Data Article

X-ray diffraction and thermoanalytical datasets of precursors of the Gd$_6$UO$_{12-\delta}$ phase processed by combined mechanochemical–thermal routes

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ABSTRACT

The datasets presented here are related to the research paper entitled “Disordered Gd$_6$UO$_{12-\delta}$ with the cation antisite defects prepared by a combined mechanochemical–thermal method” [1]. The datasets complement the findings [1] on the effect of the combined mechanochemical–thermal processing of the stoichiometric mixture of solid precursors (3Gd$_2$O$_3$ + UO$_2$) on the formation of Gd$_6$UO$_{12-\delta}$ phase. In this article, we provide (i) X-ray diffraction (XRD) data of the 3Gd$_2$O$_3$ + UO$_2$ mixture milled for 12 h, (ii) the refined XRD data of the non-milled 3Gd$_2$O$_3$ + UO$_2$ mixture after annealing at 1282°C for 3 h in air, and (iii) the thermogravimetric and differential thermal analysis (TG-DTA) data for non-milled and mechanically

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Specifications Table

| Subject                        | Materials Science, Materials Characterization |
|-------------------------------|-----------------------------------------------|
| Specific subject area         | Nuclear material, Material for nuclear fuel forms, Material for nuclear waste immobilization, Structural analysis, XRD, Thermal analysis |
| Type of data                  | Graph                                         |
| How data were acquired        | XRD                                           |
| Data format                   | Raw Analyzed                                  |
| Parameters for data collection| XRD patterns of powdered samples were taken in the range from 10° to 80° (2θ) (with angular step of 0.02°) using Cu Kα radiation and a C1702 diffractometer (Shimadzu, Japan) operating in Bragg-Brentano configuration. The TG-DTA was performed in air in the temperature range from 20 °C to 1282 °C at a heat rate of 10 K/min. |
| Description of data collection| The Rietveld refinement of XRD data was performed using the FullProf Suite software [2]. The ICSD database [3] was utilized for phase identification. |
| Data source location          | Institution: Nuclear and Energy Research Institute, IPEN/CNEN-SP |
|                               | City/Town/Region: São Paulo                   |
|                               | Country: Brazil                               |
| Data accessibility            | With the article                              |
| Related research article      | G. Darin, K. Imakuma, R.T. Santiago, K.L. Da Silva, L.F. Côtica, M. Fabián, J. Valíček, H. Hahn, V. Šepelák, Disordered Gd₆UO₁₂₋₄ with the cation antisite defects prepared by a combined mechanochemical–thermal method, J. Nucl. Mater. doi: 10.1016/j.nucmat.2021.152895 |

Value of the Data

- The datasets are important for a non-conventional mechanochemical preparation of Gd₆UO₁₂₋₄, which is less elaborative, solvent-free, and high-yielded in comparison with the conventional (thermal) synthesis of this nuclear material.
- The data provide the basis for the development of novel nuclear fuel materials.
- The XRD and TG-DTA datasets can guide other materials scientists toward designing novel U-Gd-O systems for nuclear fuel forms and nuclear waste immobilization.

1. Data Description

Fig. 1 shows the XRD pattern of the 3Gd₂O₃ + UO₂ mixture milled for 12 h before heat treatment. During the high-energy ball milling process, Gd₂O₃ and UO₂ are subjected to a continuous fragmentation accompanied by the reduction of their crystallite size to the nanometer range. The latter is documented by relatively broad XRD peaks shown in Fig. 1. The qualitative XRD analysis reveals that milling of the mixture of individual binary oxides also leads to the partial formation of the ternary Gd₆UO₁₂ phase. The early stage of mechanosynthesis of the GdU₆O₁₂ phase is indicated in Fig. 1 by the presence of a broad XRD peak at the diffraction angle of about 30.6° (2θ). During the early stages of high-energy milling the reaction precursors are mixed at the atomic level and the new mechanosynthesized phase nucleates in interfacial regions between the solid reactants during the impact period. During the subsequent thermal treatment
Fig. 1. XRD pattern of the 3Gd₂O₃ + UO₂ mixture milled for 12 h before heat treatment. The partial formation of the Gd₆UO₁₂ phase is evidenced by the presence of a broad XRD peak at the diffraction angle of about 30.6° (2θ) indicated by arrow.

Fig. 2. The refined XRD pattern of the non-milled 3Gd₂O₃ + UO₂ mixture after annealing at 1282 °C for 3 h in air. The following three phases are present in the sample: Gd₂O₃, (Gd,U)O₂, and Gd₆UO₁₂.

at 1573 K for 3 h, the total conversion of the precursors to the Gd₆UO₁₂ phase takes place [1]. Such a favorable formation of the uranate during the thermal treatment step is a consequence of an accelerated mass transfer and enhanced ionic diffusivity at contact zones between precursors due to reduced diffusion paths as a result of their mechanical preactivation and the partial mechanosynthesis of the target phase.

Fig. 2 presents the refined XRD pattern of the non-milled 3Gd₂O₃ + UO₂ mixture after annealing at 1282 °C for 3 h in air. The data document that the solely thermal processing of the mixture does not lead to the complete transformation of educts to the final Gd₆UO₁₂ phase. The quantitative analysis of XRD data reveals the presence of the following three phases in the sample: 23 wt.% of Gd₂O₃ (ICSD collection code: 230,768), 66 wt.% of (Gd,U)O₂ (236,072), and 11 wt.% of Gd₆UO₁₂ (21,945) [3].
Fig. 3 shows the TG-DTA curves for non-milled and mechanically preactivated 3Gd₂O₃ + UO₂ mixture measured in air at a heat rate of 10 K/min. At about 1200 °C, a significant increase of the relative weight for the mechanically pre-treated mixture is attributed to its oxidation resulting in the complete formation of Gd₆UO₁₂; i.e., the reaction 3Gd₂O₃ + UO₂ + ½O₂ → Gd₆UO₁₂ proceeds. This is in contrast to the TG curve of the non-milled mixture exhibiting only a slight increase at temperatures above 1250 °C. The latter is associated with the initial stages of the conventional (thermal) synthesis of Gd₆UO₁₂.

2. Experimental Design, Materials and Methods

The synthesis of the Gd₆UO₁₂ solid phase requires the presence of two solid simple oxide precursors in the stoichiometric composition (3Gd₂O₃ and UO₂) and one gas phase (oxygen); i.e., the overall heterogeneous chemical reaction leading to the formation of Gd₆UO₁₂ can be written as 3Gd₂O₃ + UO₂ + ½O₂ → Gd₆UO₁₂. At first, the stoichiometric mixture of UO₂ and Gd₂O₃ was preactivated by ball-milling in a Pulverisette 6 mill (Fritsch, Germany) for 12 h at 300 rpm in N₂ atmosphere at ambient temperature. The milling process was interrupted every 1 h for 5 min (the total number of breaks: 11). A grinding chamber and balls made of stainless steel were used. The ball-to-powder mass ratio was 11:1. The UO₂ and Gd₂O₃ precursors used for the synthesis of Gd₆UO₁₂ are products of Nuclear Materials Laboratory at the Industrial Nuclear Center of Aramar (São Paulo, Brazil) and the firm Alfa Aesar, respectively. The mixtures of non-milled and mechanically treated precursors were pressed into pellets at 390 MPa, which were subsequently heated for 3 h at 1573 K in air. XRD patterns of powdered samples were taken in the range from 10° to 80° (2θ) (with angular step of 0.02°) using Cu Kα radiation and a C1702 diffractometer (Shimadzu, Japan) operating in Bragg-Brentano configuration. The Rietveld refinement of XRD data was performed using the FullProf Suite software [2]. The ICSD database [3] was utilized for phase identification. The TG-DTA measurements were performed using a simultaneous thermal analysis apparatus STA 409 C/7/E (Netzsch, Germany). The TG-DTA was done in the temperature range from 20 °C to 1282 °C at a heat rate of 10 K/min. The pelletized samples (700 mg) of both non-milled and mechanically preactivated 3Gd₂O₃ + UO₂ mixtures were thermally treated in open platinum crucibles in air.
CRediT Author Statement

Gaspar Darin: Conceptualization, Methodology, Software, Visualization; Kengo Imakuma: Investigation, Formal analysis; Rafael Trautwein Santiago: Visualization, Investigation; Klebson Lucenildo Da Silva: Conceptualization, Supervision, Formal analysis, Resources, Writing - Original Draft, Writing - Review & Editing; Luiz Fernando Cótica: Formal analysis, Supervision; Martin Fabián: Investigation, Formal analysis; Jan Valíček: Investigation, Visualization; Horst Hahn: Supervision; Vladimír Šepelák: Supervision, Writing - Original Draft, Writing - Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

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Supplementary Materials

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.dib.2021.106972.

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