

## Supplementary Information

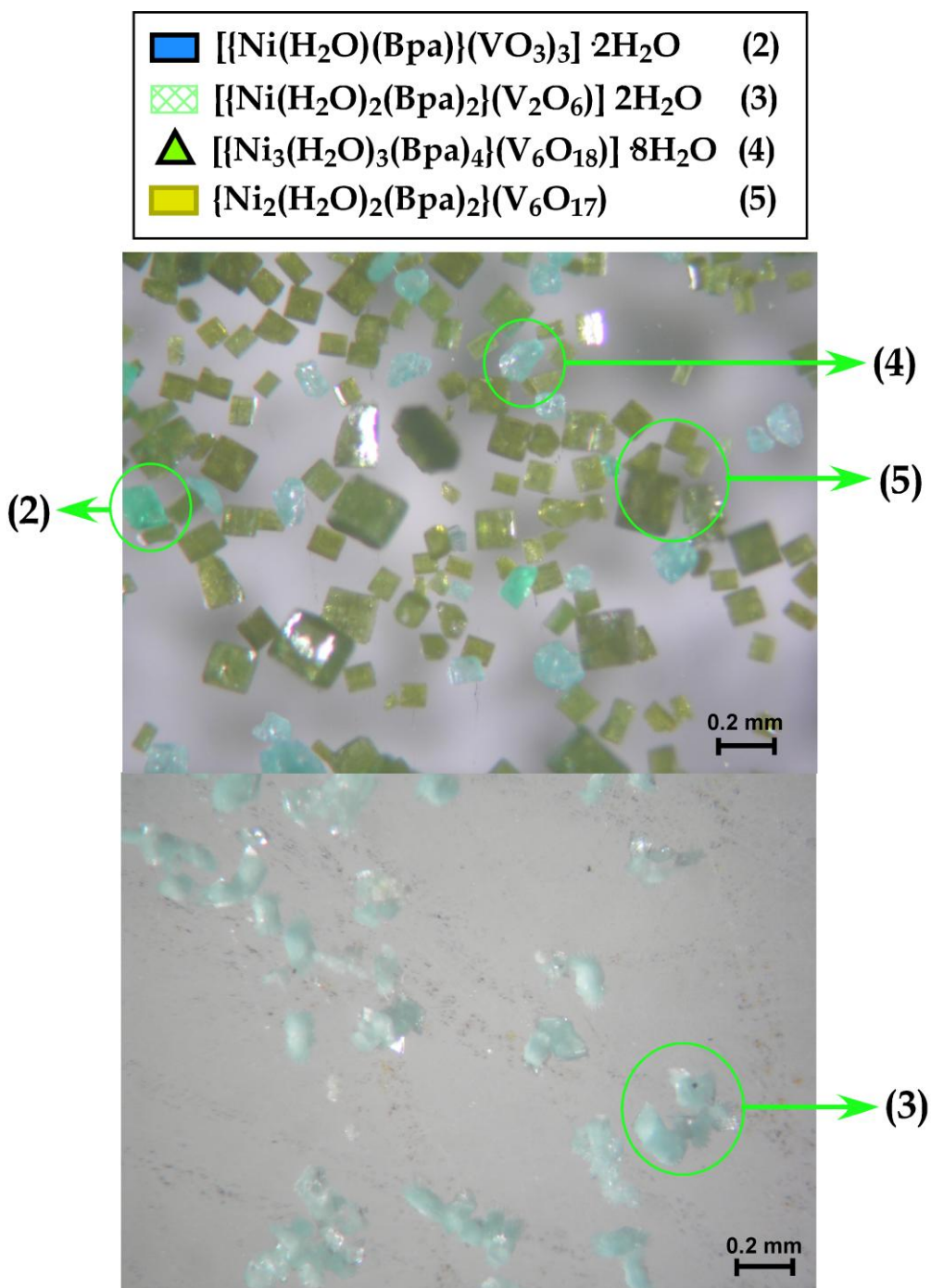
# Anisotropic thermal expansion of $\{\text{Co}(\text{Bpa})\}(\text{VO}_3)_2$ and diffuse scattering in $[\{\text{Ni}(\text{H}_2\text{O})(\text{Bpa})\}(\text{VO}_3)_2] \cdot 2\text{H}_2\text{O}$ , two new 3D hybrid vanadates

***<sup>a</sup>Roberto Fernández de Luis, <sup>a</sup>Miren Karmele Urtiaga, <sup>b</sup>José Luis Mesa, <sup>a</sup>Edurne S. Larrea, Teófilo Rojo<sup>b</sup> and María Isabel Arriortua<sup>\*a</sup>***

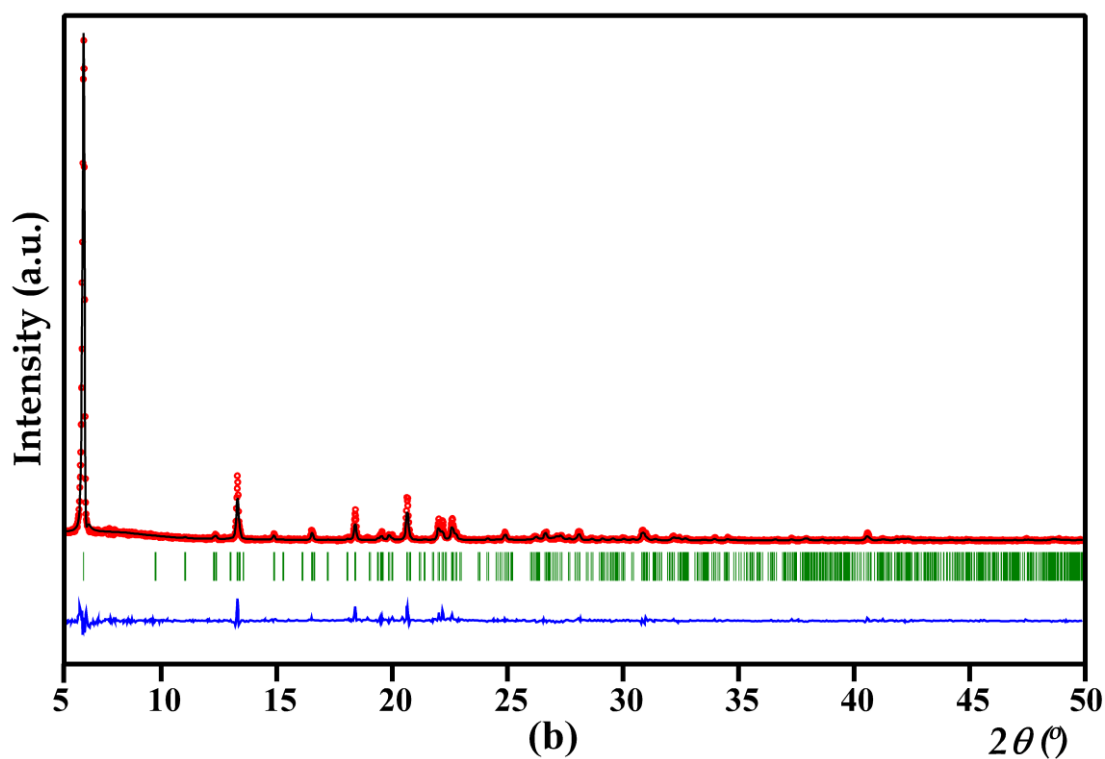
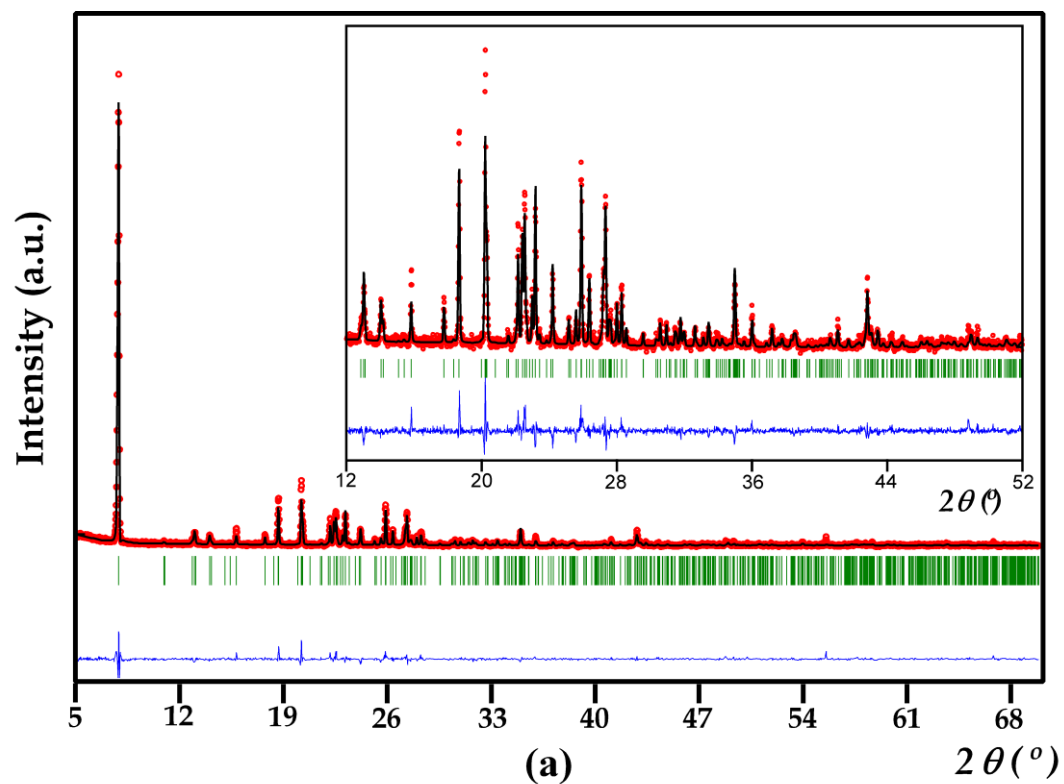
*<sup>a</sup>Departamento de Mineralogía y Petrología and <sup>b</sup>Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología. Universidad del País Vasco UPV/EHU, Apdo. 644, E-48080 Bilbao. Spain.*

roberto.fernandez@ehu.es, karmele.urtiaga@ehu.es, joseluis.mesa@ehu.es, edurne.serrano@ehu.es  
teo.rojo@ehu.es, maribel.arriortua@ehu.es

### Supplementary Information



**Figure S1.** Products after the hydrothermal reaction. The above figure shown the mixture of phases obtained at a initial 0.258:0.258:0.258 stoichiometry. The compound (3) morphology and color is shown in the below figure.



**Figure S2.** (a) Rietveld refinement for  $\{\text{Co}(\text{Bpa})\}(\text{VO}_3)_2$  (**1**). (b) Rietveld refinement for  $[\{\text{Ni}(\text{H}_2\text{O})(\text{Bpa})\}(\text{VO}_3)_2] \cdot 2\text{H}_2\text{O}$  (**2**). Red points: Experimental data; Black line: Calculated, Green bars: Reflection positions, Blue line: Experimental-Calculated.

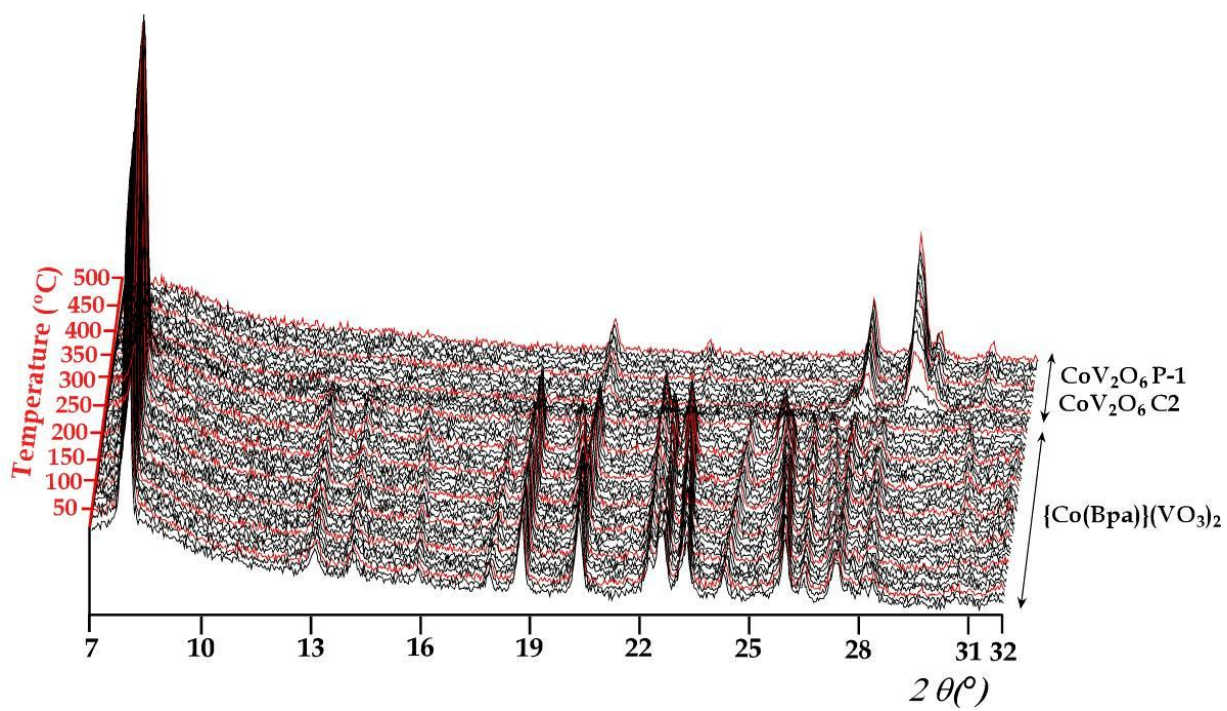


Figure S3. X-ray thermodiffractometry experiment for  $\{\text{Co}(\text{Bpa})\}(\text{VO}_3)_2$ .

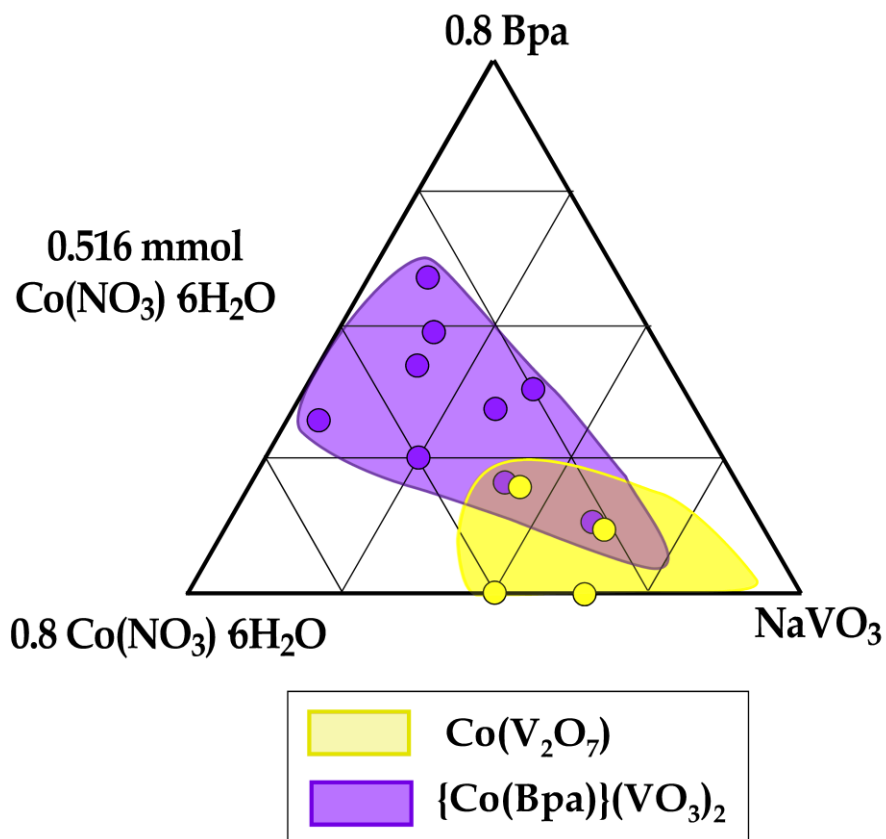
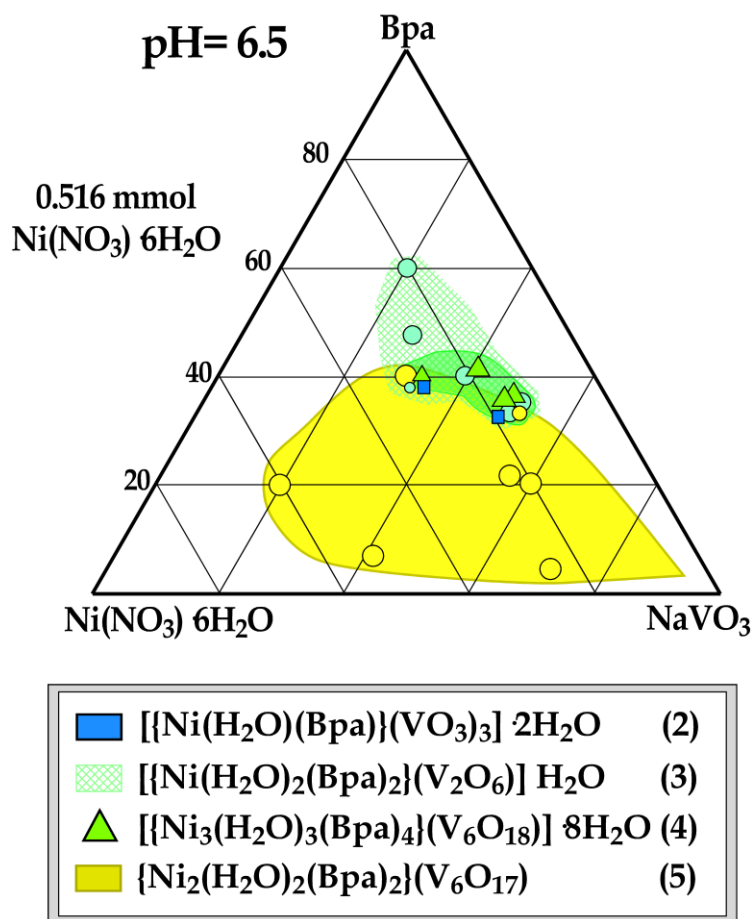
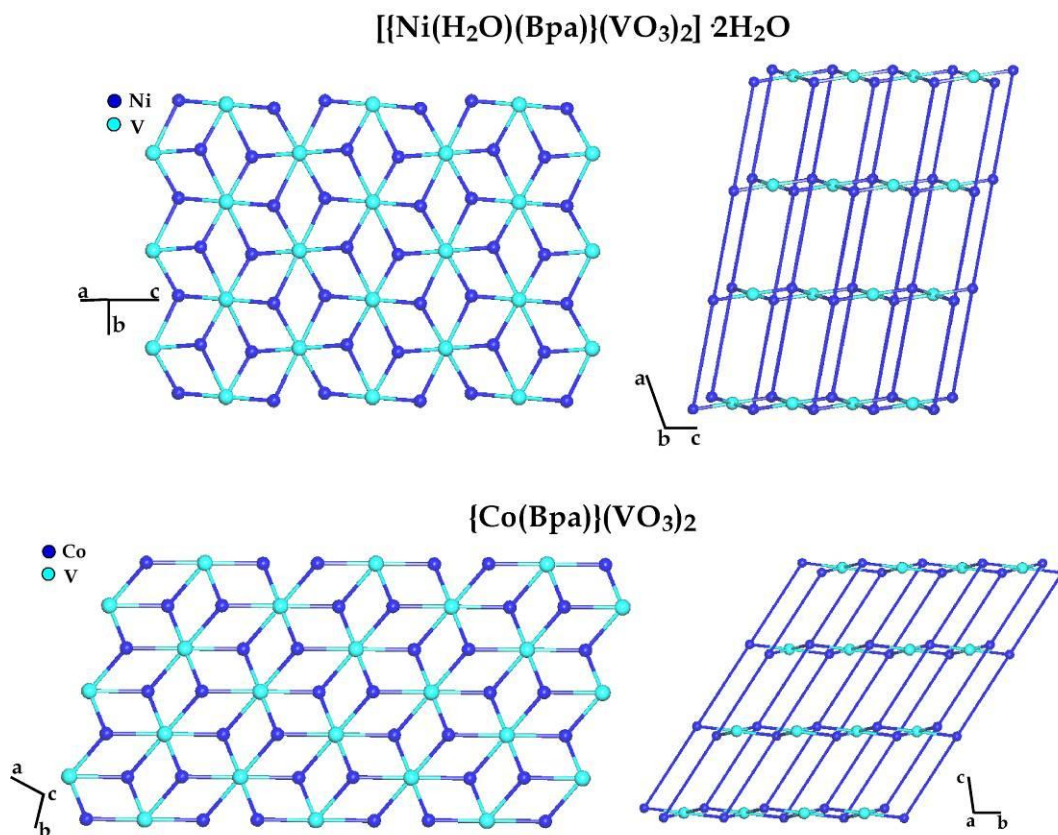


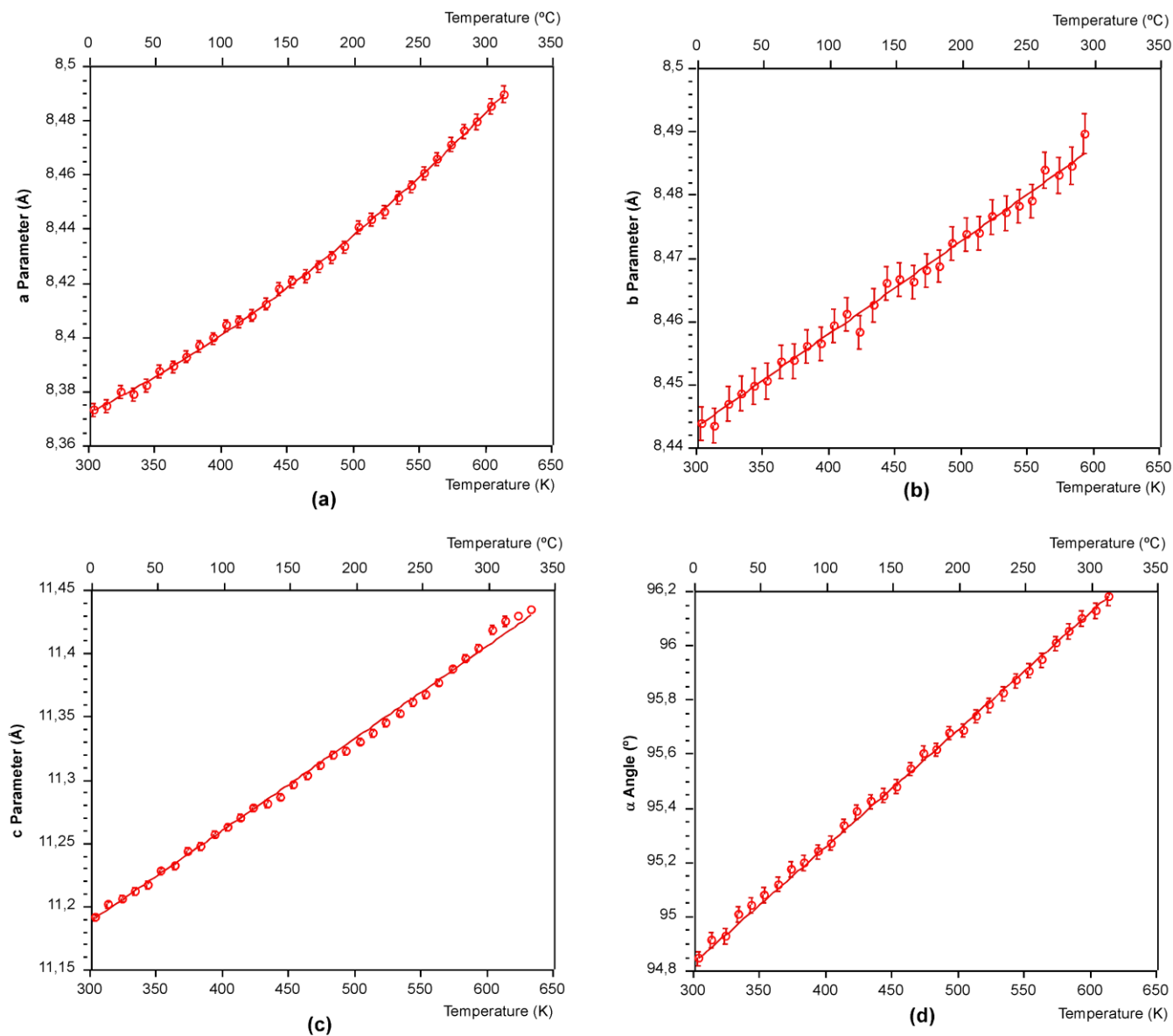
Figure S4. Compositional space diagrams for the  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NaVO}_3/\text{Bpa}$  system. (0.516 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ).



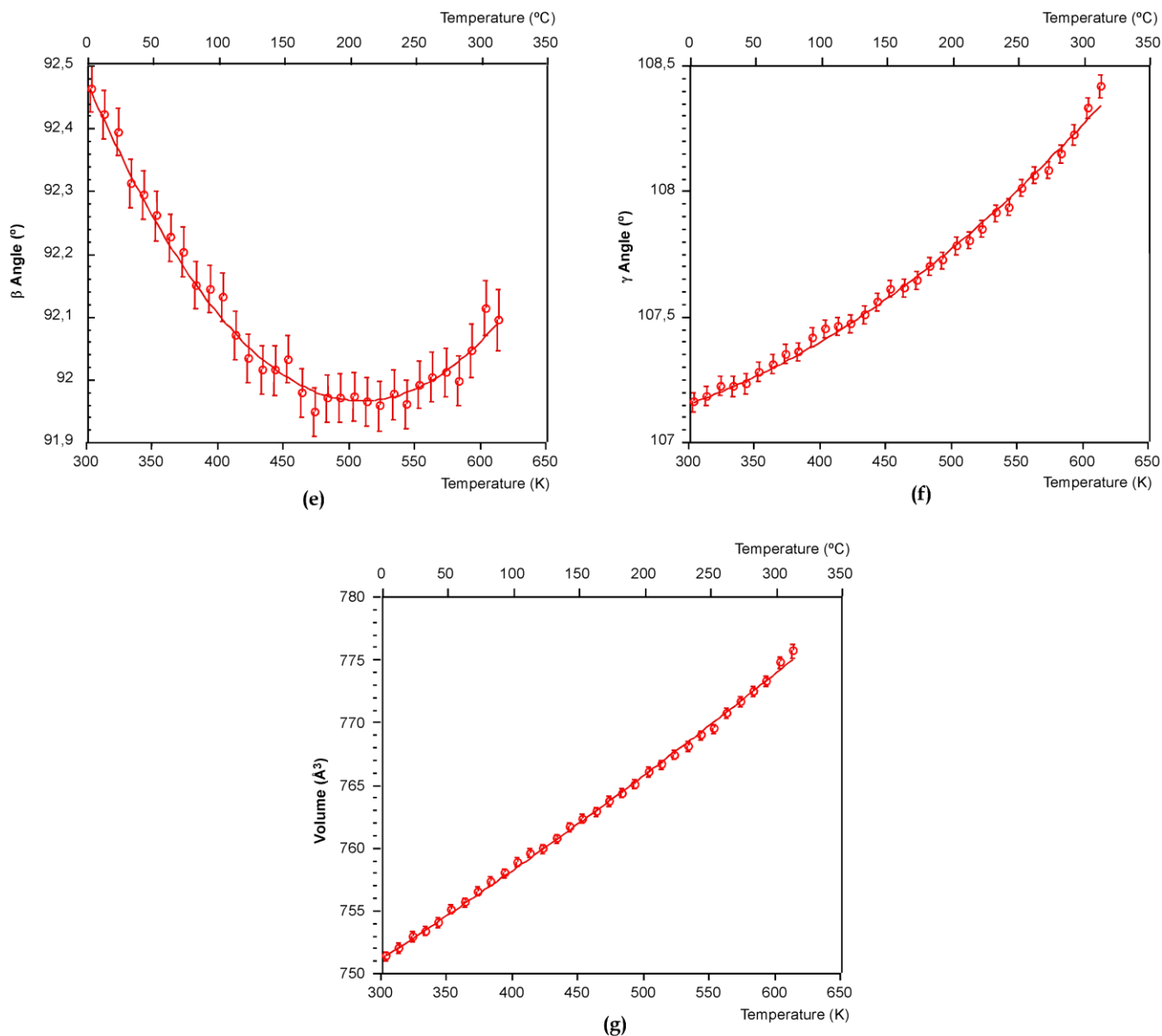
**Figure S5.** Compositional space diagrams for the Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O/NaVO<sub>3</sub>/Bpa system. (0.516 mmol of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O).



**Figure S6.** Topology of crystal structures.



**Figure S7.-** For  $\{Co(Bpa)\}(VO_3)_2$ : Fits of the thermal evolution of the cell parameters and volume considering a temperature independent thermal expansion coefficient ( $P(T)=P_{Ti}\exp[\alpha_0(T-T_i)]$ ), and temperature dependent thermal expansion coefficient ( $P(T)=P_{Ti}\exp[\alpha_0(T-T_i)]$ ;  $\alpha_0 = a_0 + a_1T$ ) for a linear and non-linear thermal variations, respectively.



**Figure S8.-** For  $\{Co(Bpa)\}(VO_3)_2$ : Fits of the thermal evolution of the cell parameters and volume considering a temperature independent thermal expansion coefficient ( $P(T)=P_{T_i}\exp[\alpha_0(T-T_i)]$ ), and temperature dependent thermal expansion coefficient ( $P(T)=P_{T_i}\exp[\alpha_0(T-T_i)]; \alpha_0= a_0 + a_1T$ ) for a linear and non-linear thermal variations, respectively.