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Supplementary Information

Synthesis and characterization of MgF_2-CoF_2 binary fluorides. Influence of the treatment atmosphere and temperature on the structure and surface properties

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Table S1 Photographs of $Mg_xCo_{1-x}F_2$ binary fluorides after thermal treatment in reducing and oxidizing atmospheres.

Sample	Dried	Reduced		Oxidized	
	120 °C	300 °C	400 °C	300 °C	400 °C
Mg100					
MgCo0.6					
MgCo7.5					
MgCo37.7					
Co100					

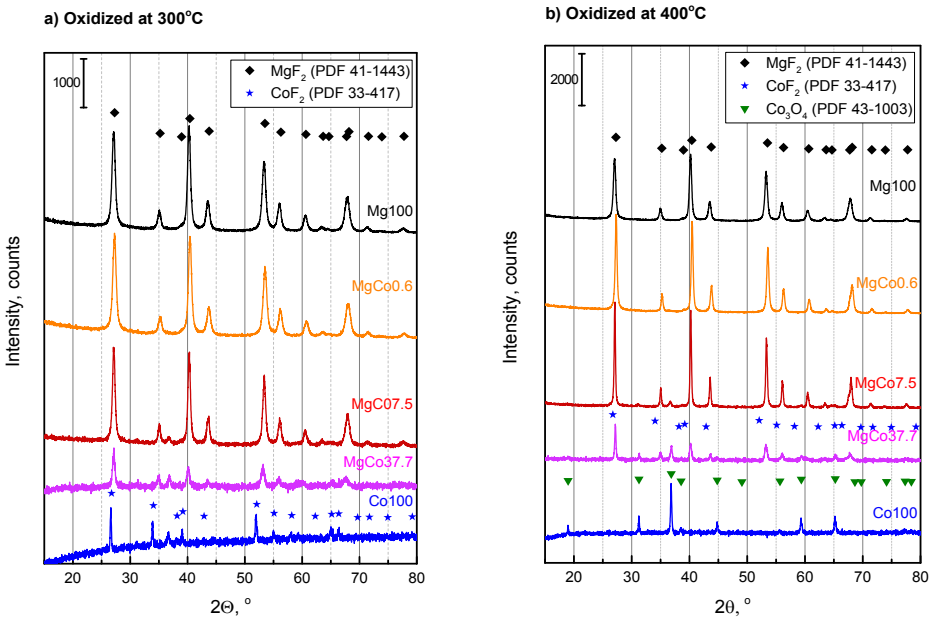

Fig. S1 Powder diffraction patterns of $Mg_xCo_{1-x}F_2$ binary fluorides calcined for 5h at 300°C (a) and 400°C (b).

In Figure S1 presented are X-ray powder diffraction patterns of the samples oxidized in air. Magnesium fluoride calcined at 300 °C (Mg100-Ox3) is characterized by a set of reflections typical of MgF_2 (sellaite, PDF 41-1443) and has tetragonal structure ($P4_2/mnm$). No other reflections (also from MgO), that could indicate the presence of other crystalline phases, were observed. The incorporation of CoF_2 in the amount of 0.6 mol% did not result in changes in the XRD pattern. At a greater Co content (the MgCo7.5-Ox3 sample), the reflections became shifted towards smaller 2θ angles which indicates the replacement of Mg^{2+} ions by Co^{2+} ions. On the other hand, no magnesium-containing sample (Co100-Ox3) is characterized by the presence of reflections originating from CoF_2 (PDF 33-417) and signals pointing to the presence of the Co_3O_4 phase (PDF 43-1003). The oxide phase also appears in the XRD pattern of the MgCo7.5-Ox3 sample and its amount increases with increasing CoF_2 content in the sample. In the diffraction pattern of MgCo37.7-Ox3 the aforementioned phase is discernible and in that of no magnesium-containing sample (Co100-Ox3) it is very clearly visible. After calcination at 400 °C, the presence of cobalt oxide becomes even more pronounced. Cobalt fluoride is not as stable as MgF_2 and during the calcination it is gradually oxidized to Co_3O_4.

Table S2 Values of a and c parameters for MgF_2 and CoF_2, according to literature data and those obtained in this work.

Fluoride	a, Å	c, Å	c/a	Year	Ref.
MgF_2	4.6218 (1)	3.0534 (2)	0.6606	1962	[1]
MgF_2	4.6213 (1)	3.0159 (1)	0.6526	1971	[2]
MgF_2	4.6213 (1)	3.0519 (1)	0.6604	1976	[3]
MgF_2	4.628 (5)	3.045 (3)	0.6580	1981	[4]
MgF_2	4.6233 (1)	3.0522 (1)	0.6602	1987	[5]
MgF_2	4.6249 (1)	3.0520 (1)	0.6599	2001	[6]
MgF_2	4.622 (7)	3.050 (3)	0.6599	2002	[7]
MgF_2	4.6258 (6)	3.0469 (4)	0.6587	2012	[8]
Mg100-R3	4.6214 (2)	3.0413 (4)	0.6581	2018	this work
CoF_2	4.6951 (1)	3.1796 (2)	0.6772	1954	[9]
CoF_2	4.6954 (4)	3.1774 (4)	0.6767	1971	[2]
CoF_2	4.6950 (7)	3.1817 (5)	0.6777	1993	[10]
CoF_2	4.6956 (5)	3.1793 (5)	0.6771	2001	[11]
Co100-R3	4.6934 (3)	3.1437 (5)	0.6699	2018	this work

Parenthesized figures represent standard deviations of the least unit cited.

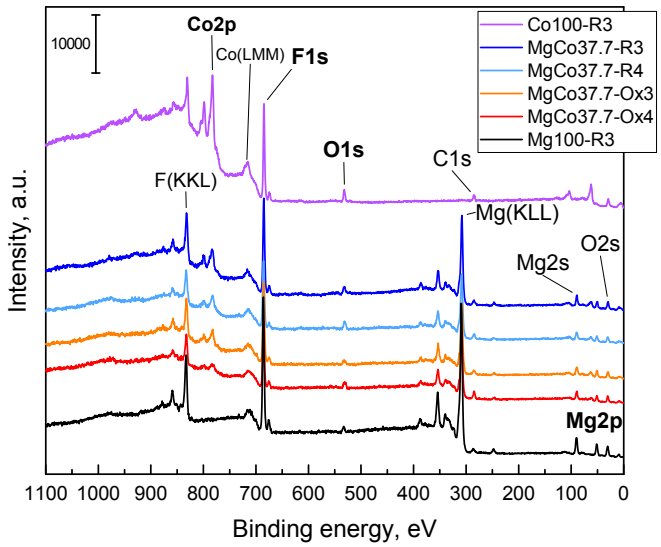

Fig. S2 XPS survey spectra of MgF_2, CoF_2 and $Mg_xCo_{1-x}F_2$ binary fluorides.

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