

The Copper Ampoule: A New Reactor for the Solid-State Synthesis of Complex Lanthanide Fluorides

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For the first time, copper ampoules have been used as reactors for the solid-state synthesis of complex lanthanide fluorides under vacuum. The high ductility of copper allows for high-vacuum tight sealing of the ampoules by cold welding. Furthermore, no chemical reactivity of copper toward solid fluorides has been observed. Thus, for an examination in view of optical upconversion properties, the superstructure phases $\text{Ba}_{4-x}\text{Y}_{3+x}\text{F}_{17+x}$ ($x \approx 0.08$) and $\text{Pb}_{4-x}\text{Y}_{3+x}\text{F}_{17+x}$ ($x \leq 0.2$) have been synthesized by annealing of mixtures of binary fluorides in evacuated copper ampoules.

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Key Words: evacuated copper ampoules; solid state synthesis in copper ampoules; solid state synthesis of complex lanthanide fluorides; synthesis of barium yttrium fluorides; synthesis of lead yttrium fluorides.

INTRODUCTION

Lanthanide (*Ln*) compounds exhibit many interesting solid-state properties, including so-called upconversion (UC). UC describes the conversion of infrared to visible or even ultraviolet light (1). UC is attractive in view of the realization of compact visible UC lasers (2, 3) or UC phosphors (4–7), which explains the interest for new and highly efficient UC materials. High UC efficiency has been found in *Ln* halides (8), showing lower phonon energies and, consequently, reduced radiationless multiphonon relaxation (9, 10). However, among *Ln* halides, only fluorides are air stable (not hygroscopic) and are therefore of interest in view of real world applications.

For the search for new and efficient fluoride UC compounds, including new as well as known phases, we have developed a screening procedure, synthesizing a broad range of compounds by annealing and assessing their UC properties using a specially designed powder test setup (11). Since *Ln* fluoride compounds are sensitive to oxygen

(oxidation) and water (hydrolysis) at elevated temperatures (formation of oxyfluorides and oxides with release of fluorine or hydrogen fluoride), synthesis has to be performed under an inert atmosphere (inert gas or vacuum) in an appropriate reactor (12, 13). As described in the literature, fluoride powders have mainly been obtained by annealing in argon-purged and sealed ampoules of tantalum, gold, platinum, or nickel (14–16). However, for a screening procedure, requiring the synthesis of a large number of compounds, a reactor material has to be found which is inexpensive and easy to handle. Furthermore, it has to be inert toward both reactants and products and resist possible corrosive gases. Dénès introduced bent copper tubes as new inexpensive and convenient reactors for fluorides of metals in suboxidation states (17). According to Gmelin (18), copper is not—or just slightly—reactive toward fluoride compounds and hydrogen fluoride. Fluorine, however, will attack copper at elevated temperatures with formation of CuF_2 . For the synthesis of SnF_2 -based fluorides, Dénès used copper tubes which were sealed under inert gas by flattening and bending the end around itself three or four times. This method is efficient for leak-free reactions under moderate heating (e.g., 1 h at 400–500°C). However, leakage occurred at higher temperatures. Furthermore, copper tubes sealed by this technique cannot be evacuated. Altogether, this reduces the value of the bent copper tube technique for the solid-state synthesis of complex *Ln* fluorides.

In this paper, we present the use of evacuated copper ampoules as reactors for the solid-state synthesis of ternary *Ln* fluorides. Copper ampoules, being tight up to 900°C and 48 h, are obtained from tubes which are cold welded using a special pair of pliers. This represents a simple sealing procedure, which can be applied on a vacuum line system or in an inert gas purged glovebox. We have developed the new ampoule technique for the synthesis of the complex *Ln* fluorides. Our interest is directed toward yttrium-containing ternary fluoride host compounds, which may be doped with, erbium as the optically active ion. By introducing a second heavy cation (barium or lead), our aim is to further enhance UC efficiency. BaY_2F_8 has already proved its

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potential as an UC laser host material (19) and established our interest for further intermediate compounds of the phase systems $\text{BaF}_2\text{-YF}_3$ and $\text{PbF}_2\text{-YF}_3$, respectively. We have found $\text{Ba}_{2\mp x}\text{Y}_{1\pm x}\text{F}_{7\pm x}$ ($x \leq 0.05$) (20,21) and $\text{Pb}_{4\mp x}\text{Y}_{3\pm x}\text{F}_{17\pm x}$ ($x \leq 0.2$) (14,22) to be attractive candidates for an assessment of their potential as an UC host. This is mainly based on interesting compositional (phase width) and structural (superstructure) features of these phases. Furthermore, they exhibit compositional analogy or proximity to highly efficient chloride UC compounds [Ba_2ErCl_7 and $\text{Ba}_2\text{YCl}_7\text{:Er}^{3+}$, respectively (23,24)]. By annealing corresponding mixtures of binary fluorides in evacuated copper ampoules, we have obtained $\text{Pb}_{4\mp x}\text{Y}_{3\pm x}\text{F}_{17\pm x}$ ($x \leq 0.2$) as a pure phase. However, annealing of the ($\text{BaF}_2\text{:YF}_3$) sample yielded a mixture of a solid solution ($(\text{Ba},\text{Y})\text{F}_{2+x}$ ($x \approx 0.28$)) and $\text{Ba}_{4-x}\text{Y}_{3+x}\text{F}_{17+x}$ ($x \approx 0.08$), a further superstructure phase. This is due to $\text{Ba}_{2\mp x}\text{Y}_{1\pm x}\text{F}_{7\pm x}$ disproportionating into the two above-mentioned phases below 945°C .

EXPERIMENTAL AND RESULTS

Yttrium fluoride was prepared from the corresponding oxide (Aldrich, 99.9%) by dissolving in hot hydrochloric acid and subsequent precipitation of the hydrated fluoride with hydrofluoric acid. Drying, dehydration, and recrystallization were performed by slow heating in a horizontal tube furnace at 800°C for 12 h under a gently flowing mixture of N_2 and HF. The YF_3 obtained in this way could be handled in a normal atmosphere without showing any sign of hygroscopic degradation for hours.

The ternary Ln fluorides were obtained by annealing anhydrous powders of YF_3 , BaF_2 (Fluka, $\geq 97\%$), and PbF_2 (Fluka, $\geq 99\%$). The mixture ratios were 4:3 for $\text{PbF}_2\text{:YF}_3$ and 2:1 for $\text{BaF}_2\text{:YF}_3$. The loose powder mixture or a pressed pellet was placed into a glassy carbon crucible (0.3 cm^3) and closed with graphite wool to minimize transport by sublimation. The crucible was put into a copper tube (commercially available oxygen-free copper; inner diameter: 8 mm; wall thickness: 1 mm) which was previously sealed on one side by squeezing using a special pair of pliers (rounded jaws, Fig. 1a). Thereafter, the loaded tube was connected to a high-vacuum line and evacuated for 2 h at 100°C and $\sim 10^{-4}$ mbar. Finally, the copper tube was sealed a second time by squeezing. This yielded an ampoule around 5 cm in length (Fig. 1b). Reaction was performed in a resistively heated furnace (nearly isothermal temperature distribution), with an argon-purged silica tube protecting the copper against oxidation by atmospheric oxygen. The ampoules were kept for 48 h at 600°C ($\text{PbF}_2\text{:YF}_3$) and 900°C ($\text{BaF}_2\text{:YF}_3$), respectively. After cooling to room temperature, they were opened using a tube cutter. The ampoules did not show any sign of collapsing or corrosion. Additionally, they were successfully checked for

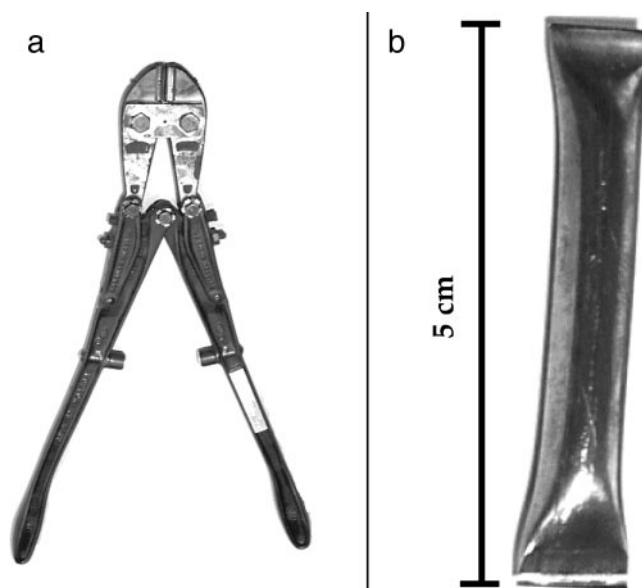


FIG. 1. Welding pliers (a) and copper ampoule (b) as used for the solid-state synthesis of ternary lanthanide fluorides.

vacuum tightness. The obtained ternary Ln fluorides were ground, yielding crystallites $50\text{--}100\ \mu\text{m}$ in diameter.

The powders were cast into an epoxy resin and analyzed by an electron microprobe (Cameca SX50, 20 kV, 20 nA), determining the composition of individual crystallites. The results showed strong scattering due to the dependence of the analysis on the surface roughness of the crystallites. However, they indicated the presence of a single phase in the ($\text{PbF}_2\text{:YF}_3$) product and of two phases in the ($\text{BaF}_2\text{:YF}_3$) sample. In the latter case, the elemental compositions were additionally determined as $\sim 16\text{ at.}\% \text{ Ba}/\sim 12\text{ at.}\% \text{ Y}$ [$\text{Ba}_4\text{Y}_3\text{F}_{17}$ (25,26): 16.7 at.% Ba/12.5 at.% Y] and $\sim 20\text{ at.}\% \text{ Ba}/\sim 8\text{ at.}\% \text{ Y}$ [$(\text{Ba},\text{Y})\text{F}_{2.28}$ (25,27): 22 at.% Ba/8.5 at.% Y], respectively. For all powder samples, no contamination with copper (detection limit = 100 ppm) could be found.

Analysis of the ($\text{PbF}_2\text{:YF}_3$) product with an X-ray powder diffraction camera (Enraf-Nonius, Guinier camera, $\text{CuK}\alpha_1$, 2 h) allowed unambiguous identification of the superstructure phase $\text{Pb}_{4\mp x}\text{Y}_{3\pm x}\text{F}_{17\pm x}$ ($x \leq 0.2$) on the basis of X-ray reflections corresponding to both the basis structure and the superstructure (14). The ($\text{BaF}_2\text{:YF}_3$) product was analyzed with an X-ray powder diffractometer (Phillips PW1800, $\text{CuK}\alpha_1$, int. stand.: LiF). Using data available on the solid solution $(\text{Ba},\text{Ln})\text{F}_{2+x}$ (27), $\text{Ba}_{4\mp x}\text{Y}_{3\pm x}\text{F}_{17\pm x}$ (26), and $\text{Ba}_{2\mp x}\text{Y}_{1\pm x}\text{F}_{7\pm x}$ (20), we could assign the reflections to $(\text{Ba},\text{Y})\text{F}_{2+x}$ ($x \approx 0.28$) and $\text{Ba}_{4-x}\text{Y}_{3+x}\text{F}_{17+x}$ ($x \approx 0.08$) (Table 1). The latter exhibited weak superstructure and split basis-structure reflections, both being characteristic for the rhombohedral distorted fluorite-type superstructure. $\text{Ba}_{2\mp x}\text{Y}_{1\pm x}\text{F}_{7\pm x}$, however, was not obtained.

TABLE 1
Measured X-Ray Powder Diffraction Pattern of the
(BaF₂:YF₃) Product and Calculated Diffraction Patterns for
Ba_{4-x}Y_{3+x}F_{17+x} [*x*=0.08, Hexagonal, *a*=11.055 Å, *c*=20.346 Å
(26)] and (Ba, Y)F_{2+x} [*x*=0.28, Cubic, *c*=6.0086 Å (27)]^a

(BaF ₂ :YF ₃) product		Ba _{4-x} Y _{3+x} F _{17+x} (26)		(Ba, Y)F _{2+x} (27)	
<i>d</i> _{obs} (Å)	Intensity (%)	<i>d</i> _{calc} (Å)	<i>hkl</i>	<i>d</i> _{calc} (Å)	<i>hkl</i>
4.2875	2	(s) 4.2847	113		
3.7434	3	(s) 3.7450	015		
3.5625	7	(s) 3.5627	211		
3.4696	100			3.4691	111
3.4114	75	(b) 3.4093	122		
3.3865	32	(b) 3.3910	006		
3.1647	10	*			
3.0036	21			3.0043	200
2.9488	29	(b) 2.9486	214		
2.7602	1	(s) 2.7638	220		
2.7030	1	(s) 2.7041	125		
2.6328	1	(s) 2.6330	131		
2.5613	2	(s) 2.5594	223		
2.4844	3	(s) 2.4845	027		
2.3784	2	(s) 2.3771	401		
2.2663	6	(s) 2.2661	217		
2.2250	3	(s) 2.2238	315		
2.1772	4	(s) 2.1837	321		
2.1249	37			2.1244	220
2.0868	33	(b) 2.0892	410		
2.0806	29	(b) 2.0807	128		
2.0070	10	(s) 1.9966	413		
1.9576	1	(s) 1.9604	137		
1.9324	2	(s) 1.9328	235		
1.9075	1	(s) 1.9064	051		
1.8132	21			1.8117	311
1.8026	12	(s) 1.8022	241		
1.7840	15	(b) 1.7813	422		
1.7789	23	(b) 1.7787	416		

^a(s), superstructure reflection; (b), basis-structure reflection; *, not identified.

With the synthetic procedure mentioned above, Er³⁺-doped samples of (Ba, Y)F_{2+x} (*x* ≈ 0.28)/Ba_{4-x}Y_{3+x}F_{17+x} (*x* ≈ 0.08) and Pb_{4-x}Y_{3+x}F_{17+x} (*x* ≤ 0.2), together with BaY₂F₈ for comparison, were prepared and their UC efficiency determined on an UC powder test setup (11). BaY₂F₈:10% Er³⁺, excited with laser light of ~980-nm wavelength, turned out to be the strongest UC system by up to one order of magnitude. As for the rest, no significant influence of the host structure type or the composition could be found. However, considerable impact could be attributed to the Er³⁺ concentration (optimum at ~10 mol%) and the excitation wavelength (being best at 980 nm).

DISCUSSION AND CONCLUSIONS

Whereas Kieser and Greis (20) found Ba₂YF₇ to be metastable at room temperature and to disproportionate into

Ba_{4-x}Y_{3+x}F_{17+x} (*x* = 0.01) and (Ba, Y)F_{2+x} (*x* = 0.25) if cooled down rather than quenched below 945°C, Rao *et al.* (21) obtained Ba₂YF₇ by solid-state reaction of BaF₂ and YF₃ at 900°C and subsequent furnace cooling to room temperature. Our observations correspond to the former.

Powders of complex lanthanide fluorides can be obtained in a solid-state reaction using evacuated and sealed copper ampoules as reactors. We have prepared vacuum-tight ampoules providing up to 4-cm³ reaction volume. The high ductility of the copper enables cold welding, leading to the formation of a joint which is high-vacuum tight (10⁻⁵ mbar) up to 900°C at least. Tightness is also maintained when an internal pressure of 5 bar is applied at 500°C for several hours. This time might be extended by applying a counter-pressure to prevent swelling of the joint. Furthermore, some problems can arise from copper recrystallization, leading to considerable grain growth and the formation of leaks in the joint region. This limits the use of evacuated copper ampoules at elevated temperatures to around 48 h, which, however, is adequate for most solid-state reactions. As for the rest, the joint is found to be mechanically robust (shock resistant) and remains tight even after repeated quenching in liquid nitrogen or water.

Focusing on the chemical properties of copper, this turns out to be both stable and inert during synthesis. Though Dénès (17) does not report any contamination of the product with copper, it appears advisable to prevent direct contact between the solid fluorides and the copper by the use of platinum or glassy carbon crucibles. The latter have proved their inertness in single-crystal melt-growth experiments of LiYF₄ (28). Furthermore, emphasis has to be laid on the elimination of traces of oxygen and water, which can attack the copper as well as reactants and products. This calls for the use of perfectly dry reactants, with heating of the loaded and evacuated tubes being necessary prior to sealing.

In conclusion, simple cold welding with a special pair of pliers yields tightly sealed copper ampoules and can be applied on a vacuum line to evacuate and/or fill ampoules with a gaseous reactant (halogenization) prior to sealing. Alternatively, sealing may be done in a glove box under an inert gas atmosphere. The ampoules can be used as reactors for the solid-state synthesis of oxygen-sensitive and/or moisture-sensitive compounds. Furthermore, they allow quenching after reaction, which might be necessary to obtain metastable phases. In summary, this new ampoule technique represents a valuable tool for solid-state chemists.

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