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Rare earth tungsten bronzes: a new method of synthesis. Perspectives for their application as inert matrices for transmutation of long-life actinide elements

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Abstract

A new method of synthesis of oxide tungsten bronzes containing lanthanide (*Ln*) Nd and Eu, based on thermal degradation of polyoxotungstate compounds, is proposed. The simplicity of the method allows to consider this class of compounds with chemical formula, Ln_xWO_3 , as potential inert target for incineration or transmutation of minor actinides, Am and Cm, in neutron reactors. Nd and Eu were used as analogues of transplutonium elements. Powder X-ray diffraction patterns of compounds synthesized reveal a cubic perovskite structure. The lanthanide content in bronzes was determined by optical spectroscopy analysis. The experimental density of the pressed bronze samples was estimated at 6.58 g cm^{-3} , i.e., 89% of the crystallographic value. The thermal stability of the bronzes synthesized was checked up to 900°C in an inert atmosphere. Leaching tests were performed for europium bronzes in nitric acid solutions using luminescence technique.

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1. Introduction

The problem of storage and incineration of long-life actinide (*An*) isotopes, especially Am and Cm produced in nuclear reactors, requires a careful screening of potential host materials possessing a high chemical and radiolytical resistance as well as a good thermal stability and conductivity. Moreover for incineration purpose, the matrix of such a target should not be strongly activated by neutrons, should not undergo amorphization during irradiation (usually accompanied by swelling effects), should exclude gas evolving and allow chemical reprocessing to recover the actinide elements that were not burnt during the transmutation process. Non-stoichiometric oxide phases of tungsten and vanadium called “oxide bronzes”, containing interstitial lanthanide/actinide ions in their structure seemed to be

interesting candidates for the incineration purpose because of their physical and chemical properties already described in literature [1–8]. Obvious substitution of lanthanide ions by actinides (Am, Cm), as well as quasi-metallic properties and a high chemical resistance deserve the use of W- or V-bronzes for targets for neutron irradiation in nuclear reactors or as a host matrix for actinide long-term storage.

A wide application of interesting compounds should not come against difficulties in synthesis. That was the case for oxide bronzes when the most commonly applied method for bronze preparation consisted in carrying out a solid-state hetero-phased reaction between *Ln* oxide, tungsten trioxide and metallic tungsten mixed together in the appropriate molar ratio. Long duration of this reaction running into hundreds of hours, at temperatures ranging from 1000°C to 1200°C , the necessity to repeat grinding and thermal treatment of the mixture for achieving the most acceptable homogeneity [2–5,7,8] did not make the oxide bronzes attractive materials for

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application. Recently, another way of tungsten bronze preparation by thermal degradation of ammonium salts of polyoxotungstates obtained by ion exchange procedure was reported [9]. This method was also investigated in our laboratory and we propose here, even an easier method of cubic bronze synthesis based on polyoxotungstate thermal degradation.

Some properties of the obtained bronzes regarding their utilization either as target for incineration or nuclear waste form for long-term actinide storage have been investigated. They concern the thermal behavior, phase transformations and estimation of the chemical resistance via drastic leaching experiments in nitric media.

2. Bronze preparation

Cubic tungsten bronzes of Nd and Eu have been prepared by thermal degradation of compounds obtained via precipitation by heteropolyanions (HPA) of lanthanide molecular complexes formed with neutral organic ligands. The possibility of such precipitation was for the first time reported in Ref. [10].

2.1. Chemicals

2.1.1. Lanthanides as transplutonium analogues

Nd and Eu were chosen as analogues for Cm and Am transplutonium elements, respectively. Nd is convenient for optical absorption measurements, whereas Eu is less suitable for this purpose especially in presence of HPA, because of overlapping between a strong HPA absorption at $\lambda < 400$ nm and a weak Eu absorption in the same energy region with a maximum at $\lambda = 394$ nm. Nevertheless, Eu is a well-known efficient fluorescent ion and this property is widely used for analytical purposes. As a matter of fact, Eu samples have been synthesized in our work for leaching tests controlled by luminescence technique to follow the chemical solubility of bronzes in acidic solutions. Furthermore, Eu is the closest Am-analogue from the chemical properties point of view.

For the bronze synthesis, initial solutions of lanthanide nitrate were prepared by dissolution in nitric acid of Nd, Eu sesquioxides obtained by calcination in air of pure oxalates. Nitric acid was added stepwise and every step was followed by evaporation up to obtaining wet salts in order to avoid excess of nitric acid.

2.1.2. Neutral organic ligands in Ln complex

Dimethylsulphoxide (DMSO), triphenylphosphin oxide (TPPO), dimethylacetamide (DMAA) and hexamethylphosphoramide (HMPA) were used, respectively, as lanthanide ion molecular ligand. The most convenient ligand, which does not lead to carbon residues during the thermal treatment, was found to be DMAA.

2.1.3. Heteropolyanions (HPA)

It is known that low solubility is a characteristic of salts formed with ions of the same electrical charge and close radii. Since cations coordinated to ligands have rather large radii, they usually need large anions to be precipitated. But such anions cannot replace a molecular ligand in the first coordination sphere of the cation (*Ln* ion) and therefore they do not offer a strong complexing character. Exception to this rule is provided by the HPA $P_2W_{18}O_{62}^{6-}$ and $XM_{12}O_{40}^{4-}$ (with $X = P^{(V)}, Si^{(IV)}$, etc. and $M = W^{(VI)}, V^{(V)}$). Depending on the oxidation state of *X* and *M*, the charge of such HPA $XM_{12}O_{40}^{4-}$ can vary in large limits, $3 \leq n \leq 8$. In addition, since HPA in acid solution can easily be protonated [11], it is possible to adjust their charge in acidic media where they are stable.

In this work, the following tungsten based HPA were tested: $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$. The first two oxopolytungstates were used as sodium salt and free acid, respectively, and the third one as ammonium salt.

All chemical reagents were supplied by Sigma-Aldrich or Merck.

2.2. Synthesis of the Ln-tungsten bronzes

In our previous work [12], it has been shown that a molar ratio *Ln*:DMAA = 1:6 and a stoichiometric quantity of polyoxoanion $PW_{12}O_{40}^{3-}$, are the optimal conditions to achieve precipitation of the molecular complex $Nd(DMAA)_6PW_{12}O_{40}$, whose composition has been determined by single-crystal X-ray diffraction.

Accordingly, the tungsten bronzes considered in this work were prepared via the following procedure: 1 mL of 0.5 M $Ln(NO_3)_3$ (*Ln* = Nd, Eu) was first mixed with 3 mL of 1 M DMAA and then, 5 mL of 0.1 M $Na_2HPW_{12}O_{40}$ was added to the obtained solution. Under strong stirring condition, a voluminous precipitate was formed and separated by filtration. After washing with a small quantity of cold water, the precipitate was dried on filter in air current. The thermal degradation of the washed precipitate was carried out in an inert gas (Ar) flow at 600°C during 1–3 h.

The compounds resulting from the thermal treatment of the DMAA complex of neodymium and europium precipitated by the polyoxoanion $PW_{12}O_{40}^{3-}$ are of deep violet and deep blue colors, respectively.

3. Tungsten bronze properties

3.1. Structural characterization

X-rays diffraction spectra were collected on a Philips PW 1050/70 diffractometer using $CuK\alpha$ radiation with Ni-filter. Patterns were recorded from 5° to 60° (2 θ) with 0.01° increment. Silicon was used as internal standard.

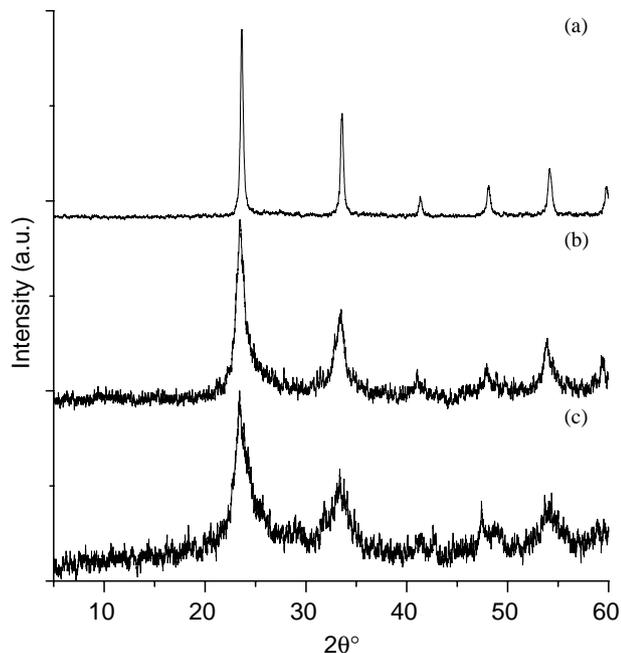


Fig. 1. Powder diffraction patterns of bronzes after thermal treatment (600°C, Ar, 3h): (A) Eu–tungsten bronze obtained from europium molecular complex formed with DMAA, precipitated by $\text{PW}_{12}\text{O}_{40}^{3-}$. (B) Nd–tungsten bronze obtained from neodymium molecular complex formed with DMAA, precipitated by $\text{SiW}_{12}\text{O}_{40}^{4-}$. (C) Poorly crystallized product obtained from Nd–molecular complex formed with DMAA, precipitated by $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$.

Nd and Eu tungsten bronzes synthesized with $\text{PW}_{12}\text{O}_{40}^{3-}$ show identical powder X-ray diffraction patterns given in Fig. 1A. That is a typical diffractogram for perovskite-like cubic Ln–tungsten bronzes [1,2,9].

Thermal treatment of bronzes obtained via $\text{SiW}_{12}\text{O}_{40}^{4-}$ and $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ precipitation also leads to the cubic structure. However, a lower crystallinity of the final product was found for the silicotungstate and even less crystallinity in the latter case (Figs. 1B and C). Additional heating of the poorly crystallized samples (600°C, Ar-flow) for 10 h did not provide any noticeable improvement of their crystallinity. Thus, it is clear that among the three HPA tested, only phosphotungstate $\text{PW}_{12}\text{O}_{40}^{3-}$ anions allow to obtain highly crystallized bronzes via our low temperature preparation method.

According to their crystal structure, the bronzes are formed with tungsten–oxygen octahedra solely linked by corners, with the rare earth ions occupying the empty cavities between these octahedra. Following literature [1,4,5], the presence of interstitial lanthanide ions in the crystalline lattice makes the bronze structure more stable. Lanthanide contents, x , in tungsten bronzes, Ln_xWO_3 , generally varied within $0.05 \leq x \leq 0.2$ limits [1–5]. It is worth noting that HPA and bronzes present identical structural arrangements and therefore, the thermal treatment of the Ln compounds precipitated

Table 1
Crystal lattice parameter (a) versus europium molar concentration (x) in tungsten bronze Eu_xWO_3

x	a (Å)	Reference
0.076	3.800	This work
0.085	3.808	[2]
0.1	3.815	[2]
0.12	3.823	[2]
0.15	3.828	[2]

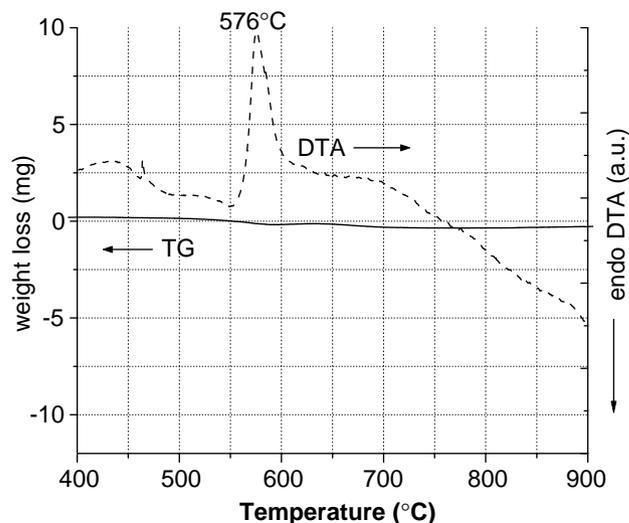


Fig. 2. TG/DTA (solid/dashed) of Nd_xWO_3 bronze: Sample weight: 49.1 mg. Heating rate: 5°C/min (He) flow. ~ 0.1 L/min.

with HPA induces only a partial structural reorganization to form the bronze phase.

In Table 1 are listed the lattice parameter values versus the lanthanide ion concentration in bronzes.

3.2. Thermal analysis

Thermal diagrams have been obtained with SETARAM TG-DTA92 instrument when isothermal heating was carried out in a tubular furnace with regulated temperature.

TG and DTA curves for $\text{Nd}(\text{DMAA})_6\text{PW}_{12}\text{O}_{40}$ samples previously dried at 400°C in an inert atmosphere, are presented in Fig. 2 for 5°C/min heating rate. The previous thermal treatment was performed in order to prevent condensation of released organics and thermal decomposition products. The samples were heated in Pt crucibles to allow accurate determination of the temperatures of possible physico-chemical transformations in the samples under study. The exothermal process of bronze formation was found to take place in a narrow temperature interval, 560–590°C, with a maximum of heat evolving at 576°C. This exothermal effect is attributed to the formation of a more energetically

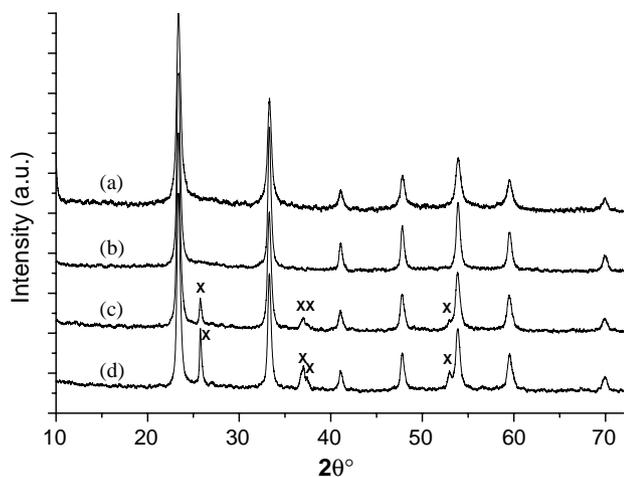


Fig. 3. Evolution of the cubic Nd-PTB phase with temperature. Treatment of the sample in Ar atmosphere for 4 h X-monoclinic WO_2 (see footnote 1,2): (A) 600°C; (B) 700°C; (C) 800°C; (D) 900°C.

stable perovskite structure. There are no other visible thermal effects in the DTA curve up to 900°C. Such a thermal stability of the obtained samples is in good agreement with the already published data on the synthesis of RE tungsten bronzes at temperatures ranging between 1000°C and 1250°C [2–5, 13]. However in Ref. [9], the X-ray powder diffraction pattern of the perovskite tungsten bronze (PTB) sample treated at 900°C in inert atmosphere shows obvious WO_2 diffraction peaks as was recorded in our samples (Fig. 3). The 700°C treatment of PTB sample in argon atmosphere for 3–20 h did not lead to changes in the XRD pattern which corresponds to the pure cubic perovskite phase (Figs. 3A and B). Starting from 800°C treatment, additional diffraction lines attributed to a new phase became noticeable in the diffraction pattern (Fig. 3C). Accordingly,^{1,2} they can be indexed to the most intense reflection lines of the WO_2 monoclinic phase. Temperature increasing to 900°C does not affect substantially the phase composition: the perovskite-type cubic bronze remains the main phase and the monoclinic WO_2 can only be considered as a weak component (Fig. 3D). A possible explanation of the WO_2 appearance is a partial oxygen loss from the WO_3 groupings forming the matrix skeleton via corner-shared WO_6 octahedra. The phenomenon of high temperature reduction of tungsten trioxide in evacuated ampoules or by action of gaseous hydrogen was already reported for pure WO_3 phase [14]. For PTB phases, it was underlined that interstitial atoms stabilize the structure [1,4]. The extent of the bronze structure stabilization depends on the nature, charge and quantity of the foreign element.

¹JCPDS-International Centre for Diffraction Data. Powder Diffraction File (PDF) 05-0431, WO_2 .

²PDF 32-1393, WO_2 .

3.3. Determination of the lanthanide contents

Lanthanide contents, x , in tungsten bronzes, Ln_xWO_3 , generally vary within $0.05 \leq x \leq 0.2$ [1–5]. The quantity of lanthanide in the compounds has been controlled during the precipitation by evaluating spectrophotometrically the neodymium (europium) concentration in the supernatant solution.

Evolution of the Nd optical absorption spectrum as polyoxoanion $\text{PW}_{12}\text{O}_{40}^{3-}$ is added dropwise to the starting solution containing Nd and DMAA in the 1:6 molar ratio is shown in Fig. 4. Absorption spectra in the visible range were recorded from solution with a Varian DMS 300 double beam spectrophotometer. The neodymium concentration is related to the area under the narrow absorption band at $\lambda = 577 \text{ nm}$ ($^4\text{I}_{9/2} - ^4\text{G}_{5/2}$ transition) with attenuation coefficient $\varepsilon \cong 6.15$. From these data, it was estimated that the neodymium concentration in the bronze phase was about 90% of the total Nd amount. The absorption spectrum of the final supernatant solution (after addition of $\text{PW}_{12}\text{O}_{40}^{3-}$ anions in the stoichiometric ratio (curve 4)) and those recorded on initial and intermediate solutions, differ in total and relative intensity.

HPA absorption at $\lambda \sim 400 \text{ nm}$ becomes noticeable in solution when no more precipitation occurs with increasing polyoxoanion concentration. Nd still in solution is probably present as a soluble complex formed with $\text{PW}_{12}\text{O}_{40}^{3-}$ anions.

As was already mentioned, europium is less convenient for spectrophotometric concentration determination in presence of HPA due to superposition of the Eu band at $\lambda = 394 \text{ nm}$ ($^7\text{F}_0 - ^5\text{L}_6$, $\varepsilon \cong 1.61$) with the HPA

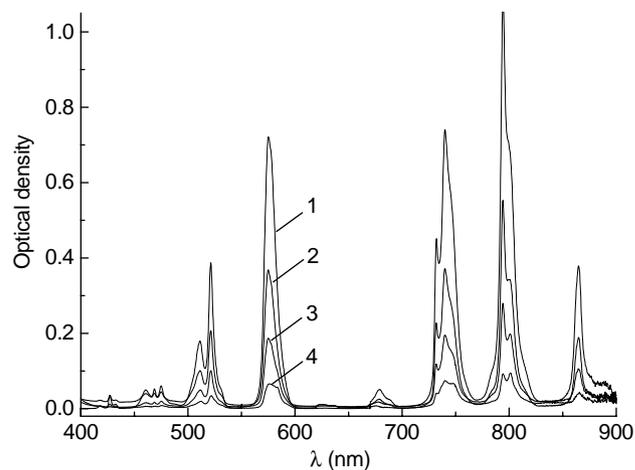


Fig. 4. Evolution of the optical absorption spectrum of Nd (supernatant solution) during precipitation of the precursor with $\text{PW}_{12}\text{O}_{40}^{3-}$: (1) starting solution, Nd:DMAA = 1:6; (2) intermediate solution, Nd:DMAA: $\text{PW}_{12}\text{O}_{40}^{3-}$ = 1:6:0.4; (3) intermediate solution, Nd:DMAA: $\text{PW}_{12}\text{O}_{40}^{3-}$ = 1:6:0.8; (4) final solution, Nd:DMAA: $\text{PW}_{12}\text{O}_{40}^{3-}$ = 1:6:1.

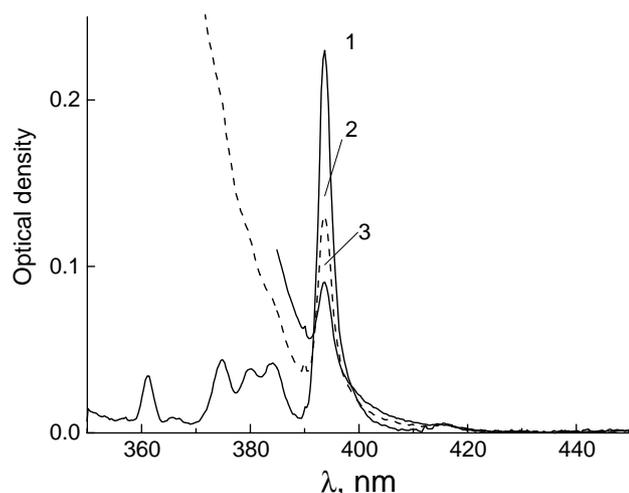


Fig. 5. Evolution of the optical absorption spectrum of Eu (supernatant solution) during precipitation of the precursor with $\text{PW}_{12}\text{O}_{40}^{3-}$: (1) starting solution, Eu:DMAA=1:6; (2) intermediate solution, Eu:DMAA: $\text{PW}_{12}\text{O}_{40}^{3-}$ =1:6:0.4; (3) final solution, Eu:DMAA: $\text{PW}_{12}\text{O}_{40}^{3-}$ =1:6:1.

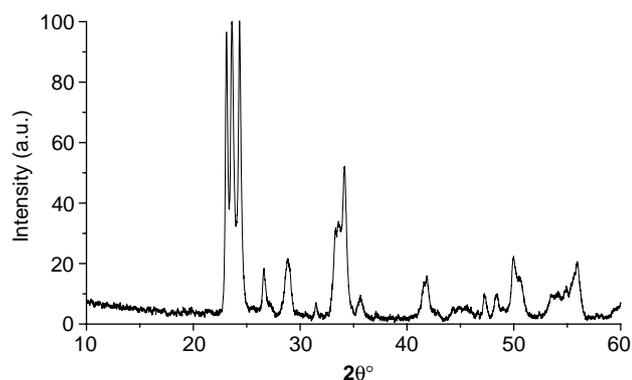


Fig. 6. Powder diffraction pattern of monoclinic WO_3 , obtained by Nd-bronze calcination in air (800°C , 1 h).

charge transfer band. Only the kinetics of Eu disappearance in solution can be observed (Fig. 5).

Nd and Eu concentrations in the prepared bronze samples were also determined by optical spectroscopy after dissolution of the respective solids. To carry out dissolution, about 1 g of the bronze compound was calcined in air at 800°C for 1 h to achieve a complete oxidation to $\text{WO}_3 + \text{Ln}_2\text{O}_3$. The yellowish-green color of the final product indicates the full oxidation of the bronze and this has been confirmed by the X-ray diffraction pattern (Fig. 6). The final product corresponds to the monoclinic tungsten trioxide.^{3,4} There are no reflection lines belonging to the lanthanide oxide in the X-ray pattern because of the low content of lanthanide homogeneously distributed in the WO_3 -

Table 2
Eu and Nd content in bronze samples

No.	Bronzes	Sample weight (mg)	Nd (mg)	Eu (mg)	wt%	x
1	Nd_xWO_3	1238.8	59.3	—	4.79	0.081
2	Nd_xWO_3	1300.7	60.8	—	4.68	0.079
3	Eu_xWO_3	1014.9	—	48	4.73	0.076
4	Eu_xWO_3	1159.2	—	57.6	4.97	0.080

phase. After cooling, the sample was treated by 1 M solution of NaOH in order to dissolve tungsten trioxide. Lanthanide hydroxide, formed during such a treatment, was flocculated and separated by centrifugation. After washing with 0.1 M NaOH and repeated centrifugation, the hydroxide precipitate was dissolved in nitric acid. Since the large specific surface area of the hydroxide can lead to adsorption of appreciable tungsten quantity, the whole operation was repeated several times up to the complete dissolution of the solid phase in a fixed volume of 2 M HNO_3 . Then, neodymium and europium concentrations were determined spectrophotometrically as reported previously. Results of Eu- and Nd-bronze analysis are given in Table 2. They can be easily extrapolated to the possible actinide content in such bronze phases.

It is worth to note that this simple dissolution procedure can be used for reprocessing and actinide recovery from the burnt-up target.

4. Eu-bronze leaching tests in acidic media

4.1. Experimental procedure

Before starting the leaching tests, enough quantity of Eu-tungsten bronze was washed by 2 M HNO_3 at moderate temperature in order to remove europium adsorbed on the solid surface as $\text{Nd}(\text{DMAA})_6\text{PW}_{12}\text{O}_{40}$ compound. Then, the compound was washed again with water and dried.

Analytical weights of europium tungsten bronze (Eu_xWO_3 , $x \approx 0.1$), containing about 0.5 mmol of Eu, were placed into 6 plastic test tubes (50 mL) filled with fixed volumes of nitric solution and the tubes were closed (Table 3). The sample weights were chosen on the basis of 10^{-2} M europium concentration for a total dissolution of the compound. Leaching tests were carried out at room temperature, with periodical stirring. Aliquots of 2 mL were taken apart after 1, 2, 3, 4, 5, 10, 15, 20 and 30 days. Before any Eu luminescence intensity measurement, aliquots were centrifuged during 5 min at 8000 rpm, neutralized by NaOH and diluted if necessary in NaNO_3 solution. The luminescence calibration curve was obtained in 0.5 M NaNO_3 solution in presence of ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ playing the role of luminescence

³PDF 72-0677, WO_3 .

⁴PDF 75-2072, WO_3 .

sensitizing agent. In accordance with Ref. [15], 0.145 M $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ was added stepwise up to a concentration of 2×10^{-3} M. The intensity of europium luminescence measured at 615 nm ($^5\text{D}_0\text{--}^7\text{F}_2$) upon excitation in $^5\text{L}_J$ multiplets with the third harmonics of YAG:Nd laser ($\lambda = 335$ nm) via a charge transfer state in paramolybdate, was measured with a Jobin–Yvon HR1000 monochromator. Typical luminescence spectra are shown in Fig. 7.

Table 3
Experimental conditions and results of leaching tests

No.	$[\text{HNO}_3]$ (M)	Weight of sample (g)	Eu content (mg)	Eu content (mmol)	$[\text{Eu}]$ (M) in leach solutions
1	0.1	1.270	78	0.51	1×10^{-6}
2	0.5	1.297	80	0.52	5×10^{-5}
3	1	1.224	75	0.49	7.5×10^{-5}
4	2	1.247	77	0.50	1.8×10^{-4}
5	5	1.362	84	0.55	3×10^{-4}
6	8	1.353	83	0.54	3.5×10^{-4}

4.2. Results and discussion

Europium concentration in leach solutions versus nitric acid concentration is shown in Table 3. It should be noted that the maximal europium concentration does not exceed 4% of the total Eu content in the bronze sample. The absence of marked correlation between leaching time and Eu concentration in leach solution may be explained by the occurrence of traces of adsorbed europium, which was not removed completely before starting the leaching tests. This hypothesis needs more prolonged leaching time to be verified.

5. Palletizing

In view of neutron reactor target application, the possibility of palletizing was considered but this study was not carried out thoroughly. The density of the obtained pellets was determined by the hydrostatic method by weighing pellets in air and in de-mineralized water at ambient temperature. The results given in

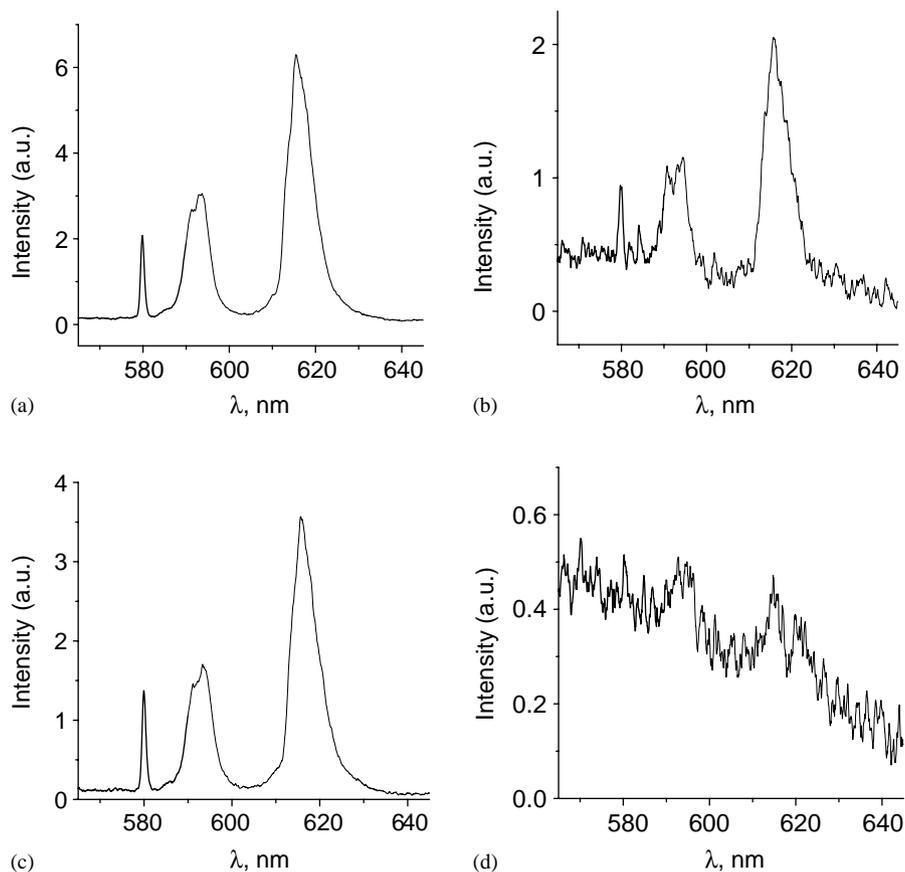


Fig. 7. Eu luminescence spectra: (A) calibration solution: $[\text{Eu}] = 5 \times 10^{-5}$ M in the presence of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, $[\text{NaNO}_3] = 0.5$ M, excitation $\lambda = 335$ nm, sensitivity 100 mV; (B) calibration solution: $[\text{Eu}] = 6 \times 10^{-5}$ M in the presence of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, $[\text{NaNO}_3] = 0.5$ M, excitation $\lambda = 335$ nm, sensitivity 20 mV; (C) solution 5 M $[\text{HNO}_3]$, 10 days leaching time, sensitivity 100 mV; (D) solution 0.1 M $[\text{HNO}_3]$, 1 day leaching time, sensitivity 20 mV.

Table 4
Density determination of Eu-bronze samples by hydrostatic weighing

Sample	(i)	(ii)	(iii)
Weight in air (g)	0.4853	0.7309	1.0176
Weight in water (g)	0.4010	0.6090	0.8630
Volume of the sample (cm ³)	0.0840	0.1220	0.1546
Density (g/cm ³)	5.77	5.99	6.58
% from theoretical density (7.35 g/cm ³)	78	81	89

Table 4 concern three samples prepared by slightly different methods: (i) cold-press of the powder obtained by thermal treatment of the initial compound at 200°C in Ar and heating of the pellet at 600°C for 3 h under Ar atmosphere, (ii) mixing of 200°C and 600°C treated powders in 1:2 ratio before cold-pressing and identical thermal treatment of the pellet, (iii) addition of 2% (wt) of stearic acid to the bronze powder obtained at 600°C followed by a thermal treatment as described above. All samples were cold-pressed under 3–4 ton/cm² for 5 min in a mould of 10 mm in internal diameter. Thermal treatment of the pellets after pressing was carried out in inert atmosphere for 3 h.

It was checked that these pressed bronze samples possess good electro-conductivity, as expected. In our further work, we plan to measure thermal conductivity as well as to carry out dilatometry experiment. Both will provide very important parameter values regarding the application considered in this study.

The highest density of the pressed bronze samples prepared in this work, was evaluated to 6.58 g/cm³, i.e., 0.89 of the crystallographic value. It should be noted that bronze polycrystalline powders prepared in this work show good ability of pelletizing. However, determination of the best pelletizing conditions is a special technical task that is not one of the present goals.

6. Conclusion

Untill recently, only high-temperature heterogeneous solid state reactions dealing with many components or high-temperature electrolysis of molten salts were used for tungsten bronzes preparation, first synthesized more than 150 years ago. All of these methods could not provide homogeneity in obtained compounds and therefore could not serve as universal methods of

synthesis of such a class of compounds. The present work solves this problem and allows to achieve synthesis at moderate temperature with fixed molar ratios Ln/An . This simple and one-step way of preparation as well as specific properties of oxide bronzes allows considering them as potential matrices for transmutation of long-life radionuclides or as nuclear waste form for their long-term safe storage.

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