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USING THE SINTERING METHOD FOR THE SYNTHESIS OF A DUPLEX STRUCTURE WHICH IS BASED ON SOLID ELECTROLYTES SCSZ AND CEO2, STABILIZED BY GD2O3 (GDC)

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In this research used two kind of initial powders: commercial powder of electrolyte GDC and powder of electrolyte ScSZ-n, which was obtained by method of laser evaporation [1]. The characteristics of the powders are presented in table 1. As you can see, the particle size corresponds to ScSZ-n, according to the BET analysis, it is almost two times smaller than the particle size of the GDC measurement. For making sizes of particles closer to each other particles of ScSZ-n powder were calcined at 600°C for 4 hours, followed by grinding in an agate mortar. The resulting powder was designated ScSZ-600, and its characteristics are also presented in table 1.

Table 1. Nomenclature and characteristics of initial powders.

Designation	Chemical composition	S_{BET}, m^2/g	d_{BET}, μm	Γ_{theor}, g/sm^3
GDC	$Ce_{0,9}Gd_{0,1}O_{2-\delta}$	34,2	24	7,21
ScSZ-n	$Zr_{0,81}Sc_{0,19}O_{1,905}$	81,5	13	5,67
ScSZ-600	$Zr_{0,81}Sc_{0,19}O_{1,905}$	54,9	19	5,67

Pictures of initial powders GDC and ScSZ-n was shown in fig.1. Scanning microscope (LEO 982) and transmission electron microscope (Jeol Jem 2100) used to obtain pictures of initial nano powders. We can see, that powder ScSZ-n was not agglomerated and particles of this powder has spherical shape. While particles of powder GDC was agglomerated and they have size near to 0.2 μm.
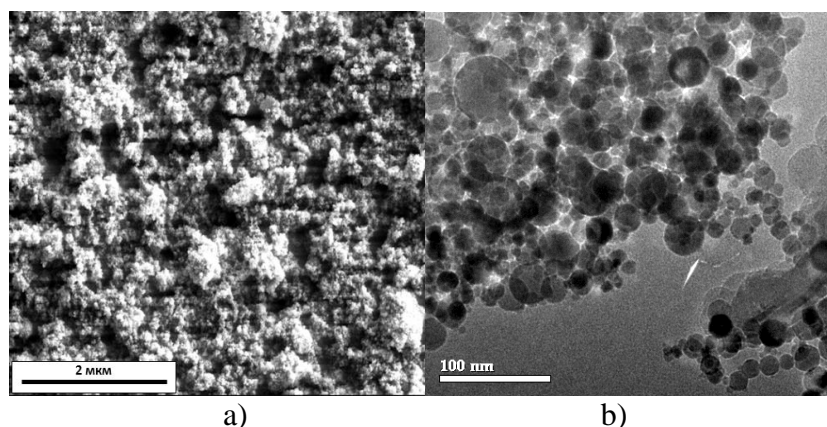

a)   b)

Fig. 1. Pictures of powders a) – GDC and b) ScSZ-n.

Joint sintering of two different layers is possible with agreed shrinkage in the process of sintering of materials. The main characteristics of powders, which affects to kinetics of sintering, are particle size distribution and chemical compositions. All powders used in this work are nano sized. However, firstly, we knew GDC powder sinters worse than ScSZ, and for obtain high density layers of powder GDC necessary high temperatures near to 1400-1600ºC [1,2]. Secondly, commercial powder GDC agglomerated and this factor leads to difficulty for sintering.

Results of dilatometric researches of initial powders shown in a fig. 2. As we can see temperature of sintering start of GDC higher almost to 100 ºC compare with temperature of

sintering start of ScSZ. Also processes of sintering of powders ScSz-n and ScSZ-600 are faster and ends up near to ~1150ºC and 1200ºC, while sintering of GDC was continued till 1500ºC. So, unlikely, we can do joint sintering of duplex structure of these two initial powders.

The literature shows that the kinetics of sintering of a solid electrolyte GDC can be significantly changed by introducing a second dopant (sodopant) into its composition [1]. Therefore, theoretically, it is possible to select a sodopant that will "fit" the GDC sintering kinetics to ScSZ to realize joint sintering.
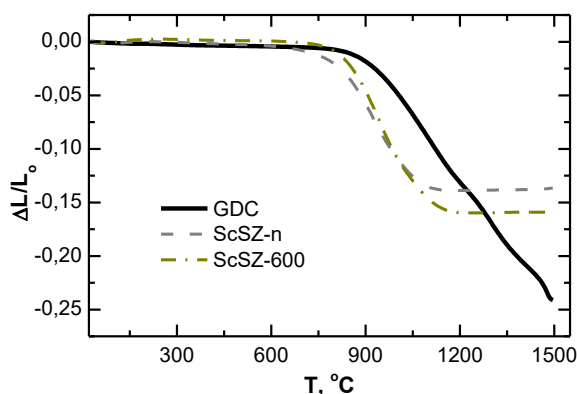

Fig. 2. Linear shrinkage curves of the initial electrolyte materials GDC and ScSZ.

Sodopants improve GDC sintering due to the fact that during sintering they form a liquid phase, which increases the rate of interparticle diffusion. Therefore, the introduced dopant should be segregated at the grain boundaries, and not dissolved in the grain volume. In [1] was proposed an estimated criterion for the solubility of dopants in the host lattice.

Thus, sodopants that do not dissolve in the GDC lattice must be characterized by |X| significantly greater than zero. However, if value of X is very large, it is possible to form a secondary phase in which the GDC does not dissolve, which does not allow sintering in the liquid-phase. In addition, positive X dopants (large size and/or electron-donating) will lead to a decrease in the concentration of oxygen vacancies near the grain boundaries and therefore to an increase in the sintering temperature. Dopants with negative X (small size and/or electron acceptor) will contribute to sintering.

Table 2 presents the slope of Vegard X values for dopants. Based on these data and literature analysis, the following elements were selected as sodopants for the study: Co, Cu, Mn and Zn.

Table 2. The slope of Vegard for dopants.

Element	r_i*, Å	X (x 100000)
Si^{4+}	0,5	-95
Al^{3+}	0,69	-77
Ni^{2+}	0,83	-61
Ga^{3+}	0,77	-59
Mn^{3+}	0,78	-58
Fe^{3+}	0,78	-57
Cu^+	0,92	-56
Li^+	0,92	-56
Cu^{2+}	0,89**	-48
Mg^{2+}	0,89	-48
Co^{2+}	0,90	-45
Zn^{2+}	0,90	-45
Fe^{2+}	0,92	-41
Sc^{3+}	0,87	-37
Mn^{2+}	0,96	-32
Hf^{4+}	0,83	-31
Zr^{4+}	0,84	-29
In^{3+}	0,92	-26
Lu^{3+}	0,98	-13

The introduction of sodopants in the electrolyte GDC.

The method of introduction of sodopants into the composition of GDC included the following stages:

1. Preparation of nitrate solution of the sodopants.
2. Dispersion of nanoscale GDC powder in isopropyl alcohol.
3. Adding to the resulting slurry the required amount of an aqueous solution of nitrate sodopants and stirring with a stirrer.
4. Solvent removal for several hours with constant stirring and heating up to 60ºC.
5. Drying at 120°C for at least 2 hours (decomposition of nitrate salts occurred during sintering of ceramics).
6. Grinding of the obtained powders in agate mortar.

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Salts of Co(NO3)2, Cu(NO3)2, Mn(NO3)2, (Fluka Analytical) and Zn(NO3)2, which were dissolved in distilled water, were used as initial reagents for preparation of nitrate solutions. The concentration of the solution was calculated from the mass of salt and the volume of water taken for dissolution.

Each sodopant was used to manufacture three compositions, wherein the number of entered sodopant: 1, 3 and 5 mol.%. The amount of sodopant was calculated on the assumption that the sodopant would equally replace Ce and Gd, without reducing Ce to an oxidation state of 3+, and the change in charge was compensated by a change in the amount of oxygen. For example, the composition, which was supposed to contain 3 mol.% Mn was defined as $Mn_{0,03}Ce_{0,873}Gd_{0,097}O_{1,922}$, and composition with 1 mol.% Cu – $Cu_{0,01}Ce_{0,891}Gd_{0,099}O_{1,941}$. Further, for simplicity, compositions with sodopants will be denoted as *GDC -xM*, where *x* is the amount of sodopant introduced into the mol.% (1, 3 or 5), and *M* is a sodopant (Co, Cu, Mn or Zn).

Method of research

Two types of samples were formed from powders prepared according to the method described above: 1) for the study of sintering kinetics and 2) for the study of conductivity. Samples for dilatometric studies were disks with a diameter of 8 mm and a thickness of 2 mm compressed to a relative density of ~ 0.5. Sintering kinetics was researched in the air atmosphere in the temperature range 20-1500°C using dilatometer Dil 402C. To measure the conductivity, the samples were pressed into blocks of rectangular cross-section, 3×2×30 mm, to a relative density of 0.6. For this purpose, the mass of backfill and pressing pressure were selected. The resulting products were sintered in an air atmosphere. Compositions containing Co and Mn were sintered at 1150ºC, and for compositions c Zn and Cu-at 1250ºC and 1050ºC, respectively. Exposure in all cases was 4 hours. Probes made of platinum wire with a diameter of 0.2 mm were applied to sintered samples. Conductivity measurements were carried out by 4-probe method at direct current in the temperature range 600-900°C with help of the automatic data acquisition system based on the controller ADAM-5000. After dilatometric studies on samples containing 5 mol.% of sodopants was determined phase composition. The diffractograms were taken on a D8 DISCOVER diffractometer on copper radiation (Cu KA1, 2 λ = 1,542 Å) with a graphite monochromator on a diffracted beam. The processing was performed using the TOPAS 3 program with the Rietveld algorithm for refinement of structural parameters. The correction factor K (in Scherer's formula) = 0.89 was used to estimate the average crystallite size (OCD).

The influence of sodopants on the characteristics of the GDC

The results of the analysis of the structure of samples GDC-5M (M = Co, Cu, Mn, Zn) after sintering dilatometer are in table 3. It is seen that the material of all samples contains one crystalline phase-a solid solution based on the cubic form CeO2 (Cerianite) with a cubic lattice parameter of 0.5422±0.0003 µm.

Table 3. Structural characteristics of GDC-based ceramics.

Designation	T_{sint}, °C	$C_{куб.}$, %	OKP, µm	a, µm	γ_m*, г/см^3	γ_{XRD}**, г/см^3	γ_{calc}***, г/см^3
GDC	1500	100	52(3)	0,5422(3)	7,08	7,21	7,21
GDC-5Co	1115	100	47(2)	0,5422(3)	6,70	7,00	7,19
GDC-5Cu	1150	100	54(3)	0,5421(3)	6,69	7,01	7,19
GDC-5Mn	1150	100	48(2)	0,5420(3)	6,87	7,02	7,15
GDC-5Zn	1150	100	52(3)	0,5422(3)	6,63	7,02	7,16

* γm is the density of the sample measured by underwater weighing;
** γXRD-density of solid solution (x-ray data);
*** γcalc-density of the composite (calculation).

On diffractograms of compositions containing Co and Zn there is a tightening of lines towards small angles, which may be due to the heterogeneity of the composition. For these samples, the value of OCD is probably underestimated.

Table 3 shows that the lattice parameter of all materials within the error is the same. No secondary phases were also detected. Therefore, to assess the degree of dissolution of Stepanov in the matrix of ceria difficult. On the one hand, most sodopants are characterized by ion radii close to the radius of Ce4+ (table 4) and their entry into the solid solution should not significantly change the lattice parameter. On the other hand, it is possible that sodopants in the form of nanoscale inclusions are distributed along the grain boundaries (due to the method of their introduction) and because of their smallness are not fixed on diffractograms.

Table 4. Characteristics of the ions.

Element	r_{ion}, μm *	χ**
Ce^{4+}	0,097	1,12
Gd^{3+}	0,105	1,20
Co^{2+}	0,090	1,88
Cu^{2+}	0,073***	1,90
Mn^{2+}	0,096	1,55
Zn^{2+}	0,090	1,65

* ionic radius by Scherer and Pruitt for coordination number 8;
** electronegativity according to Pauling;   *** coordination number 6.

In addition, Goldschmidt's rule claims that a significant solubility of ions of a substance (dopant) in the lattice of another substance (host) will be observed if 1) the ion radius of the host and dopant differ by no more than 15% and 2) the electronegativity of the host and dopant differ by no more than 0.4 [1]. Therefore, for good solubility in the CeO_2 lattice, the dopant ion must have an ionic radius in the range of 0.082 - 0.112 μm and an electronegativity of 0.72-1.52. As can be seen from table 3.4 these two conditions are satisfied by the main dopant Gd^{3+}. Mn^{2+} is characterized by close values to the specified ranges. Although Co^{2+} and Zn^{2+} have ionic radius suitable for entering the lattice, their electronegativity does not fit to range. Both parameters of the Cu^{2+} ion do not correspond to the Goldschmidt rule, indicating poor solubility of copper in CeO_2.

Since the x-ray phase analysis was performed on the compositions with the highest content of the alloying additive, we believe that the introduction of 1 and 3 mol.% sodopants should also not affect the structure of the GDC.

Conclusion

The influence of small additives of transition metal oxides (sodopants) on the properties of the solid electrolyte $Ce_{0,9}Gd_{0,1}O_{2-\delta}$ (GDC) was investigated. Samples of dense ceramics of compositions $Ce_{0,9(1-x)}Gd_{0,1(1-x)}M_xO_{2-\Delta}$ (x = 0,01, 0,03, 0,05; M = Co, Cu, Mn, Zn) were synthesized by sintering compacts at a temperature of 1050-1250°C depending on the type of additive. The grain size in the synthesized samples was about 50 μm.

The introducing of any of the studied sodopants leads to an intensification of GDC sintering. Moreover, the temperature of the end of shrinkage decreases in a number of sodopants Zn → Mn → Co →Cu, i.e. the composition containing copper is characterized by the lowest temperature of the end of shrinkage.

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