

On the Photochemical Synthesis of Nano- and Microscale Rare Earth Oxides

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Due to their unique electronic structure rare earth compounds are widely applied as the key component in many functional materials, for example for optics, electrics, magnetics and radiation shielding. Nanoscale rare earth materials can exhibit special properties including small size effect, high specific surface effect, quantum size effect, high optical, electronic, magnetical properties, superconductive property and high reactivity, which can improve the properties of nanoscale materials at a large extent. Therefore the controllable synthesis of micro- and/or nanoscale rare earth oxides is a challenge because new method of synthesis of particle rare earth oxides and the study of their size is of fundamental importance in the development of recent researches. For practical point of view it is very important to control the particle size cause of their size-dependent properties. Obtaining materials under neutral conditions have been a goal of many researches. Traditional methods usually need high temperature, or high pressure, or toxic precursors and it is difficult to obtain nano-scale r

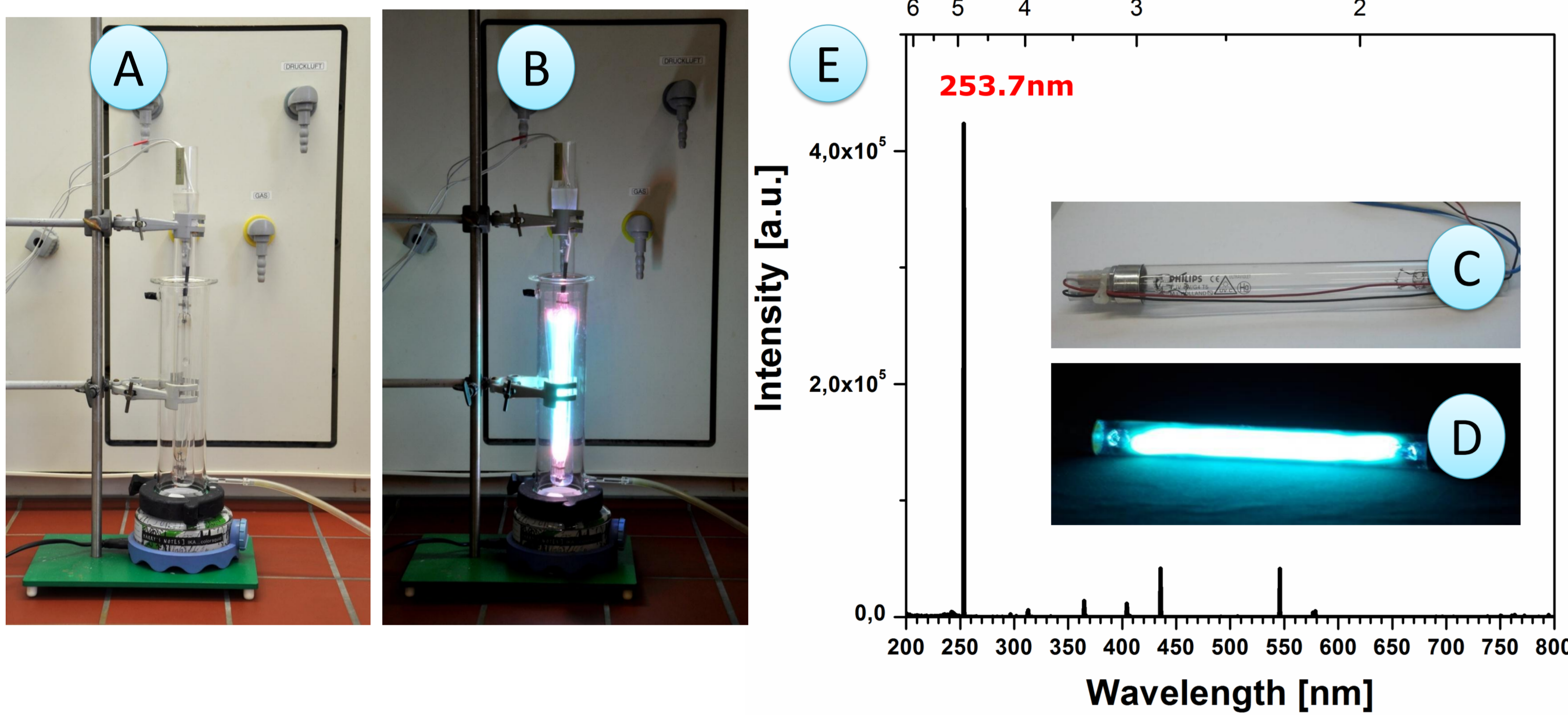


Fig. 1. A and B: A Photochemical Reactor; C and D: Low-pressure Hg discharge lamp (VUV/UV-TUV lamp emitting at 253.7 nm, 40 W).

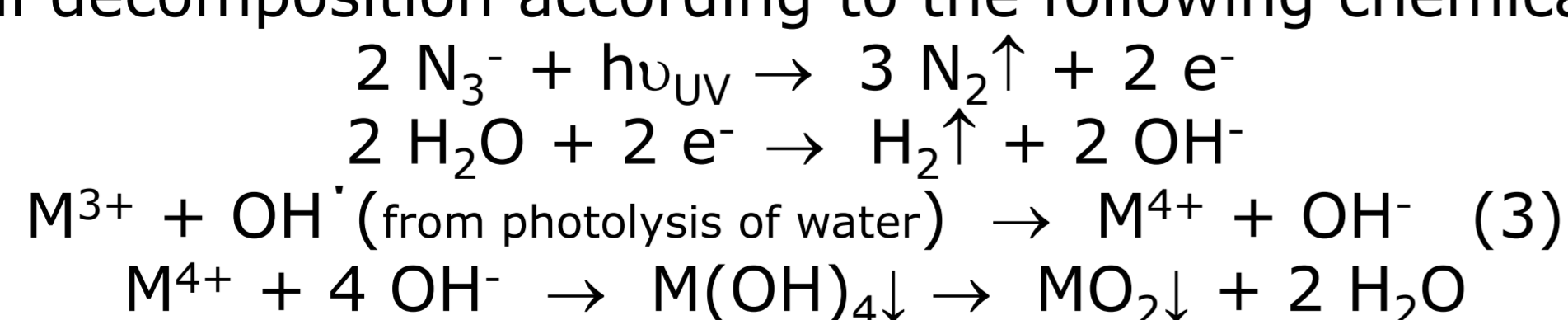
In this presentation we report a facile photochemical method to synthesize micro- and/or nanoparticles of some rare earth oxides at room temperature by a very simple reaction between rare earth chlorides or rare earth acetates and sodium azide in the presence of protecting agent polyvinylpyrrolidone (PVP) using ultraviolet photoirradiation. The particles of rare earth oxides were characterized by X-ray diffraction (XRD) and UV-visible (UV-Vis) spectrometer. The sizes of the samples were obtained by a Zetasizer Nano ZS.

Preparation of rare-earth oxide nanoscale particles

Table 1. Compositions of sample.

Number of sample	Rare earth compound	Rare earth compound 3.070 mmol [g]	Sodium azide NaN ₃	PVP [g]
1	TbCl ₃ · 6 H ₂ O	1.100	9.22 mmol = 0.6 g	2.4
2	Tb(CH ₃ COO) ₃ · x H ₂ O	1.000	9.22 mmol = 0.6 g	2.4
3	EuCl ₃ · 6 H ₂ O	1.127	9.22 mmol = 0.6 g	2.4
4	Eu(CH ₃ COO) ₃ · x H ₂ O	1.010	9.22 mmol = 0.6 g	2.4
5	PrCl ₃ · 6 H ₂ O	1.000	9.22 mmol = 0.6 g	2.4
6	Pr(CH ₃ COO) ₃ · x H ₂ O	0.976	9.22 mmol = 0.6 g	2.4

Preparation of micro and/or nano-scale rare-earth oxides particles from water solution is based on the observation that sodium azides are sensitive towards the irradiation with UV radiation, which is obvious from the absorption spectrum of NaN₃. After absorption of a UV photon sodium azide undergoes a photochemical decomposition according to the following chemical equations:



Conclusions

We have developed a facile and effective solvent-phase method for fabrication of rare earth oxides micro- and/or nanoscale particles by ultraviolet light irradiation of the aqueous solution of rare earth salts with sodium azide. Our photochemical method approach does not require any additional conditions, and thus offers not only an attractive possibility for the manufacture of micro- and/or nanoscale particles rare earth. The main advantages of this process are that it is a simple and efficient for producing particles. We can foresee the up-scaling of the process to form large quantities of micro- and/or nanosized rare earth particles. These particles could find use in different kind of technological applications.

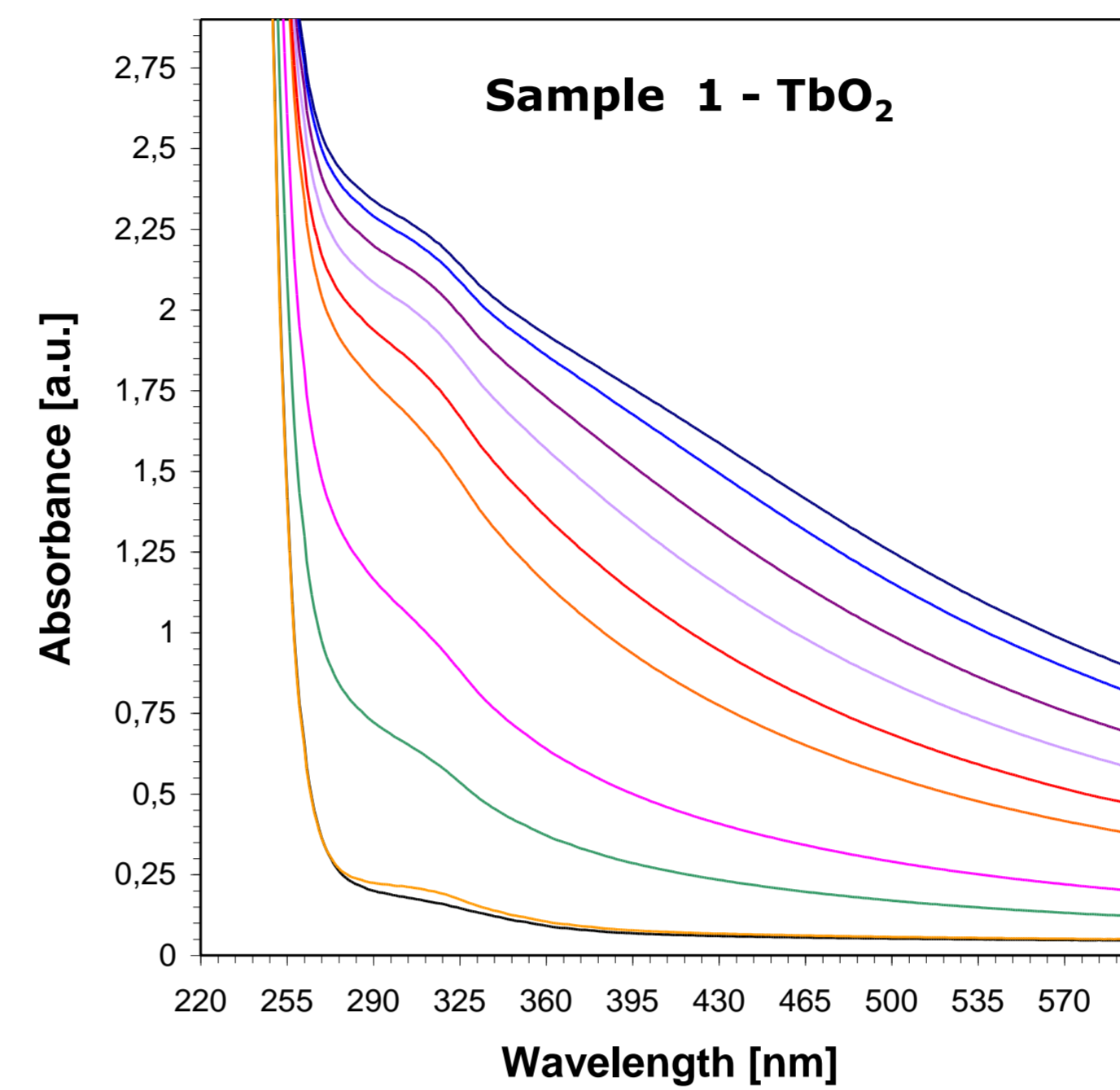


Fig. 2. The change of absorption spectrum of reaction mixture of sample 1.

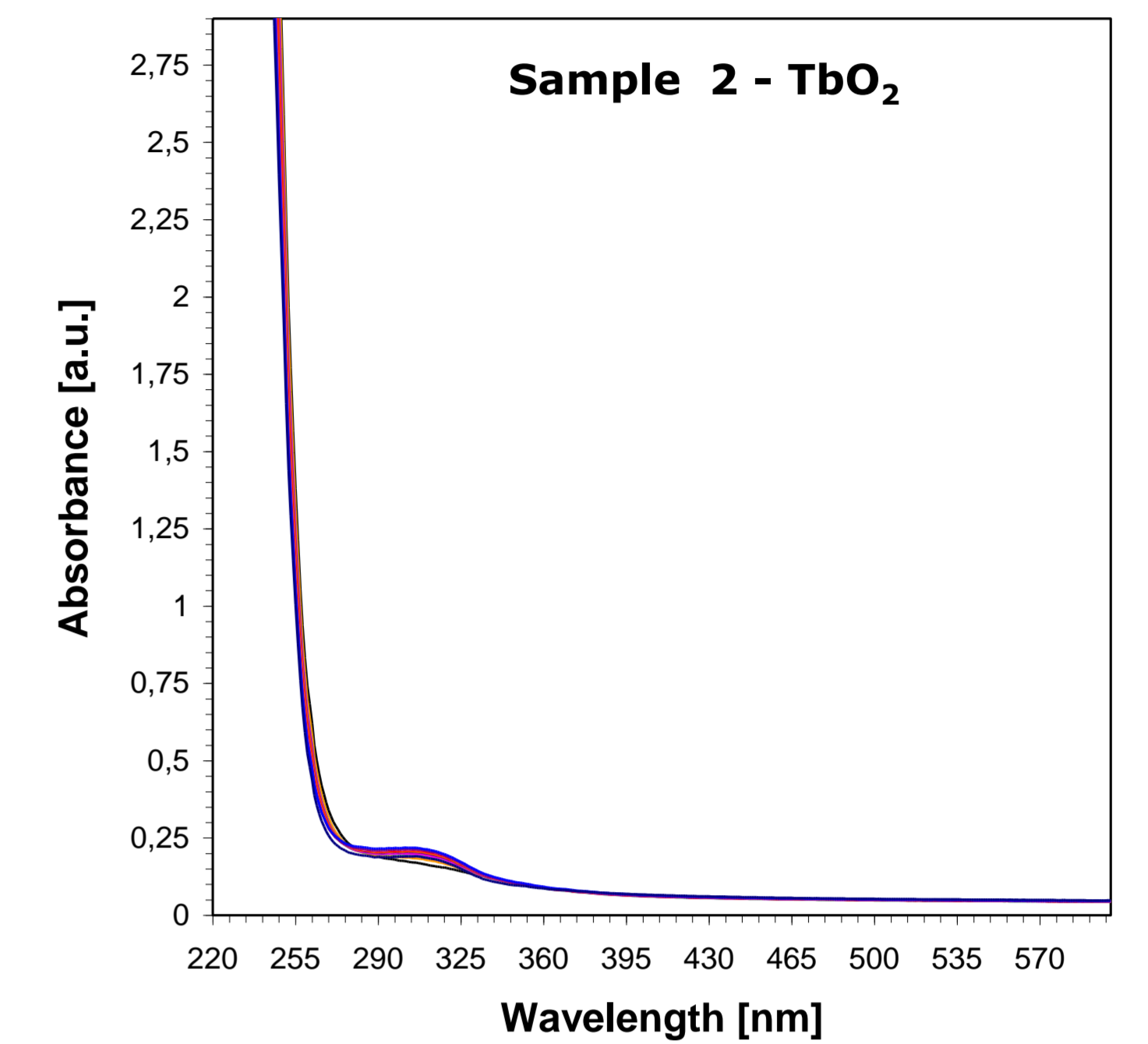


Fig. 3. The change of absorption spectrum of reaction mixture of sample 2.

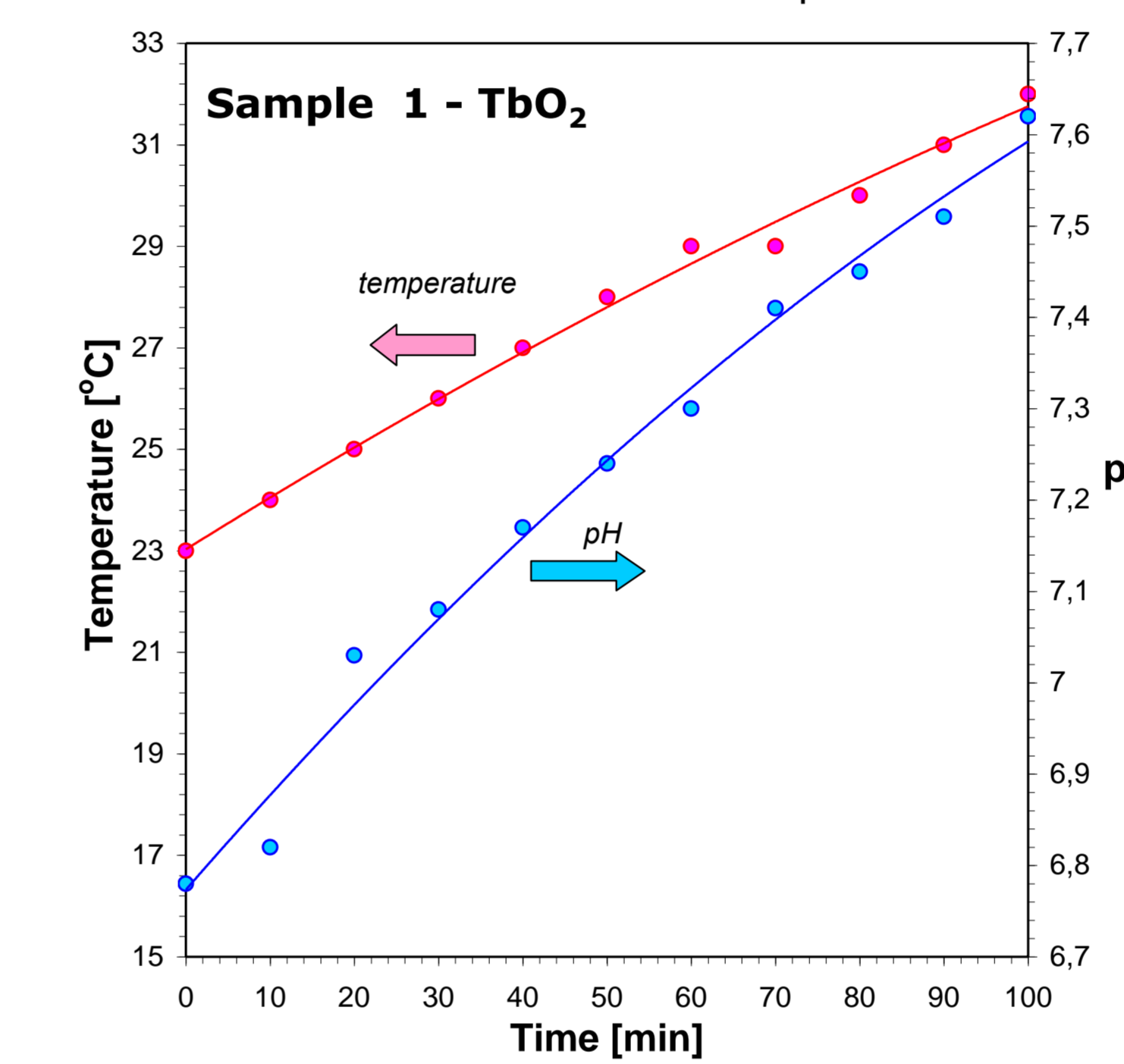


Fig. 4. The change of temperature and pH values of reaction mixture 1 during UV irradiation.

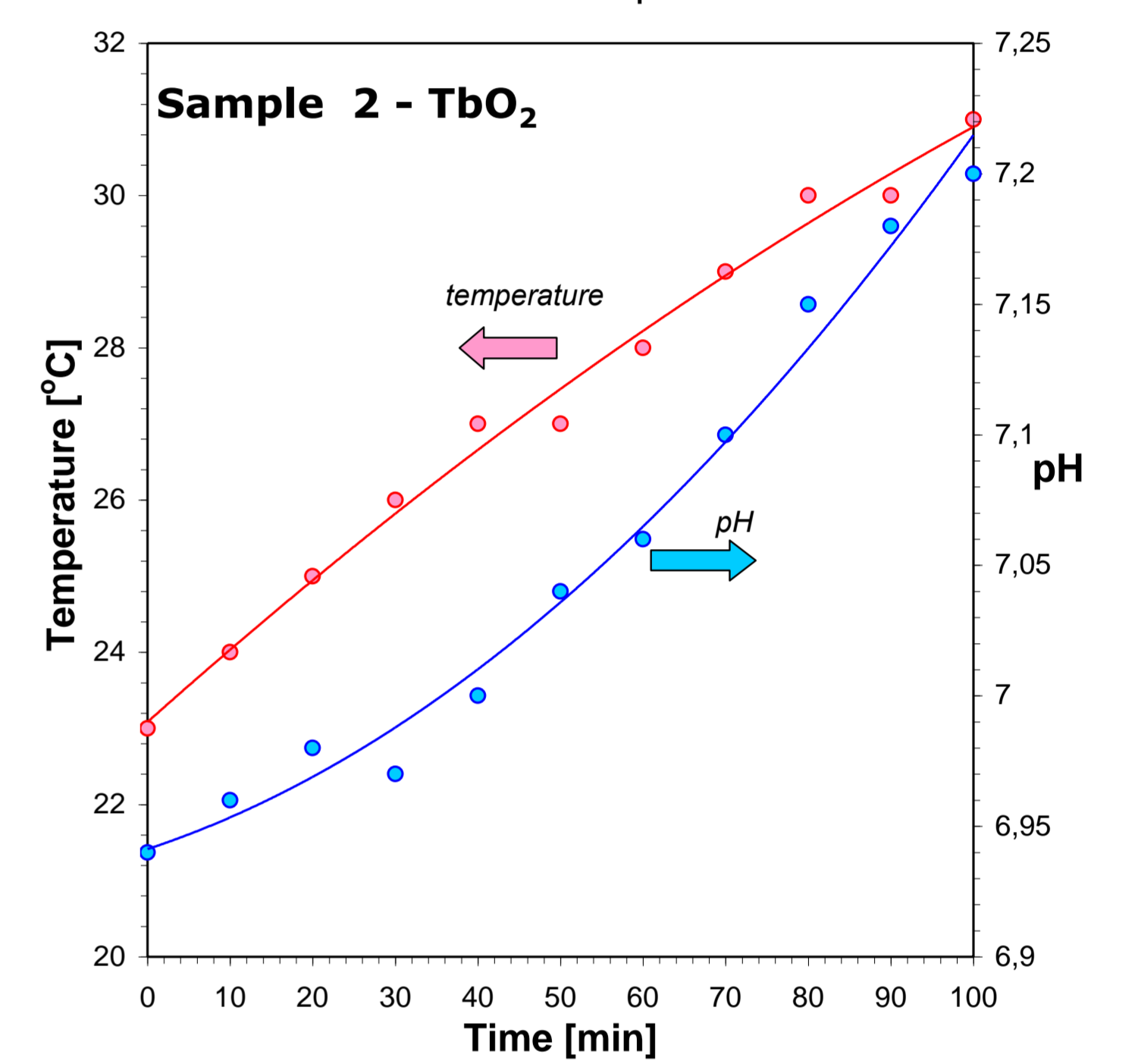


Fig. 5. The change of temperature and pH values of reaction mixture 2 during UV irradiation.

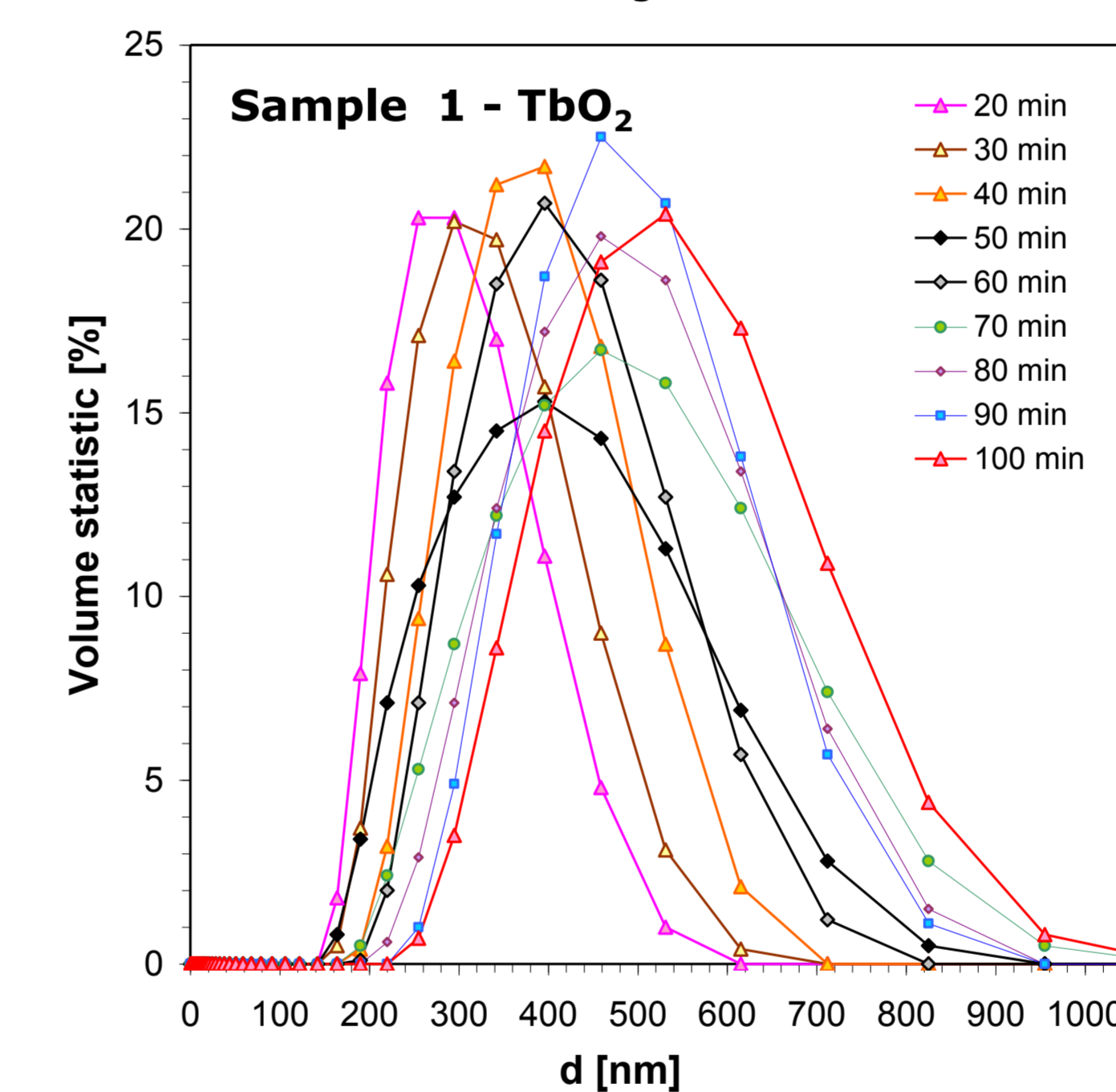


Fig. 6. The change of size of particles for reaction mixture (sample 1) during UV irradiation.

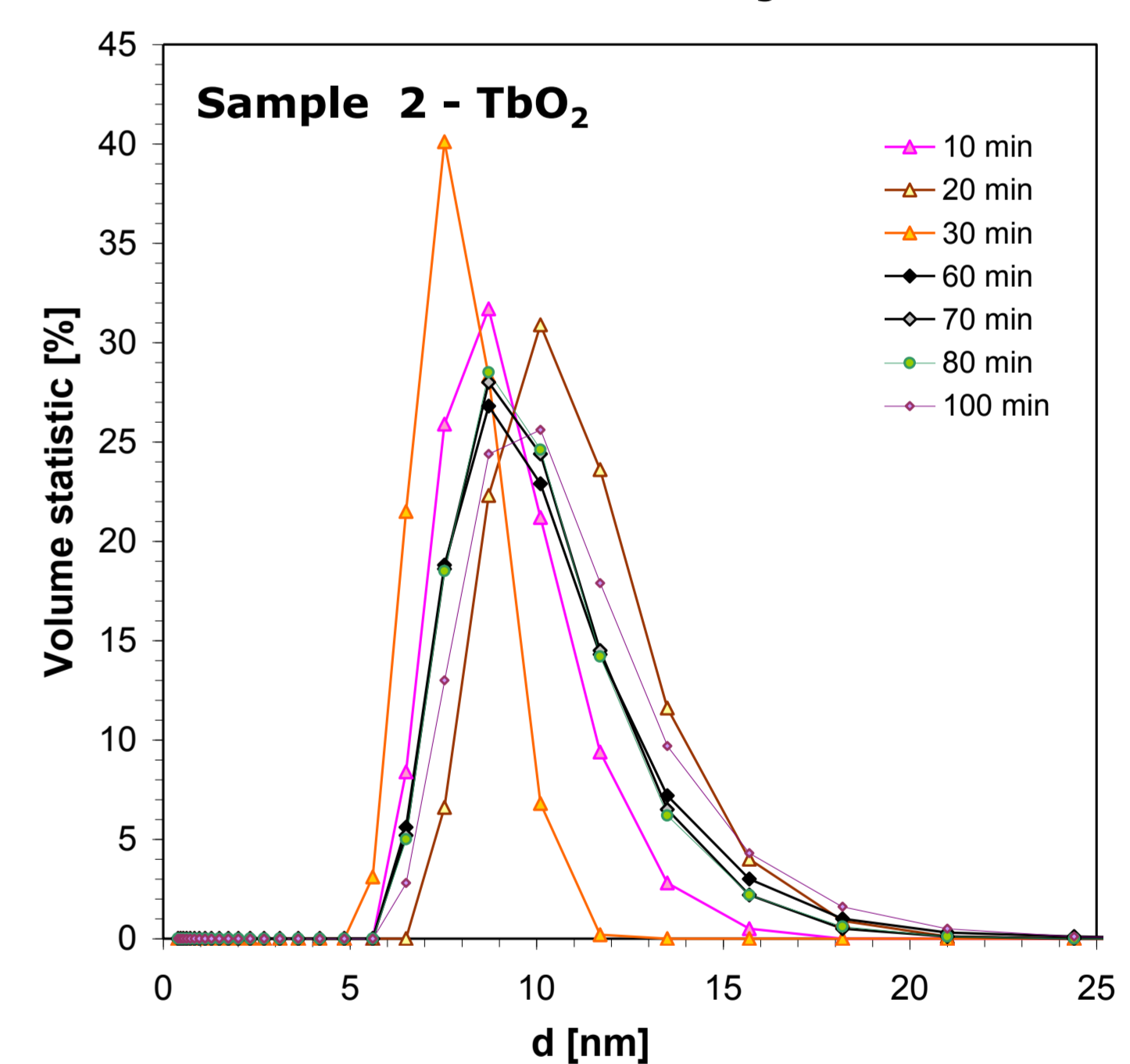


Fig. 7. The change of size of particles for reaction mixture (sample 2) during UV irradiation.

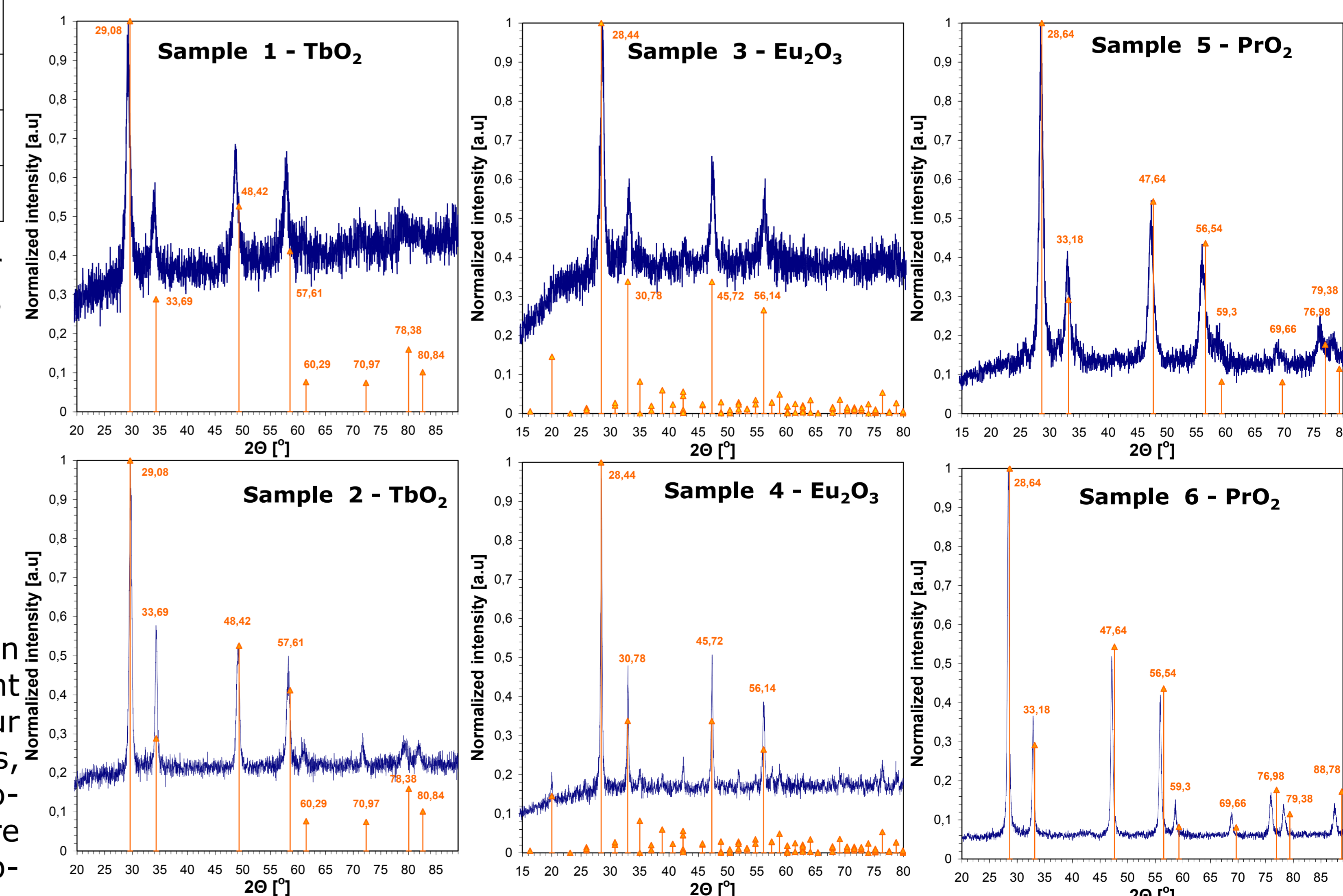


Fig. 8. XRD patterns for samples 1-6 after the calcinations step in comparison to the reference pattern of TbO₂, Eu₂O₃ and PrO₂.