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Disentangling the Structure, Optical, and Photoluminescence Emissions of NiW1–xMoxO4 (x = 25, 50, and 75%) Solid Solutions: Experimental and DFT Study†

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Supporting Information

Elemental analysis – XRF spectrometry

Table SI-1. Elemental analysis of W and Mo atoms in the samples obtained by XRF spectrometry.

Elements	Nominal					Experimental				
	NW	**NW75**	**NW50**	**NW25**	**NM**	**NW**	**NW75**	**NW50**	**NW25**	**NM**
W	100.0	75.0	50.0	25.0	0.0	100.0	77.6	47.5	22.6	0.0
Mo	0.0	25.0	50.0	75.0	100.0	0.0	22.4	52.5	77.4	100.0

Bond distances and Jahn-Teller distortion

In **Figure SI-1**, the NW structure and its constituent [NiO_6] and [WO_6] clusters are illustrated, along with the substitution sites in the NW75, NW50, and NW25 solid solutions that lead to the formation of [MoO_6] clusters. The bond distances and Jahn-Teller distortion (σ_{JT}) values are reported in **Table SI-3**.

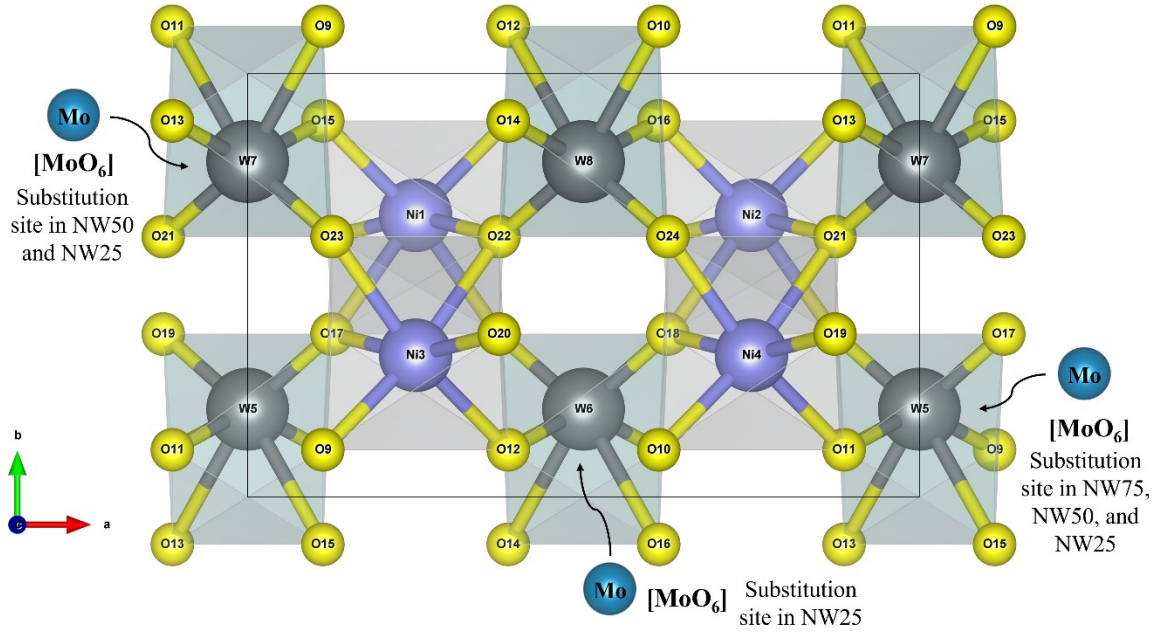

Figure SI-1. Schematic illustration of the NW structure, showing the [NiO_6] and [WO_6] clusters, and the substitution site where W is replaced by Mo in the solid solutions.

Table SI-2. Bond distances (Å) of Ni–O, W–O, and Mo–O in each cluster within the NW structure and the solid solutions.

Bond	**NW**	**NW75**	**NW50**	**NW25**
Ni1 – O14	2.0089	2.0152	2.0143	2.0307
Ni1 – O15	2.0089	2.0255	2.0063	2.0138
Ni1 – O22	2.0402	2.042	2.0504	2.0528
Ni1 – O23	2.0402	2.0425	2.0187	2.0196
Ni1 – O17	2.1064	2.0811	2.0942	2.0862
Ni1 – O20	2.1064	2.0983	2.0908	2.0668
σ_{JT}	**0.042**	**0.031**	**0.037**	**0.026**
Ni2 – O16	2.0089	2.0154	2.0149	2.0318
Ni2 – O13	2.0089	2.0258	2.0069	2.0133
Ni2 – O24	2.0402	2.0418	2.0503	2.0533
Ni2 – O21	2.0402	2.0426	2.0186	2.0189
Ni2 – O19	2.1064	2.0811	2.0938	2.0861
Ni2 – O18	2.1064	2.0980	2.0898	2.0666
σ_{JT}	**0.042**	**0.031**	**0.037**	**0.026**
Ni3 – O9	2.0089	1.9883	2.0069	2.0057

Ni3 – O12	2.0089	2.0075	2.0149	1.9946
Ni3 – O17	2.0402	2.0171	2.0186	2.0252
Ni3 – O20	2.0402	2.0485	2.0503	2.0252
Ni3 – O22	2.1064	2.0971	2.0898	2.1060
Ni3 – O23	2.1064	2.1233	2.0938	2.0859
σ_{JT}	**0.042**	**0.051**	**0.037**	**0.044**
Ni4 – O10	2.0089	2.0074	2.0143	1.9942
Ni4 – O11	2.0089	1.9883	2.0063	2.0061
Ni4 – O18	2.0402	2.0483	2.0504	2.0247
Ni4 – O19	2.0402	2.0171	2.0187	2.0257
Ni4 – O21	2.1064	2.1234	2.0942	2.0859
Ni4 – O24	2.1064	2.0971	2.0908	2.1062
σ_{JT}	**0.042**	**0.051**	**0.037**	**0.044**
W/Mo5 – O17	1.7458	1.8108	1.8019	1.8023
W/Mo5 – O19	1.7458	1.8109	1.8020	1.8017
W/Mo5 – O11	1.8349	1.8751	1.8951	1.8950
W/Mo5 – O9	1.8349	1.8752	1.8950	1.8973
W/Mo5 – O13	2.3231	2.2143	2.1924	2.1891
W/Mo5 – O15	2.3231	2.2143	2.1924	2.1937
σ_{JT}	**0.287**	**0.199**	**0.180**	**0.179**
W/Mo6 – O18	1.7458	1.7456	1.7460	1.8113
W/Mo6 – O20	1.7458	1.7454	1.7456	1.8106
W/Mo6 – O10	1.8349	1.8366	1.8400	1.8802
W/Mo6 – O12	1.8349	1.8366	1.8395	1.8783
W/Mo6 – O14	2.3231	2.3189	2.3098	2.2019
W/Mo6 – O16	2.3231	2.3191	2.3107	2.208
σ_{JT}	**0.287**	**0.283**	**0.277**	**0.192**
W/Mo7 – O21	1.7458	1.7334	1.8019	1.8023
W/Mo7 – O23	1.7458	1.7334	1.8020	1.8019
W/Mo7 – O13	1.8349	1.8612	1.8950	1.8993
W/Mo7 – O15	1.8349	1.8613	1.8951	1.8970
W/Mo7 – O9	2.3231	2.2881	2.1924	2.1821
W/Mo7 – O11	2.3231	2.2883	2.1924	2.1872
σ_{JT}	**0.287**	**0.257**	**0.180**	**0.174**
W8 – O22	1.7458	1.7462	1.7460	1.7337
W8 – O24	1.7458	1.7461	1.7456	1.7330
W8 – O14	1.8349	1.8385	1.8400	1.8676
W8 – O16	1.8349	1.8382	1.8395	1.8642
W8 – O10	2.3231	2.3117	2.3098	2.2758
W8 – O12	2.3231	2.3118	2.3107	2.2813

σ_{JT}	**0.287**	**0.283**	**0.277**	**0.250**

Density of States – DOS

An analysis of the partial DOS reveals that the orbitals at the VB and CB are non-degenerated with different contribution of the d orbitals of the transition metals and p orbitals from O atoms. For the NW model (**Figure SI-2**), the VB is formed by a homogeneous contribution of Ni $3d$ orbitals, and O $2p$ orbitals. However, the CB is mainly for by Ni $3d_{xz} + 3d_{yz} + 3d_{xy}$ orbitals and mainly by the W e_g ($5d_{z^2} + 5d_{x^2-y^2}$) orbitals. At the top of the VB in the α channel at NW involves the hybridization of Ni $3d_{xz} + 3d_{xy}$ orbitals and O $2p_z$ orbitals, whereas the bottom of the CB is formed mainly by empty W $5d_{z^2} + 5d_{xz} + 5d_{x^2-y^2}$ orbitals. For the β channel, the VB is formed by Ni $3d_{x^2-y^2}$ orbitals hybridized with O $2p_z$ orbitals, while the CB is composed of the hybridization between the W $5d_{z^2} + 5d_{xz}$ orbitals with Ni $3d_{xz} + 3d_{xy}$ orbitals.

For the NM in **Figure SI-3**, the VB is formed also by contribution of Ni $3d$ orbitals, and O $2p$ orbitals, while the CB is mainly formed by Ni $3d_{xy}$ orbitals and mainly by a homogenous contribution of the W e_g ($5d_{z^2} + 5d_{x^2-y^2}$) and W $5d_{xz} + 5d_{yz}$ orbitals. The top of the VB is composed by only Ni $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals in the α and β channels, respectively. Concerning the bottom of the CB, the α channel is composed by empty Mo $4d_{z^2} + 4d_{xz} + 4d_{x^2-y^2}$ orbitals, while at the β channel, there is a hybridization between the Mo $5d_{z^2} + 5d_{xz}$ orbitals with Ni $3d_{xz}$ orbitals.

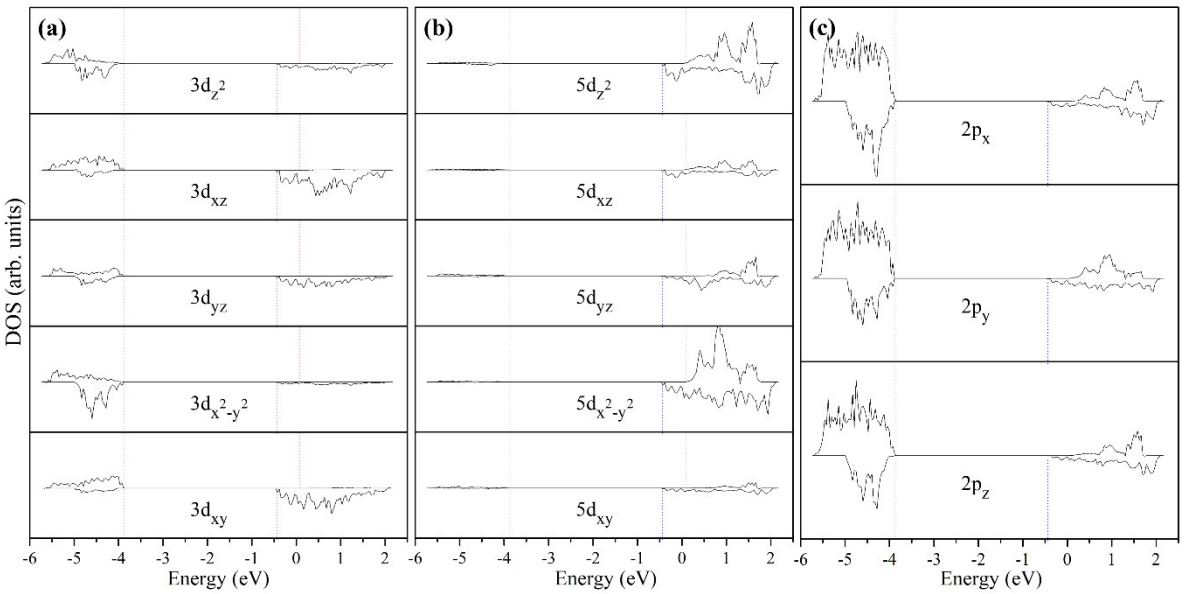

Figure SI-2. Partial DOS projected on **(a)** Ni, **(b)** W, and **(c)** O orbitals at the pure NW.

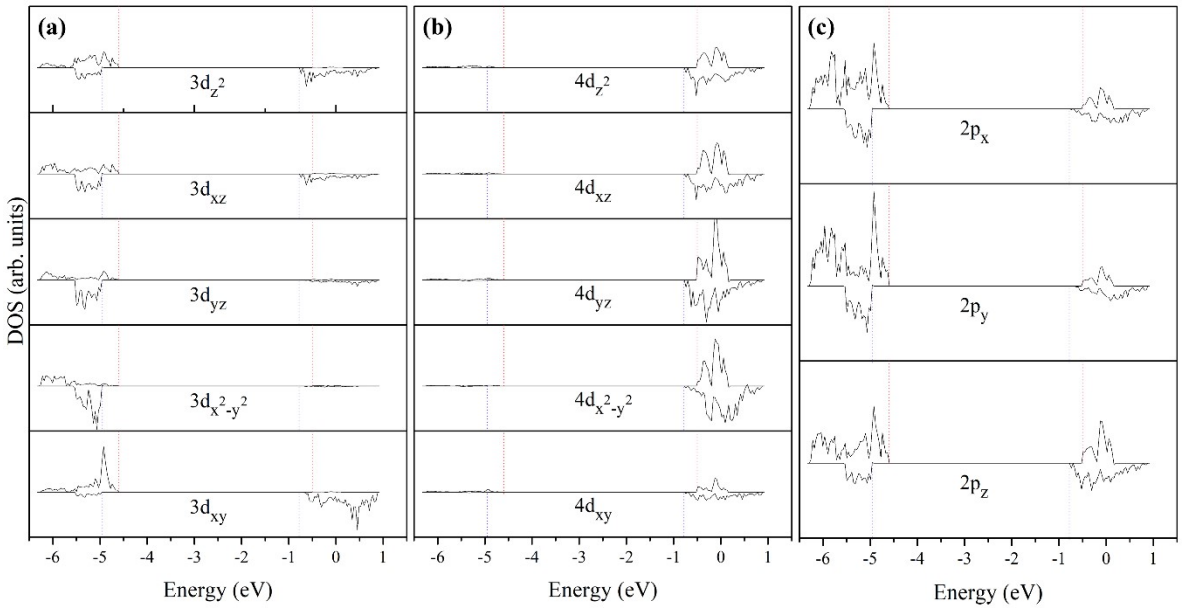

Figure SI-3. Partial DOS projected on **(a)** Ni, **(b)** Mo, and **(c)** O orbitals at the pure NM.

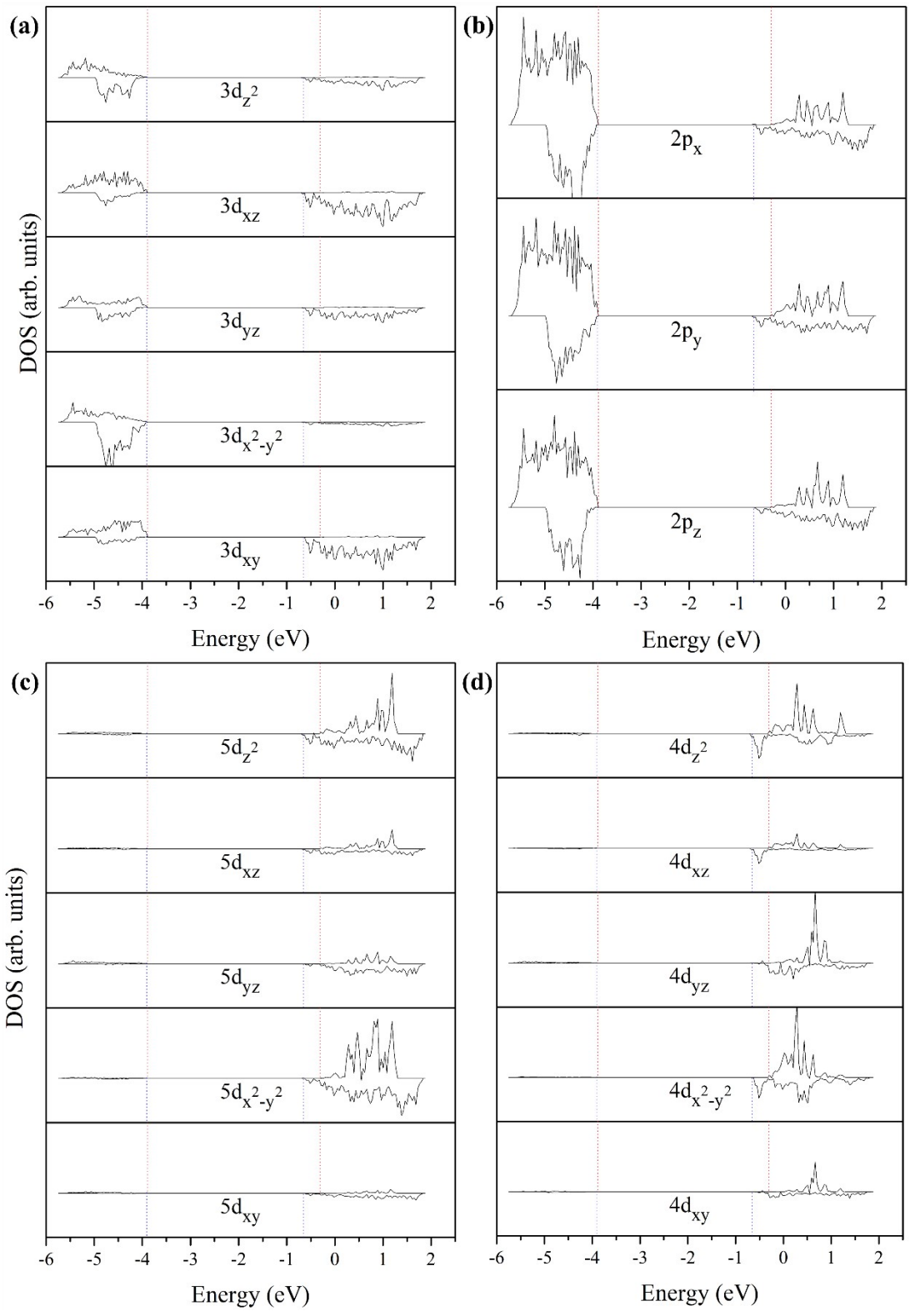

Figure SI-4. Partial DOS projected on **(a)** Ni, **(b)** O, **(c)** W, and **(d)** Mo orbitals at the NW75 solid solutions.

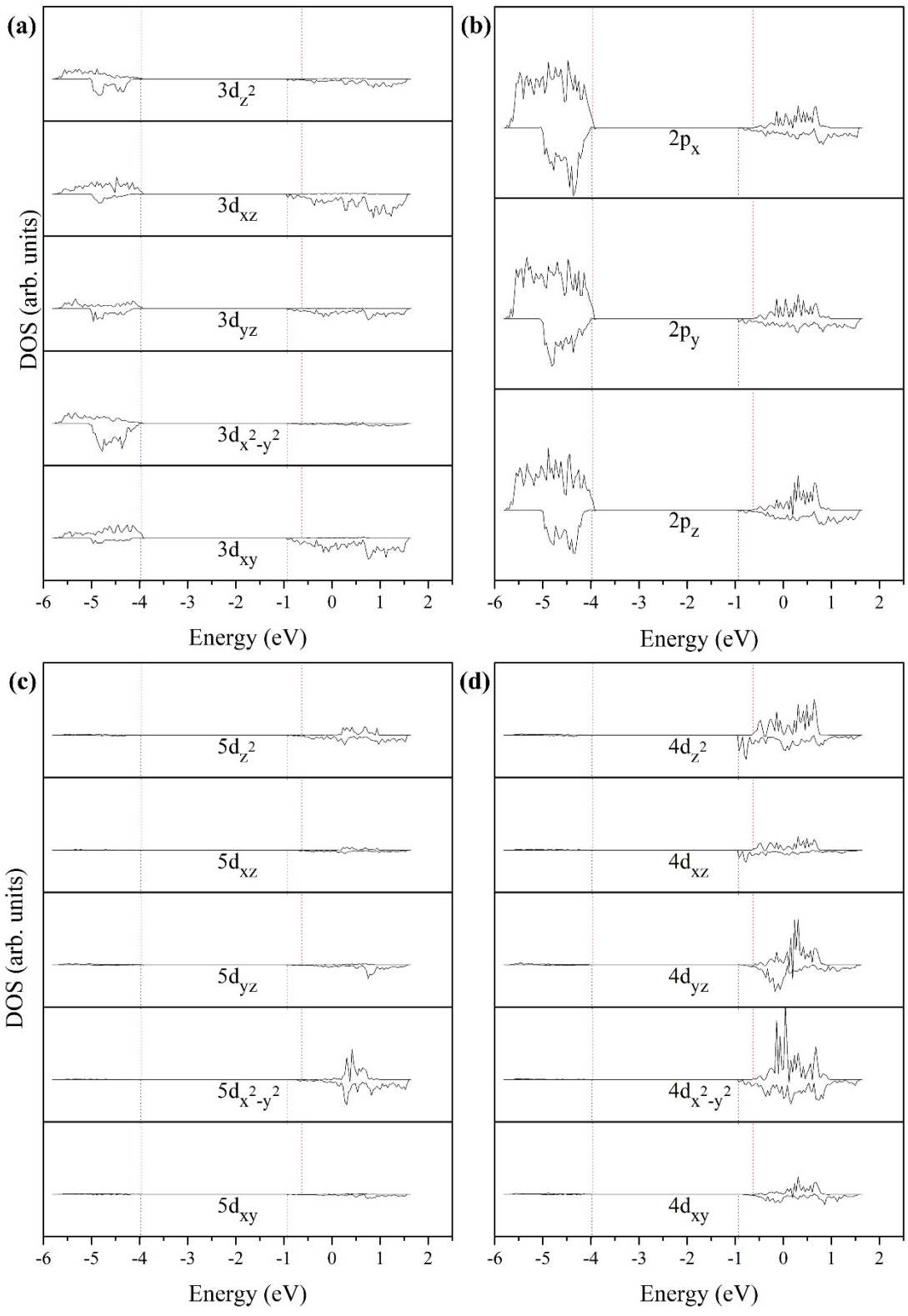

Figure SI-5. Partial DOS projected on **(a)** Ni, **(b)** O, **(c)** W, and **(d)** Mo orbitals at the NW50 solid solutions.

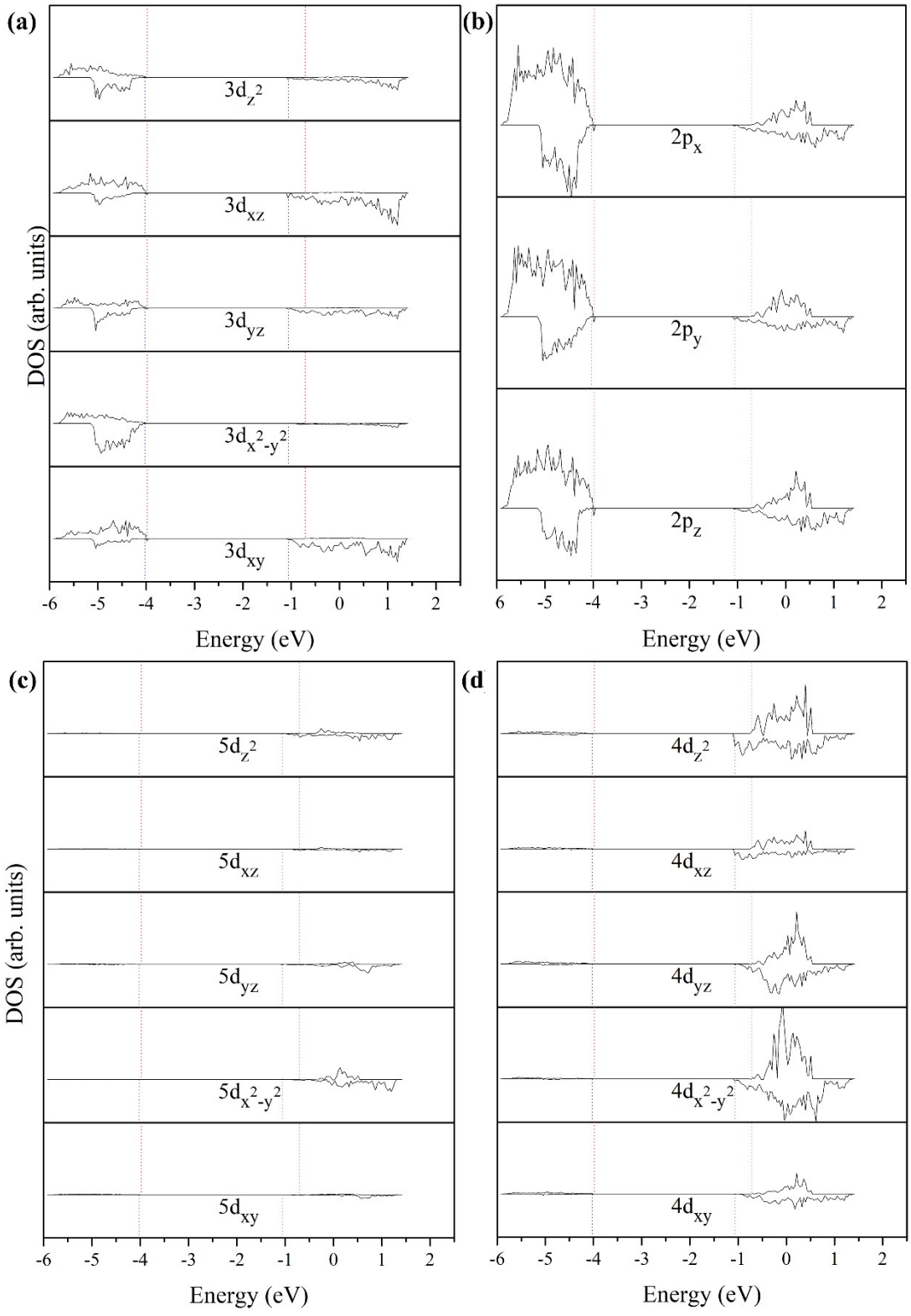

Figure SI-6. Partial DOS projected on **(a)** Ni, **(b)** O, **(c)** W, and **(d)** Mo orbitals at the NW25 solid solutions.