypothesized that the origin of the aluminum impurity is the corundum crucible that the specimens contacted during annealing. Analysis of literary data reveals evidence of the low solubility of aluminum oxide in ZrO₂-Y₂O₃. It was reported [28–31] that the solubility limit of Al₂O₃ in ZrO₂-9 mol.% Y₂O₃ at T = 1700 °C is 0.7 mol.%. At higher Al₂O₃ concentrations, aluminum oxide in the ZrO₂-Y₂O₃ ceramics is present in the form of particles located inside the grains and at the grain boundaries or forms grain-boundary phases with high Al₂O₃ content.

Taking into account the results of this work and earlier studies [28–31], one can conclude that some of the Al₂O₃ impurity is dissolved in the ceramics whereas most of the impurity is localized at the grain boundaries and, to a smaller extent, on the ceramic surface in the form of inclusions. Al₂O₃ solubility in (ZrO₂)₀.₉₀₉(Y₂O₃)₀.₀₉(Eu₂O₃)₀.₀₀₁ ceramic solid solutions can be the cause of the decrease in the lattice parameter of the solid solutions in comparison to the single crystals of similar composition.

Figure 4. Microstructure images of the (ZrO₂)₀.₉₀₉(Y₂O₃)₀.₀₉(Eu₂O₃)₀.₀₀₁ ceramic specimens synthesized using different methods from crushed single crystals: (a) uniaxial compaction; (b) slip casting.

Figure 3. Raman spectra of (ZrO₂)₀.₉₀₉(Y₂O₃)₀.₀₉(Eu₂O₃)₀.₀₀₁...
Figure 6 shows the luminescence spectra of the (ZrO$_2$)$_{0.990}(Y_2O_3)_{0.09}(Eu_{2}O_3)_{0.001}$ single crystal and ceramic solid solutions recorded with excitation of the $^3$D$_1$ level of the Eu$^{3+}$ ions by a 532 nm laser at room temperature.

![SEM image of the (ZrO$_2$)$_{0.990}(Y_2O_3)_{0.09}(Eu_{2}O_3)_{0.001}$ ceramic specimen synthesized using slip casting.](image)

**Figure 5.** SEM image of the (ZrO$_2$)$_{0.990}(Y_2O_3)_{0.09}(Eu_{2}O_3)_{0.001}$ ceramic specimen synthesized using slip casting. The + symbols show areas (1, 2, 3, 4) in which the ZrO$_2$, Y$_2$O$_3$ and Al$_2$O$_3$ oxide concentrations were measured.

**Table 2.** Elemental analysis data for (ZrO$_2$)$_{0.990}(Y_2O_3)_{0.09}(Eu_{2}O_3)_{0.001}$ ceramics synthesized using slip casting.

| Area | ZrO$_2$ | Y$_2$O$_3$ | Al$_2$O$_3$ |
|------|---------|------------|-------------|
| 1    | 87.1    | 9.6        | 3.3         |
| 2    | 89.6    | 9.9        | 0.6         |
| 3    | 89.2    | 10.0       | 0.8         |
| 4    | 89.2    | 9.9        | 0.9         |

![Luminescence spectra](image)

**Figure 6.** Luminescence spectra of (ZrO$_2$)$_{0.990}(Y_2O_3)_{0.09}(Eu_{2}O_3)_{0.001}$ single crystal and ceramic solid solutions synthesized using different methods from crushed single crystals: (1) uniaxial compaction; (2) slip casting. $\lambda = 532$ nm, $T = 300$ K. Inset: luminescence bands (R$_1$ and R$_2$) of Cr$^{3+}$ ions in Al$_2$O$_3$ for the $^2$E$\rightarrow$$^4$A$_2$ transition.

Analysis of the luminescence spectra for the transitions between the $^5$D$_0$ and $^7$F$_{j}$($j=4$) multiplets of the Eu$^{3+}$ ions in the (ZrO$_2$)$_{0.990}(Y_2O_3)_{0.09}(Eu_{2}O_3)_{0.001}$ ceramic solid solu-
tions recorded with excitation of the $^5D_1$ level of the Eu$^{3+}$ ions by a 532 nm laser at $T = 300$ K shows that they contain the same spectral bands as the respective spectra of the $(\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.009}(\text{Eu}_2\text{O}_3)_{0.001}$ single crystal solid solutions. The luminescence spectra of the $(\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.009}(\text{Eu}_2\text{O}_3)_{0.001}$ single crystals for the $^3D_0 \rightarrow ^7F_{0-2}$ transitions of the Eu$^{3+}$ ions, which are superimpositions of the bands of the Eu$^{3+}$ optical centers with different neighborhoods, were reported earlier [17]. The numbers I, II and IV in Figure 6 mark the respective Eu$^{3+}$ optical centers. Optical center I is where the Eu$^{3+}$ ions have one oxygen vacancy and are surrounded by seven oxygen atoms. Optical center II is where the Eu$^{3+}$ ions do not have oxygen vacancies in the first coordination shell but have one oxygen vacancy in the second coordination shell. Optical center IV’ represents the centers in which oxygen vacancies are located in the farthest coordination shells of the Eu$^{3+}$ ions.

It can be seen from Figure 6 that the intensity ratio of the spectral bands for the $^5D_0 \rightarrow ^7F_{0-2}$ transitions of the Eu$^{3+}$ ions pertaining to different optical centers in the synthesized $(\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.009}(\text{Eu}_2\text{O}_3)_{0.001}$ ceramic specimens is the same as the respective intensity ratio of the optical centers for the single crystal material of similar composition. The difference in the luminescence spectra for the ceramics is the presence of two intense and narrow bands near 693 and 694.5 nm and a change in the shape of the spectral bands in the 665–730 nm region. Taking into account the results of earlier studies [17–22], one can conclude that these changes in the luminescence spectra of the ceramics are not caused by the optical transitions of the Eu$^{3+}$ ions. It can also be seen from Figure 6 that the bands near 693 and 694.5 nm for different ceramic specimens have different intensities relative to the luminescence bands of the Eu$^{3+}$ ions.

Figure 7 shows the luminescence spectra of the $(\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.009}(\text{Eu}_2\text{O}_3)_{0.001}$ single crystal and ceramic solid solutions recorded with excitation of the $^5D_1$ level of the Eu$^{3+}$ ions by a 527 nm laser at room temperature.

![Figure 7. Luminescence spectra of $(\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.009}(\text{Eu}_2\text{O}_3)_{0.001}$ single crystal and ceramic solid solutions synthesized using different methods from crushed single crystals: (1) uniaxial compaction; (2) slip casting. $\lambda = 527$ nm, $T = 300$ K.](image)

Analysis of the luminescence spectra of the Eu$^{3+}$ ions in the $(\text{ZrO}_2)_{0.909}(\text{Y}_2\text{O}_3)_{0.009}(\text{Eu}_2\text{O}_3)_{0.001}$ single crystal and ceramic solid solutions shown in Figure 7 shows that the luminescence spectra of the ceramic specimens are identical to each other and to the luminescence spectrum of the single crystal specimen. The luminescence spectra of the ceramic specimens differ from those of the single crystal specimen through the presence of two narrow bands at 693 and 694.5 nm whose intensities differ for the two ceramic specimens. It should be noted that the intensities of the bands in the luminescence spectrum of the Eu$^{3+}$ ions under excitation by a 527 nm laser are lower than the intensities of the bands in the luminescence spectrum recorded with 532 nm excitation.

Analysis of literary data shows that the Cr$^{3+}$: Al$_2$O$_3$ luminescence spectrum excited by a 532 nm laser contains two intense and narrow bands near 692.8 and 694.2 nm (the
so-called R-bands) caused by the $^2E \rightarrow ^4A_2$ transition of the Cr$^{3+}$ ions and also contains several additional weak bands near 660, 670, 706 and 714 nm (the N-bands and the side-bands) [32–34]. The positions of these bands are similar to those of the bands found in the luminescence spectra of the (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ ceramics (Figures 6 and 7). Thus, all the ceramic specimens contained a chromium impurity along with aluminum oxide, as suggested by the presence of additional bands in the luminescence spectra of the ceramic specimens.

The chromium impurity probably originates from the use of lanthanum chromite (LaCrO$_3$) heaters during specimen heat treatment in insufficiently closed aluminum oxide (Al$_2$O$_3$) crucibles. Since the ceramic specimens were sintered at a high temperature (1680 °C), chromium ions could evaporate from the heater material LaCrO$_3$. The volatility of chromium in LaCrO$_3$ at high temperatures is a well-known problem [35]. It was hypothesized that chromium evaporation occurs by the following reaction:

$$2\text{LaCrO}_3(s) = \text{La}_2\text{O}_3(s) + \text{Cr}_2\text{O}_3(g) \quad (1)$$

Chromium oxide may also reduce to metallic chromium at above 1200 °C [36].

According to literary data, Cr$_2$O$_3$ solubility in Al$_2$O$_3$ is unlimited [37], and given that the luminescence spectra (Figures 6 and 7) only contain bands typical of the Cr$^{3+}$ ions in Al$_2$O$_3$, one can conclude that Cr$_2$O$_3$ interacts mainly with Al$_2$O$_3$ to form the Cr$_2$O$_3$-Al$_2$O$_3$ solid solution. The chromium impurity seems to not enter into the ZrO$_2$-Cr$_2$O$_3$ solid solution since the experimental luminescence spectra did not contain the wide band in the 700–1100 nm region which is typical of Cr$^{3+}$ ion luminescence in ZrO$_2$-Cr$_2$O$_3$ [38,39]. Furthermore, Cr$_2$O$_3$ solubility in ZrO$_2$-Y$_2$O$_3$ was quite low, only 0.7 mol.% for the ZrO$_2$-8 mol.% Y$_2$O$_3$ ceramics at $T = 1450$ °C [36,40].

An inhomogeneous distribution of the uncontrolled impurity in the ceramic specimens is suggested by the change in the R$_1$ and R$_2$ luminescence band intensities of the Cr$^{3+}$ ions in Al$_2$O$_3$ in comparison to the luminescence bands of the Eu$^{3+}$ ions in different ceramic surface areas (Figures 8 and 9). The R$_1$ and R$_2$ luminescence band intensity distribution map for the Cr$^{3+}$ ions in Al$_2$O$_3$ in a 50 µm × 50 µm surface area (Figures 8a and 9a) is shown in Figures 8b and 9b. Figures 8c and 9c show the luminescence spectra for different surface areas of the test ceramics excited with a 473 nm laser. Figures 8d and 9d separately show the R$_1$ and R$_2$ luminescence bands of the Cr$^{3+}$ ions in Al$_2$O$_3$ for the $^2E \rightarrow ^4A_2$ transition.

These spectra are shown in relative units normalized to unity relative to the luminescence band peaking at 606.4 nm caused by the $^3D_0 \rightarrow ^7F_2$ transition of the Eu$^{3+}$ ions. The color of the R$_1$ and R$_2$ luminescence bands of the Cr$^{3+}$ ions in Figures 8c,d and 9c,d corresponds to the color in the scale shown to the right of the intensity distribution maps in Figures 8b and 9b characterizing the intensity of these bands.

Thus, analysis of the R$_1$ and R$_2$ luminescence band intensity distribution maps for the Cr$^{3+}$ ions in Al$_2$O$_3$ on the ceramic specimen surfaces, as shown in Figures 8b and 9b, showed that the uncontrolled Cr$^{3+}$: Al$_2$O$_3$ impurities in the test ceramic specimens were in the form of discrete inclusions.

Figure 10 shows the luminescence excitation spectra of (ZrO$_2$)$_{0.879}$(Y$_2$O$_3$)$_{0.12}$(Eu$_2$O$_3$)$_{0.001}$ single crystal and (ZrO$_2$)$_{0.909}$(Y$_2$O$_3$)$_{0.09}$(Eu$_2$O$_3$)$_{0.001}$ ceramic solid solutions. The recording wavelength of 606 nm corresponds to the position of the most intense $^3D_0 \rightarrow ^7F_2$ transition band of the Eu$^{3+}$ ions.
Chromium oxide may also reduce to metallic chromium at above 1200 °C. The excitation spectra of the (ZrO₂)₀.₉₀₉(Y₂O₃)₀.₀₉₀(Eu₂O₃)₀.₀₀₁ ceramics (Figure 10) contain a sufficiently wide symmetrical band in the 220 to 290 nm region peaking at ~253 nm, which according to earlier data [41] originates from the O²⁻→Eu³⁺ charge transfer transition. For the (ZrO₂)₀.₈₇₉(Y₂O₃)₀.₁₂(Eu₂O₃)₀.₀₀₁ single crystal, this band is at a greater wavelength (~265 nm). Along with the O²⁻→Eu³⁺ charge transfer band, the luminescence excitation spectra of the (ZrO₂)₀.₈₇₉(Y₂O₃)₀.₁₂(Eu₂O₃)₀.₀₀₁ single crystal and (ZrO₂)₀.₉₀₉(Y₂O₃)₀.₀₉₀(Eu₂O₃)₀.₀₀₁ ceramic solid solutions contain bands corresponding to intraconfigurational f-f transitions between the multiplets of the 7F main state and the 5D, 5L and 5G excited states of the Eu³⁺ ions. The most intense band is the one at 528 nm that pertains to the ⁷F₀₁→⁵D₂ transition. The difference in the spectral band intensities between the single crystals and the ceramics for the group of optical transitions in the 380–430 nm region seems to be caused by stronger scattering from the non-transparent ceramic specimens.

Figure 8. (a) Surface image of a ceramic specimen synthesized using uniaxial compaction; (b) R₁ and R₂ luminescence band intensity distribution map for the Cr³⁺ ions in Al₂O₃ on the surface area shown in Figure 8a; (c) luminescence spectra of the ceramic specimen excited with a λ = 473 nm laser (T = 300 K) corresponding to the intensity scale in Figure 8b; (d) R₁ and R₂ luminescence bands of the Cr³⁺ ions in Al₂O₃ for the ²E→⁴A₂ transition.
The surface morphology of the ceramic specimens synthesized using different methods from crushed single crystals is shown in Figure 9a. The ceramic solid solutions synthesized using different methods from crushed single crystals are single crystal and diffuse. The ceramic specimens were sintered in air directional melt crystallization in a cold skull. The ceramic specimens have more homogeneous surfaces. The grain size of the ceramic specimens was approx. 10 to 40 µm.

Figure 9. (a) Surface image of a ceramic specimen synthesized using slip casting; (b) R1 and R2 luminescence band intensity distribution maps for the Cr3+ ions in Al2O3 on the surface area shown in Figure 9a; (c) luminescence spectra of the ceramic specimen excited with a λ = 473 nm laser (T = 300 K) corresponding to the intensity scale in Figure 9b; (d) R1 and R2 luminescence bands of the Cr3+ ions in Al2O3 for the 2E→2A2 transition.

Figure 10. Luminescence excitation spectra of (ZrO2)0.879(Y2O3)0.12(Eu2O3)0.001 single crystal and (ZrO2)0.909(Y2O3)0.09(Eu2O3)0.001 ceramic solid solutions synthesized using different methods from crushed single crystals: (1) uniaxial compaction; (2) slip casting. λem = 606 nm, T = 300 K.
4. Discussion

In this work ceramic specimens were synthesized using uniaxial compaction and slip casting from powders of crushed \((ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}\) single crystals grown by directional melt crystallization in a cold skull. The ceramic specimens were sintered in air at 1680 °C for 2 h. The density of the as-synthesized ceramic specimens was 98% of the density of the single crystal specimens.

The \((ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}\) ceramic solid solutions synthesized using different methods from crushed single crystals are single-phase and have a fluorite-type cubic structure with close lattice parameters. For uniaxially compacted ceramics, \(a = 5.1381(3)\ \text{Å}\); for slip cast ceramics, \(a = 5.1368(3)\ \text{Å}\). Raman spectroscopy showed that the structure of the test ceramic specimens consists of a \(t^\prime\) phase.

The surface morphology of the ceramic specimens synthesized using different methods differs, but the microstructures of the specimens are quite similar. The \((ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}\) slip cast ceramic specimens have more homogeneous surfaces. The grain size of the ceramic specimens was approx. 10 to 40 \(\mu\text{m}\).

Comparison of the luminescence spectra of the \(\text{Eu}^{3+}\) ions in the \((ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}\) ceramic and single crystal solid solutions did not reveal any tangible difference. The luminescence excitation spectra of the \(\text{Eu}^{3+}\) ions in the \((ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}\) ceramics are similar in band shape and position to the luminescence excitation spectra of the \(\text{Eu}^{3+}\) ions in the single crystals except for the \(\text{O}^{2-} \rightarrow \text{Eu}^{3+}\) charge transfer band’s shift towards smaller wavelengths.

Elemental analysis revealed the presence of aluminum impurities, and optical spectroscopic study of the \((ZrO_2)_{0.909}(Y_2O_3)_{0.09}(Eu_2O_3)_{0.001}\) ceramic specimens showed the presence of uncontrolled \(\text{Cr}^{3+}:\text{Al}_2\text{O}_3\) impurities originating from conditions related to the synthesis process.

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