Mechanochemical route for the synthesis of $VNbO_5$ and its structural re-investigation using structure solution from powder diffraction data

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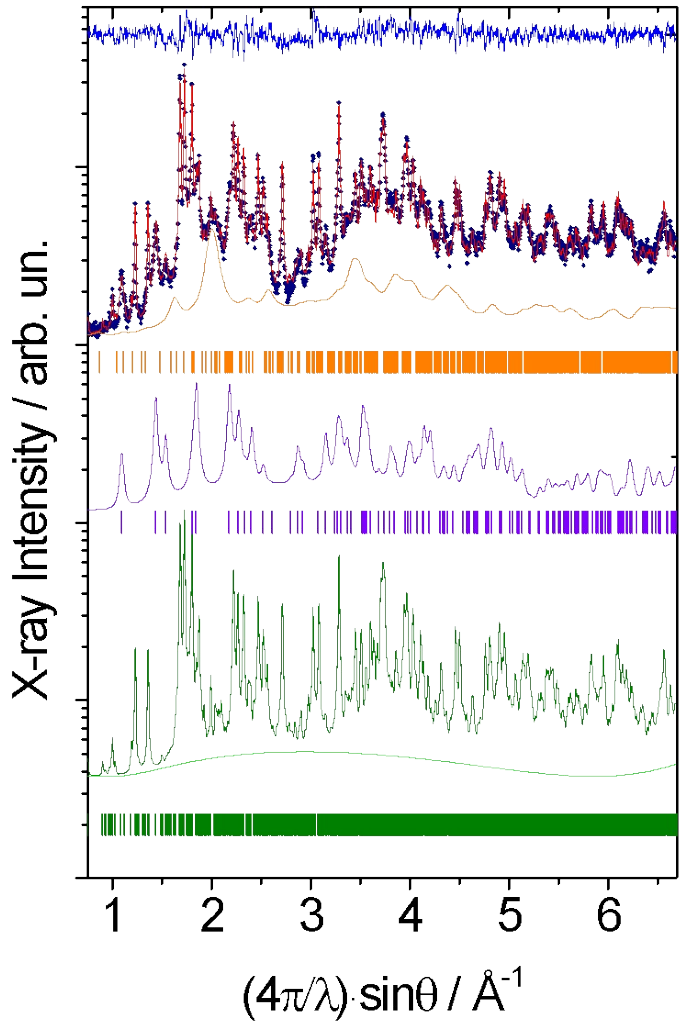

Figure S1. The Rietveld fit (red curve) of the powder pattern (dots) for equimolar shcherbianite-niobia mixture ball milled for 2 h. The top line (blue curve) represents the residuals obtained at the end of the fit. The background (green line) is displaced by a scale factor because of the logarithmic scale used to express the intensity weighted by the reciprocal vector. The total fit at this stage involves not only the orthorhombic V_2O_5 (violet curve) phase and monoclinic Nb_2O_5 (olive curve), but also an orthorhombic Nb_2O_5 component (orange curve), whose formation is very likely assisted by the inclusion of V_2O_5 fragments, affected by the prolonged mechanical treatment. The bar sequence reported under the calculated patterns of each phase marks the expected peak position on account of their space group symmetry. Notice also for the orange phase the considerable peak broadening, corresponding to average crystallite size of 200 Å. While the peaks of shcherbinaite appear also broadened, the monoclinic niobia peaks seems less affected by the mechanical treatment process.

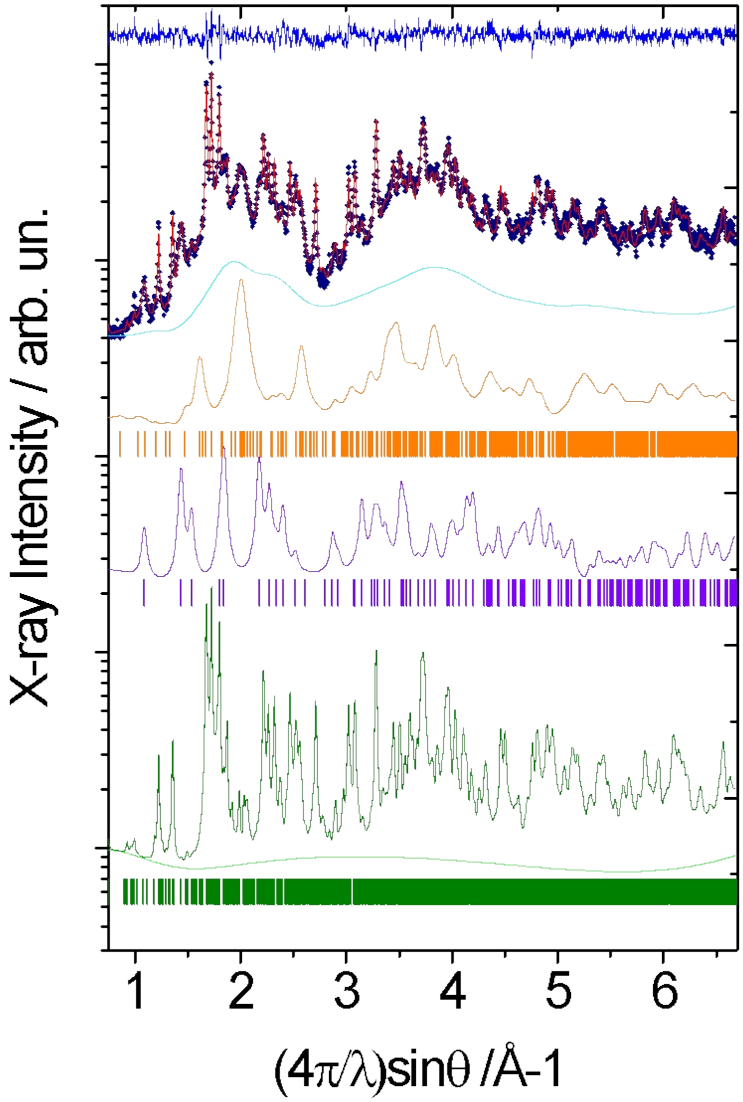

Figure S2. The Rietveld refinement results for the powders processed mechanically for 4h. To obtain a relatively uniform curve of residuals (top curve, blue line) it is necessary to introduce a supplementary amorphous/nanocrystalline phase (cyan curve) to account for a wavy background. The approach used was proposed for the first time by Le Bail. The olive, violet and orange lines account for the scattering crystallographic contributions from monoclinic niobia, orthorhombic shcherbinaite and orthorhombic mixed (niobium vanadium) phases, respectively. The amorphous contribution at this stage amounts at ca. 30.0 wt%

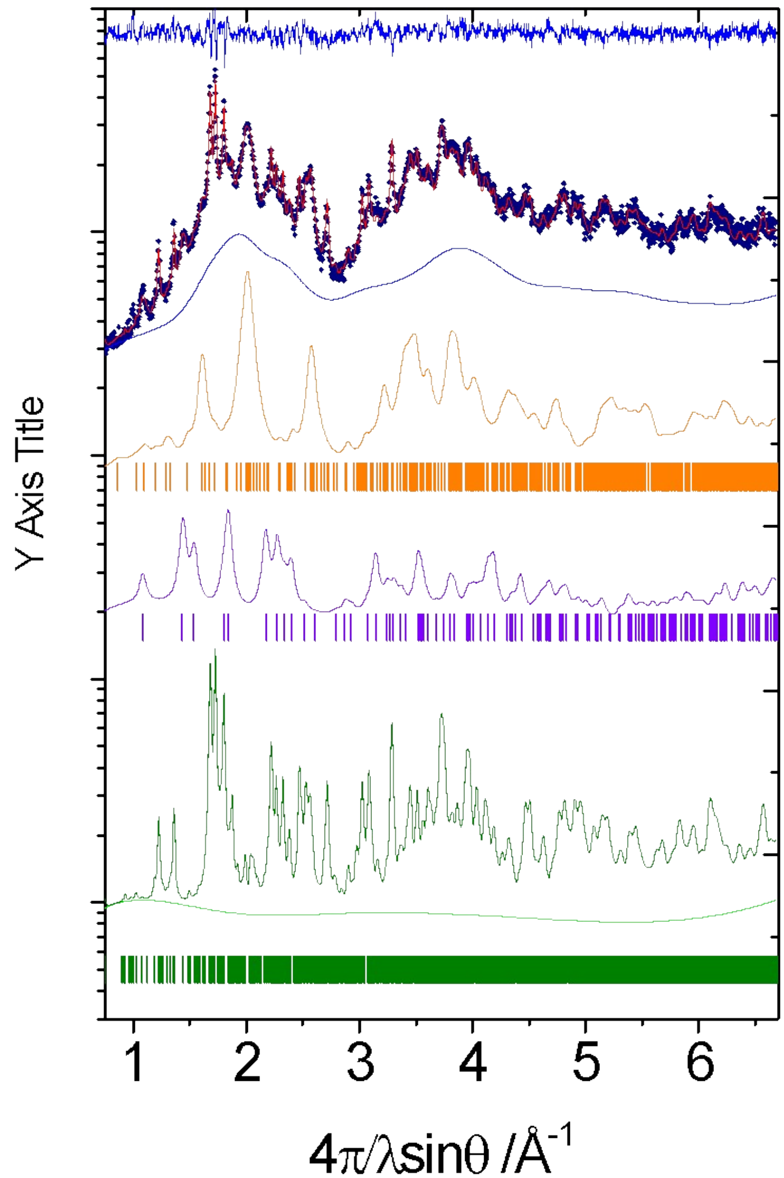

Figure S3. The Rietveld fit results obtained for the powders processed for 8 h of ball milling. It can be surmised that the original component due to V_2O_5 is going to be consumed, while the amorphous component is increasing to 40.0 wt.% its relative presence in the pattern.

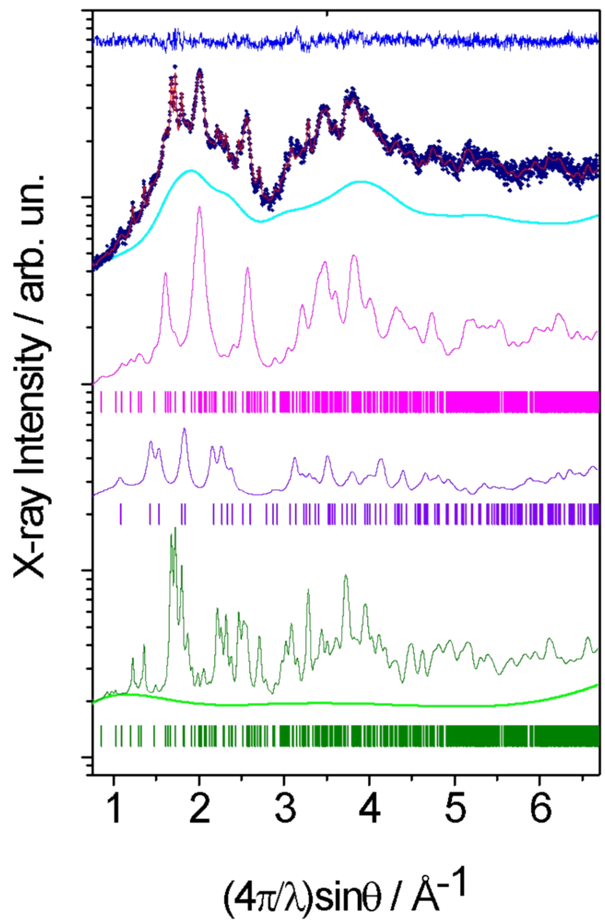

Figure S4. The Rietveld fit of the mixture processed mechanically for 12 h with its four component phases. Now the amount of the supposed amorphous/nanocrystalline phase amounts to ca. 50.0 wt.%. As it will be shown after the heat treatment at 750 K, such mixture is able to deliver almost totally the $VNbO_5$ orthorhombic phase. Its chemical behavior is very effective to decrease the substantially the hudrogen desorption process from powdered MgH_2.

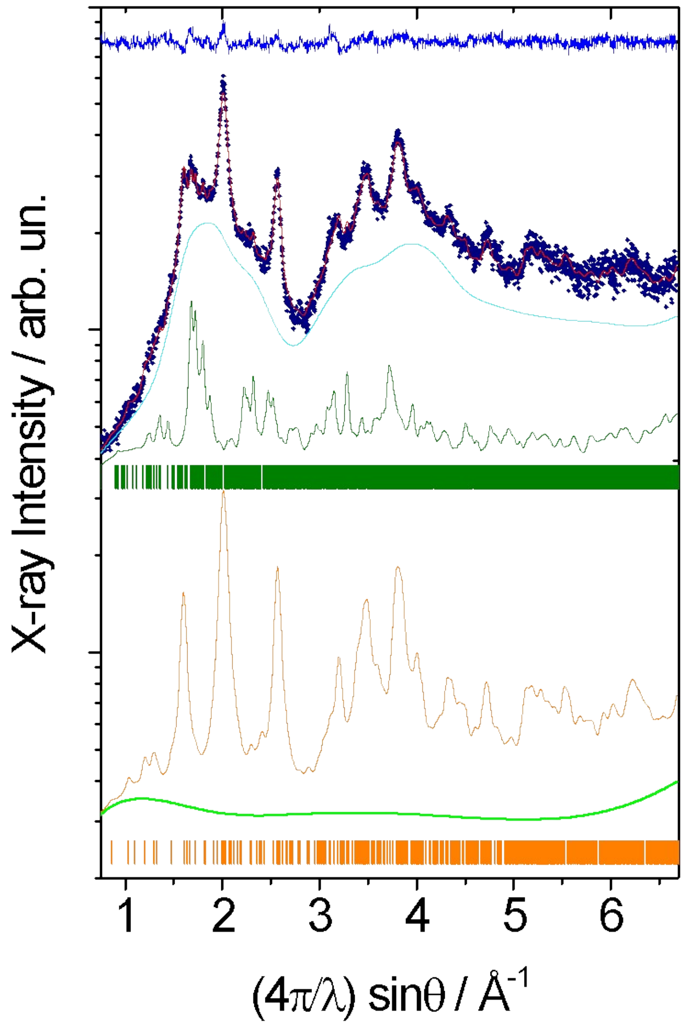

Figure S5. The Rietveld numerical process to fit the experimental data is simplified after 20 h of ball milling, since the shcherbinaite phase has completely reacted to form the amorphous component that now amounts to 65.0 wt.%. The rest is mainly constituted by Nb2O5 phase, still resisting to the damaging action of the attritor tools and media..

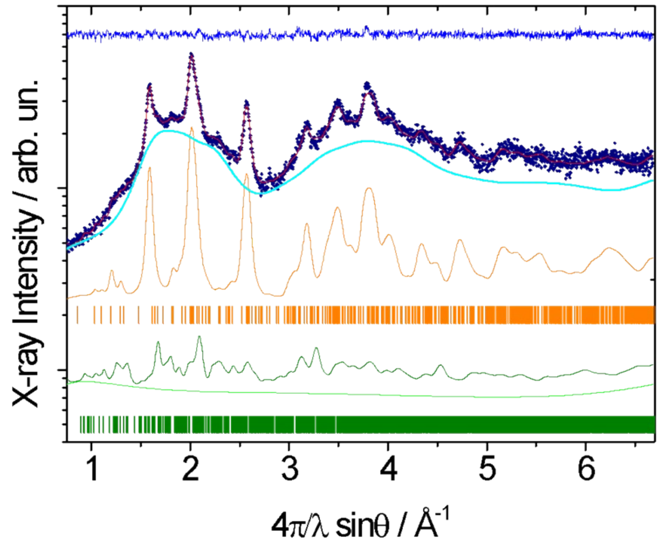

Figure S6. XRD Rietveld fit of the powders ball milled 30 h. The quantitative analysis conducted using MAUD assigns 75.0 wt% to the amorphous/nanocrystalline component (cyan line), accompanied by the 20 wt% of orthorhombic $(Nb,V)_2O_5$ (space group Pbam, orange line) and a tiny quantity of deformed monoclinic Nb_2O_5 (4.0 wt.%, olive line). It turns out that all the original shcherbinaite has disappeared and/or transformed.

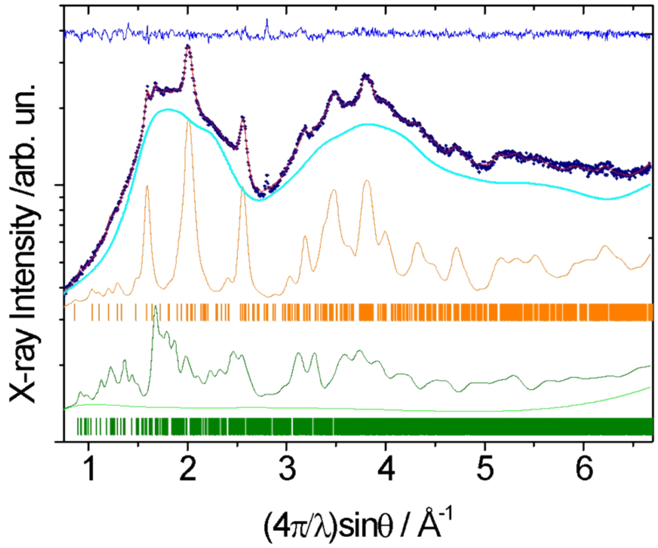

Figure S7. Rietveld fit of the powders ball milled for 50 h. With respect to the previous patterns, here the evident tendency is to privilege the amount of amorphous phase (cyan line) with a yet persisting quantity of orthorhombic $(Nb,V)_2O_5$ phase (10.0 wt.%) and some small quantity of monoclinic niobia.

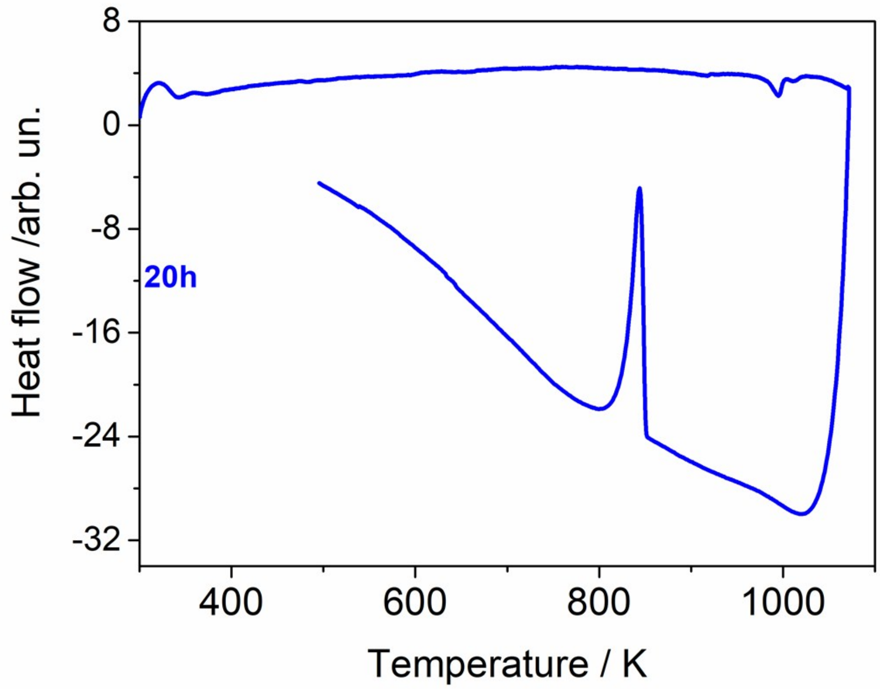

Figure S8. DSC trace collected for the powders ball milled for 12 h. Heating and Cooling steps have been reported.

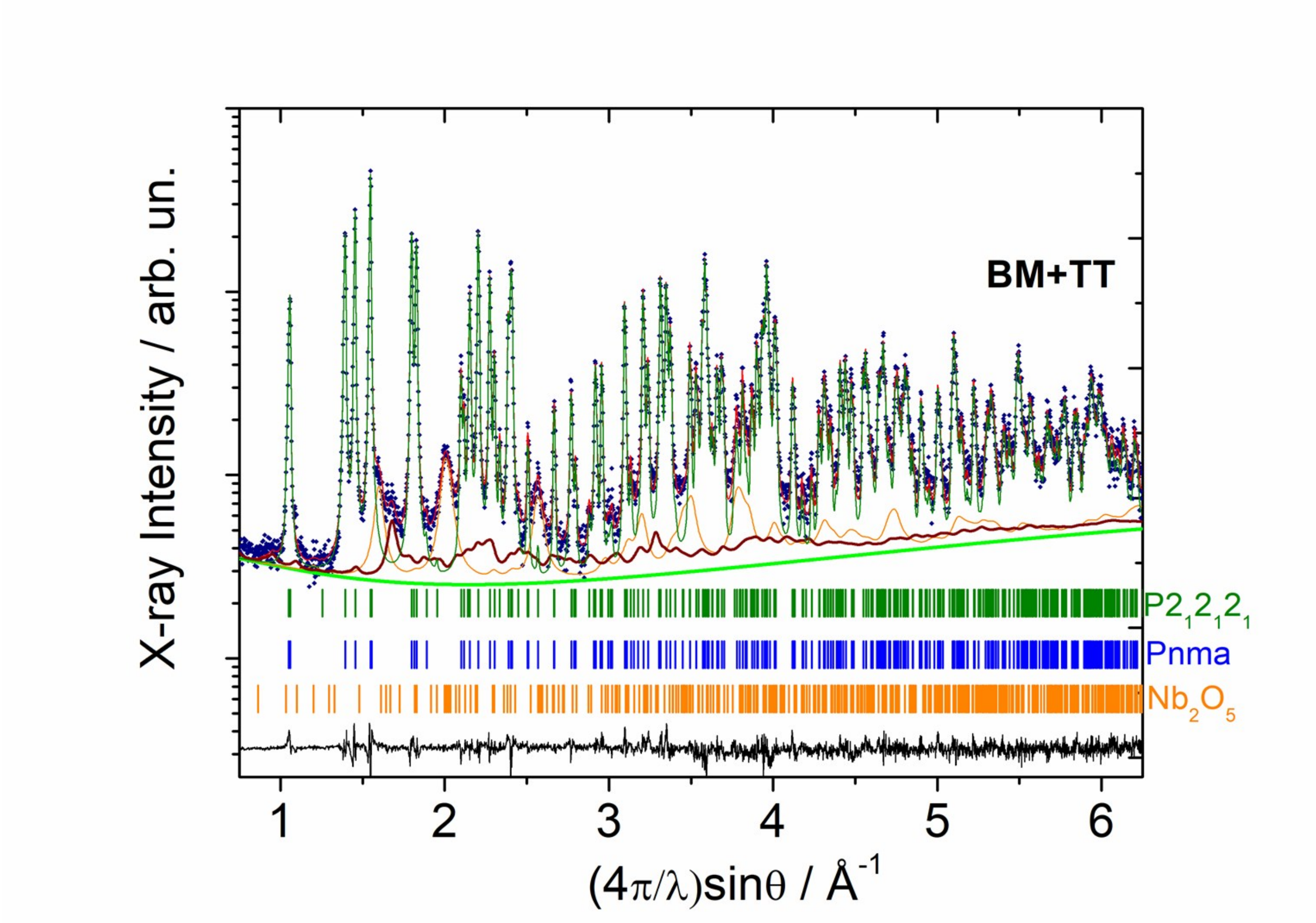

Figure S9. Rietveld interpolation of the crystalline $VNbO_5$ orthorhombic phase obtained after heating at 750 K the equimolar V_2O_5-Nb2O5 mixture ball milled for 50 h. the powders ball milled for 50 h.