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$_{x}$Co$_{1-x}$F$_2$ binary fluorides after thermal treatment in reducing and oxidizing atmospheres.

| Sample   | Dried 120 °C | Reduced 300 °C | Reduced 400 °C | Oxidized 300 °C | Oxidized 400 °C |
|----------|--------------|----------------|----------------|-----------------|-----------------|
| Mg100    | ![Image]     | ![Image]       | ![Image]       | ![Image]        | ![Image]        |
| MgCo0.6  | ![Image]     | ![Image]       | ![Image]       | ![Image]        | ![Image]        |
| MgCo7.5  | ![Image]     | ![Image]       | ![Image]       | ![Image]        | ![Image]        |
| MgCo37.7 | ![Image]     | ![Image]       | ![Image]       | ![Image]        | ![Image]        |
| Co100    | ![Image]     | ![Image]       | ![Image]       | ![Image]        | ![Image]        |
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 MgF₂ (sellaite, PDF 41-1443) and has tetragonal structure (P4/mnm). No other reflections (also from MgO), that could indicate the presence of other crystalline phases, were observed. The incorporation of CoF₂ 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 Mg²⁺ ions by Co²⁺ ions. On the other hand, no magnesium-containing sample (Co100-Ox3) is characterized by the presence of reflections originating from CoF₂ (PDF 33-417) and signals pointing to the presence of the Co₃O₄ 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 CoF₂ 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 MgF₂ and during the calcination it is gradually oxidized to Co₃O₄.

### Table S2

| Fluoride | a, Å   | c, Å   | c/a   | Year | Ref. |
|----------|--------|--------|-------|------|------|
| MgF₂     | 4.6218 (1) | 3.0534 (2) | 0.6606 | 1962 | 1   |
| MgF₂     | 4.6213 (1) | 3.0159 (1) | 0.6526 | 1971 | 2   |
| MgF₂     | 4.6213 (1) | 3.0519 (1) | 0.6604 | 1976 | 3   |
| MgF₂     | 4.628 (5) | 3.045 (3) | 0.6580 | 1981 | 4   |
| MgF₂     | 4.6233 (1) | 3.0522 (1) | 0.6602 | 1987 | 5   |
| MgF₂     | 4.6249 (1) | 3.0520 (1) | 0.6599 | 2001 | 6   |
| MgF₂     | 4.622 (7) | 3.050 (3) | 0.6599 | 2002 | 7   |
| MgF₂     | 4.6258 (6) | 3.0469 (4) | 0.6587 | 2012 | 8   |
| Mg100-R3 | 4.6214 (2) | 3.0413 (4) | 0.6581 | 2018 | this work |
| CoF₂     | 4.6951 (1) | 3.1796 (2) | 0.6772 | 1954 | 9   |
| CoF₂     | 4.6954 (4) | 3.1774 (4) | 0.6767 | 1971 | 2   |
| CoF₂     | 4.6950 (7) | 3.1817 (5) | 0.6777 | 1993 | 10  |
| CoF₂     | 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 MgF₂, CoF₂ and MgₓCo₁₋ₓF₂ binary fluorides.

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