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1 Conversion of actinide nitrate surrogates into oxide using combustion synthesis process:

2 A facile approach

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14

15 Abstract

16 In recent years, the focus of research in the conversion routes for the actinide nitrates into oxides for the generation
17 IV nuclear fuel cycle have attracted rapidly growing interest. One process is the self-sustained exothermic reaction
18 of Solution Combustion Synthesis (SCS) methodology. It was applied here to the reaction of an actinide surrogate
19 $Gd(NO_3)_3 \cdot 6H_2O$ with glycine in air to produce $\sim 10^{-3}$ mol amounts of Gd_2O_3 . The primary process parameters were
20 the Gd/glycine ratio and heating rate, which affected the ignition temperature of the precursor mixture. An
21 optimum ratio of one and a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ resulted in nearly complete SCS conversion over the 483-
22 573 K temperature range and ultrafine gadolinia powders. The 100- to 500-fold swelling of the reactant mixture
23 plays a dynamic role in the reactivity of the system. Final products were characterized by X-Rays Diffraction
24 (XRD), surface area analysis, carbon content, and Scanning Electron Microscopy (SEM). The structural
25 characteristics of the final gadolinia phases have been interpreted by the adiabatic flame temperature calculation.

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29 Keywords

30 Actinide conversion - Gadolinium nitrate - Glycine - Combustion synthesis

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36 Introduction

37 The recycling of actinides, in particular uranium and plutonium, resulting from the treatment of spent
38 nuclear fuel, is of great interest for the deployment of Generation IV reactors (GEN IV) [1-2]. This recycling
39 process involves a step of conversion of the actinides obtained in the form of nitrate in solution into an oxide form
40 or more precisely a solid solution of mixed oxides (MOX). The conversion path should facilitate the formation of
41 homogeneously mixed oxide compounds, containing different amounts of Pu (GEN III / GEN IV transition), in a
42 continuous process. The resulting powders of mixed oxides must be adapted to a subsequent shaping of the fuel
43 without any grinding step or sieving of the powders, in order to reduce the generation of dust.

44
45 In this direction, new routes have been experimented for the effective conversion of nitrates of actinides into
46 oxides. Among the various routes, Solution Combustion Synthesis (SCS) is a simple and convenient path.
47 Moreover, this is a self-sustaining exothermic redox reaction process between an oxidant (metal nitrate) and a
48 reducing agent (organic fuel) mixed in an aqueous solution at the molecular level [3-7]. Under the thermal
49 treatment of aqueous precursor, a self-sustaining reaction will occur when it reaches the ignition temperature.
50 During this thermal treatment, the water is evaporated which leads to the conversion of the aqueous mixture into
51 a gel (~ 373 K), and then, the gel is allowed to pyrolysis at a temperature of about 573 K. These two-step processes
52 generate a large amount of gas, which makes the final product in porous and finely dispersed form [8]. These
53 peculiarities of the SCS reactions seem interesting as regards to the synthesis of the solid solution of nanoscale
54 actinide oxides [9-17]. However, the various controlling processing parameters plays a vital role to obtain the good
55 characteristics for the finished products, but it is not well documented. In addition, the mechanism involved in the
56 SCS reaction is not fully understood. The mechanism of SCS reaction mainly depends on the techniques used for
57 the conversion reaction. Two modes can be distinguished: volume combustion, also known as a thermal explosion,
58 and self-propagating combustion mode [18-19]. In the first mode, the entire volume of the precursor is uniformly
59 heated to the ignition temperature and the temperature increases to a maximum value. In the second case, the
60 precursor is heated locally to trigger the exothermic reaction, which propagates automatically over the entire
61 volume of the precursor in the form of a combustion front. In this, the maximum temperature reached is lower than
62 that observed in "volume combustion" mode [18].

63 Several equilibria such as thermal, chemical and structural are involved in a SCS reaction, and it depends on the
64 kinetics of the reactions. The kinetics of the reaction could be strongly influenced by the various processing
65 parameters. It is well known that the heating/cooling rate affects the SCS reaction leading to metastable phases
66 [17]. The heating rate can also act on the generation of the gaseous compounds produced during the process, which
67 can induce swelling of the viscous gel obtained by the dehydration of the precursors and it indirectly results in a
68 modification of the reactivity. The fuel to oxidizer molar ratio, also called richness (see SI-1 for definition of ϕ),
69 is another parameter which can affect the kinetic and the thermodynamic of the SCS reaction. For example, the
70 adiabatic temperature reached during the SCS reaction is dependent on this parameter, and consequently it changes
71 the characteristic of the powders synthesized.

72
73 In this present study, we studied the specific parameters such as swelling of the gel, temperature rate that provide
74 a new and unique information for the SCS process. The experiments were carried out with gadolinium nitrate and
75 glycine. The oxidation-reduction rate might be important in the conversion of actinides. So, gadolinium has been

76 considered as a surrogate for trivalent actinides (Cm, Am). Syntheses were carried out in a tubular furnace to
77 perform a homogeneous volume heating of the sample and to control the thermal treatment. To gain better insights,
78 modifications in the controlling parameters (heating rate, richness) were applied in the combustion process. The
79 precursor was characterized by infrared spectroscopy (IR), thermal analysis coupled with mass spectrometry (TG-
80 MS), the final products were analysed by X-ray diffraction (XRD), elemental analyses, scanning electron
81 microscopy (SEM) and nitrogen adsorption-desorption isotherms (BET).

84 **Experimental procedure**

85 Gadolinium (III) nitrate hexahydrate (purity: 99.9%), Glycine anhydrous (purity: 99.5%) was purchased from
86 Sigma Aldrich. Gd/Glycine was prepared by dissolving under stirring $2 \cdot 10^{-3}$ mole of gadolinium nitrate
87 hexahydrate in 3 mL of purified water, and an appropriate quantity of glycine to obtain the targeted richness ϕ (0.3
88 $< \phi < 2.2$).

89 Syntheses were performed in a tubular furnace (Nabertherm, Controller P320) under static air atmosphere. The
90 heat treatment consists of rapid heating, up to 393 K, followed by a temperature plateau (dwell time 15 minutes)
91 to dehydrate it and to obtain a gel called “dried gel” containing a mass of about 65-490 mg of Glycine and 550 mg
92 of gadolinium nitrate. The resulting gel is then heated to 573 K with a variable heating rate ($1 - 10 \text{ K} \cdot \text{min}^{-1}$). The
93 ignition of the SCS reaction was observed visually for a temperature in the range of 458 K and 513 K depending
94 on the mixture chemical composition. After this treatment, a white powder was obtained.

95 IR spectra were recorded by using a spectrometer (Perkin-Elmer IR-ATR, spectrum 100) with a typical resolution
96 of 8 cm^{-1} in the range of $300-1800 \text{ cm}^{-1}$. The Gd/Glycine gel was analysed after dehydration of the solution on a
97 hot plate at 398 K and powders obtained after syntheses on tubular furnace were pressed on the lens thanks to a
98 poppet.

99 The volume increase of the gel was measured in operando by direct observation of a graduated test tube (volume
100 equal to 25 mL or 50 mL) put in the furnace. The initial volume of the dried gel is about 3 ml. A thermometer put
101 on the test tube checked the temperature of the mixture.

102 ThermoGravimetric and Differential Thermal Analyses coupled with Mass Spectrometry (TGA-DTA-MS)
103 analyses were performed in air atmosphere on a sample of about 3 mg obtained after dehydration on a hot plate at
104 393 K of $7.5 \mu\text{L}$ of the Gd/Glycine mixture solution. These analyses were performed in a Setaram Setsys Evolution
105 16 apparatus coupled to a mass spectrometer Hiden QGA300 for gas analysis.

106 X-Ray Diffraction patterns were obtained by a Bruker D8 diffractometer equipped with a Lynxeye detector and
107 using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). XRD patterns were recorded at room temperature in the $10^\circ \leq 2\theta \leq 60^\circ$
108 range with a time of analysis equal to $2'47''$, and Debye-Scherrer calculation has been used to determine average
109 crystallites size.

110 Nitrogen adsorption/desorption analysis (77 K) was carried out with a Micromeritics Tristar 3020 instrument.
111 Before each measurement, samples were outgassed at 398 K for 24 hours. The specific surface area was calculated
112 by using the classic BET equation (Brunauer, Emmett, Teller).

113 Scanning electron microscope (SEM) observations were directly conducted on powder samples without prior
114 preparation, using a FEI Quanta 200 electronic microscope, equipped either with a Back-Scattered Electron

115 Detector, in high vacuum conditions with a low accelerating voltage equal to 2 kV. These conditions were chosen
 116 in order to induce a beam deceleration effect that led to high resolution images.

117 Finally, the amount of carbon in the powder was evaluated by the means of a LECO CS230 analyser using the
 118 complete combustion of the samples in a large excess of O₂. Added Fe powder was used to assist the combustion.
 119 The IR detection of the CO₂ formed was used to detect the carbon content. In order to get quantitative values, a
 120 blank and a series of standards (steel containing wt% of carbon) were analysed before the samples.

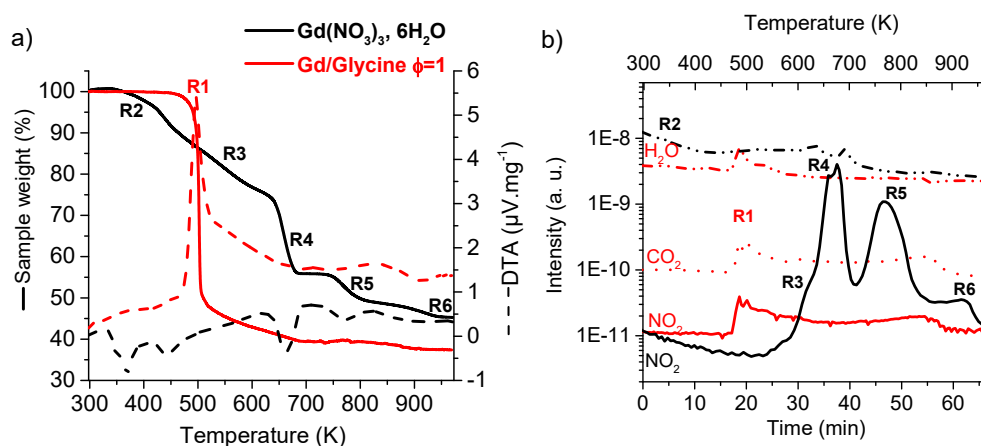
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122

123 Results

124 1) Comparison of SCS / thermal conversion of Gd(NO₃)₃

125 The comparison of TGA curves (Fig. 1a) of Gd/Glycine dried gel ($\phi = 1$) and gadolinium nitrate shows a clear
 126 difference in the evolution of the mass losses according to the temperature. Concurrently with these mass losses,
 127 DTA analyses show a small endothermic peak at 673 K for the former and a broad exothermic peak at 483 K for
 128 the latter. These results confirmed that the ignition has occurred by the SCS reaction of the Gd/Glycine dried gel
 129 according to reaction R1 (Table 1). The TGA analysis of glycine presented in SI-2 is identical to that presented in
 130 [19].



131

132 **Fig. 1.** a) TGA, DTA, and b) MS curves of gadolinium nitrate, $\phi = 1$ Gd/Glycine gel during a thermal treatment
 133 (air atmosphere, heating rate 10 K.min⁻¹)

134

135 **Table 1**

136 Equations and mass losses associated to thermal events observed during the TG analyses of Gd/Glycine ($\phi = 1$)
 137 dried gel and of gadolinium nitrate hexahydrate. m_i and m_f : mass before and after the reaction. The thermal
 138 treatment was done in air under a heating rate of 10 K / min. (*) Reactions described in reference [20]

139

Reaction		Theoretical m_f/m_i (%)	Experimental m_f/m_i (%)	Temperature onset (K)
$Gd(NO_3)_3 \cdot 6H_2O + \frac{5}{3}\phi NH_2CH_2CO_2H + \left(\frac{15}{4}(\phi - 1)\right) O_2$				
$\rightarrow \frac{1}{2} Gd_2O_3 + \frac{10}{3}\phi CO_2 + \left(\frac{25}{6} + 6\right)\phi H_2O + \left(\frac{5}{6}\phi + \frac{3}{2}\right) N_2$	R1	37.5 (for $\phi = 1$)	38 (for $\phi = 1$)	483
$4(Gd(NO_3)_3 \cdot 6H_2O) \rightarrow Gd_4(NO_3)_{12} \cdot 4H_2O + 20H_2O$	R2(*)	80	83	323

$\text{Gd}_4(\text{NO}_3)_{12}, 4\text{H}_2\text{O} \rightarrow \text{Gd}_4\text{O}(\text{NO}_3)_{10}, 4\text{H}_2\text{O} + \text{N}_2\text{O}_5$	R3(*)	92.5	87	513
$\text{Gd}_4\text{O}(\text{NO}_3)_{10}, 4\text{H}_2\text{O} \rightarrow \text{Gd}_4\text{O}_4(\text{NO}_3)_4, \text{H}_2\text{O} + 3\text{N}_2\text{O}_5 + 3\text{H}_2\text{O}$	R4(*)	71.7	74	626
$\text{Gd}_4\text{O}_4(\text{NO}_3)_4, \text{H}_2\text{O} \rightarrow \text{Gd}_4\text{O}_5(\text{NO}_3)_2 + \text{N}_2\text{O}_5 + \text{H}_2\text{O}$	R5(*)	86.8	87	738
$\text{Gd}_4\text{O}_5(\text{NO}_3)_2 \rightarrow 2\text{Gd}_2\text{O}_3 + \text{N}_2\text{O}_5$	R6(*)	87	93	850

140

141 More precisely, TGA curve of the gel (Gd/Glycine) displayed a mass loss of ~4% between 298 and 483 K caused
 142 by evaporation of water, a quick mass loss of ~ 52% at 483 K was caused by the ignition of the gel, and a total
 143 mass loss of ~ 62% at 973 K, is in agreement to theoretical mass loss 62.5% which is calculated on the basis of
 144 the SCS reaction of the dried gel (Table 1). At the end of ignition step, a white powder was formed, and regular
 145 decrease of mass of the SCS product was observed beyond 573 K, which was due to an elimination of organic
 146 residues as attested by carbon analyse showing a decrease of the carbon content from 0.5 wt% to 0.01 wt%
 147 respectively for powders heated at 573 K and 973 K.

148 The thermal decomposition of gadolinium nitrate hexahydrate reported by Melnikov [20] in nitrogen atmosphere,
 149 presents 5 endothermic steps (from R2 to R6). Although the TGA analyses were carried out under different
 150 atmospheres, the results are agreed with the report (Fig. 1a). All mass losses and peaks were assigned to the
 151 formation of oxynitrate as described in table 1.

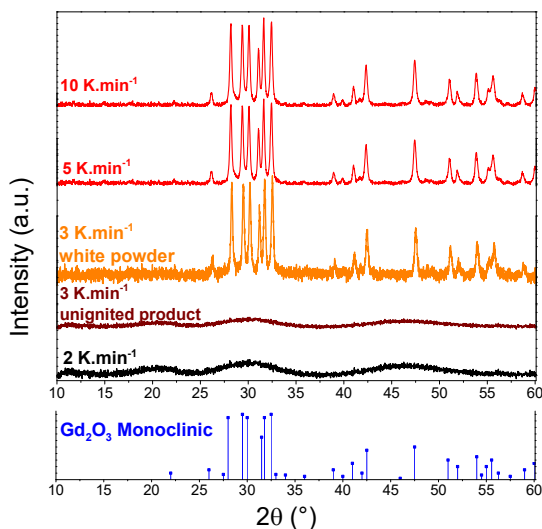
152 MS curves (Fig. 1b) confirm the release of CO_2 and H_2O , during the ignition step of the SCS reaction, in agreement
 153 with reaction R1. N_2 is used as gas vector during the analysis that is why it cannot be detected as a product of the
 154 reaction R1. In addition, the release of NO_2 gas corresponds to a secondary reaction. This gas is also detected
 155 during the thermal decomposition of gadolinium nitrate hexahydrate in agreement with the reactions R3, R4, R5,
 156 R6.

157 Final products obtained after the TGA-DTA analyses were analysed by XRD (SI-3). XRD patterns show the
 158 formation of a cubic gadolinium oxide after a thermal treatment up to 973 K of gadolinium nitrate alone, whereas
 159 the products of the SCS reaction from synthesis in tubular furnace is a monoclinic gadolinium oxide obtained at
 160 483 K (SI-2). This difference, which is a consequence of the temperature increase during the SCS reaction, will
 161 be discussed in the next part of this article.

162

163 2) Effect of processing parameters on the characteristics of the final products

164 As said previously, the SCS reaction was performed in a furnace leading to a volume combustion mode for the
 165 reactants. This mode of heating allows a precise control of the temperature ramp. Syntheses were done with
 166 Gd/Glycine ($\phi = 1$) mixtures with different ramp and XRD analyses of the final products were performed according
 167 to this parameter (Fig. 2). The results show that the crystalline compound Gd_2O_3 monoclinic was obtained for a
 168 heating rate higher than $3 \text{ K}\cdot\text{min}^{-1}$, in these conditions, the final product is a white powder and ignition phenomenon
 169 were observed. On the contrary, tests carried out at lower heating rate did not lead to the ignition phenomenon. So
 170 the colour of the obtained powder is brown, associated to the high carbon content of these samples ($> 4.7\%$). At
 171 heating rate of $3 \text{ K}\cdot\text{min}^{-1}$, the powder was heterogeneous, the upper part of the sample was white, and the bottom
 172 was brown, which can mean a suffocation of the reaction at the bottom. For $\phi = 1$, the ratio C/Gd in the precursor
 173 is equal to 3.3 (see R1), depending on the processing conditions this ratio change from 0.08 to a value higher than
 174 2 in the final product. The highest values were obtained when the ignition did not take place.



175

176 **Fig. 2.** XRD patterns of SCS reactions applied to Gd/Glycine $\phi = 1$ mixture with different heating rates (Gd_2O_3
 177 monoclinic JCPDS 043-1015 (C))

178

179 Based on these results, a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ was selected for the elaboration of the following samples (Table
 180 2).

181 In order to have a better understanding of the effect of glycine on the SCS reaction, we have undertaken several
 182 tests with various amounts of glycine ($0.3 < \phi < 2.2$). Several authors studied the effect of fuel/nitrate molar ratio
 183 on the final material, and their results provided a strong basis for the next studies [9, 21-29]. By comparing these
 184 studies, it clearly shows an effect of fuel richness on the morphology of the material and chemical composition,
 185 which changes with the mixture and the process (SI-1).

186 XRD patterns on the final products give several information's (SI4). The first one was the loss of crystallinity of
 187 the oxide when ignition does not occur, for low heating rate ($< 3 \text{ K}\cdot\text{min}^{-1}$) and with the lowest and the highest
 188 richness. The final products have a black colour, and a relatively high amount of carbon, meaning a low rate of
 189 transformation. The second observation relates to the phase transition observed according to the value of the
 190 richness in between 0.8 and 1.2. For $0.8 < \phi < 1.2$, monoclinic Gd_2O_3 was formed and cubic structure for the higher
 191 value of the richness. Not only the phase obtained, but also the morphology (specific area, crystallites size...) was
 192 affected by the change in the processing parameters (Table 2). For $\phi = 1$, the specific surface area increases with
 193 respect to the heating rate, and it is inversely proportional to the carbon content which can be likened to the
 194 efficiency of the SCS reaction. The high heating rate at $10 \text{ K}\cdot\text{min}^{-1}$, is the best condition for the conversion, the
 195 specific surface area increasing slowly according to the richness in the range of $0.8 < \phi < 2.2$. As said previously,
 196 for the lowest richness ($\phi = 0.5$) the obtained amorphous powder has a quite high specific surface area which could
 197 be the result of the incomplete thermal decomposition of the mixture glycine/gadolinium nitrate. The increase of
 198 the richness leads also to an increase in the amount of carbon in the final products, which ultimately has the effect
 199 of reducing the size of the crystallites. However, the calculated surface area representative of the surface of the
 200 crystallites is higher than the measured one that can be explained by the embedment of the nanoparticles in a
 201 carbon matrix. This is revealed through the SEM observations, which clearly shows a porous structure for the
 202 sample obtained in the best conditions of reactivity ($\phi = 1$, heating rate = $10 \text{ K}\cdot\text{min}^{-1}$). During ignition, the

203 decomposition reaction of reagents caused a large emission of gaseous species, which causes the formation of this
 204 porous structure (Figure 3).

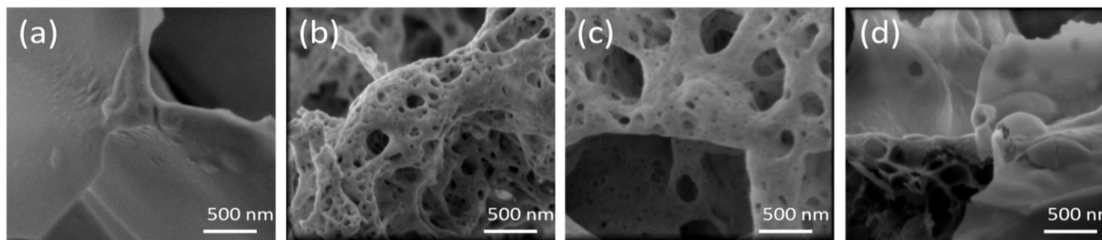
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206 **Table 2.**

207 Characteristics of final products obtained after SCS reaction of Gd/Glycine. The calculated surface area S ($\text{m}^2\cdot\text{g}^{-1}$)
 208 is obtained by the classical formulae $S = 3/d*\rho$ (d (nm) calculated by Debye-Scherrer formulae, ρ density of Gd_2O_3
 209 = $7.41 \text{ g}\cdot\text{cm}^{-3}$). The error bars are about 1% for carbon content, 10% for crystallites size and 1% for the surface
 210 area. Phases : amorphous (am.), Monoclinic (mon.), Cubic (cub.)

Fuel richness ϕ	Heating rate ($\text{K}\cdot\text{min}^{-1}$)	Structure	Carbon (wt%)	C/Gd (at./at.)	Average crystallites size (nm)	Calculated specific area ($\text{m}^2\cdot\text{g}^{-1}$)	Measured specific area ($\text{m}^2\cdot\text{g}^{-1}$)
0.3		am.	2.6	0,4	-	-	27.2
0.5	10	am.	1.8	0,27	-	-	25.3
0.8		mon., cub.	0.7	0,1	28.6	14.2	10.3
1.0	1		8.8	1,4	-	-	0.3
	2	am.	7.8	1,27	-	-	0.5
	3		4.7	0,74	-	-	0.5
	3		0.5	0,08	29.3	13.7	2.0
	5	mon.	0.5	0,08	29.5	13.7	8.8
	10		0.5	0,08	29.5	13.7	9.8
1.2		mon., cub.	1.4	0,21	22.3	18.1	12.1
1.5		cub.	1.8	0,27	12.4	32.7	14.6
1.7	10	cub.	2.0	0,31	8.0	50.4	15.0
2.0		am.	11.2	1,9	-	-	16.1
2.2		am.	12.1	2,1	-	-	18.1

211



212

213 **Fig. 3.** SEM images of final products obtained after SCS reaction of Gd/Glycine mixtures a) 2 K.min⁻¹ – $\phi = 1$,
214 b) 10 K.min⁻¹ – $\phi = 1$, c) 10 K.min⁻¹ – $\phi = 1.5$, d) 10 K.min⁻¹ – $\phi = 2$
215

216 On the contrary, SEM images of the amorphous product (Fig. 3a) shows the formation of a coarse structure led to
217 the low specific area. An amorphous compound was also obtained for $\phi = 2$ (Fig. 3d), but in this case, the high
218 value for a specific area could be caused by the release of gas arising from the incomplete conversion, i.e.
219 suffocation of the SCS reaction.

220

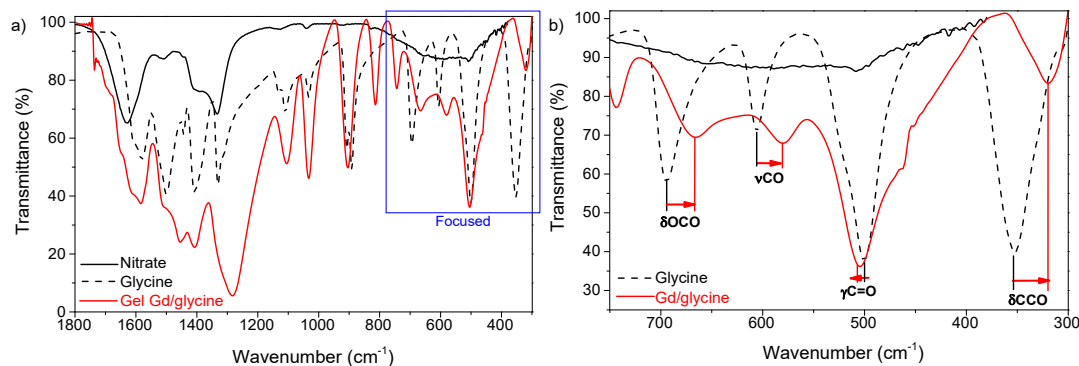
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222 Discussion

223 1) Complexation

224 Glycine is used as a fuel for the SCS reaction, but can also be considered as a complexing agent for gadolinium
225 nitrate in particular because of amino and carboxyl functional groups in its structure. To understand these
226 interactions, comparative IR spectroscopy analyses were performed on glycine and Gd/Glycine gel at $\phi = 1$ (Fig.
227 4).

228



229

230 **Fig. 4.** IR spectra of the gel Gd/Glycine ($\phi = 1$) compared to the glycine alone and the gadolinium nitrate

231 hexahydrate in the wavenumber range a) 1800-300 cm⁻¹ and b) 750-300 cm⁻¹ [26, 30-31]

232

233 It is difficult to obtain information from the domain of organic vibration bond between 1800 and 1000 cm⁻¹ because
234 of simultaneous detection of nitrates and fuel bonds. The missing of organic vibrating bonds modification suggests
235 there was no chemical transformation of the reagents during gel formation step.

236 Information about interactions between gadolinium and glycine has been obtained by observing the shift of the
237 carboxylate function peaks between 750 and 300 cm⁻¹. This shift in the characteristic band associated with the
238 stretching of carboxylate is due to the strong interactions between the carboxylates and gadolinium. This
239 interaction was caused by a complexation of gadolinium ions with glycine during the formation of the gel. The
240 interaction between Gadolinium and Glycine is possible in with the mesomeric form of Glycine, which is a dipolar
241 molecule with a complexing carboxylate function. This complexation is very important for the combustion redox
242 reaction between the fuel and the nitrates. Indeed, results obtained during TG and MS analyses (Fig. 1, and SI-2)

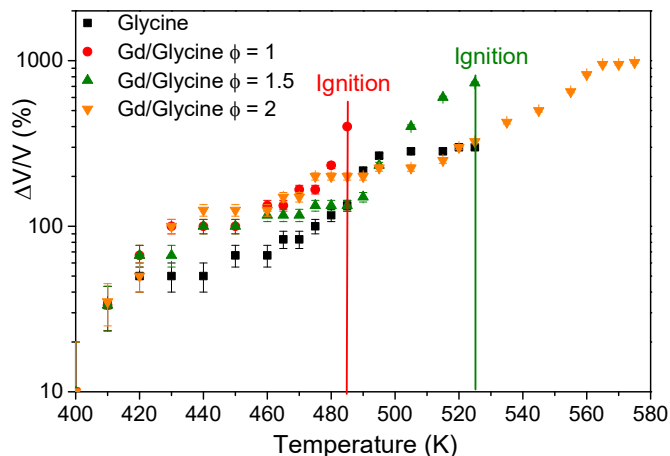
243 show a transition from two endothermic thermal decompositions of reagents alone to one exothermic simultaneous
244 decomposition of nitrates and glycine during the ignition.

245

246 2) Swelling effect and ignition

247 Only a few studies [22-23] report a swelling during the heat treatment of the gel obtained after mixing the nitrate
248 with fuels (glycine, urea...). This phenomenon was not well studied, but it seems to have an impact on the ignition
249 step as shown in Figure 5. It can be observed that the ignition was inhibited for the precursor, that has the highest
250 swelling (Gd/Glycine $\phi=2$).

251



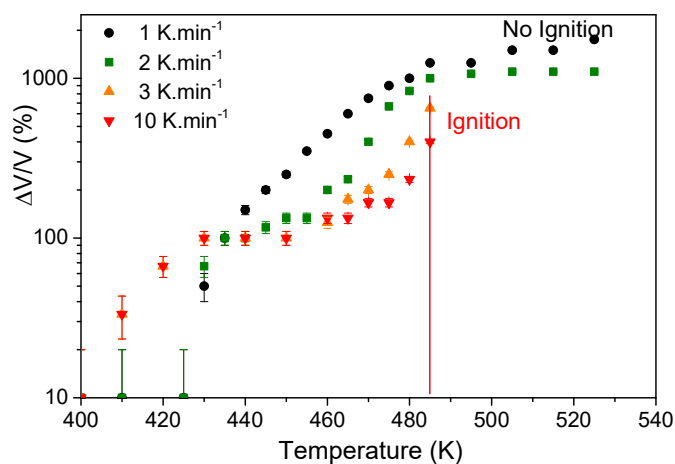
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253 **Fig. 5.** Effect of the richness on the thermal swelling of the precursors (heating rate 10 K.min⁻¹)

254

255 For a temperature of 483K, the volume of glycine alone increases more than twice, which is the same order of
256 magnitude as the swelling of the precursors Gd/Glycine. This means that glycine has an important role in this
257 process. This swelling is a consequence of the high viscosity of the gel and the generation of gases due to thermal
258 decomposition. It is feasible that the viscosity of the gel with respect to glycine alone, is increased due to the
259 interaction between the chemical groups of glycine and nitrates (see Fig. 4). However, two regimes can be
260 highlighted: one corresponding to the thermal decomposition of a gel having a richness close to 1, i.e. in these
261 conditions the final product obtained is a crystalline oxide, and the other corresponding to a higher richness (> 2)
262 leading to an amorphous oxide (table 2).

263



264

265 **Fig. 6.** Swelling of the precursors during the heat treatment: Effect of the heating rates Gd/glycine ($\phi = 1$)

266

267 In the first case (richness close to 1), the heating rate has an effect on the ignition phenomom. For a heating rate
 268 lower than 3 K.min⁻¹ the ignition was not observed (Fig. 6). This effect can be a consequence of the too low density
 269 of matter in the system induced by the higher volume increase. In these conditions, even if ignition can occur at a
 270 local scale, the reaction can not be self-propagated. At the transition-heating rate of 3 K.min⁻¹, two products were
 271 obtained, an amorphous brown powder with high carbon content (0.74%) on the bottom of the sample and a
 272 crystalline white powder with lower carbon content (0.08%) on the top (see table 2).The heterogeneity observed
 273 in this sample is probably due to the release of gaseous products by reaction R1. These gases rise from the bottom
 274 to the top of the mixture, and influenced the swelling and the reactivity of the system. For higher heating rates (>
 275 3 K.min⁻¹), the SCS reaction occurs easily, because the density of matter is high enough to generate self-
 276 propagation of the reaction.

277 In the last case ($\phi > 2$), not only the swelling of glycine but also the penetration of oxygen is limiting factor for the
 278 reactivity. Indeed, under these conditions according to R1, oxygen is necessary for this reaction. The large volume
 279 of gas released by the reaction when the ignition occurs (500 liters / mol Gd for $\phi = 1$ to 500K) limits the ingress
 280 of oxygen and the progress of the reaction as indicated by the high carbon content measured in the final products
 281 (~2%wt.).

282 To conclude, the density of matter or more precisely the density of the chemical complex is a key parameter for
 283 the reactivity of the SCS reaction and for the ignition phenomena. In the case of an excess of glycine ($\phi > 2$), the
 284 access of oxygen could be another parameter that explains the lack of reaction (Fig. 2, Table 2).

285

286 3) Phase transformation

287 Powders obtained from the SCS reaction of different Gd/Glycine mixtures shows a transition phenomenon of
 288 gadolinium oxide crystalline structure formation when the fuel richness increases. The effect of fuel richness on
 289 SCS reaction can be explained through the estimation of the temperature attained during ignition. This temperature
 290 can be measured experimentally or calculated by thermodynamic considerations. In the former case, the
 291 temperature (T_c) is generally called “flame temperature” or “combustion temperature”. Several reports [32-33]
 292 described that an increase of T_c with richness up to a value in the range of $1 < \phi < 1.5$ and after, a decrease of this

293 parameter for higher values of ϕ . In the latter case, the adiabatic temperature (T_{ad}) can be calculated using a simple
 294 thermodynamic approach. T_{ad} increases substantially with the richness [34-35]. However, in a general point of
 295 view, T_c is lower than T_{ad} . Several factors have been invoked to explain this difference: the experimental conditions
 296 are not purely adiabatic [19], the fuel does not completely reacts with oxygen especially for fuel-rich conditions
 297 [19, 33] and a part of heat produced by the ignition is dissipated by the considerable amount of gas generated. As
 298 said previously, T_c decreases for high values of ϕ , which is the opposite trend compared to T_{ad} . This difference can
 299 be caused by the utilization of an incorrect reaction route, which can change the energy balance of the process and
 300 finely the calculation of T_{ad} . Only one report elucidated [9] the decrease of T_{ad} for $\phi > 1$, in the system of iron-
 301 nitrate-glycine, certainly because of the set of the thermodynamic data used is representative of the SCS reaction.
 302 To conclude, it is not so easy to obtain the value of the temperature reached during the ignition, especially when
 303 $\phi \neq 1$. In this study, for stoichiometric conditions ($\phi = 1$), a low amount of residual carbon was measured in the
 304 final products obtained by the SCS reaction R1 (Table 2), indicating that the reaction route proposed in Table 1 is
 305 consistent. This result allows us to use a basic calculation to estimate T_{ad} as follow:

306

$$307 \quad T_{ad} = T_0 - Q/\bar{c}_p \quad (1)$$

308

$$309 \quad Q = \sum_j n_j \Delta_f H_j^0 - \sum_i n_i \Delta_f H_i^0 \quad (2)$$

310

$$311 \quad \bar{c}_p = \sum_j n_j c_j \quad (3)$$

312

313 Where Q is the heat release during the reaction and, \bar{c}_p the average specific heat capacity of the products at room
 314 temperature. T_0 is the ambient temperature, i and j respectively specify reactants and products and n_i and n_j are the
 315 amounts of each compound. The ΔH_f^0 and c_j values of the compounds are presented Table 3.

316

Table 3.

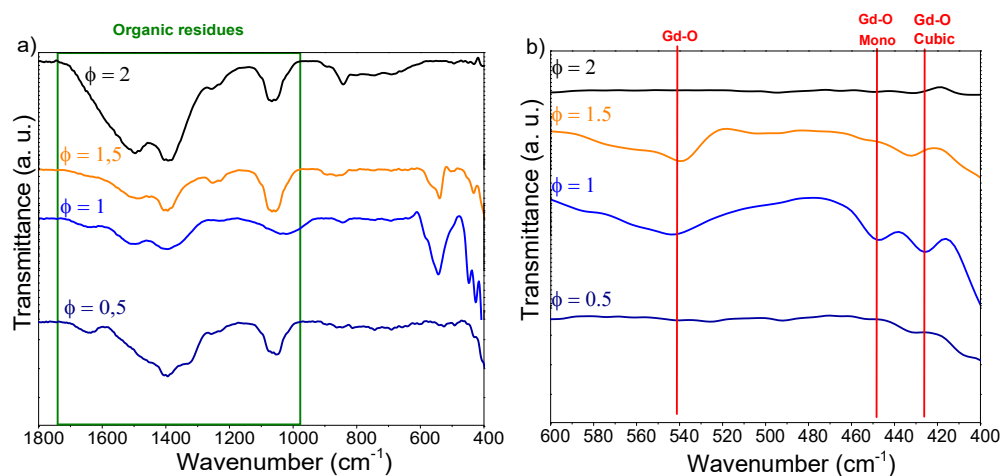
317 Standard enthalpies of formation and heat capacities for Gadolinium nitrate hexahydrate – Glycine system from
 318 [19, 36]
 319

Compounds	ΔH_f^0 (kJ.mol ⁻¹)	c_p (J.mol ⁻¹ .K ⁻¹)
Gd(NO ₃) ₃ , 6H ₂ O	-3072.3	
Glycine, solid	-528.5	
Gd ₂ O ₃ , solid	-1825	106.7
H ₂ O (g)	-241.8	30
CO ₂ (g)	-393.1	43
N ₂ (g)	0	27
O ₂ (g)	0	25

320

321 The adiabatic temperature calculated (T_{ad}) for $\phi = 1$ is close to 1600 K, which is higher than the temperature of
 322 1473 K proposed in reference [37] for the transition cubic/monoclinic of gadolinium oxide. The monoclinic

323 structure of the gadolinium oxide powders synthesise in this study is in agreement with this result (Table 2). As
 324 discussed previously for $\phi \neq 1$, a decrease of the temperature reached by the SCS reaction was observed, that can
 325 explain the formation of the cubic gadolinium oxide structure obtained under the same combustion temperatures
 326 for fuel-lean or fuel-rich ($\phi = 0.8$ and $1.5 < \phi < 1.7$). However, the thermodynamic calculation is not able to
 327 predict the lack of ignition and the formation of amorphous final products, for large excess of one of the reagents
 328 ($\phi < 0.5$ or $\phi > 2$). In these conditions, the reagent acts as a diluting compound for the SCS reaction and was
 329 associated with a diluting effect and its endothermic decomposition induces an inhibition for ignition.
 330 The lack of ignition with $\phi = 0.5$ and $\phi = 2$ Gd / Glycine mixtures and the optimal ignition of Gd / Glycine
 331 stoichiometric richness mixtures were confirmed by IR analyses on the final powders (Fig. 7).



332
 333 **Fig. 7.** IR spectra of SCS reaction final products obtained with Gd/Glycine mixtures with different ϕ , in the
 334 wavenumber range a) 1800 - 400 cm^{-1} and b) zoom in the area 600 - 400 cm^{-1} (air atmosphere, heating rate 10
 335 $\text{K}\cdot\text{min}^{-1}$)

336
 337 IR spectra of the compound obtained without ignition ($\phi = 0.5$, $\phi = 2$, Fig. 7) show a lack of gadolinium-oxygen
 338 bonds between 700 and 400 cm^{-1} , and the main presence of organic compounds between 1800 and 1000 cm^{-1} .
 339 These organic bonds are also present in the IR spectra of the final products, but gadolinium-oxygen bonds were
 340 detected too. Furthermore, organic residues are fewer presents in IR spectra of final powders obtained with
 341 stoichiometric richness mixtures, which was confirmed by carbon content measures (Table 2). IR spectra of
 342 powders are similar than their XRD patterns (SI-4) and confirm the formation of crystalline nanoparticles after
 343 ignition and of organic residues at $\phi = 0.5$ and $\phi = 2$. In the case of $\phi = 0.5$ and $\phi = 2$ Gd/Glycine mixtures, a
 344 thermal treatment at 973 K is necessary to obtain the final cubic gadolinium oxide.

345
 346

347 Conclusion

348 The conversion of gadolinium nitrate into oxide was obtained by SCS reaction with glycine as fuel at temperature
 349 about 723 K lower than the classical thermal denitration temperature. For a stoichiometric ratio of glycine /
 350 gadolinium nitrate ($\phi = 1$), monoclinic Gd_2O_3 powder are obtained with a specific surface area of about $10 \text{ m}^2\cdot\text{g}^{-1}$,

351 a small amount of residual carbon and good crystallinity. The ignition of the precursors leading to the conversion
352 nitrate / oxide, was observed at a temperature of about 483 K.

353 The implementation of this reaction with glycine causes significant swelling of the precursors during the
354 temperature increase up to the ignition. This swelling is related to the decomposition of glycine. Several
355 experimental parameters: the heating rate, the richness influence the amplitude of this phenomena. When the
356 swelling is too high (rate of heating rate $< 3 \text{ K}\cdot\text{min}^{-1}$, richness $\phi > 2$), the ignition is not observed and an amorphous
357 compound is obtained. These results indicate that the density of matter before the ignition is a key parameter for
358 the reaction that modifies the reactivity of the system and induces structural changes. For intermediate richness
359 ($\phi = 0.8, 1.5, 1.7$), the end-products have a cubic structure, which is the stable structure of this oxide at low
360 temperature, or a mixture of monoclinic and cubic Gd_2O_3 . Adiabatic temperature calculations of the reaction are
361 consistent with the crystalline phases observed.

362 These findings of actinide surrogates suggest that, the new route will be a promising path for the recycling of
363 actinides of the Generation IV reactors systems. However, the high swelling of the glycine would be a drawback
364 for the application of such fuel in an industrial process, notably for the conversion of actinides. Works are in
365 progress to evaluate other fuels such as citric acid, β -alanine.

366

367

368

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Measure of the swelling of the Gel

