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Effect of ytterbium oxide co-doping impurity on the structure and transport characteristics of $(ZrO_2)_{0.91-x}(Sc_2O_3)_{0.09}(Yb_2O_3)_x$ (x = 0 - 0.01) single crystals

M.A. Borik[1], G.M. Korableva[2], A.V. Kulebyakin[1,*], I.E. Kuritsyna[2], E.E. Lomonova[1], V.A. Myzina[1], P.A. Ryabochkina[3], N.V. Sidorova[3], N.Yu. Tabachkova[1,4] and T.V. Volkova[3]

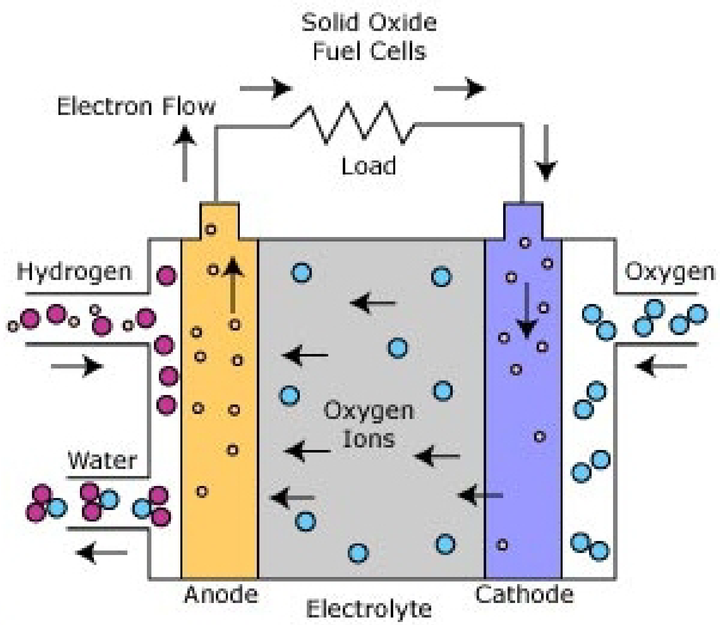
[1] Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia;
[2] Institute of Solid State Physics of the Russian Academy of Sciences, Chernogolovka, Russia;
[3] Ogarev Mordovia State University, Saransk, Russia;
[4] National University of Science and Technology «MISIS», Moscow, Russia.

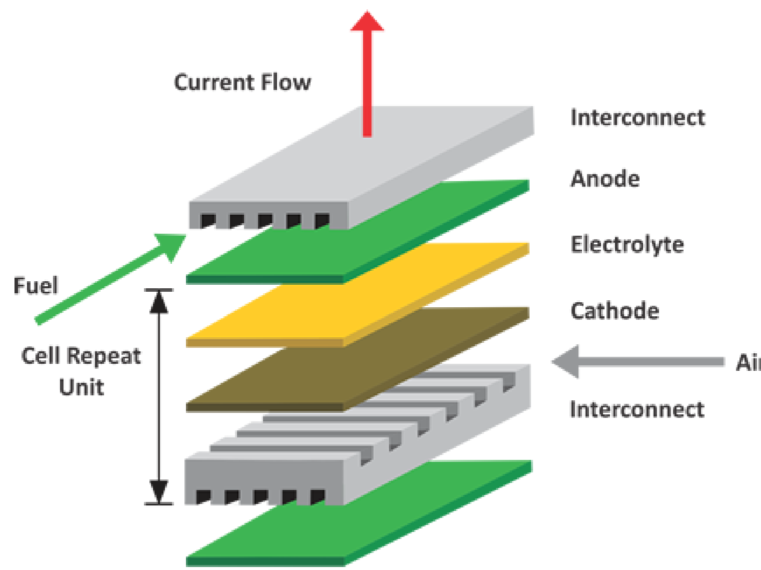
* Corresponding author: kulebyakin@lst.gpi.ru

INTRODUCTION

Materials based on zirconia are a promising electrolyte for an application in solid oxide fuel cells (SOFC) that can operate at 1100 K. Scandia stabilized zirconia (ScSZ) have the highest conductivity at moderate temperatures. However, a major disadvantage of these materials is the degradation of their conductivity during long-term operation due to an unstable phase composition. Partial replacement of scandia for other oxides in the ZrO_2-Sc_2O_3 system aimed at increasing the stability of the high-conductivity cubic phase proves to be one of the most efficient solutions to these problems.

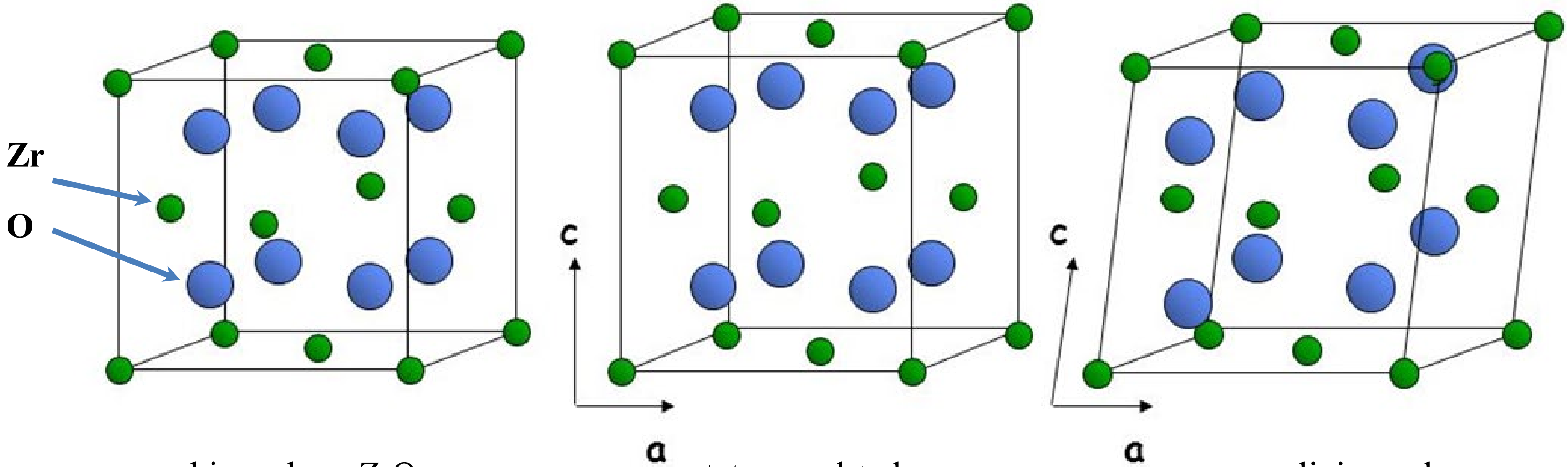
The aim of this work is to assess the effect of the introduction of dopant ytterbium oxide into ZrO_2 – 9 mol.% Sc_2O_3 solid solutions on the phase composition, structure, and electrophysical properties of the material.





Planar SOFC configuration

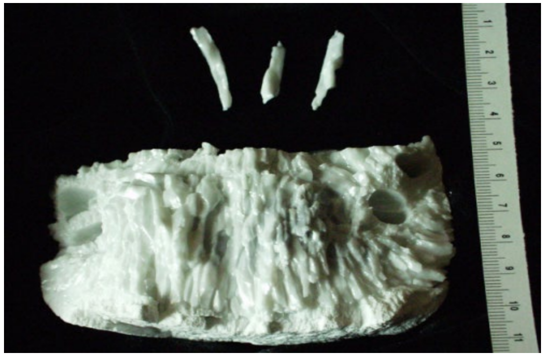
The three zirconia polymorphs



cubic *c*-phase ZrO_2
Fm3m
2680 -2370 ºC
a=b=c
α=β=γ=90º

tetragonal *t*-phase
$P4_2/nmc$
2370 - 1160 ºC
a=b≠c
α=β=γ=90º

monoclinic *m*-phase
$P2_1/C$
< 1160 ºC
a ≠ b≠c
α=γ=90º β>90º

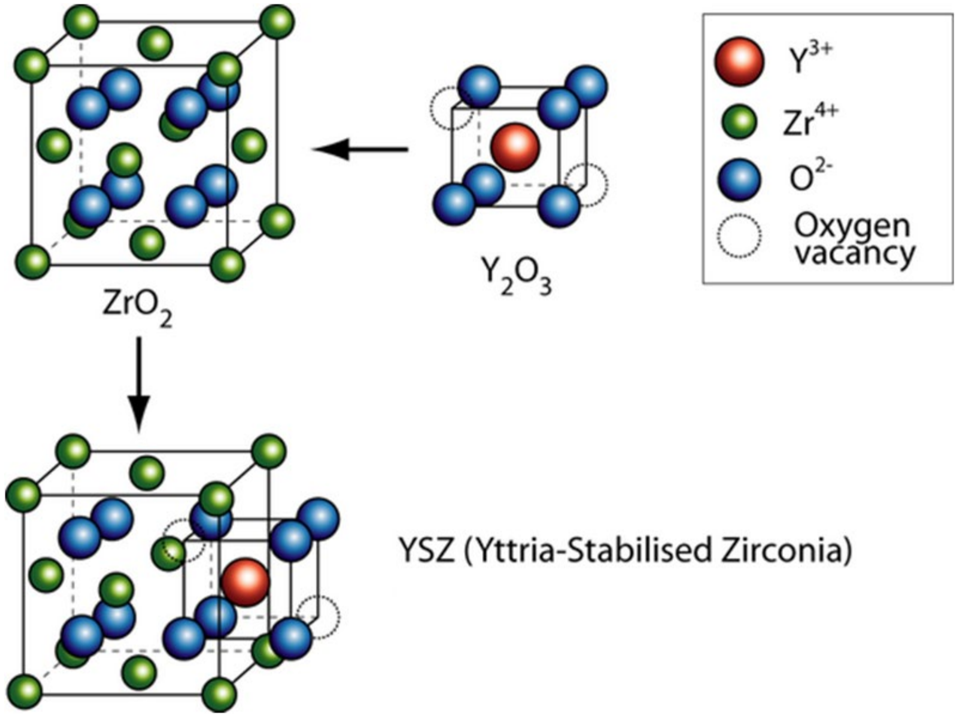


Crystals of the monoclinic phase of zirconia are needle-shaped and very small, so they do not find practical application.

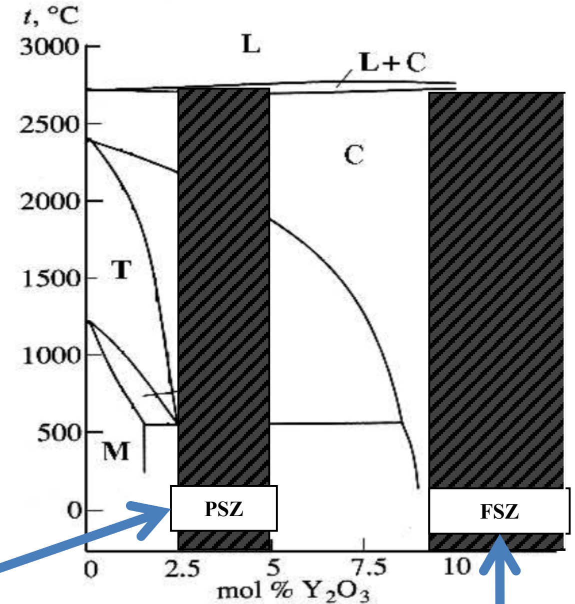
The tetragonal and cubic phases are of interest!

Stabilization of high-temperature zirconia phases

The cubic and tetragonal phases can be stabilized by doping with Y_2O_3, Sc_2O_3, CeO_2 …



Phase diagram of the zirconia rich portion of ZrO_2 –Y_3O_3 system [1]



ZrO_2- (2.5-5) mol.%Y_2O_3
Partially Stabilized Zirconia (*PSZ)*
tetragonal phase

ZrO_2- (9-40) mol.%Y_2O_3
Fully Stabilized *Zirconia (FSZ)*
cubic phase

[1]H. G. Scott. ''Phase Relationships in the Zirconia–-Yttria System,'' J. Mater. Sci., 10, 1527–35 (1975).

Crystal synthesis technology

The crystals were grown by directional crystallization technique with direct high-frequency heating in a cold container (skull melting)

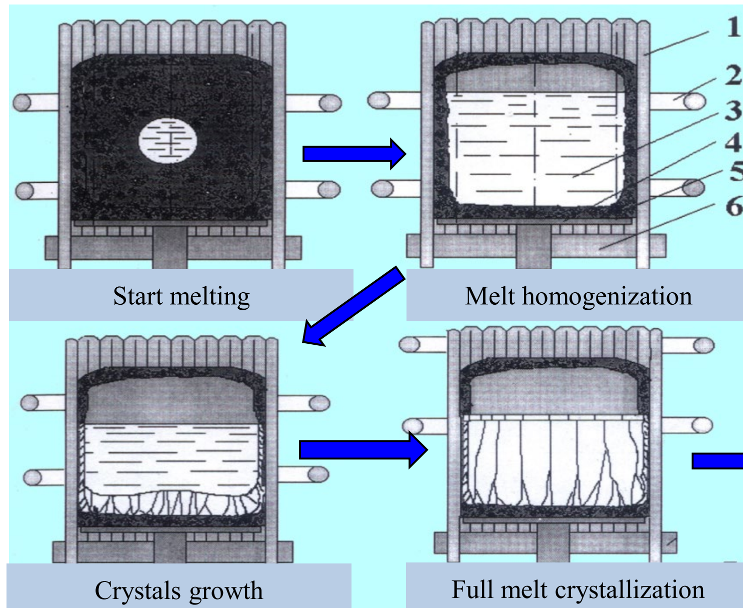
The main advantages of this method of synthesis :

No temperature limits (up to 3000 ºC)

No contact with crucible material

No requirements for the particle size distribution of raw materials

The possibility of re-melting crystalline waste



1 – cold container wall;
2 – inductor;
3 – melt;
4 – cooled crucible bottom;
5 – skull;
6 – insulating ring

Extracting of the bulk

The separation of the bulk into individual crystals

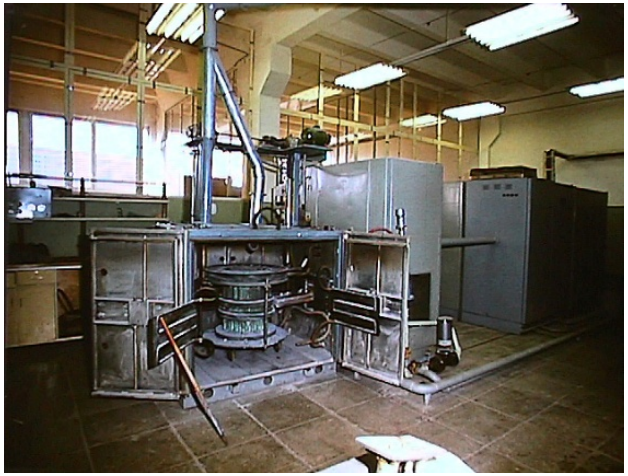
The "Kristall-407" installation

Electric power	60 kW
Electromagnetic field frequency	5.28 MHz
Container diameter	130 mm
Mass of melt	4 -6 kg
Working atmosphere	air

Growth installations for the synthesis of the crystals

A view of cold container (CC)
of 130 mm diameter

The "Kristall-401" installation
(CC of 180 mm diameter)



The "Kristall-403" installation
(CC of 300 mm diameter)

The "Kristall-403M" installation
(CC of 700 mm diameter)

Growth of the $(ZrO_2)_{0.91-x}(Sc_2O_3)_{0.09}(Yb_2O_3)_x$ single crystals

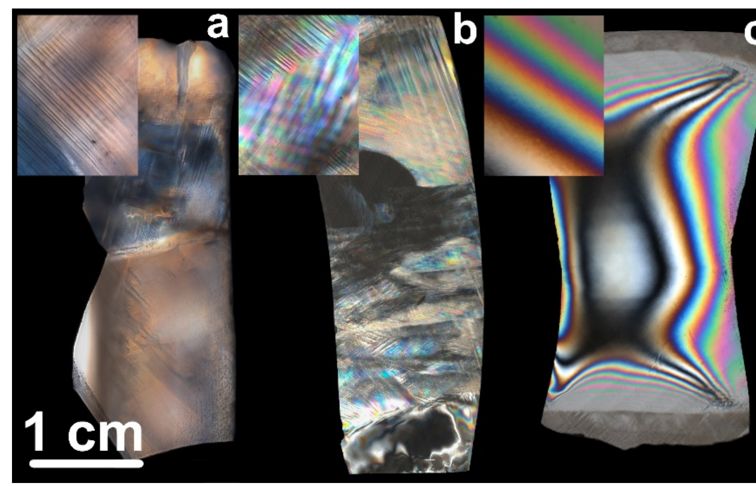
The compositions of the grown crystals and their symbols

Compositions of the crystals	Symbol
$(ZrO_2)_{0.91}(Sc_2O_3)_{0.09}$	9ScSZ
$(ZrO_2)_{0.905}(Sc_2O_3)_{0.09}(Yb_2O_3)_{0.005}$	9Sc0.5YbSZ
$(ZrO_2)_{0.90}(Sc_2O_3)_{0.09}(Yb_2O_3)_{0.01}$	9Sc1YbSZ

Appearance of crystals

9ScSZ 9Sc0.5YbSZ 9Sc1YbSZ

Images of the microstructure of crystals in polarized light



9ScSZ 9Sc0.5YbSZ 9Sc1YbSZ

Phase composition, density and lattice parameters for $(ZrO_2)_{0.91-x}(Sc_2O_3)_{0.09}(Yb_2O_3)_x$ crystals

The phase analysis of crystals was studied by X-ray diffractometry on plates cut from different parts of the crystal perpendicular to the <100> direction.

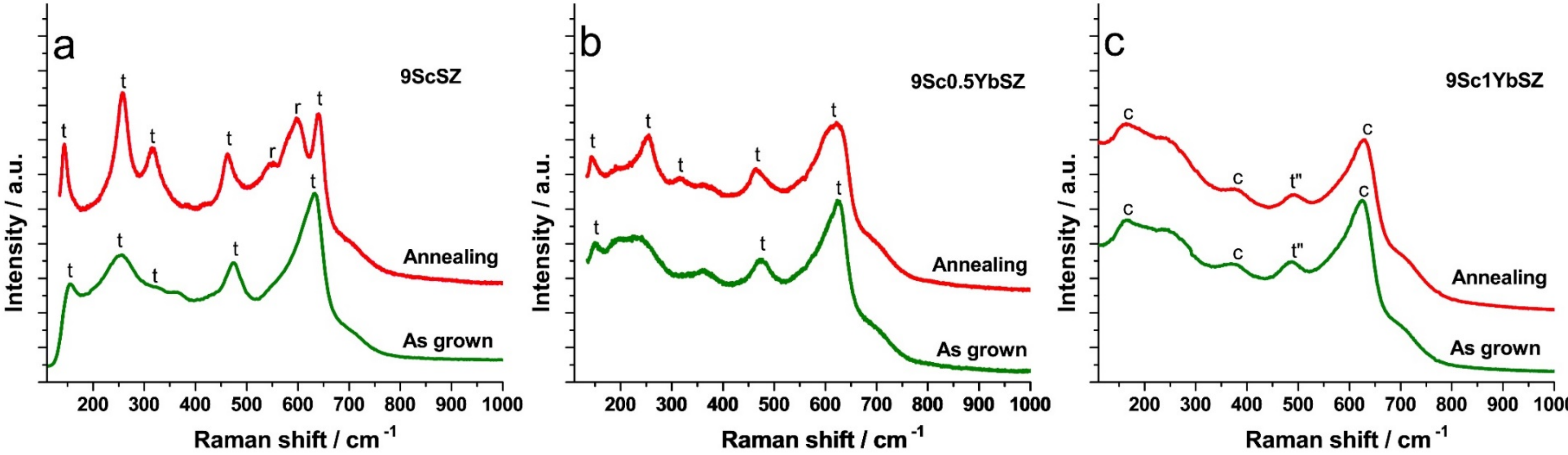
Sample	As-Grown			As-Annealed, 1000 °C, 400 hours, air		
	Phase	Lattice Parameters, nm	Density, g/cm3	Phase	Lattice Parameters, nm	Density, g/cm3
9ScSZ	t	a=0.3595(1); c=0.5122(1)	5.786(3)	t r	a=0.3596(1); c=0.5124(1) a=0.3559(2); c= 0.9007(2)	5.783(3)
9Sc0.5YbSZ	t c	a=0.3597(1); c=0.5106(1) a=0.5092(1)	5.816(3)	t	a=0.3597(1); c=0.5110(1)	5.818(3)
9Sc1YbSZ	c	a=0.5094(1)	5.863(3)	c	a=0.5094(1)	5.862(3)

t, c and r - tetragonal, cubic and rhombohedral phases

Prolonged high-temperature annealing affects the phase composition and lattice parameters of the crystals.

Phase composition of the crystals before and after annealing

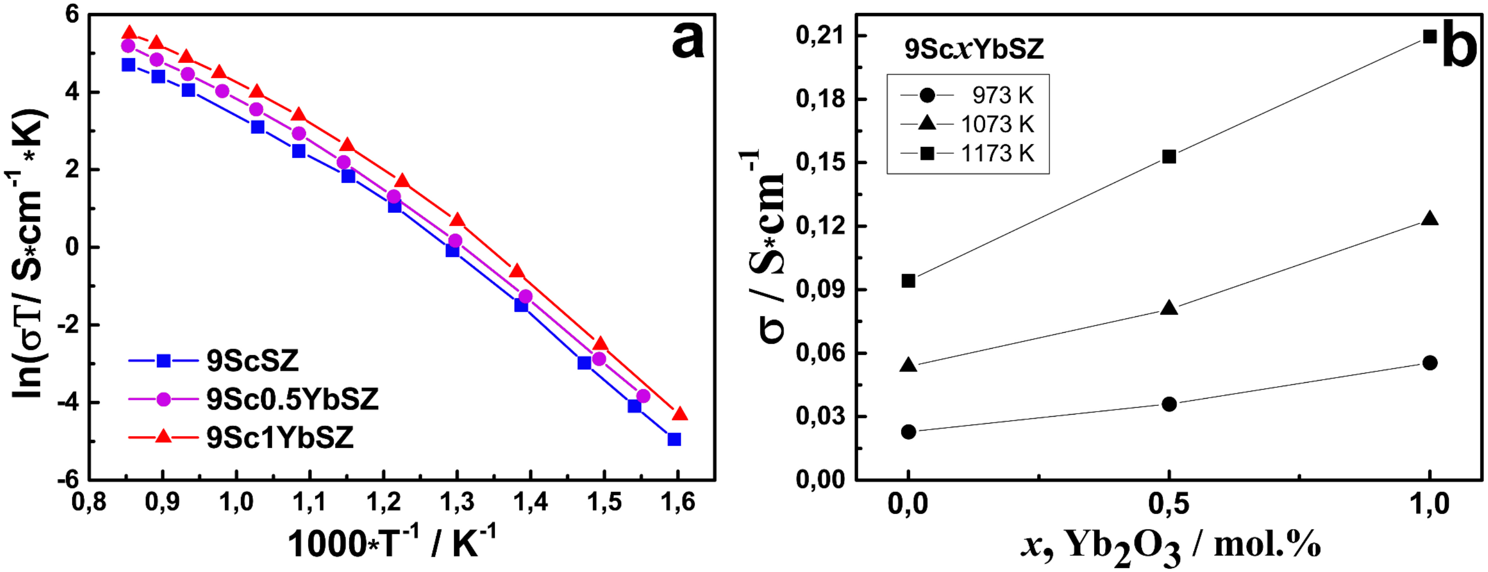
The phase composition of the crystals was also studied by Raman scattering. This method makes it possible to reveal even insignificant changes in the local structure that occur in crystals during prolonged annealing.



Codoping the ZrO_2 - 9 mol% Sc_2O_3 solid solution with ytterbium oxide at a concentration of 1 mol% leads to the formation of single-phase crystals with a pseudocubic structure of the t’’-phase, which is stable upon prolonged annealing in air.

Properties of the $(ZrO_2)_{0.91-x}(Sc_2O_3)_{0.09}(Yb_2O_3)_x$ crystals

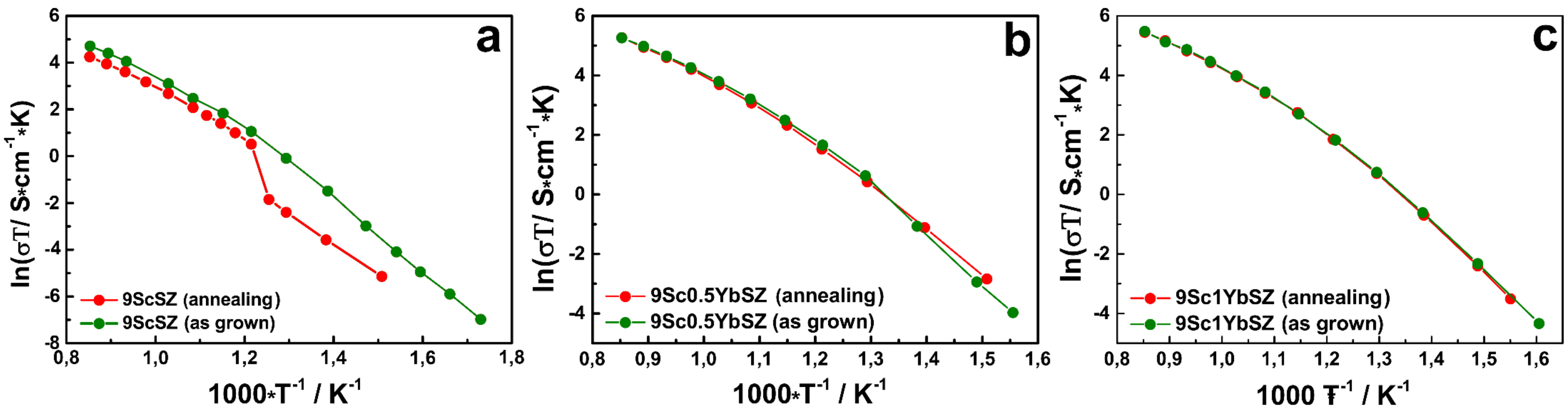
The 9Sc1YbSZ crystals with a t"-phase structure have the maximum conductivity values over the entire temperature range.



Temperature dependence of the conductivity of crystals in Arrhenius coordinates (a) and the conductivity of crystals depending on the concentration of Yb_2O_3 (b)

Properties of the $(ZrO_2)_{0.91-x}(Sc_2O_3)_{0.09}(Yb_2O_3)_x$ crystals

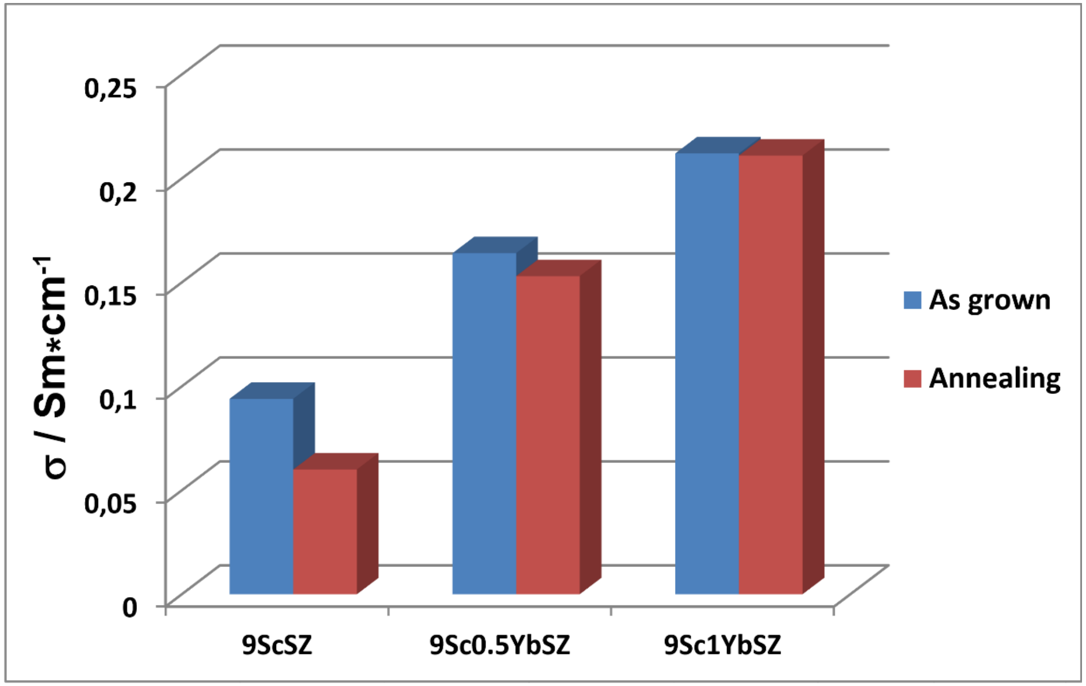
After annealing, the temperature dependence of the conductivity of the 9ScSZ crystal shows a jump in the conductivity in the temperature range of ~ 600 °C, associated with the transition of the rhombohedral phase to the cubic. For the 9Sc0.5YbSZ crystal, the values of the conductivity after annealing slightly decrease. For the 9Sc1YbSZ crystal, the conductivity values before and after annealing practically coincide in the entire temperature range.



Temperature dependences of the conductivity of (a) 9ScSZ, (b) 9Sc0.5YbSZ, and (c) 9Sc1YbSZ crystals before and after annealing.

Properties of the $(ZrO_2)_{0.91-x}(Sc_2O_3)_{0.09}(Yb_2O_3)_x$ crystals

After annealing in air at 1000 ° C for 400 hours, the conductivity at 1173 K of the 9ScSZ crystal decreases by 35%. For the 9Sc0.5YbSZ crystal, after annealing, the conductivity decreases by less than 10%. For the 9Sc1YbSZ crystal, no degradation of conductivity after annealing at 1000 ° C for 400 hours was observed.

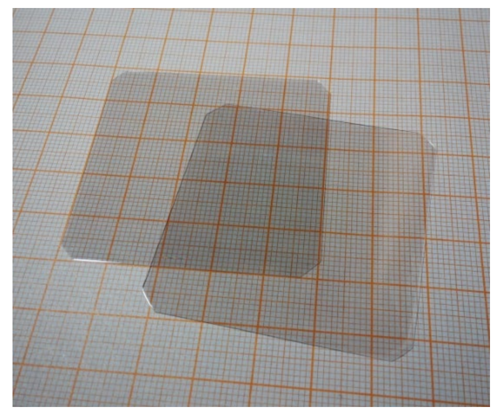


Conductivity values at 1173 K before and after annealing at 1000 ° C for 400 hours

Summary

- It is shown that the stabilization of ZrO_2 together with 9 mol.% Sc_2O_3 and 1 mol.% Yb_2O_3 makes it possible to obtain transparent homogeneous crystals with a pseudocubic structure, which have high phase stability.
- The conductivity of the crystals depending on the concentration of Yb_2O_3 is nonmonotonic.
- The $(ZrO_2)_{0.9}(Sc_2O_3)_{0.09}(Yb_2O_3)_{0.01}$ crystals have a maximum conductivity in the investigated temperature range.

Single crystal based on zirconia



Single-crystal membranes (solid electrolyte).
The size of 50x50 mm, h = 200 μm

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