Supplementary Information for

Low- and high-temperature oxidation of Mn_{1.5}Al_{1.5}O₄ in relation to decomposition mechanism and microstructure

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Construction and application of Vegard's plot for the determination of the composition of

Mn-Al spinel-like oxides

Vegard's plot was constructed on the base of data from Powder Diffraction File (PDF, JCPDS-ICDD)¹⁹ for the compounds β -Mn₃O₄, Mn₂AlO₄, MnAl₂O₄ and γ -Al₂O₃ (Table S1). Because Mn₂AlO₄, MnAl₂O₄ and γ -Al₂O₃ has cubic spinel structure with a=b=c and β -Mn₃O₄ is tetragonal spinel with a=b≠c, we utilized normalized unit cell volume Vn instead of lattice parameter and plotted the dependence of Vn on the content of Al ions x in Mn_{3-x-γ}Al_{x □ γ}O₄ (Figure S1). The volume and quantity of Al ions were normalized to 4 oxygen atoms. The end member γ -Al₂O₃ can be written as Al_{2.67}□_{0.33}O₄, where □-vacancy. Figure S1 shows that in the range of Al content x=0–2 there is almost a linear dependence of Vn on x. Increase in Al content from x=2 to x=2.67 leads to quicker decrease of unit cell volume. This can be explained by different types of substitution. In the range of x=0–2 (solid solutions between Mn₃O₄ and MnAl₂O₄) Mn³⁺ ions are substituted by Al³⁺ ones. A further increase in the content of Al³⁺ ions (solid solutions between MnAl₂O₄ and γ -Al₂O₃) leads to the appearance of cationic vacancies because three Mn²⁺ ions are substituted by two Al³⁺ ones due to charge balance. We made also a linear approximation of the dependence of Vn on x in the range x=2–2.67. Constructed plot makes it possible to estimate the content of Mn and Al ions as well as concentration of cation vacancies if lattice constants (or unit cell volumes) of Mn-Al spinel oxides are known.

Lattice constants were refined by Rietveld method with use of TOPAS software¹⁸. Figure S2 shows an example of Rietveld refinement for the sample calcined at T=700°C and then quenched. One can see that XRD pattern contains peaks of two spinel-like phases: cubic and tetragonal. Refined lattice constants and calculated normalized unit cell volumes are represented in the Table S2. The volumes and Vegard's plot (Figure S1) was used to determine the phase composition. If accuracy of Vn is less than 0.3 Å³ (x=0–2) and 0.5 Å³ (x=2–2.67) the accuracy in Al content is less than 0.05 (shown by red rectangles on the Figure S1).

| Compound | PDFNumber | Space group | Lattice constants, Å | V, Å ³ | Vn, Å ³ |
|--|-----------|----------------------|----------------------|-------------------|--------------------|
| β -Mn ₃ O ₄ | 24-0734 | I4 ₁ /amd | a=b=5.7621, c=9.4696 | 314.41 | 78.60 |
| Mn_2AlO_4 | 29-0881 | Fd3m | 8.371 | 586.59 | 73.32 |
| MnAl ₂ O ₄ | 29-0880 | Fd3m | 8.204 | 552.18 | 69.02 |
| γ -Al ₂ O ₃ | 10-0425 | Fd3m | 7.90 | 493.04 | 61.63 |

Table S1. Space group, lattice constants, unit cell volume V and normalized volume Vn for β -Mn₃O₄, Mn₂AlO₄, MnAl₂O₄ and γ -Al₂O₃ (PDF data).



Figure S1. Dependence of normalized unit cell volume (Vn) on the Al content (x).



Figure S2. Rietveld refinement of the lattice constants for the sample calcined at 700°C and then quenched.

Table S2. Refined lattice constants, normalized unit cell volume Vn and phase composition for the cubic and tetragonal Mn-Al spinel-like oxides

| Crystal system | Lattice constants, Å | Vn, Å ³ | Phase composition |
|----------------|----------------------|--------------------|--|
| Cubic | a = 8.040(3) | 65.0(1) | Mn _{0.4} Al _{2.4} O ₄ |
| Tetragonal | A = b = 5.721(2), | 77.5(1) | Mn _{2.8} Al _{0.2} O ₄ |
| | c = 9.471(2) | | |

Comparison of two approaches for the determination of the composition of Mn-Al spinel-like oxides: Vegard's plot and Rietveld refinement of atomic parameters

It is known that Vegard's low is valid for the homogeneous solid solutions. In the case of segregation of Mn ions to the surface of parent spinel it is interesting to determine Mn-Al spinel composition with use

of Rietveld refinement of all atomic parameters including occupancies and compare it with composition received on the base of Vegard's plot.

Let us consider all cases arising during $Mn_{1.5}Al_{1.5}O_4$ heating in air leading to the Mn oxidation and segregation to the particle surface. We think that highest degree of segregation should be in the sample heated and calcined at T=400°C because lattice constants reduced from a=8.285(1) to a=8.273(1). According to the Vegard's plot it means that $Mn_{1.5}Al_{1.5}O_4$ is transformed into the $Mn_{1.42}Al_{1.58}O_4$ loosing Mn ions but second phase enriched by Mn ions is not observed by XRD. It seems to be that there is a lower degree of Mn segregation in other cases. XRD analysis of the initial sample was made without contact with air, so there are no reasons for the oxidation and consequently for the segregation of Mn ions to the particle surface. Calcination at T=300°C doesn't lead to the change of lattice constant (according to the XRD data) and there is no oxygen addition (according to TG data). Final products of decomposition (T=700°C) represent two phases formed just as a result of strong segregation of Mn to the particle surface. We think that these two phases represent homogeneous solid solutions because $Mn_{1.5}Al_{1.5}O_4$ decomposition is finished. Calcination at 500 or at 600°C leads to very high rate of oxidation and very rapid increase in sizes of hausmannite-like particles that cause appearance of peaks of hausmannite-like phase on the XRD pattern. This case is closer to the case of the full decomposition where two phases coexist.

We determined Mn-Al oxide composition for the sample calcined at 400°C with use of Rietveld refinement of atomic parameters by such a way. We took several compositions Mn_{1.3}Al_{1.7}O₄, Mn_{1.4}Al_{1.6}O₄, Mn_{1.5}Al_{1.5}O₄, Mn_{1.6}Al_{1.4}O₄ and Mn_{1.7}Al_{1.3}O₄ and distributed Mn and Al atoms over spinel octahedral 16d and tetrahedral 8a positions. We varied occupancy of 16d position by Mn atoms. Other occupancies are dependent parameters and can be calculated from spinel composition. Hear it should be taken into account that quantity of atoms in 16d positions is twice larger then quantity of atoms in 8a positions. Partial occupancies for Mn or Al were varied parameters, but total occupancies of 8a, 16d and 32e positions were fixed at 1. Peak shape parameters U, V, W and coordinates of oxygen atoms in 32e position were refined parameters. Temperature factors were fixed as 0.5 for Mn, Al and 1.0 for oxygen for all cases. Calculated dependence of R-factors on occupancy of 16d position by Mn atoms is shown on the Figure S3.

One can see that there is a good correspondence between two approaches. First approach (Vegard's low) gives composition $Mn_{1.42}AI_{1.58}O_4$. As it was shown above the estimated accuracy of this approach is determined by accuracy in determination of lattice constants and is less than 0.05. Second approach (Rietveld refinement) gives $Mn_{1.4}AI_{1.6}O_4$ composition. Estimated accuracy can be considered as equal to 0.1 because R-factors are minimal and have almost the same values for the three compositions: $Mn_{1.3}AI_{1.7}O_4$, $Mn_{1.4}AI_{1.6}O_4$ and $Mn_{1.5}AI_{1.5}O_4$. Example of Rietveld refinement for the $Mn_{1.4}AI_{1.6}O_4$ (occupancy of 16d position by Mn ions is equal to 0.25) is shown on Figure S4.

So it can be concluded that Vegard's low is also applicable in the case of segregated solid solutions but probably with lower accuracy (0.1 instead of 0.05).



Figure S3. Dependence of R-factor on the occupancy of 16d position by Mn.



Figure S4. Rietveld refinement for the sample calcined at 400°C and quenched.

XPS spectra



5 650 655 Binding energy, eV

Figure S6. Mn2p XPS spectra of the samples prepared by thermal treatment and quenched a) initial $Mn_{1.5}Al_{1.5}O_4$; b) heated to T=300°C; c) heated to T=500°C; d) cooled to T=800°C.