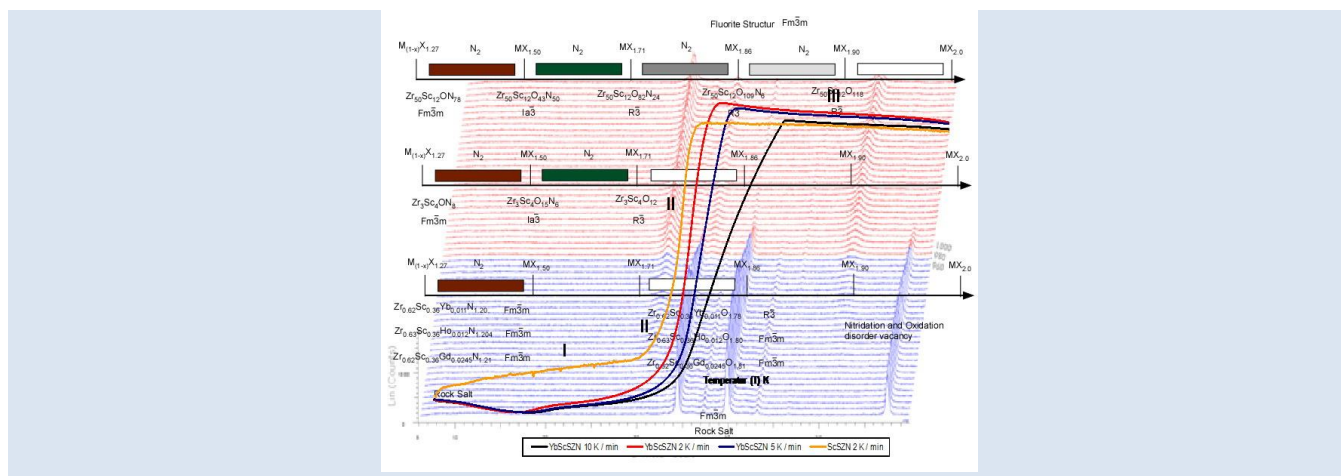


SCANDIA STABILIZED ZIRCONIA MATERIALS CODOPED WITH Gd, Ho AND Yb. NITRIDATION AND STABILITY

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ABSTRACT

The cubic and rhombohedral structures of scandia stabilized-zirconia (ScSZ) co-doped with the rare earth ions Gd, Ho, and Yb were determined. The cubic fluorite structures obtained for Gd⁺³ and Ho⁺³ co-doped ScSZ have lattice constants of $a = 508.88(0.02)$ pm and $a = 508.52(0.01)$ pm respectively. Due to the ionic radii of Gd⁺³ (97 pm) and Ho⁺³ (91 pm), the lattice constant for the Gd compound is slightly larger than the Ho doped compound.

For the ytterbium (86.8 pm) co-doped ScSZ, the rhomboedral ($R\bar{3}$) fluorite related superstructure the following cell parameters $a = 953.58(0.03)$ pm and $c = 1747.12(0.06)$ pm were found: After the nitridation under NH₃ for 24 h at 1200 °C, all 3 compounds exhibit a deficient rock salt structure with cell parameters: $a = 454.18(0.03)$ pm for Gd⁺³, $a = 454.59(0.01)$ pm for Ho⁺³ and $a = 454.26(0.02)$ pm for Yb⁺³. The decomposition of all these nitrides was investigated with thermal analysis. It was found that the reoxidation process is diffusion controlled.

Keywords: Thermal stability of nitrides, crystal Structure, Zirconium -Scandium Codoped Rare Earth.

MATERIALES DE CIRCONIA ESTABILIZADAS CON ESCANDIO Y CODOPADAS CON GD, HO, Y YB. NITRURACIÓN Y ESTABILIDAD

RESUMEN

Se determinó la estructura cúbica y romboédrica del sistema zirconia estabilizada con escandia, co-dopados con elementos de tierras raras Gd, Ho, and Yb. La estructura cúbica con el elemento Gd⁺³ and Ho⁺³ poseen los siguientes parámetros de red cristalina $a = 508.88(0.02)$ pm and $a = 508.52(0.01)$ pm respectivamente. A consecuencia de los radios iónicos del Gd⁺³ (97 pm) and Ho⁺³ (91 pm), la constante de celda para el compuesto derivado de Gd es ligeramente más grande que para el compuesto dopado con Ho.

Para el sistema codopado con Yb (86.8 pm) fue obtenida una estructura fluorita romboédrica ($R\bar{3}$) con parámetro de celda $a = 953.58(0.03)$ pm and $c = 1747.12(0.06)$ pm. Después de la nitridación bajo una atmosfera de Amoniaco (NH₃) por 24 h a 1200 °C. Los tres compuestos obtenidos presentan una estructura de sal de roca con los siguientes parámetros de celda $a = 454.18(0.03)$ pm para Gd⁺³, $a = 454.59(0.01)$ pm para el Ho⁺³ and $a = 454.26(0.02)$ pm para el Yb⁺³. La reacción de descomposición de los nitruros obtenida fue investigada mediante análisis térmico, encontrándose un mecanismo de oxidación controlado por un proceso de difusión.

Palabras Claves: Estabilidad térmica de nitruros. Estructuras Cristalina. Circonio estabilizado con Escandio y Tierras Raras.

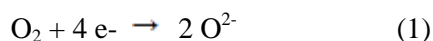
Abbreviations: ScSZ - Scandium stabilized zirconia; REScSZ - Rare earth (Gd, Ho, Yb) codoped scandium stabilized zirconia; ZrN - zirconium nitride; ScSZN - Scandium stabilized zirconium nitride.

1. INTRODUCTION

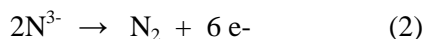
ScSZ receives an attention as a substitute of YSZ for the electrolyte of low temperature which operating solid oxide fuel cells SOFC. But ScSZ with concentration over 10% shows a rhombohedral to cubic phase transition around 650°C [1]. This phase transformation is not favourable for SOFC applications because of the sudden thermal expansion which causes mechanical failures. In order to avoid this problem, additional dopants like as Yb₂O₃ [2], CeO₂ [3] and Gd₂O₃ [4] were investigated.

Attempts to avoid this phase transition in doped ScSZ by anion substitution, e.g. by the replacement of 3 O²⁻ by 2 N³⁻ and a vacancy, lead to the oxynitrides Zr₅₀Sc₁₂O₁₀₉N₆, Zr₅₀Sc₁₂O₈₂N₂₄, Zr₅₀Sc₁₂O₄₃N₅₀ [5]. The structures and the thermal behaviour of such oxynitrides were evaluated in situ by powder XRD and for Zr₅₀Sc₁₂O₄₃N₅₀ also by powder neutron diffraction [6]. For the stability of these compounds, thermal analysis was used to investigate the reoxidation behaviour of the different compounds and to elucidate the decomposition mechanism [7].

The reoxidation from nitrides of ScSZ and REScSZ are a reactions with a diffusion controlled mechanism. The whole reaction can be explained by a reduction process of oxygen



which is endothermic and requires the dissociation energy of O₂ (498 kJ/mol) as well as the electron affinity (704 kJ/mol) to sum 1202 kJ/mol and an oxidation process of N³⁻



that is exothermic and calculated from the association energy (-945 kJ/mol) and the negative electron affinity (N³⁻ → N -2300 kJ/mol) to be -3245 kJ/mol. So this redox reaction



will produce at the end one strong exothermic signal in the DTA measurements.

N₂ bubbles are formed at an interface between the nitride and an O₂ saturated reoxidized surface layer, the release of dinitrogen might be delayed. The dissolution of N₂ gas bubbles will release the surface energies of the bubbles resulting in a second exothermic peak in the DTA measurements.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation

Gd, Ho, Yb codoped ScSZ was prepared by sol gel methods (Pechini) [8]. ZrOCl₂·8H₂O was dissolved in water and Sc₂O₃/Gd₂O₃/Ho₂O₃/Yb₂O₃ subsequently in HNO₃ with the molar relation Zr/Sc = 48/14 and 5% molar RE (Gd₂O₃ / Ho₂O₃ / Yb₂O₃). After adding a solution of a 1:1 mixture of ethylene glycol and citric acid, the whole mixture was stirred under reflux for 8 h until a gel has formed. Freeze drying of this gel and annealing at 1200 °C for 72 h led to a white powder, which was identified by X-ray powder diffraction to be cubic (fluorite structure for Gd Ho) and rhombohedral (fluorite related superstructure for Yb).

The nitridation process was executed in a tubular reactor using a mass flow controller for the NH₃ flow (6 l/h) for 24 h at 1200 °C until the red colored crystals of the nitrides were formed [8].

2.2 X-ray powder diffraction and SEM/EDS

The measurements were collected at room temperature with a Siemens D500 diffractometer operating in Bragg- Brentano geometry, using Cu-Kα radiation (λ = 154.06 pm) (Ge monochromator, Scintillation counter). This instrument was working in a θ/2θ configuration, at 40 kV and 30 mA. The diffractograms were recorded in the angular range of 2θ = 6°-109°, the scan step size Δ2θ = 0.02° and the time of counting 12 s. In situ XRD studies were performed, with a Siemens D 500 diffractometer (θ/θ set up) operating in reflexion geometry and parallel beam optics using a multilayer reflector (Göbel mirror) and a position sensitive detector (Braun OED).

The Scanning Electron Microscopy Analysis were realized with the equipment JEOL model JSM 6390, and the detector EDS Oxford INCA. The Elemental analysis (no quantitative) from the different compositions were collected and presented.

2.3 Rietveld refinement

The structural and profile parameters were improved by Rietveld analysis using the program FULLPROF [9]. The structural parameters of RE-ScSZ were refined in space group *Fm*3*m* using the following structural model:

Metals (Zr, Sc, Gd and Ho) on Wyckoff position 4(a) (0,0,0) and oxygen on 4b (1/4,1/4,1/4). and for

$R\bar{3}$ for $M_x = (\text{Zr, Sc and Yb}) M_1$ on Wykoff position 3a (0,0,0), M_2, M_3 18f (x,y,z), M_4 3b (0,0,1/2), O_x (x=1,2,3,4) 18f (x,y,z) O_5 3b (1/2, 1/2,1/2).

For the nitrides in $Fm\bar{3}m$ the following structural (Rock Salt) model was used : Metals (Zr, Sc, Gd and Ho) on Wykoff position 4(a) (0,0,0), N 4(b) (1/2, 1/2,1/2)) and Oxynitride $R\bar{3}$ (using same notation M (Zr,Sc,RE) M_1 3(a) (0,0,0), M_2 18(f) (x,y,z), M_3 18(f) (x,y,z), M_4 3(b) (0,0,1/2) O_x/N_x (x=1,2,3,4) 18f (x,y,z) O_5 3b (1/2, 1/2,1/2).

During refinement the site occupancy parameter of all atoms were fixed at a composition ratio of Zr/Sc = 48/14 and 5% molar RE and the temperatur factor between 0.1 - 0.8 [10].

2.4 Thermal analysis

TG/DTA experiments were carried out using a Netzsch STA 449F3 thermoanalyser. Scans were measured in an atmosphere of air at heating rate 10 K/min at ambient temperature to 1200°C. The DDTA and diagram were represented with the program Origin and Excel.

3. RESULTS AND DISCUSSION

3.1 RE (Gd, Ho, Yb) co-doped scandium-stabilized zirconium

Gadolinium, holmium and ytterbium co-doped ScSZ solid solutions, $Zr_{0,60}Sc_{0,175}Gd_{0,225}O_{1,8}$, $Zr_{0,60}Sc_{0,175}Ho_{0,225}O_{1,8}$, crystallize in the cubic fluorite structure ($Fm\bar{3}m$) and $Zr_{0,60}Sc_{0,175}Yb_{0,225}O_{1,8}$ rhomboedral $R\bar{3}$ with in a fluorite related superstructure . In the Table 1 was summarized the structural parameters. For Gd and Ho co-doped ScSZ the cell parameters are approximately identical because the ionic radii to Gd^{+3} and Ho^{+3} rather to Zr^{+4} . By the Yb^{+3} with ionic radii (72 pm) is also very close to that Zr^{+4} and was obtained finally a rhomboedral structure.

In the table 2 was summed up the EDS-SEM analysis from the different compositions from RE-ScSZ. The micro Crystalline compound evidence the RE incorporation and the structure stabilized from zirconium. The morphology presented from the differents compound were cluster and agglomerations (solids solutions).

Table 1. Cell parameter of Gd, Ho, Yb Codoped Scandium Zirconium Oxide.

	Gd₂O₃-ScSZ	Ho₂O₃-ScSZ	Yb₂O₃-ScSZ
Crystal System, Space Group	cubic $Fm\bar{3}m$	cubic $Fm\bar{3}m$	rhomboedral $R\bar{3}$
a /pm	508.88(0.03)	508.52(0.01)	953.58 (0.02)
c /pm			1747.12
V/ Å³	131.7798	131,4976	1375.8414
Formula units /cell	4	4	3
Reflection collected	11	11	400
Parameter refined	13	13	16
R_p	8.68	13.0	34.3
R_w	12.4	17.8	33.6
R_e	8.53	15.1	25.0
R² (%)	2.116	1.391	1.812

Table 2. Gd,Ho,Yb Codoped Scandium Zirconium Oxide, SEM/EDS qualitative analysis in weight %.

Element	Gd ₂ O ₃ -ScSZ	Ho ₂ O ₃ -ScSZ	Yb ₂ O ₃ -ScSZ
O-K	47.28	45.67	51.46
Sc-K	6.11	6.37	6.41
Zr-L	42.63	43.7	36.97
RE-K	3.98	4.18	5.16

3.2 Rare earth (Gd, Ho, Yb) co- doped scandium stabilized zirconium nitrides

The material obtained after nitridation of RE-ScSZN using NH₃ during 24 h at 1200°C was analysed and the XRD-patterns refined. Figures 1, 2 and 3 show the diffractograms and the Rietveld refinement for RE-ScSZN.

The diffractogram for the solid solution Gd-ScSZN (figure 1) shows the rock salt phase and an additional compound which counts for incomplete nitridation with still some oxynitride present. By approximate 2θ = 14°, 22° and 30°,the reflexion corresponds to an additional compound, that is iso-structural with the solid solutions Zr₇O₈N₄ and

Zr₅₀Sc₁₂O₈₂N₂₄ reported by N.J. Martinez and Et.al [5].

In the figures 2 and 3 were showed the solid solution for Ho₂O₃-ScSZN and Yb₂O₃-ScSZN respectively. The refinement of the structures reveals a rock salt phase of the nitride: Their cell parameter for the Ho₂O₃-ScSZN a/ pm = 454.59 and for Yb₂O₃-ScSZN a/ pm = 454.26 is lightly more small for Yb, as a consequence of ionic radii for Yb 86.8 pm.

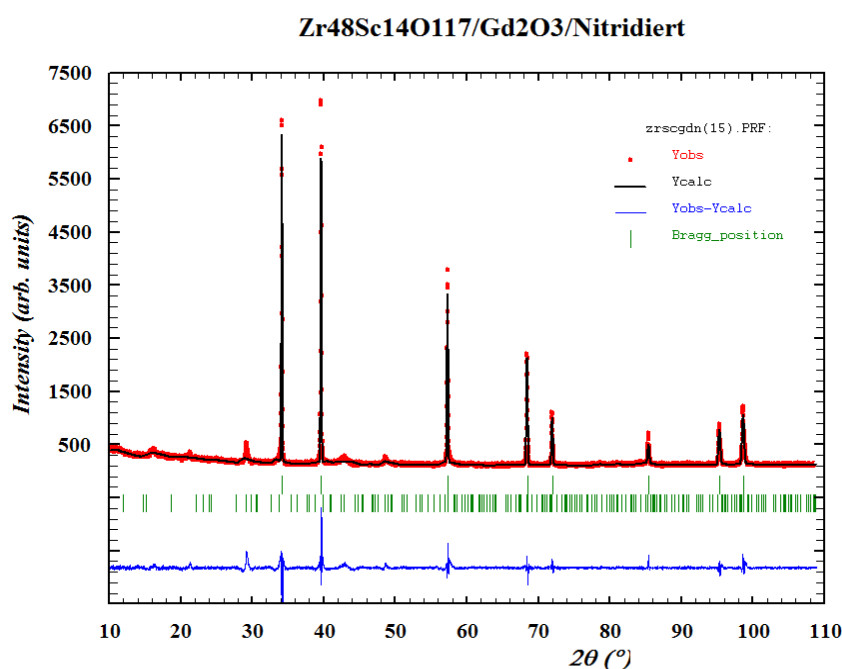


Figure 1. Gd₂O₃-ScSZN. Observed and calculated X-Ray powder pattern. Tick marks indicate the Bragg positions. (Related to both structure).

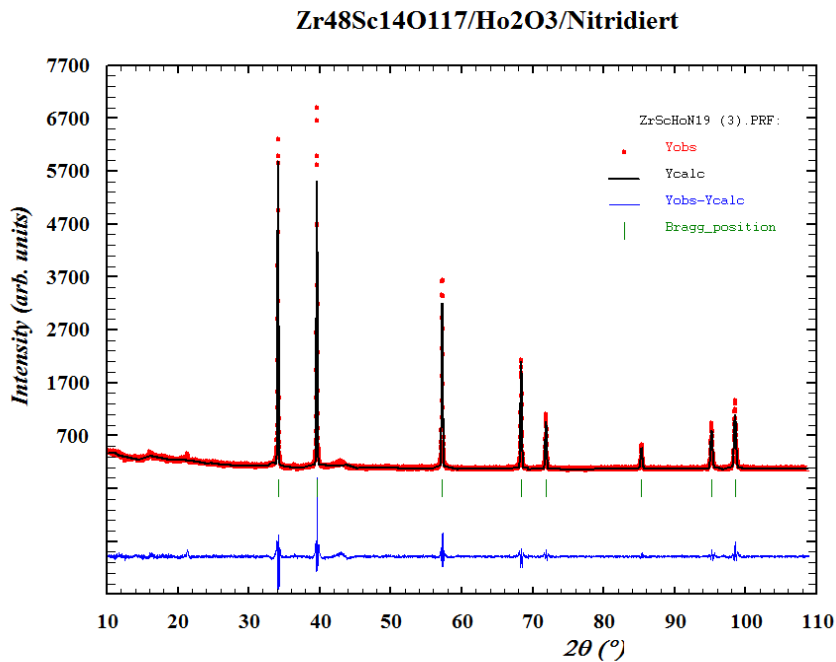


Figure 2. Ho₂O₃-ScSZN. Observed and calculated X-Ray powder pattern. Tick marks indicate the Bragg positions.

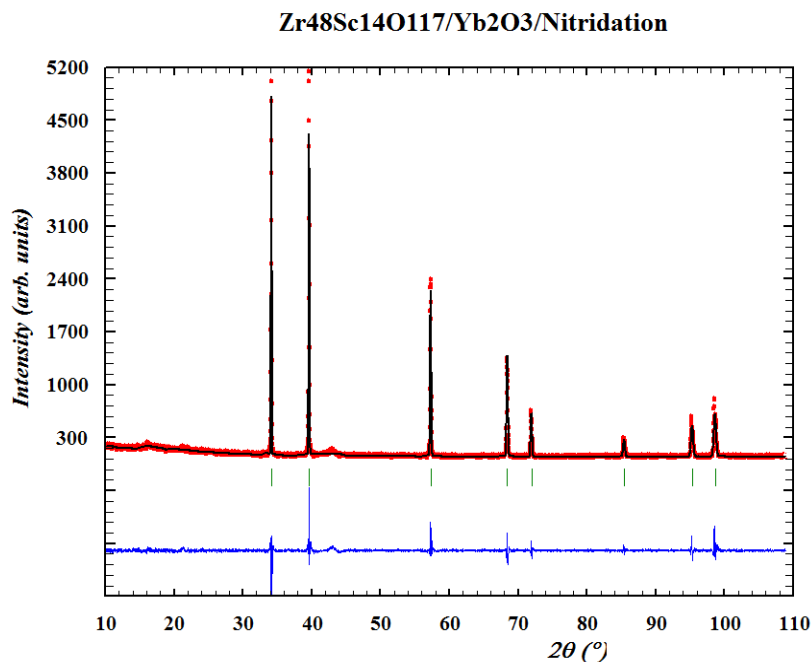


Figure 3. Yb₂O₃-ScSZN. Observed and calculated X-Ray powder pattern. Tick marks indicate the Bragg positions.

In table 3 are summarized all the crystal obtained with the refined parameter.

3.3 TG/DTA/ and in situ XRD analysis for the reoxidation of RE-ScSZN

In the Fig. 4 can be observed the oxidation in air to RE-(Gd,Ho,Yb) ScSZN under no isothermal conditions. The DTA curves for all compounds

show one bigger exothermic peak with a height of -2 μV. This behaviour is attributed to O₂ / N₂ adsorption/desorption mechanism in the oxidation process. In the table 4, the peak position for all nitride compounds is displayed.

Table 3. Gd, Ho, Yb codoped Scandium Zirconium Nitrides.

	Gd₂O₃-ScSZN		Ho₂O₃-ScSZN	Yb₂O₃-ScSZN
Crystal System, Space Group	(1)cubic <i>Fm$\bar{3}m$</i>	(2)rhomb. <i>R$\bar{3}$</i>	cubic <i>Fm$\bar{3}m$</i>	cubic <i>Fm$\bar{3}m$</i>
a/ pm	454.18 (0.08)	948.59 (0.02)	454.59 (0.01)	454.26 (0.02)
c/ pm		1747.13 (0.01)		
V/ Å³	93.6875	1359.0239	93.9392	93.7377
Formula units cell	4	3	4	4
Reflection collected	8	397	8	8
Parameters refined	17	17	76	76
R_p		41.0		18.2
R_w /		28.9		20.6
R_c /		15.4		9.06
R² (%)		3.533		8.6528
Phase (%)	(1) 99.52 % (2) 0.48 %		8.6528	5.159

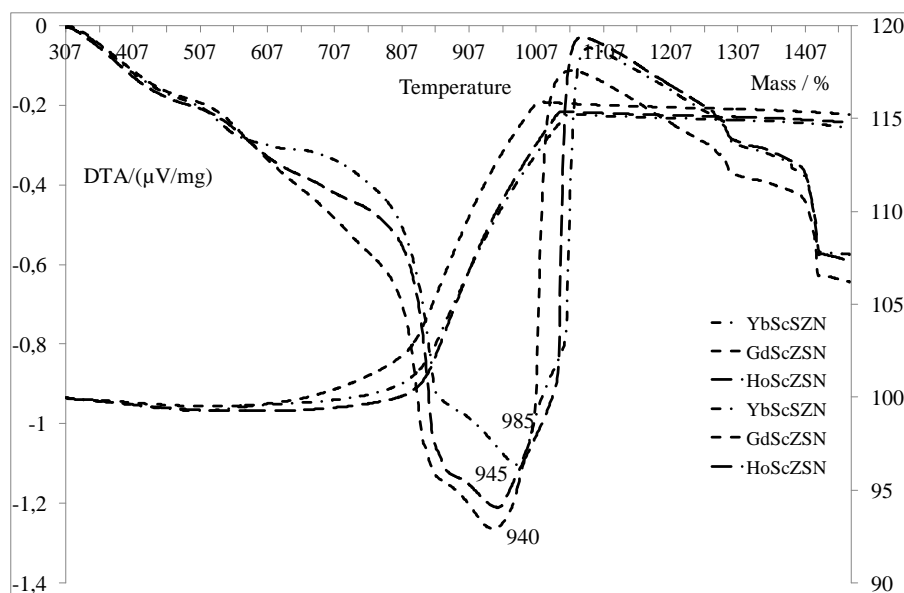


Figure 4. The results of thermogravimetric analysis (TG/DTA) of REScSZN showing that N₂ is release during the reoxidation.

This result clearly indicates that the diffusion mechanism decrease with radius ionic of the element, and the phase transition (NaCl) rock Salt structure to cubic Fluorite like no controlled the oxidation process and the new Fluorite like structure no was formed (see Figure 5). This behaviour is a consequence from their radius ionic $Gd > Ho \sim Yb$, that refrained the move in the diffusion process.

In the figure 5 is shown the direct and fast decomposition reaction from Nitride to oxide. In this process, intermediates Oxynitride compound are not presented in the reaction and is evident the transformation from the Rock Salt to cubic Fluorite Structure by 980 K.

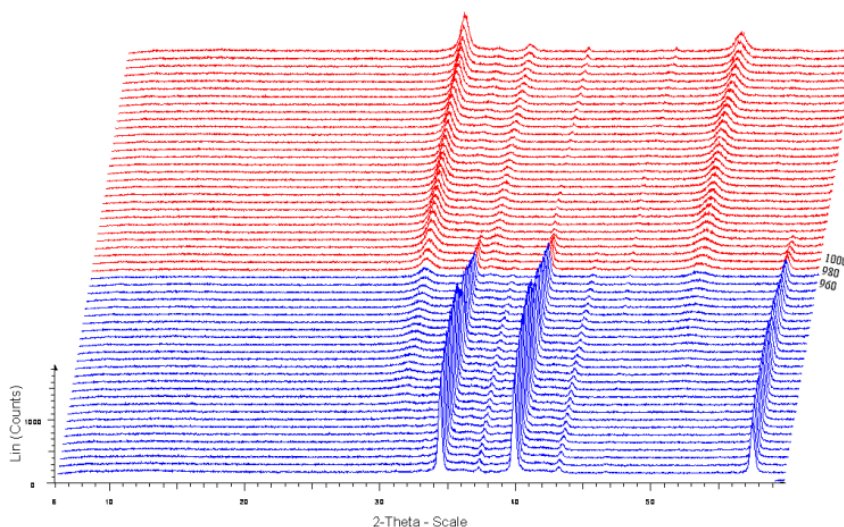


Figure 5. Time and temperature-controlled X-ray diffractogram (angular range $2\theta=5-60^\circ$) for the decomposition reaction of (YbScSZN) between 25-1200°C showing the formation only of the Fluorite phase.

4. CONCLUSIONS

The codoping from zirconium scandium compound with 5 % RE (Gd,Ho,Yb) and molar relation Zr/Sc 48/14, stabilized the cubic like fluorite structure for Gd and Ho. Yb presents ionic radii (86.8 pm); this radii is practically equal to Zirconium (86.0 pm), and consequently stay the initial structure. The nitridation reaction for all compounds results in the formation of the nitride with Rock Salt structure. The decomposition reaction from RE-ScSZN is a diffusion process, wherein O_2 and N_2 plays an important role. The movement of these ions through the interstices of the crystal may be inhibited, as consequence of these atoms additional, and their

Table 4. DTA behaviour and peak position of the Transition NaCl and - Fluorite likes structure.

Compound (Radius Ionic pm)	DTA Peak Position
Gd-ScSZN (97)	~ 940 K
Ho-ScSZN (91)	~ 945 K
Yb-ScSZN (86,8)	~ 985 K

kinetics decline.

5. ACKNOWLEDGEMENT

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