A NEW TYPE OF MIXED FRAMEWORK
IN THE CRYSTAL STRUCTURE OF BINARY
MOLYBDATE $Nd_2Zr_3(MoO_4)_9$

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Single crystals of binary molybdate $Nd_2Zr_3(MoO_4)_9$ were grown. The crystal structure of this compound was investigated by X-ray diffraction analysis (CAD-4 diffractometer, MoK_α radiation, 2844 reflections, $R = 0.0230$), and a new type of structure was found. The crystals are trigonal with cell dimensions $a = 9.804(1)$, $c = 58.467(12)$ Å, $V = 4867(1)$ Å^3, $Z = 6$, $d_{calc} = 4.098$ g/cm^3, space group $R\bar{3}c$. The structure involves polyhedra of three types: MoO_4 tetrahedra, ZrO_6 octahedra, and NdO_9 tricapped trigonal prisms linked by their common vertices into an original three-dimensional framework.

Seeking new binary molybdates of rare-earth elements and zirconium, we investigated phase equilibria in the subsolidus region of Ln_2O_3–ZrO_2–MoO_3 systems at 700°C. It was found that the composition and number of phases vary in the REE series. Molybdates with the following compositions were synthesized: $Ln_2Zr_3(MoO_4)_9$ (La–Tb), $Ln_2Zr_2(MoO_4)_7$ (Sm–Ho, Y), $Ln_2Zr(MoO_4)_5$ (Tb–Lu, Y) [1, 2].

Here we report on the results of our crystal structure analysis for $Nd_2Zr_3(MoO_4)_9$, a compound from the group which is the first member of the above series of isostructural compounds.

Neodymium and zirconium binary molybdate crystals were obtained by spontaneous crystallization from a solution in a MoO_3 melt with a charge to solvent ratio of 1:2 (w/w). The compound synthesized previously by stepwise annealing of a mixture of Nd_2O_3, ZrO_2, and MoO_3 (450-750°C, 150 h) was used as a batch. Nucleation and crystal growth started when the temperature of the solution melt was lowered from 900 (homogenization time 4 h) to 800°C at a rate of 2 deg/h.

A pink transparent crystal of irregular form (chip) with approximate dimensions $0.45 \times 0.30 \times 0.40$ mm was selected for X-ray structure analysis. The unit cell parameters were refined and the intensities of 8068 reflections were measured on an Enraf-Nonius CAD-4 automatic diffractometer using the standard procedure (λMoK_α radiation, graphite monochromator, $\theta/2\theta$ scan mode, variable rate, maximal $2\theta = 75°$). An empirical absorption correction based on φ-scan data was applied, $\mu(MoK_\alpha) = 75.18$ cm^{-1}. The crystals are trigonal with unit cell parameters $a = 9.804(1)$, $c = 58.467(12)$ Å, $V = 4867(1)$ Å^3, $Z = 6$; $d_{calc} = 4.098$ g/cm^3. The space group, $R\bar{3}c$, was determined by analyzing extinctions in $F(hkl)$ and confirmed by subsequent calculations. The structure was solved by direct methods using SHELXS-86 [3] and refined by the full-matrix least-squares procedure in an anisotropic approximation with SHELXL-93 [4]. The final $R = 0.0230$ corresponds to 2844 independent nonzero reflections with $I > 2\sigma(I)$ (78 refined parameters). Table 1 lists the final values of positional and equivalent isotropic thermal parameters of basic atoms; Table 2 gives selected interatomic distances and angles. The local valence force balance calculated according to [5] is presented in Table 3. Its good convergence with $D = 0.9\%$ (balance quality criterion [6]) confirms the composition and the refined model of the structure. The tables of anisotropic thermal parameters and structural factors are available from the authors.

The crystal structure of $Nd_2Zr_3(MoO_4)_9$ is a new formula and structural type of binary molybdate, where no mono- and bivalent metal cations are present.

TABLE 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of the Structure of $Nd_2Zr_3(MoO_4)_9$

Atom	x	y	z	U_{eq}
Nd	0.66667	0.33333	0.0293(1)	0.007(1)
Zr(1)	0	0	0	0.008(1)
Zr(2)	0.33333	0.66667	0.0713(1)	0.007(1)
Mo(1)	0.0962(1)	0.7254(1)	0.0249(1)	0.008(1)
Mo(2)	0.2798(1)	0.2798(1)	0.25	0.009(1)
O(1)	−0.0999(2)	0.5951(2)	0.0299(1)	0.017(1)
O(2)	0.1563(2)	0.6594(2)	0.0018(1)	0.021(1)
O(3)	0.2101(3)	0.7356(3)	0.0494(1)	0.023(1)
O(4)	0.1214(2)	0.9174(2)	0.0192(1)	0.016(1)
O(5)	0.2935(2)	0.4680(2)	0.2445(1)	0.016(1)
O(6)	0.1623(2)	0.1924(2)	0.2734(1)	0.023(1)

$*U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE 2. Selected Interatomic Distances (Å) and Angles (deg) in $Nd_2Zr_3(MoO_4)_9$

Mo(1) tetrahedron		Mo(2) tetrahedron	
Mo(1)–O(1)	1.720(2)	Mo(2)–O(6)	1.715(2)× 2
Mo(1)–O(2)	1.724(2)	Mo(2)–O(5)	1.811(2)× 2
Mo(1)–O(3)	1.790(2)	⟨Mo–O⟩	1.768
Mo(1)–O(4)	1.801(2)		
⟨Mo–O⟩	1.759		
		O(6)–Mo(2)–O(6)	108.2(2)
		O(6)–Mo(2)–O(5)	107.5(1)× 2
O(1)–Mo(1)–O(2)	108.6(1)	O(6)–Mo(2)–O(5)	109.8(1)× 2
O(1)–Mo(1)–O(3)	109.9(1)	O(5)–Mo(2)–O(5)	113.8(1)
O(2)–Mo(1)–O(3)	109.1(1)	⟨O–Mo–O⟩	109.3
O(1)–Mo(1)–O(4)	109.0(1)		
O(2)–Mo(1)–O(4)	110.8(1)		
O(3)–Mo(1)–O(4)	109.4(1)		
⟨O–Mo–O⟩	109.5		
Zr(1) octahedron		Nd polyhedron	
Zr(1)–O(4)	2.074(2)× 6	Nd–O(1)	2.439(2)× 3
Zr(2) octahedron		Nd–O(2)	2.489(2)× 3
Zr(2)–O(5)	2.059(2)× 3	Nd–O(6)	2.510(2)× 3
Zr(2)–O(3)	2.091(2)× 3	⟨Nd–O⟩	2.479
⟨Zr–O⟩	2.075		

TABLE 3. Local Valence Force Balance (s) in $Nd_2Zr_3(MoO_4)_9$

Atom	Mo(1)	Mo(2)	Zr(1)	Zr(2)	Nd	Σs_a
O(1)	1.658	—	—	—	0.405	2.063
O(2)	1.640	—	—	—	0.354	1.994
O(3)	1.372	—	—	0.644	—	2.016
O(4)	1.332	—	0.674	—	—	2.006
O(5)	—	1.296	—	0.702	—	1.998
O(6)	—	1.680	—	—	0.335	2.015
Σs_c	6.002	5.952	4.044	4.038	3.282	

As in most structures of binary molybdates, in $Nd_2Zr_3(MoO_4)_9$ the molybdenum atoms have a tetrahedral oxygen environment with Mo(1) lying on the general position and Mo(2) on the twofold axis. The mean Mo–O distances are 1.759 Å and 1.768 Å; the average O–Mo–O angles are 109.5° and 109.3° for the two sorts of molybdenum-oxygen tetrahedron, respectively; these values lie within the range of mean values for c.n.(Mo) = 4 [7].

The two independent zirconium atoms lie on the 3 axis inside the oxygen octahedra; one of them, Zr(1), is at the center of inversion. The Zr–O bond lengths are close to each other: 2.074 and 2.075 Å, respectively. These values are comparable to the Zr–O distances in the structures of $K_8Zr(MoO_4)_6$ [8] and $Zr(MoO_4)_2$ (high-temperature modification) [9], where the zirconium atom also has an octahedral environment.

The Nd atom also lies on the threefold axis. The surrounding oxygen atoms form a tricapped trigonal prism, which is a typical coordination polyhedron of REE [10]. The Nd–O distances vary within a narrow range of 2.439-2.510 Å, the mean value being 2.479 Å. These values are close to those for many oxygen-containing REE compounds such as $Nd_2TeMo_6O_{24} \cdot 18H_2O$ ($\langle Nd-O \rangle$ 2.506 Å) [11], $Nd_2P_6O_{18} \cdot 12H_2O$ ($\langle Nd-O \rangle$ 2.500 Å) [12], and $Nd_2V_{10}O_{28} \cdot 28H_2O$ ($\langle Nd-O \rangle$ 2.518 Å) [13].

The three types of coordination polyhedron around cations are clearly seen in Fig. 1 showing a projection of a small layer of the structure $(0.32 < z < 0.52)$ of neodymium-zirconium molybdate cut out perpendicularly to the threefold axis. The linkage between the polyhedra along the long axis c is more clearly seen in Fig. 2 presenting a section of the structure along the (110) plane.

As mentioned above, the Nd and Zr polyhedra lie on the special positions on the threefold axes; they have no common structural elements and form some kind of rods along the c axis with "material" polyhedra alternating with slightly twisted empty trigonal prisms. The coordination polyhedra of cations form the following sequence on the threefold axis: Zr1–Zr2–Nd–↑–Nd–Zr2–Zr1–Zr2–Nd–↑–Nd–Zr2–Zr1 (10 polyhedra per translation; ↑ — the 2 axis, which is perpendicular to the 3 axis; the centrosymmetric polyhedra are underlined). The crystal structure may be represented as (Nd, Zr) rods (with three symmetrically equivalent rods rhombohedrally shifted relative to each other per unit cell) linked to each other by their common oxygen vertices of the bridging Mo tetrahedra of two sorts to form a three-dimensional mixed framework. To derive this structure, it is sufficient that the following formal conditions be satisfied [14, 15]: 1) all vertices of coordination polyhedra are shared; 2) edge and bow type contacts are absent; 3) the amphoteric cations Zr^{4+} and Nd^{3+} are therefore recognized as performing an acid function. Although the mean valence force in neodymium polyhedra is moderate $(s = 1/3)$, the polyhedra are fittingly built in the mixed framework, reinforcing the latter. To confirm the ability of nine-vertex polyhedra to play the leading role in construction of a mixed net, one can cite the apatite-like structures $Yb(ReO_4)_3$ [16] and $CdTh(MoO_4)_3$ [17]; the latter differs from the former
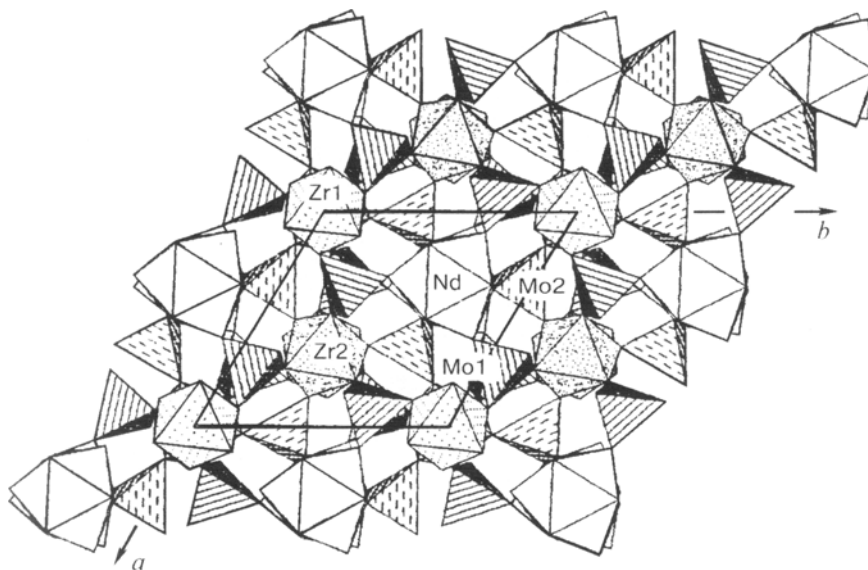

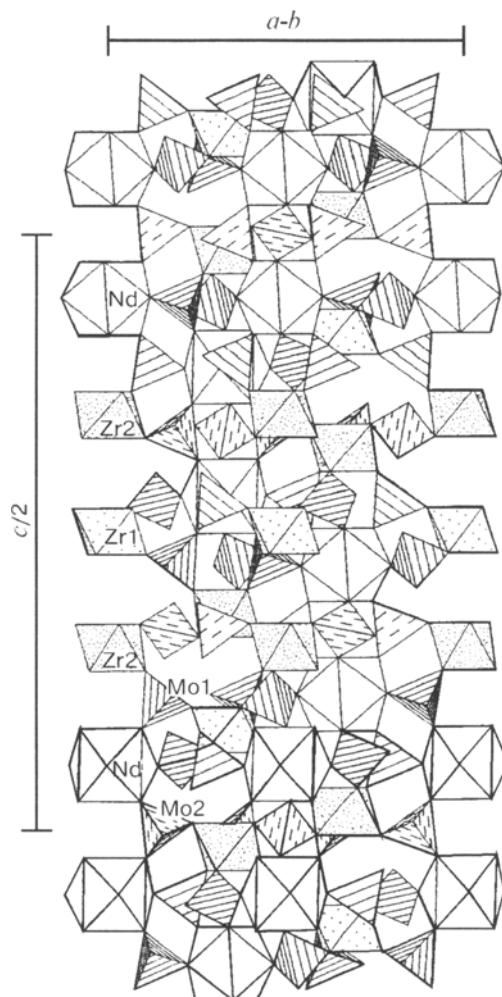**Fig. 1.** Fragment of the structure of $Nd_2Zr_3(MoO_4)_9$. The layer at $z = 0.4$ projected on the (001) plane is lined out.

Fig. 2. Structure of $Nd_2Zr_3(MoO_4)_9$ projected on the (110) plane. The polyhedra stringed on the 3 axis are well discernible of the right and on the left: two sorts of Zr octahedron and Nd nine-vertex polyhedra.

in having the octahedrally coordinated positions occupied by Cd atoms in the voids of the structure consisting of the $Yb(Th)O_9$ tricapped trigonal prisms and $Re(Mo)O_4$ tetrahedra.

On the other hand, this structure may be interpreted in a more traditional way, as a much looser three-dimensional "subnet" $\{[Zr(MoO_4)_3]^{2-}\}_{3\infty}$ of hexadentate ZrO_6 octahedra and bridging bidentate MoO_4 tetrahedra linked by their common oxygen vertices with large voids accommodating the Nd atoms which coordinate the free vertices of MoO_4 tetrahedra. A net of analogous stoichiometry and type of mutual coordination of octahedra and tetrahedra (hexadentate and bridging bidentate), $\{M(TO_4)_3\}_{3\infty}$, is observed in the rhombohedral structure of $K_5(Mg_{0.5}Zr_{0.5})Zr(MoO_4)_6$ [18]. However, it is characterized by a more "rarefied" topology with intranet space sufficient for accommodating the large potassium cations. By analogy with the previous two structures, the rhombohedral $Ba_9Sc_2(SiO_4)_6$ [19] has hexagonal basis dimensions and a mixed radical anion stoichiometry, but here the large cations are differentiated from the small ones, and the structural motif is layered: $\{M(TO_4)_3\}_{2\infty}$. Clearly, here we have a "volume effect" (increased content of large compensator cations) on the polymorphism of the mixed radical $\{M(TO_4)_3\}$.

As for practical uses, the compound is expected to be effective as laser material (high content of Nd^{3+} and short contacts Nd–Nd 6.31 Å). On the other hand, the openwork structure of the binary molybdate may be completed by the mobile ions Li^+, Na^+, Cu^+, and Ag^+. These ions may be inserted in the structure by heterovalent substitution $Zr^{4+} \rightarrow A^+ + M^{3+}$ and occupy both the empty trigonal prisms in the (Nd, Zr) rods and the voids between the rods having enough room for the cations. The framework character of the structure and, probably, the three-dimensional

283

net of sites accessible for the mobile ions prompt that this structural motif is promising for creation of solid electrolytes on its basis.

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