

## Supplementary Materials

### *(Sc<sub>0.2</sub>Nd<sub>0.2</sub>Er<sub>0.2</sub>Yb<sub>0.2</sub>Lu<sub>0.2</sub>)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> Reactivity with Steam: TEM EELS Analysis*

To gain further insight to the compositional and microstructural character of the steam-reacted (Sc<sub>0.2</sub>Nd<sub>0.2</sub>Er<sub>0.2</sub>Yb<sub>0.2</sub>Lu<sub>0.2</sub>)DS sample with higher spatial resolution we use STEM-EDS, as shown in Figure SM1. The atomic number contrast of the high-angle annular dark-field image (HAADF) (Figure SM1(a)) shows a higher density monosilicate reaction layer containing pores on the right and the unreacted disilicate material on the left. Intensity variations in the reaction region and streaks in the porous region result from thickness fluctuations during sample preparation. The uniform contrast in the HAADF image of the unreacted region shows that the average atomic number density in the disilicate is relatively uniform. The reaction front appears to progress non-uniformly, with one example indicated by the white arrows in Figure SM1. The preferential progression of the reaction front between the two grains suggest that the phase transformation occurs faster along the grain boundaries that separate grains. In addition to the suggested faster propagation along grain boundaries, the curvature of the interface indicated by the white and cyan arrow shows that the reaction has preferentially consumed a small grain leaving behind a pore, which is also shown in the diffraction contrast of the annular dark-field image in Figure SM1(b). The O and Si maps (Figure SM1(c,d)) show the expected mono- and disilicate compositions. Figure SM1(e,f) shows the presence of Nd rich (other RE lean) REDS particles in the unreacted layer and a nearly equimolar concentration of RE in the steam-reacted REMS phase. Concentrations of the three phases marked with rectangles in Figure SM1 are shown in Table SM1. The geometry of the interface marked by the white arrow therefore suggests that the reaction occurs faster at boundaries separating disilicate grains and faster at Nd-rich grains.

## Supplementary Materials

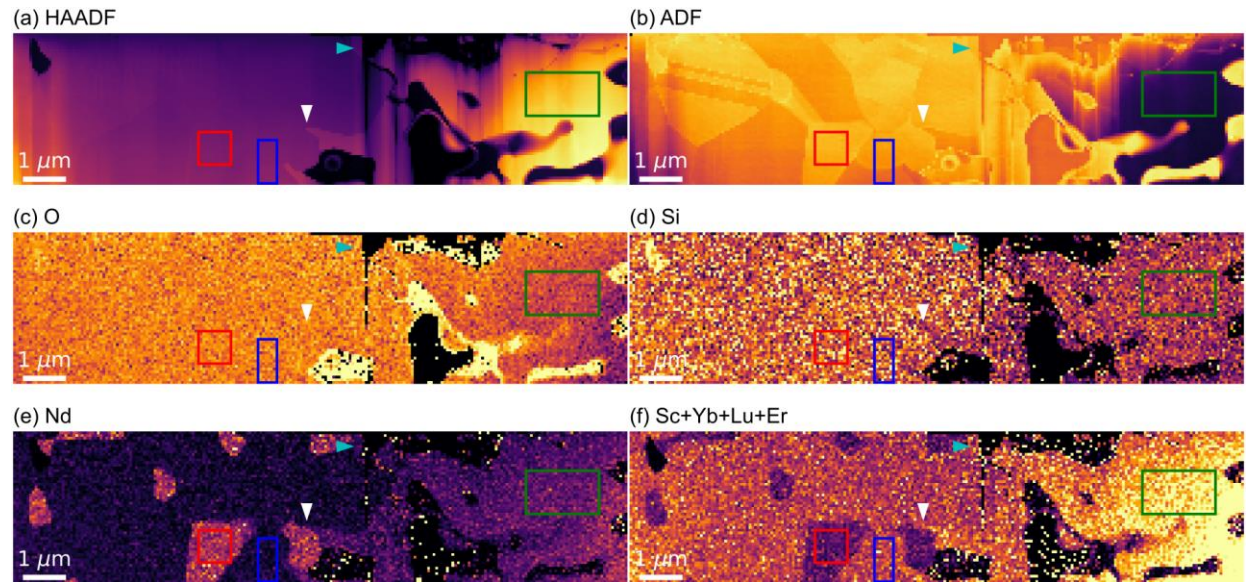


Figure SM1. STEM-EDS of  $(Sc_{0.2}Nd_{0.2}Er_{0.2}Yb_{0.2}Lu_{0.2})DS$  after exposure to steam at 1400 °C for 125h. The two-phase unreacted disilicate (left) and porous monosilicate reaction product (right) interface were both characterized. The three rectangular regions were analyzed for composition, and the steam reaction front is denoted by the two arrows

Table SM1. Elemental concentrations (at%) of the three phases marked in Figure SM1.

Element	Area 1 (Red)	Area 2 (Blue)	Area 3 (Green)
O	67.47	67.67	52.99
Si	16.41	15.16	11.45
Nd	11.05	1.93	6.25
Sc	0.31	3.58	6.90
Er	2.15	3.79	7.34
Yb	1.47	3.78	7.45
Lu	1.13	4.09	7.63
<b>sum (no Nd)</b>	<b>5.07</b>	<b>15.24</b>	<b>29.31</b>
<b>mean (no Nd)</b>	<b>1.27</b>	<b>3.81</b>	<b>7.33</b>

The stoichiometry of the Nd-rich REDS phase has approximately a 1:2:3 ratio of RE(no Nd):Nd:Si and is very Sc-lean. The Nd-lean REDS phase has equimolar RE(no Nd) to Si, and small amounts of Nd (2 at%). The steam-reacted REMS layer has approximately equimolar amounts of all RE. The low O and Si concentration in the steam-reacted REMS region could be in part to mass absorption, affecting EDS quantification. NdDS has been shown to be more reactive in high-velocity steam than other REDS (RE = Sc, Er, Yb, Lu) [6]. The increased

## Supplementary Materials

reactivity of Nd-silicates in conjunction with the progression of the reaction interface around the Nd-rich particles shows that the Nd-rich phase is preferentially being consumed and providing Nd to the stable X2 phase.

The near-edge structure of the  $(\text{Sc}_{0.2}\text{Nd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2})\text{DS}$  interface was examined with monochromated EELS after steam reaction to further understand the site occupancy and the apparent preferential segregation of RE elements. Figure SM2(a) shows the HAADF image, taken during the spectrum image acquisition, of the triple point indicated by the white arrows in Figure SM1. K-means clustering was performed on the loadings of a singular valued decomposition to obtain a characteristic spectrum of each phase. The average of the raw data was then taken for each cluster. This approach provides a characteristic high signal-to-noise spectrum for each phase without introducing artifacts or removing subtle features, which can occur during singular valued decomposition denoising. The clusters are shown in Figure SM2(b) and spectrum from each phase is shown in Figure SM2(c). The colors in Figure SM2(c-f) match the clusters in Figure SM2(b). The same Nd-rich disilicate (red), Nd-lean disilicate (green), and monosilicate reaction product (blue) phases that are observed with EDS data are also seen with EELS. Monochromated EELS spectrum images of the Sc-L<sub>23</sub>, Nd-M<sub>45</sub>, and O-K edges acquired with higher dispersion (smaller eV/channel) are shown in Figure SM2(d-f).

## Supplementary Materials

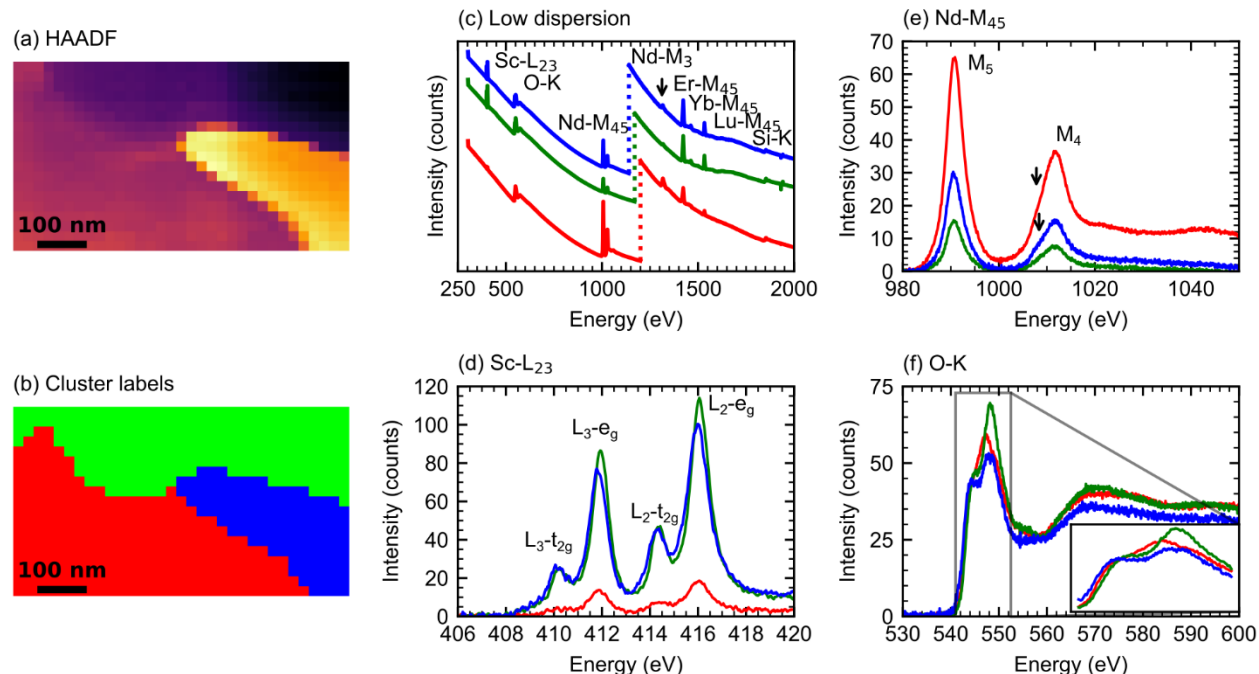


Figure SM2. EELS analysis of the  $(\text{Sc}_{0.2}\text{Nd}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2})\text{DS}$  interface after steam reaction at 1400 °C for 125h.

To begin we consider the occupation of Sc in the three phases. The Sc- $L_{23}$  peak is related to transitions from the  $2p_{3/2}$  to the  $2d-e_g$  and  $-t_{2g}$  bands. The  $t_{2g}$  energy is identical in the reacted and unreacted phase, where the reacted phase has a lower  $e_g$  energy than the unreacted phase. This can be understood by considering the average bond lengths, coordination, and volumes in the two phases. The X2 REMS steam reaction phase has two polyhedra: one with a large volume and effective coordination of 7.2, and the other with low volume and effective coordination of 4.6. The  $\beta$ -phase REDS has one polyhedron with an effective coordination of 6.0. The average bond length in  $\beta$ -phase YbDS is the same as the small polyhedron of the X2 YbMS phase. It is reasonable to hypothesize that Sc preferentially occupies the smaller site in the X2 phase due to its smaller radius. Occupying the smaller site in the X2 phase reduces the coordination of the Sc atoms to 4.6 relative to the  $\beta$ -REDS phase coordination of 6.0. This is in essence a comparison between a tetrahedrally coordinated and octahedrally coordinated atom, which correspond to lower and higher crystal field splitting, respectively. The  $e_g-t_{2g}$  splitting in the unreacted REDS

## Supplementary Materials

phase (green) is larger than in the reacted phase, which confirms that the Sc preferentially occupies a lower coordinated site. The small radius Sc atoms therefore preferentially occupy the smaller RE site in the steam reacted REMS phase.

We next consider the electronic structure of Nd to understand possible preferential site occupancies. The splitting of the two high-intensity peaks can again be related to the local bonding environment and spin-orbit coupling. Apart from the overall intensity of the edges (related to the before mentioned Nd concentration differences) there are not any major differences in the splitting or integrated intensity ratio of the  $M_4$  and  $M_5$  edges, which indicates minimal changes in the  $3d_{3/2}$   $3d_{5/2}$  spin-orbit coupling and implies negligible site preference for the Nd cation in any of the three phases present. The satellite peak, indicated by arrows in Figure SM2(e), is more prominent in the steam reacted phase (blue) curve than the unreacted Nd-rich REDS phase (red) curve. The prominence of the satellite peak in the steam reacted phase could be from crystal field splitting associated with polyhedra of the two phases. The unreacted phase has two polyhedra with minimal variation in bond length, while the steam reacted phase's polyhedron have large variations in bond length. This hypothesis is consistent when examining the O-K edge, as shown in Figure SM2(f). The first doublet, which is also shown as an enlarged inset, is related to the O hybridization with the RE elements. The single, broad peak of the Nd-rich phase (red) indicates a range of orbital energies associated with RE-O bonding. Both the Nd-lean and reacted phases that have smaller distribution of bond length within polyhedral again have well defined peak splitting. Therefore, preferential segregation of Nd to specific atomic sites cannot be determined from the Nd- $M_{45}$  and O-K near edge fine structures, yet the effect of crystal structure on Nd-O bonding and other RE-O bonding is apparent.

## Supplementary Materials

Taking the EDX and EELS results together, we observe the preferential progression of the reaction front around Nd-rich phase suggesting that the phase is reacting faster. The Sc from the Nd-lean disilicate phase lowers its average coordination and occupies the smaller polyhedron of the reacted X2 phase.