Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information:

Phase transition and negative thermal expansion in orthorhombic $Dy_2W_3O_{12}$

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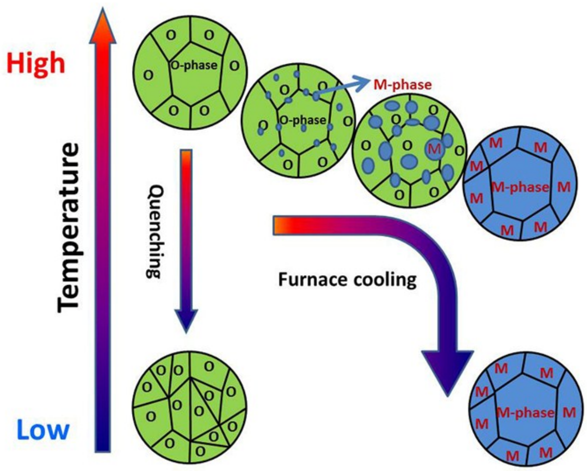

Fig. S1 Diagram of the mechanism for achieving the orthorhombic phase. O represents orthorhombic phase, and M represents monoclinic phase.

The phase transition from orthorhombic phase to monoclinic phase is a reconstruction phase transition, which mainly includes the nucleation and growth. And the phase transition needs enough time and energy to complete the nucleation and growth. However, the high temperature quenching can't provide these two conditions. That is to say, the high temperature quenching prevents the orthorhombic phase from the phase transition. The orthorhombic phase is metastable phase at low temperature, which is stabilized by lattice strain, grain boundary surface energy and other factors.

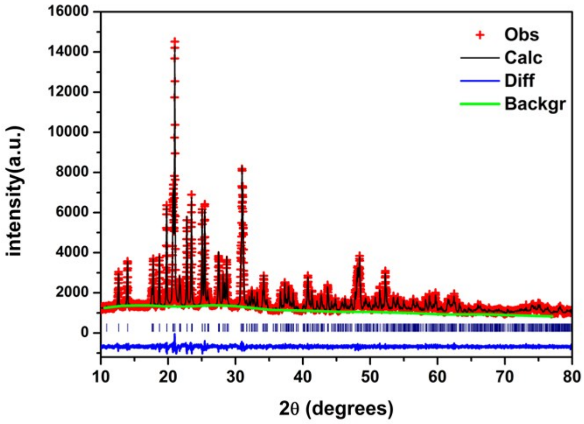

Fig. S2 Le Bail fit of XRD data of quenched sample at 200°C in space group Pnca

Table S1. The cell parameters of orthorhombic $Dy_2W_3O_{12}$ versus temperature from XRD results

Temperature(°C)	Cell parameter(Å)			Chi2
	a	b	c	
150	10.09058(8)	13.99580(11)	10.00783(8)	1.61
200	10.08458(8)	13.99545(10)	10.00420(8)	1.72
250	10.07585(8)	13.98876(10)	9.99726(8)	1.41
300	10.07058(9)	13.98789(10)	9.99387(8)	1.66
350	10.06577(9)	13.98532(10)	9.98993(8)	1.66
400	10.05962(9)	13.98189(11)	9.98506(9)	1.63
450	10.05389(9)	13.97722(12)	9.98018(9)	1.53
500	10.04830(9)	13.97305(12)	9.97543(9)	1.62

Table S2. The cell parameters of orthorhombic $Dy_2W_3O_{12}$ versus temperature from SXRD results

Temperature(°C)	Cell parameter(Å)			Chi2
	a	b	c	
250	10.08133(7)	13.99282(10)	10.00256(7)	1.22
300	10.07521(8)	13.98988(10)	9.99807(7)	1.22
350	10.06916(8)	13.98675(11)	9.99807(8)	1.41
400	10.06302(8)	13.98328(12)	9.99807(8)	1.54
450	10.05767(9)	13.97983(12)	9.99807(9)	1.61
500	10.05211(9)	13.97578(12)	9.99807(9)	1.71

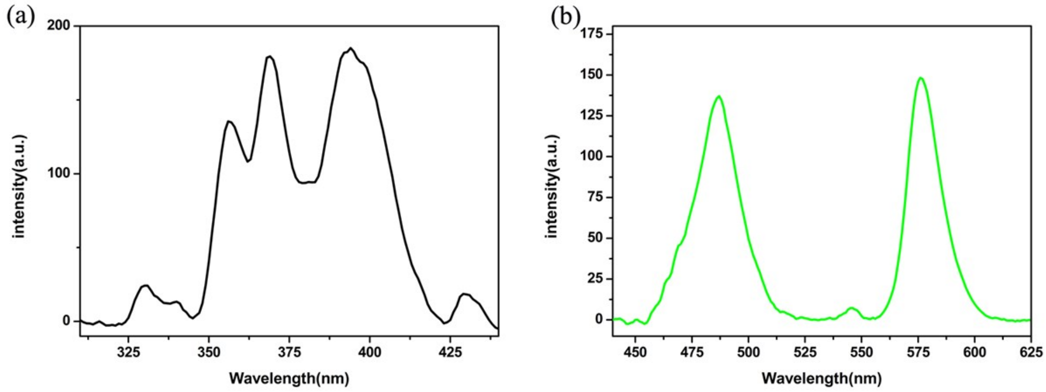

Fig. S3 Excitation spectrum of the quenched sample (λex=576nm)(a), Emission spectrum of the quenched sample (λex=356nm) (b)

Due to the unique 4f electronic configuration of Dy^{3+}, the photoluminescence and the magnetic properties of the quenched sample ($Dy_2W_3O_{12}$•$2.7H_2O$) were also investigated, which will be the guidance for the further research on the orthorhombic $Dy_2W_3O_{12}$. Fig. S3(a) exhibits the excitation spectra of the quenched sample with the monitoring emission at 576nm. There are three main excitation peaks at 356nm, 369nm and 393nm observed. Among them, the peak around 356nm is attribute to the electronic transitions of $^6H_{15/2} \rightarrow (^4M_{15/2},^6P_{7/2})$, the peak at 369nm is assigned to $^6H_{15/2} \rightarrow ^4I_{11/2}$, and the band centered at 393 is due to the electronic transition of $^6H_{15/2} \rightarrow ^4F_{7/2}$. The transition (356nm) was selected to collect the emission spectra, which is shown in Fig. S3(b). There are two emission bands in the emission spectrum. The band at 487nm is owing to the transition of $^4F_{9/2} \rightarrow ^6H_{15/2}$, and the peak around 576nm is assigned to $^4F_{9/2} \rightarrow ^6H_{13/2}$.[1] The photoluminescence of the quenched sample make it have potential to be used for white light LED.

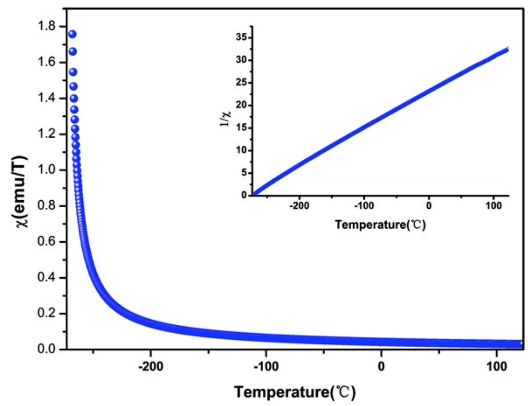

Fig. S4 the magnetic susceptibility as a function of temperature for the quenched sample, the inset shows 1/χ versus T

The magnetic property of the quenched sample was measured in the temperature range of -268℃~127℃ by SQUID under 0.2T field. Fig. S4 presents the magnetic susceptibility as a function of temperature for quenched sample, and the representative inverse magnetic susceptibility as a function temperature is exhibited in the inset Fig.S4. It is evident that $1/\chi$ vs T curve of quenched sample is well fitted by the Curie-Weiss law $1/\chi=CT$， where C is the Curie constant. This indicates that the quenched sample shows paramagnetic behavior, which is due to the strong paramagnetic property of Dy^{3+}.

references:

1 L. C. ZHANG Wenyan, NI Yaru, SONG Jianbin, HUANG Wenjuan,TAO Jing, XU Zhongzi, *Journal of Wuhan University of Technology (Materials Science Edition)*, 2013, **5**, 002.