Figures

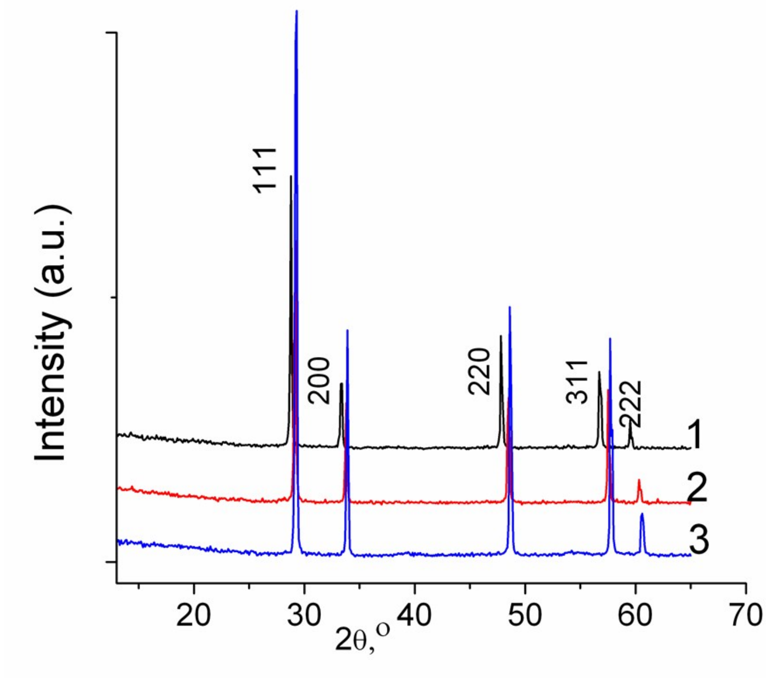


Fig.S1. XRD of high – temperature fluorites: (1) $Gd_{10}Mo_2O_{21}$, (2) $Dy_{10}Mo_2O_{21}$, (3) $Ho_{10}Mo_2O_{21}$.

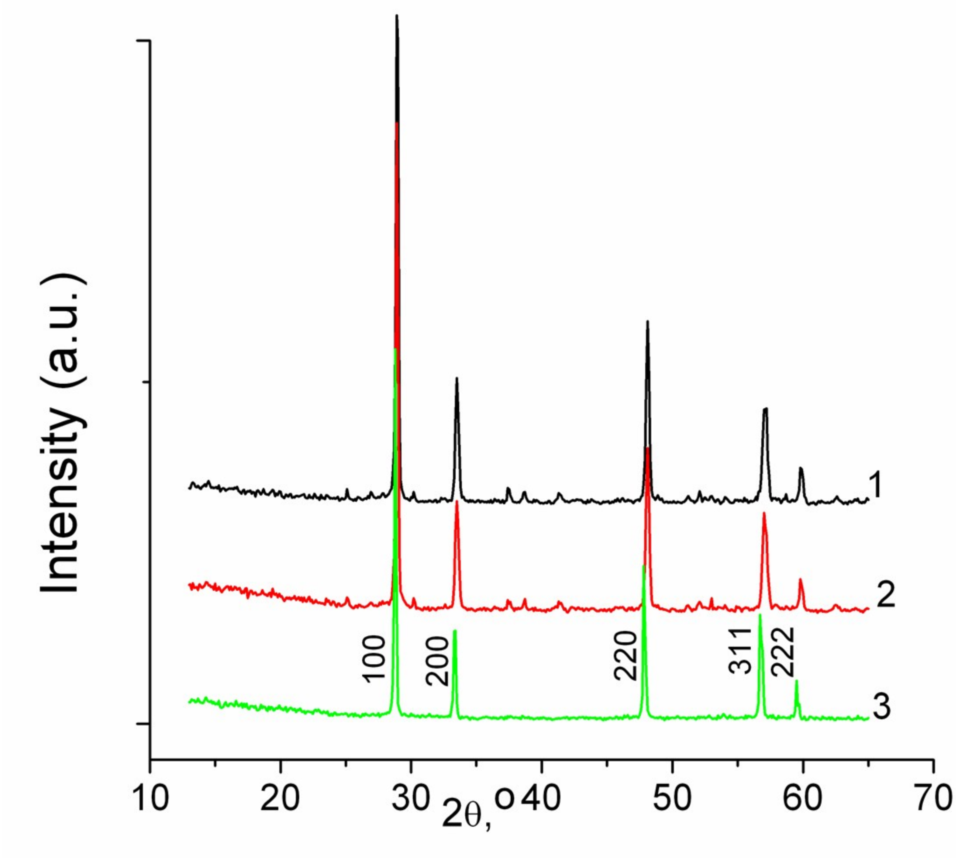


Fig.S2 XRD data illustrating the phase changes of $Gd_{10}Mo_2O_{21}$: (1)1200°C, 40 h; (2) 1200°C, 80 h; (3) 1600°C, 3 h.

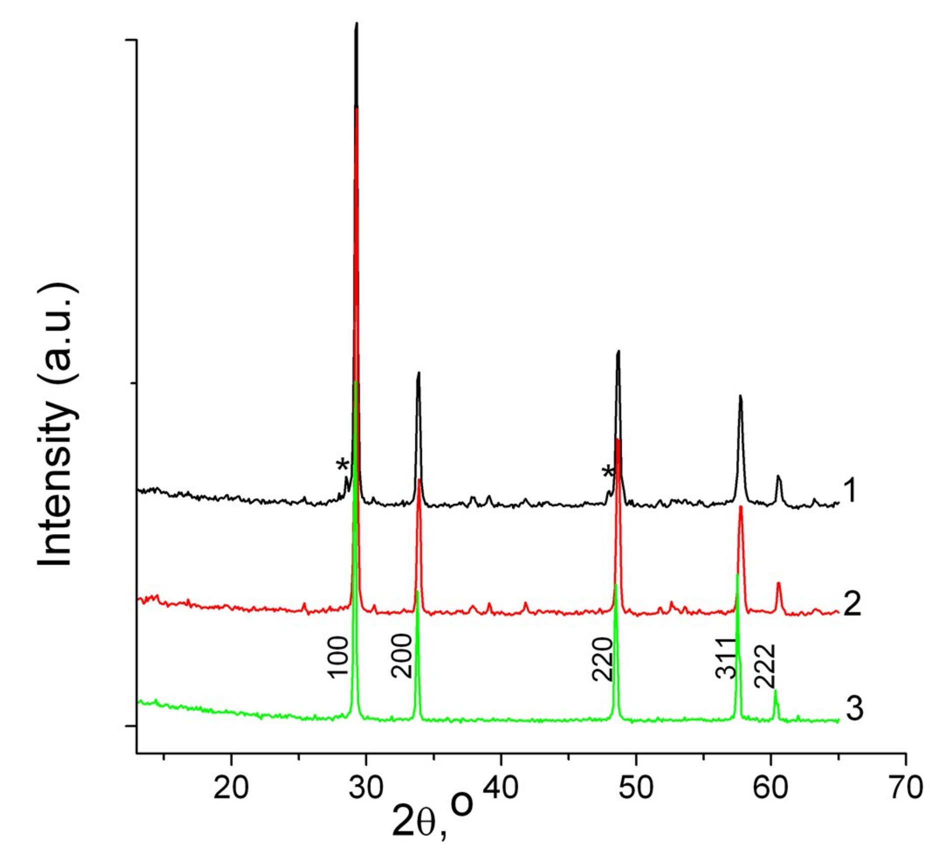


Fig.S3 XRD data illustrating the phase changes of $Dy_{10}Mo_2O_{21}$: (1) 1200°C, 40 h; (2) 1200°C, 80 h; (3) 1600°C, 3 h (asterisks mark reflections from Dy_2O_3).

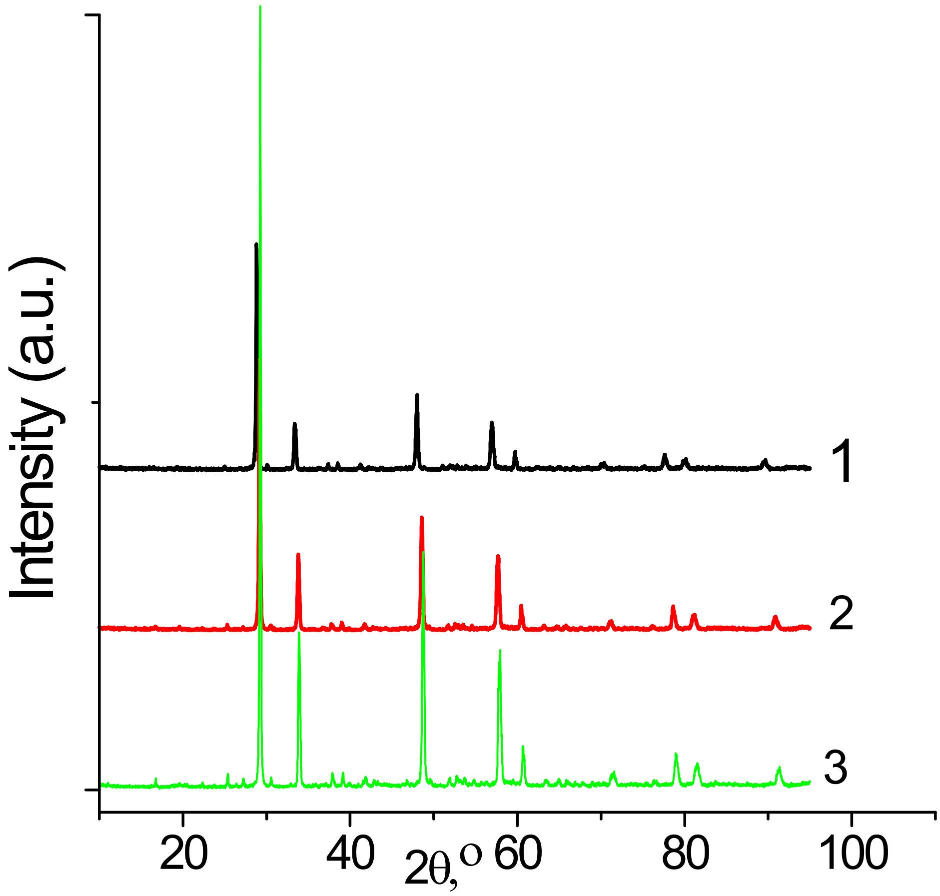


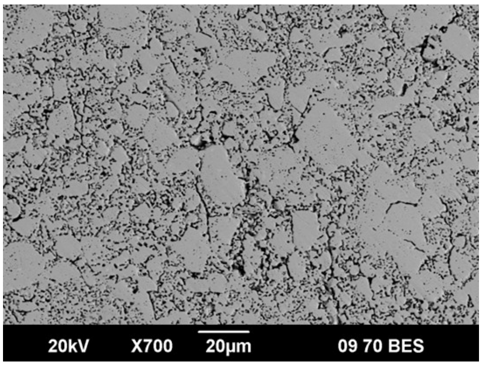
Fig.S4 XRD of low – temperature phases: (1) $Gd_{10}Mo_2O_{21}$, (2) $Dy_{10}Mo_2O_{21}$, (3) $Ho_{10}Mo_2O_{21}$.

Supplement A.

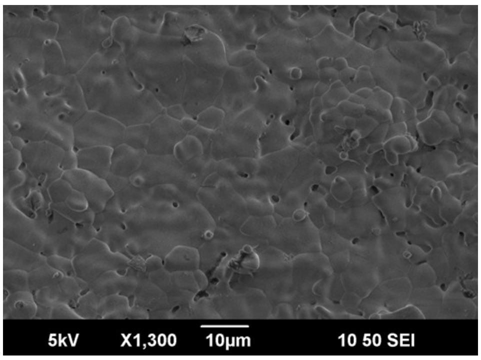
The microstructure of the *Ln*MoO-1200 (*Ln* = Gd, Dy, Ho) ceramics produced at 1200°C and *Ln*MoO-1600 *(Ln* = Gd, Dy, Ho) ceramics produced at 1600 °C is illustrated in **Figs. S5 – S7**. **Figs. S5a, S6a** present cross-section of the ceramics of the orthorhombic *Ln*MoO-1200 (*Ln* = Gd, Dy) molybdates, obtained in single-phase form at 1200 °C. They are similar in microstructure. The orthorhombic *Ln*MoO-1200 (*Ln* = Gd, Dy) ceramics consists mainly of smaller grains, 0.2 to 0.5 µm in size, but there are also grains ~35 µm in size (**Figs. S5a, S6a**). The orthorhombic HoMoO-1200 ceramics is more porous than the *Ln*MoO-1200 (*Ln* = Gd, Dy) ceramics and was investigated by SEM earlier **[44]**.

Figs. S5b, S6b show the fresh surface of the fluorite *Ln*MoO-1600 (*Ln* = Gd, Dy) ceramics, obtained in single-phase form at 1600 °C. SEM of ceramics cross-section of the high-temperature fluorite modifications after polishing and thermal etching at 1450°C for 0.5 h are shown in **Figs. S5c, S6c.** The grain size in the gadolinium molybdate fluorite sample is 10–15 μm. Note the unusual microstructure of the surface of the fluorite DyMoO-1600 ceramics (**Fig. S6b**). Some of its grains have the form of the square plates (10×10×4 μm), and the size of some grains cannot be determined (**Fig. S6b**). The fluorite HoMoO-1600 ceramics is more inhomogeneous than the gadolinium molybdate and dysprosium molybdate fluorite ceramics **(Fig. S7)**. Its grains range in size up to 5 μm, and some are even 25 μm in size.

As a rule, in the series of rare-earth tungstates **[40]** and molybdates **[31]**, the density decreases significantly with a decrease in the ionic radius of lanthanides following the same trend in the binary RE oxides.



a



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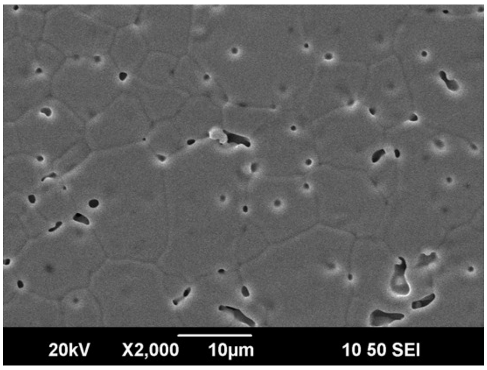
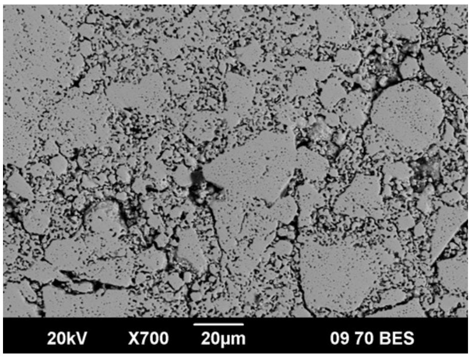


c

Fig.S5 Microstructure of the gadolinium ceramics prepared by firing (a) at 1200 °C for 80 h, then polished and thermally etched at 1050°C (ceramics cross-section surface; back-scattered electron image), (b) at 1600 °C for 3 h, and (c) at 1600 °C for 3 h, then polished and thermally etched at 1450°C (ceramics cross-section surface).



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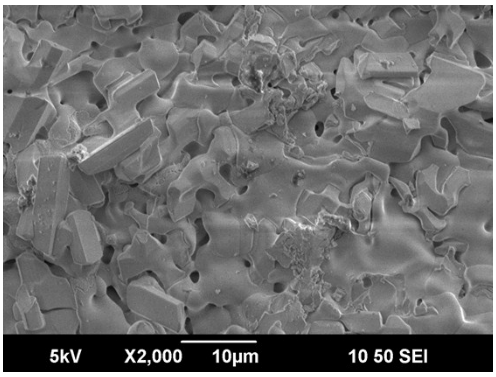

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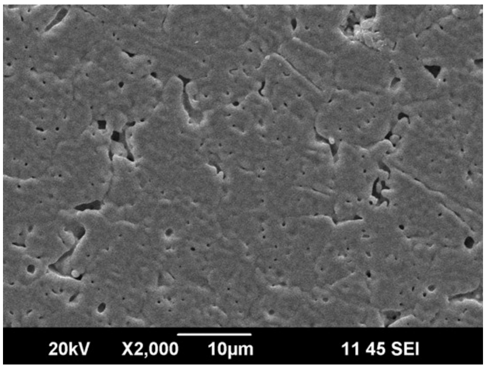

c

Fig.S6 Microstructure of the dysprosium ceramics prepared by firing (a) at 1200 °C for 80 h, then polished and thermally etched at 1050°C (ceramics cross-section surface; back-scattered electron image), (b) at 1600 °C for 3 h, and (c) at 1600 °C for 3 h, then polished and thermally etched at 1450°C (ceramics cross-section surface).

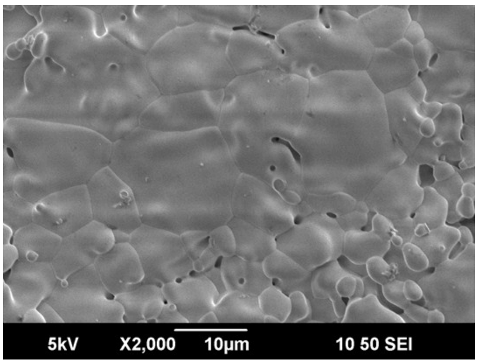

Fig.S7 Microstructure of the holmium ceramics prepared by firing at 1600 °C for 3 h.

Table S1. Crystal structural parameters for $Ho_{10}Mo_2O_{21}$ refined against NPD data collected at room temperature. Space group Pbnc (# 60). Numbers in parentheses are standard deviations of the last significant digit. *a* = 15.8751(6) Å, *b* = 10.5318(3) Å, *c* = 10.5672(4) Å, V = 1766.76(11) Å^3, overall isotropic temperature factor U_{iso} = 0.0047(3) Å^2

Atom	Wyckoff site	x	y	z
Mo1	8d	0.5868(10)	0.2438(25)	0.1193(12)
Ho1	8d	0.0732(9)	-0.0047(12)	0.1365(13)
Ho2	8d	0.2720(6)	0.2437(20)	0.1322(13)
Ho3	8d	0.0798(11)	0.4934(12)	0.1210(16)
Ho4	8d	0.6001(7)	0.7495(20)	0.1447(11)
Ho5	8d	0.7456(15)	0.0067(18)	0.1410(13)
O1	8d	0.3408(11)	0.3857(20)	-0.0026(22)
O2	8d	0.5473(10)	0.3710(17)	0.0176(19)
O3	8d	0.3579(12)	0.3570(19)	0.2678(22)
O4	8d	0.3209(15)	0.6172(21)	0.2186(17)
O5	8d	0.5147(12)	0.1126(21)	0.0537(19)
O6	8d	0.3246(14)	0.1975(16)	0.4721(17)
O7	8d	0.6694(14)	0.9074(18)	0.0043(19)
O8	8d	0.1434(12)	0.6331(21)	0.2525(20)
O9	8d	0.1825(15)	0.3847(20)	0.2170(15)
O10	4c	0.5	0.3023(25)	0.25
O11	4c	0.5	0.6350(26)	0.25
O12	4c	0.0	0.3940	0.25