



Article **Crystal Growth of the** R_2SiO_5 **Compounds (**R = Dy, Ho, and Er) by the Floating Zone Method Using a Laser-Diode-Heated Furnace

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Abstract: In recent years, rare earth silicate compounds have attracted the extensive attention of researchers owing to their potential for applications in scintillation crystals in gamma ray or X-ray detectors, as well as in thermal or environmental barrier coatings. Large high quality crystals of three members of the rare earth monosilicates family of compounds, R_2SiO_5 (with R = Dy, Ho, and Er), have been grown by the floating zone method, using a laser-diode-heated floating zone furnace. Crystal growths attempts were carried out using different parameters in order to determine the optimum conditions for the growth of these materials. The phase purity and the crystalline quality of the crystal boules were analysed using powder and Laue X-ray diffraction. Single crystal X-ray diffraction experiments were carried out to determine the crystal structures of the boules. The optimum conditions used for the crystal growth of R_2SiO_5 materials are reported. The phase purity and high crystalline quality of the crystals produced makes them ideal for detailed investigations of the intrinsic physical and chemical properties of these materials.



1. Introduction

Rare earth silicates have been thoroughly investigated over the past seven decades owing to their high potential for use in applications. To date, several chemical phases have been identified in the *R*-Si-O systems [1–23], e.g., rare earth monosilicates, R_2SiO_5 , disilicates, $R_2Si_2O_7$, apatite-type phases, $R_{4.67}(SiO_4)_3O$ or $R_4(SiO_4)_3$, and $R_4(Si_3O_{10})(SiO_4)$. The majority of the studies have been focused on the first two families of compounds, R_2SiO_5 and $R_2Si_2O_7$, mainly due to the polymorphism exhibited by these materials and their physical and chemical properties [19]. The structural phase diagram of the $R_2Si_2O_7$ shows a relatively high number of structural types possible in these materials [24–28], whereas R_2SiO_5 compounds exhibit a lower degree of polymorphism [19].

Two types of crystal structures can be found in the literature for the rare earth monosilicates, labelled in the literature as X1 (or A) and X2 (or B) [19]. The compounds R_2SiO_5 containing larger rare earth ions (with $R = La \rightarrow Gd$) crystallize in the X1-type structure. Rare earth monosilicate compounds that incorporate smaller rare earth ions (with $R = Tb \rightarrow Lu$) are dimorphic with temperature, at low temperature these systems crystallize in the X1-type, and at relatively high temperature (900 $\leq T \leq 1100$ °C), they undergo a structural phase transition to the X2-type structure [29,30].

The X1- R_2 SiO₅ polymorphs have a monoclinic ($P2_1/c$) crystal structure that is comprised of three different cation sites, and five anion sites. The larger trivalent rare earth R^{3+}



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). ions occupy a nine-fold and a seven-fold oxygen coordinated sites, whereas the smaller tetravalent Si⁴⁺ ion sit at the centre of tetra-fold coordinates sites [31]. The X2- R_2 SiO₅ polymrophs crystallize in a monoclinic (given in the literature as the different settings B2/b, C2/c and I2/a) crystal structure, containing the same number of cation and anion sites as the X1-type structure. The main difference to the X1-type is that the rare earth R^{3+} ions occupy a six-fold and a seven-fold oxygen coordinated sites, with the latter polyhedron described previously as a capped octahedron [32].

Rare earth monosilicates, R_2SiO_5 , have been extensively investigated due to their performance as laser host materials [33], scintillation crystals in gamma ray or X-ray detectors [34], as well as environmentally benign thermal barrier coatings (TBC/EBC) [35], and more recently, as quantum memory-storage materials [36]. Despite the communities interest for these materials, studies of the intrinsic properties of R_2SiO_5 have been hindered by the difficulties in preparing bulk phase pure samples [19,37], due to the presence, in the polycrystalline samples, of impurities consisting of other rare earth silicate compounds. The drawback arises from the similar thermal stability ranges of the various chemical and structural phases existing in the temperature-composition phase diagrams of the *R*-Si-O systems. To overcome this drawback and to study the fundamental properties of the rare earth monosilicates, high quality single crystal samples are required.

Pure and doped R_2SiO_5 crystals have been previously grown using the Czochralski [33,38–47], flux [19,29,41,48–50], micropulling-down [51,52] techniques. Er₂SiO₅ crystals were also obtained when attempting to synthesize the intermetallic compound ErFeRe [32]. Nevertheless, the $R_2 SiO_5$ crystals previously grown were prepared using solvents, yielding crystals of relatively small size, employing crucibles or relatively slow growth rates (1–6 mm/h). One of the "ideal" methods for the growth of relatively large, high quality single crystals is the floating zone technique. The effectiveness of this method arises from the lack of crucible or solvent during the growth process, preventing thus the contamination of the boules. A Tb doped Gd_2SiO_5 crystal was obtained using an optical floating zone (FZ) furnace, however, the authors reported limited information regarding the growth process and crystal quality of the grown boule [53]. Other related compounds, $R_2Si_2O_7$, have been previously grown using optical FZ furnaces, however, the boules tended to have a high number of thermally generated cracks, and single grains isolated from the crystal boules were of relatively small sizes [54,55]. Previous studies [31,56–61] have demonstrated the feasibility of the FZ technique using a laser floating zone furnace for preparing single crystals of relatively large size of members of the rare earth monosilicate family, Gd_2SiO_5 , $Nd_xGd_{2-x}SiO_5$ and $Lu_xGd_{2-x}SiO_5$ (pure and Nd or Yb doped).

In the present work, we report the growth, for the first time, of single crystals of the rare earth monosilicate compounds, R_2SiO_5 (with R = Dy, Ho, Er), by the FZ method, using a laser-diode-heated floating zone (LDFZ) furnace. This is especially important for the study of the physical and chemical properties intrinsic to these materials, and especially for the optical, thermal, mechanical properties, as well as chemical reactivity, degradation and corrosion, i.e., the key characteristics that would allow the use of the R_2SiO_5 compounds in applications, such as scintillation crystals in gamma ray or X-ray detectors, as well as in TBC/EBC. Furthermore, the results of our work point to the possibility of producing crystals of other *R*-Si-O systems by the floating zone method using a laser-diode-heated furnace, opening up the route to detailed investigations of this vast class of materials.

2. Materials and Methods

 R_2SiO_5 (with R = Dy, Ho, Er) were first synthesized in polycrystalline form by reacting powders of the starting oxides, Dy_2O_3 , Ho_2O_3 or Er_2O_3 (all of 99.99% purity), and silica, SiO_2 (\geq 99.995%). The results of our efforts to synthesise R_2SiO_5 in polycrystalline form are described elsewhere in a more detailed paper [62]. The polycrystalline material previously synthesised was used to prepare feed rods for the crystal growth experiments.

Crystals of the rare earth monosilicate compounds, R_2SiO_5 (with R = Dy, Ho, Er), were then grown using a LDFZ furnace (Model FZ-LD-5-200W-II-VPO-PC, Crystal Systems Corporation, Hokuto, Japan), using different growth conditions. The quality of the crystal boules was investigated using a Laue X-ray imaging system with a Photonic Science CCD camera. Small quantities of each crystal boule were then ground for phase purity analysis, whilst small pieces were cleaved from the crystals for investigations of the crystal structures of the R_2SiO_5 crystals.

Room temperature powder X-ray diffraction (PXRD) patterns were collected on a Panalytical X'Pert PRO MPD (Bragg-Brentano geometry) using Cu radiation ($\lambda_{K\alpha 1} = 1.5406$ Å and $\lambda_{K\alpha 2} = 1.5444$ Å, CuK α_1 to CuK α_2 ratio ~ 1:0.023), over an angular range of 10–110 ° in 2 θ , with a step size of 0.00835 °. For the Dy-containing sample, the pulse height distribution (PHD) settings were changed in order to reduce the fluorescence-induced background [63,64]. The lower level PHD setting of the X-celerator line (1D) detector was increased to 56%, while the upper level was maintained at 80%. The analysis of the diffractograms was performed using the Fullprof software suite [65].

Single crystal X-ray diffraction (SCXRD) experiments were carried out on small pieces (~20–40 µm) cleaved from R_2SiO_5 boules. SCXRD measurements were firstly performed on the as-grown Dy₂SiO₅, Ho₂SiO₅, and Er₂SiO₅ crystal fragments, at room temperature, on an Oxford Diffraction Xcalibur diffractometer. Data over large regions of reciprocal space were collected using Mo radiation ($\lambda_{K\alpha} = 0.71073$ Å). SCXRD data were then collected, at room temperature, on annealed crystal fragments isolated from the as-grown R_2SiO_5 boules. All the SCXRD data were indexed and integrated using CrysAlisPro (Rigaku) [66]. An empirical absorption correction was used, with the automatic configuration implemented in the ABSPACK module. The crystal structure was refined using SHELXL [67,68], as implemented in Olex2 [69].

3. Results and Discussion

Following our efforts in optimizing the synthesis of polycrystalline material of R_2SiO_5 (with R = Dy, Ho, Er), we have successfully prepared samples with considerably reduced levels of the impurity phases, following the same strategy as in Reference [62]. The polycrystalline material contained mainly the desired X2- R_2SiO_5 phase, and a small amount of impurities, $R_2Si_2O_7$ and $R_{4.67}(SiO_4)_3O$ phases (see Figure 1a–d).



Figure 1. Cont.



Figure 1. (a) Room temperature PXRD patterns of polycrystalline samples of rare earth monosilicates, R_2 SiO₅. PXRD profiles of (b) Dy₂SiO₅, (c) Ho₂SiO₅, and (d) Er₂SiO₅ polycrystalline samples in the range 31.5–34.5° scattering angle 2 θ (grey coloured region), with the reflections belonging to different phases marked using arrows (X2- R_2 SiO₅ in black, $R_{4.67}$ (SiO₄)₃O in light blue, D- R_2 Si₂O₇ in light purple, and other unidentified phase(s) in green colour).

3.1. Floating Zone Crystal Growth Using a Conventional Floating Zone Furnace

We first tried to grow a crystal boule of Ho_2SiO_5 in air atmosphere, in a flow of 1 L/min, using a four-mirror halogen lamp optical image furnace (Model FZ-T-10000-H-VI-VP-PC, Crystal Systems Corporation, Hokuto, Japan), equipped with four 1 kW halogen lamps, in similar conditions to the ones used for the crystal growth by the FZ method of similar rare earth silicate compounds [53,55]. Despite the fact that the feed rod could be molten, our attempts to form a stable molten zone failed. The feed rod did not appear to melt congruently, and it was not possible to ensure a good viscosity of the liquid that would allows us to maintain a molten zone and proceed further with the crystal growth experiment. Nonetheless, we were able to solidify a very small amount of the liquid on top of the seed rod. Phase purity analysis (not shown) carried out on the ground tip of the seed rod shows the presence of two phases, $X2-Ho_2SiO_5$ and $Ho_{4,67}(SiO_4)_3O$. The stabilisation of the Ho_{4.67}(SiO₄)₃O impurity is consistent with the observations made as a result of our attempts to synthesise pure, polycrystalline R_2SiO_5 samples. Annealing at high temperature and/or for an increased amount of time appears to facilitate the formation of the $Ho_{4.67}(SiO_4)_3O$ phase. Due to the temperature profile characteristic for the conventional halogen-heated FZ furnace [70], exposure to the high heat generated by the halogen lamps during the warming up phase of the growth process produces a similar effect, thus favoring the stabilisation of the $Ho_{4.67}(SiO_4)_3O$ phase to the detriment of the X2-Ho₂SiO₅ phase. Moreover, this result is in agreement with our hypothesis that the areas of thermal stability of the various chemical and structural phases existing in the R-Si-O systems overlap [19,27,55].

3.2. Floating Zone Crystal Growth Using a Laser-Diode-Heated Floating Zone Furnace

Following our failed attempts to grow $R_2 SiO_5$ crystals by the FZ method, using a conventional, halogen-heated, floating zone furnace, we then tried to prepare crystals of the rare earth monosilicates using a LDFZ furnace equipped with five 200 W InGaAs lasers ($\lambda = 976$ nm).

We have successfully grown crystals of the R_2SiO_5 (with R = Dy, Ho, and Er) by the FZ method, using the LDFZ furnace. A series of experiments were performed to optimize the crystal growth parameters and to obtain crystal boules of high crystalline quality. Several rare earth monosilicate crystal boules were obtained using different growth conditions, and a summary of the parameters used is given in Table 1. In all cases, polycrystalline rods were used as seeds to allow for a systematic study of the effect of the growth conditions on the quality of the crystals.

Chemical Composition	Growth Rate (mm/h)	Gas Atmosphere/ Pressure/Flow	Feed & Seed Rotation Rate (rpm)	Remarks					
Dy ₂ SiO ₅	10	air, ambient, 1 L/min	10	very fragile boule, with a few cracks					
	12	Ar:O ₂ (80%:20%), 5 bars	10	robust boule, despite a few cracks *					
Ho ₂ SiO ₅	10–15	air, ambient, 1 L/min	10	robust boule, without cracks					
	10	air, ambient	10	robust boule, despite one crack					
	12	Ar:O ₂ (80%:20%), 5 bars	10	robust boule, without cracks *					
Er ₂ SiO ₅	15	air, ambient, 1 L/min	10	very fragile boule, with a lot of cracks					
	8–15	air, ambient	10	very fragile boule, with a lot of cracks					
	12	Ar:O ₂ (80%:20%), 5 bars	10	less fragile boule, despite some cracks *					
	5	Ar:O ₂ (80%:20%), 5 bars	10	less fragile boule, despite some cracks					

Table 1. Summary of the conditions used for the growth using a LDFZ furnace of R_2SiO_5 (with R = Dy, Ho, and Er) crystal boules. All the boules grown were transparent to light, with a bright yellow (Dy₂SiO₅), a pale yellow/pink (Ho₂SiO₅), and a pink (Er₂SiO₅) colour.

* The sign marks the crystal boules of the best crystalline quality, and thus, the optimal growth conditions that allowed us to obtain these boules.

We have first attempted to grow crystal boules of R_2SiO_5 in air, at ambient pressure, in dynamic conditions (in a flow of air of 1 L/min), applying a similar strategy as for the crystal growth using the FZ technique of related compounds, the rare earth disilicates, $R_2Si_2O_7$ [55]. Although the R_2SiO_5 crystal boules appear to melt congruently, during the growth of the Dy₂SiO₅ and Er₂SiO₅ boules, small bubbles appeared in the molten zone (see Figure 2a). Moreover, as the growth progressed, the bubbles grew larger and, after a while, they were able to overcome the surface tension and disappear. The disappearance of a bubble did not lead to the separation of the molten zone owing to a sufficiently high viscosity and surface tension of the liquid. Nevertheless, analysis of the boules grown revealed the incorporation of gas bubbles into some of the crystal boules. Despite the presence of bubbles during the growth process, no signs of evaporation were observed, for any the growths, on the quartz tube surrounding the feed and seed rods.

Almost all the crystal boules tended to have a high number of thermally generated cracks, except in the case of the Ho₂SiO₅ boules. In all cases, the cracks developed in the first few millimetres of the crystal boules, and as the crystal growth progressed, the cracks propagated into the growing Dy₂SiO₅ and Er₂SiO₅ crystals. In the case of Ho₂SiO₅, the cracks disappeared almost completely after 5–10 mm from the beginning of the boule. Moreover, the Dy₂SiO₅ and Er₂SiO₅ crystal boules were very fragile and they cleaved or broke when removing them from the LDFZ furnace.

To reduce the thermal strain on the crystal boules during the crystal growth process and to prevent the formation of cracks, we have also carried out growth attempts of R_2SiO_5 in air, at ambient pressure, but in static conditions (without a flow of gas). In all cases, the change from dynamic to static conditions did not appear to have a significant effect in reducing the number of cracks in the crystal boules. Nevertheless, we observed that the formation of bubbles in the liquid seems to occur more often.

Previous studies highlighted the effect of employing higher gas pressure on the occurrence of bubbles in the melt during the growth process [70–72]. We have thus performed a new series of crystal growth trials, in an argon/oxygen gas mixture (Ar:O₂ = 80:20%), at 5 bars pressure. Our experiments showed that the application of a higher gas pressure suppresses the formation of bubbles in the melt for the growths of the R_2SiO_5 (with R = Dy, Ho, and Er) crystal boules, thus improving considerably the stability of the molten zone during the growth process (see Figures 2b and 3). During our growth experiments, the temperature of the melt was monitored continuously as a function of time. These data, shown in Figure 3, indicate that the during the crystal growths of the R_2SiO_5 compounds carried out in an argon/oxygen gas mixture (Ar:O₂ = 80:20%), at 5 bars pressure, the molten zone appeared to be more stable than the during the growth attempts performed in air, at ambient pressure, in static conditions. Furthermore, for almost the entire duration of the growth processes, the temperatures of the molten zones measured using the infrared thermometer were constant for the growth experiments that were stable and determined to be ~1896 °C for Dy₂SiO₅, 1922 °C in the case of Ho₂SiO₅, and 1945 °C for Er₂SiO₅, respectively. For comparison, the temperature profile recorded during the growth of a Ho₂SiO₅ crystal boule prepared in air, at ambient pressure, in static conditions, and at a growth rate of 10 mm/h, shows fluctuations in the temperature of the melt associated with the instability of the molten zone due to the formation of bubbles during the growth process. To test the accuracy of the infrared thermometer, we have grown crystal boules of TiO₂ using the LDFZ furnace, in air, at ambient pressure. During these growth experiments, the temperature of the melt (not shown) was found to vary in the temperature range 1835–1845 °C. These values are consistent with the previously reported value for the melting point of TiO₂ [73], suggesting thus that the temperatures of the melt for the *R*₂SiO₅ compounds may be well approximated using the infrared thermometer.



Figure 2. Floating zone growth of a boule of: (a) Dy_2SiO_5 in a flow of air of 1 L/min, at ambient pressure, at a growth rate of 10 mm/h. (b) Dy_2SiO_5 in an argon/oxygen gas mixture (Ar:O₂ = 80%:20%), at 5 bars pressure, at a growth rate of 12 mm/h.



Figure 3. Temperature profiles measured in situ, using an infrared thermometer, during the growths of R_2SiO_5 compounds using the LDFZ furnace, in a mixed argon/oxygen (Ar:O₂ = 80:20%) gas atmosphere, at a pressure of 5 bars and at a growth rate of 12 mm/h. The data corresponding to the crystal growth of Dy₂SiO₅ is shown in red, Ho₂SiO₅ in blue and Er₂SiO₅ in orange, respectively. The temperatures of the melts measured by the infrared thermometer are marked for each compound using horizontal dashed lines. For comparison, the temperature profile recorded during the growth of a Ho₂SiO₅ crystal boule prepared in air, at ambient pressure, in static conditions, and at a growth rate of 10 mm/h, is shown in light purple colour.

In all cases, applying a gas pressure had a positive effect in reducing the number of cracks in the crystal boules. During the growths of Dy₂SiO₅ and Ho₂SiO₅, the cracks completely disappeared after ~ 5 mm from the beginning of the boule. Note that the cracks that can be seen at the end of the Dy_2SiO_5 crystal boule on Figure 5a appeared after separation, upon cooling and at the moment when the lasers were switched off. Despite our attempts to reduce the occurrence of the thermally induced cracks, either by employing slower growth rates or changing the atmosphere conditions, we were not able to prepare a crack-free Er_2SiO_5 crystal boule. Nevertheless, our experiments suggest that the number of cracks can be reduced upon applying a high gas pressure, and furthermore, the grown boules are less fragile. A previous study reports on the effect of gas pressure on the temperature profile during the growth process [70]. The authors argue that the decrease in temperature observed at higher pressure of oxygen gas at all points along the crystal boule can be explained by a larger heat exchange between the grown crystal and greater number of gas molecules at higher pressure. The same study suggests that increasing the gas pressure could lead to an increased occurrence of cracks in the crystals, due to the a sharper gradient of temperature along the sample. Our results suggest that, in the case of the R_2SiO_5 compounds, known for their low thermal conductivities [31,74–79], the sharper temperature gradient characteristic of the LDFZ furnace coupled with a higher gas pressure of an argon/oxygen gas mixture help to promote the heat exchange between the crystal boule and the gas molecules and minimise the internal strain responsible for the formation of cracks. These two parameters were found to be crucial for the successful growth of large, high quality crystals of these materials by the FZ method.

Our results suggest that the cracks form to help to relieve the internal thermal strain of the crystal boule. The temperature profile measured using the infrared thermometer (see Figure 4) shows that the temperature along the crystal boule is much lower in the crack-free regions of the crystal boule (temperature profile measured at the surface of the boule at \sim 28 mm from the beginning of the crystal boule), while in the regions of the boule with cracks (at \sim 15 mm from the beginning of the crystal boule), anomalies can be observed in the data, possibly due to a reduced heat exchange between the boule and the gas atmosphere. The apparent lower temperature at the surface of the the polycrystalline seed (at \sim 8 mm) than at the surface of the grown crystal (at \sim 28 mm) can be explained by a heat exchange between the polycrystalline seed rod and the alumina holder used for mounting the seed.



Figure 4. Vertical temperature profiles measured in situ, using an infrared thermometer, during the growth of a Ho₂SiO₅ crystal boule in a mixed argon/oxygen (Ar:O₂ = 80:20%) gas atmosphere, at a pressure of 5 bars and at a growth rate of 12 mm/h. The maximum in temperature corresponds to the relative position of the molten zone. The black, red and orange curves are taken at 8, 15 and 28 mm, respectively, from the beginning of the boule.

Crystal boules of Dy₂SiO₅, Ho₂SiO₅ and Er₂SiO₅ were thus successfully grown by the FZ method, using the LDFZ furnace. The boules were typically 4–5 mm in diameter and 20–45 mm long. All the boules grown were transparent to light, with a bright yellow (Dy₂SiO₅), a pale yellow/pink (Ho₂SiO₅), and a pink (Er₂SiO₅) colour. Figures 5a–c show the photographs of the R_2 SiO₅ crystal boules grown in optimal conditions, i.e., in a mixed argon/oxygen (Ar:O₂ = 80:20%) gas atmosphere, at a pressure of 5 bars and at a growth rate of 12 mm/h.



Figure 5. Crystal boules of rare earth monosilicates, (a) Dy_2SiO_5 , (b) Ho_2SiO_5 , and (c) Er_2SiO_5 , grown using a LDFZ furnace and optimal conditions, i.e., in a mixed argon/oxygen (Ar:O₂ = 80:20%) gas atmosphere, at a pressure of 5 bars and at a growth rate of 12 mm/h.

All R_2SiO_5 crystal boules developed facets as they grew (at ~10 mm from the beginning of the crystal boule), and two to four strong facets were present for the remaining of the length of all grown crystals. All the crystal boules separated from the seed at ~3–4 mm from the beginning of the crystal boule. The quality of the grown boules was investigated by X-ray Laue diffraction and all the crystals showed similar crystalline quality despite the cracks and the different conditions employed during the crystal growth process. Figure 6 shows the Laue photographs taken along the length and on the cross section of the Ho₂SiO₅ crystal boule grown in air, at ambient pressure, and at a growth rate of 10 mm/h. The Laue patterns were identical along the whole length of the crystal boule, and moreover, the Laue photographs taken on the cross section (the crystal boule cleaved naturally at the position where the horizontal crack formed) were consistent with one another at several points.



Figure 6. X-ray Laue back reflection photographs taken at different points along the crystal length on the sides of the Ho_2SiO_5 crystal boule grown in air, at ambient pressure, and at a growth rate of 10 mm/h. Laue patterns taken on a cleaved cross section (where the crack can be seen) are consistent with one another at several points.

Structural and phase purity analysis was carried out at room temperature on ground crystal pieces cut from the as-grown R_2SiO_5 (with R = Dy, Ho, and Er) crystal boules and the PXRD patterns are displayed in Figures 7a–c. Profile matching to the monoclinic (I2/a) structure show no trace of impurities and confirm that the R_2SiO_5 crystals are belonging to the X2-type. The lattice parameters determined by PXRD are given in Table 2. The lattice parameters of the R_2SiO_5 crystal boules are in agreement with our results obtained for polycrystalline samples. Figure 7d shows the dependence of the lattice parameters on the effective ionic radii for the R_2SiO_5 (with R = Dy, Ho, and Er) crystals. All lattice parameters exhibit a monotonic decrease in agreement with the lanthanide contraction.



Figure 7. Room temperature PXRD patterns of ground as-grown R_2SiO_5 crystal pieces, presented in the following order: (a) Dy₂SiO₅, (b) Ho₂SiO₅, and (c) Er₂SiO₅. The experimental profiles (red closed circles) and full profile matching refinements (black solid lines) made using the X2-type with a monoclinic (I2/a) structure are shown, with the differences given by the blue solid lines. (d) Evolution of the lattice parameters, *a*, *b*, *c* and β , as a function of the effective ionic radii reported in Reference [80] for hexacoordinated R^{3+} ions.

Table 2. Lattice parameters for R_2SiO_5 (with R = Dy, Ho, and Er), refined from the room temperature PXRD data collected on ground pieces isolated from the as-grown crystal boules. The Bragg peaks were indexed with the monoclinic (I2/a) structure of the X2 polymorphs.

Chamical Composition		COF				
Chemical Composition	a (Å)	b (Å)	c (Å)	β (°)	GOF	
Dy ₂ SiO ₅	10.46578(2)	6.75135(1)	12.54282(2)	102.7299(1)	1.34	
Ho ₂ SiO ₅	10.41830(1)	6.72696(1)	12.50449(2)	102.6148(1)	1.76	
Er ₂ SiO ₅	10.37192(1)	6.70451(1)	12.46547(2)	102.5388(1)	1.96	

To determine the crystal parameters, small pieces were cleaved from the as-grown R_2SiO_5 crystal boules and SCXRD measurements were performed at room temperature. The crystal details obtained from the refinement of the SCXRD data measured at room temperature are given in Supplementary Data and Figure 8 shows the crystal structure

of X2- R_2 SiO₅ polymorphs. The characteristics of the oxygen polyhedra formed around the rare earth and silicon ions are given in Supplementary Data (data were obtained from VESTA software [81], based on bond valence parameters from Reference [82]). In all $R_2 SiO_5$ crystals, the average bond R-O lengths are larger in the seven-fold coordinated polyhedron, R_2O_7 , than in the six-fold oxygen coordinated rare earth sites, R_1O_6 . It should also be noted that the values of the quadratic elongation and bond angle variance for the R_1O_6 and SiO₄ polyhedra indicate that these polyhedra are distorted in comparison to the ideal octahedra and tetrahedra, respectively. Attempts to fit SCXRD data using different models for the occupancies of the cationic sites showed that the best model is the one in which the occupancies of the R and Si sites were fixed to the nominal value of 1. The crystal structures were refined using anisotropic thermal displacement parameters for the cationic sites, and isotropic thermal displacement parameters for the anionic sites. Attempts to fit the data using anisotropic displacement parameters for the oxygen sites yielded "pancake"-like ellipsoids due to the smaller weight of the O compared to the heavier R and Si. Further experiments of SCXRD at higher angles and/or using a different X-ray source (e.g., Ag radiation [83]), or alternatively single crystal neutron diffraction measurements, would yield data that would allow us to refine with a higher precision the thermal parameters for the oxygen sites.



Figure 8. Crystal structure of X2- R_2SiO_5 obtained from the refinement of the SCXRD data measured at room temperature. Representation of the local coordination around the cationic sites and the connection between the polyhedra (right).

Previous reports demonstrated that R_2SiO_5 (with $R = Tb \rightarrow Yb$, and Y) can also crystallize in the structural type stable at lower temperature, i.e., X1-structure [29,30]. In an attempt to obtain large, high quality crystals of the X1-type of R_2SiO_5 (with R = Dy, Ho, and Er), crystal fragments isolated from the as-grown boules were annealed, following the post-annealing procedure carried out on crystals of other materials that undergo thermally induced structural phase transitions [84,85]. Small R_2SiO_5 crystal fragments were annealed in air, at 950 °C, a temperature lower than the X1 \rightarrow X2-type structural phase transition temperature [29,30], for 30 days, and then slowly cooled to room temperature at a rate of 50 °C/h. The results of the long post-annealing experiments are confirmed by SCXRD data collected at room temperature on annealed R_2SiO_5 crystal fragments (see Supplementary Data; for simplification only the SCXRD data for the annealed Dy₂SiO₅ crystal fragment is shown). The crystal data of all annealed samples were identical with the parameters obtained for as-grown crystals. These results suggest that the X1 \rightarrow X2-type structural phase transition is irreversible in the conditions employed for the post-annealing of the R_2SiO_5 crystals.

4. Conclusions

High quality phase pure R_2 SiO₅ (with R = Dy, Ho, and Er) crystals were grown by the floating zone method using a laser-diode-heated floating zone furnace using different growth conditions. A summary of the crystal growth conditions used for the growths experiments is given in Table 1. The steep temperature gradient characteristic of the LDFZ furnace and a relatively high gas pressure were found to be essential for the growth of large, high quality, crack-free crystals of these materials by the FZ method. The quality and composition of the as-grown crystal boules was investigated using X-ray diffraction techniques. Powder and single crystal X-ray diffraction studies confirmed that the as-grown crystals belong to the X2-type. The results of the refinements of the room temperature powder X-ray data collected on the R_2SiO_5 crystals are listed in Table 2, while the results of the room temperature single crystal X-ray data can be found in the Supplementary Data. Annealing of the as-grown boules in air, for an extended period of time, at a temperature lower than the X1 \rightarrow X2-type structural phase transition confirms the irreversible nature of the phase transition in the conditions employed in the current study and the robustness of the X2 polymorphs at relatively high temperature and for a relatively long period of time. The availability of large size, pure phase crystals of R_2SiO_5 opens up the route for characterization experiments of the intrinsic physical and chemical properties of these materials with high potential for applications in scintillation crystals and TBC/EBC. Furthermore, our work demonstrates the feasibility of growing large, high quality, pure phase crystals of other R-Si-O systems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13121687/s1, Crystal parameters refined from the room temperature single crystal X-ray diffraction data collected on crystal pieces isolated from the as-grown Dy_2SiO_5 crystal (Tables S1–S3), annealed Dy_2SiO_5 crystal (Tables S4–S6), as-grown Ho_2SiO_5 crystal (Tables S7–S9), and as-grown Er_2SiO_5 crystal (Tables S10–S12).

Author Contributions: V.C.C.H.: Investigation, Formal analysis, Validation, Data Curation, Visualization, Writing—Original Draft. A.P.: Conceptualization, Methodology, Supervision, Project administration, Writing—Review & Editing. A.S.: Validation, Resources, Supervision, Writing—Review & Editing. M.C.H.: Conceptualization, Methodology, Resources, Validation, Project administration, Writing—Review & Editing. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of the R_2SiO_5 compounds (with R = Dy, Ho, and Er) are available from the authors.

Abbreviations

The following abbreviations are used in this manuscript:

TBCThermal barrier coatingEBCEnvironmental barrier coatingFZFloating zoneLDFZLaser-diode heated floating zonePXRDPowder X-ray diffractionPHDPulse height distributionSCXRDSingle crystal X-ray diffraction

References

- Toropov, N.A.; Bondar, I.A. Rare-earth silicates Communication 1. Phase diagram of the system La₂O₃-SiO₂. *Russ. Chem. Bull.* 1960, *9*, 145–148. [CrossRef]
- 2. Leonov, A.I.; Rudenko, V.S.; Keler, É.K. Reactions between Ce₂O₃ and SiO₂ at high temperatures. *Russ. Chem. Bull.* **1961**, 10, 1797–1804. [CrossRef]
- 3. Toropov, N.A.; Bondar, I.A. Lanthanum silicate 2La₂O₃·3SiO₂. Russ. Chem. Bull. 1959, 8, 528–530. [CrossRef]
- 4. Toropov, N.A.; Galakhov, F.Y.; Konovalova, S.F. Silicates of the rare earth elements Communication 2. Phase diagram of the binary system gadolinium oxide-silica. *Russ. Chem. Bull.* **1961**, *10*, 497–501. [CrossRef]
- 5. Toropov, N.A.; Bondar, I.A. Silicates of the rare earth elements Communication 3. Phase diagram of the binary system yttrium oxide-silica. *Russ. Chem. Bull.* **1961**, *10*, 502–508. [CrossRef]
- 6. Toropov, N.A.; Bondar, I.A. Silicates of rare-earth elements Comunication 4. New silicates in the system La₂O₃-SiO₂. *Russ. Chem. Bull.* **1961**, *10*, 682–687. [CrossRef]
- Toropov, N.A.; Galakhov, F.Y.; Konovalova, S.F. Silicates of the rare earth elements Communication 5. phase diagrams of the Dy₂O₃-SiO₂ and Er₂O₃-SiO₂ systems. *Russ. Chem. Bull.* **1961**, *10*, 1271–1277. [CrossRef]
- Toropov, N.A.; Bondar, I.A. Silicates of the rare earth elements Communication 6. Phase diagrams of the binary systems Sm₂O₃-SiO₂ and Yb₂O₃-SiO₂, and comparison of these silicates with the other rare earth element silicates which have been studied. *Russ. Chem. Bull.* **1961**, *10*, 1278–1285. [CrossRef]
- 9. Lazarev, A.N.; Tenisheva, T.F. The vibration spectra and structures of some rare earth element silicates. *Russ. Chem. Bull.* **1961**, *10*, 894–901. [CrossRef]
- 10. Keler, É.K.; Godina, N.A.; Savchenko, E.P. Reactions in the solid phase of silica with oxides of rare earth elements (La₂O₃, Nd₂O₃, Gd₂O₃). *Russ. Chem. Bull.* **1961**, *10*, 1613–1618. [CrossRef]
- 11. Keler, É.K.; Godina, N.A.; Savchenko, E.P. Reactions in the solid phase between silica and praeseodymium oxide. *Russ. Chem. Bull.* **1961**, *10*, 1619–1623. [CrossRef]
- 12. Bondar, I.A.; Galakhov, F.Y.; Toropov, N.A. Silicates of the rare earths Part 7. Solid solutions between silicates of lanthanum and samarium, gadolinium, and dysprosium. *Russ. Chem. Bull.* **1962**, *11*, 351–355. [CrossRef]
- Bondar, I.A. Silicates of the rare earths Part 8. Solid solutions between silicates of lanthanum and ytterbium. *Russ. Chem. Bull.* 1962, 11, 356–360. [CrossRef]
- 14. Toropov, N.A.; Galakhov, F.Y.; Konovalova, S.F. Silicates of the rare earths Part 9. Solid solutions between silicates of yttrium and erbium. *Russ. Chem. Bull.* **1962**, *11*, 689–693. [CrossRef]
- 15. Leonov, A.I. The valence of cerium in synthetic and natural cerium aluminates and silicates. Part 2. Cerium silicates. *Russ. Chem. Bull.* **1963**, *12*, 1922–1926. [CrossRef]
- 16. Felsche, J. A new cerium(III) orthosilicate with the apatite structure. Naturwissenschaften 1969, 56, 325–326. [CrossRef]
- 17. Felsche, J. A new silicate structure containing linear [Si₃O₁₀] groups. Naturwissenschaften 1972, 59, 35–36. [CrossRef]
- 18. Felsche, J. Rare earth silicates with the apatite structure. J. Solid State Chem. 1972, 5, 266–275. [CrossRef]
- 19. Felsche, J. The crystal chemistry of the rare-earth silicates. In *Proceedings of the Rare Earths*, Spring: Berlin/Heidelberg, Germany, 1973; pp. 99–197.
- 20. Bondar, I. Rare-earth silicates. Ceram. Int. 1982, 8, 83-89. [CrossRef]
- 21. Zhang, F.X.; Xiao, H.Y.; Lang, M.; Zhang, J.M.; Zhang, Y.; Weber, W.J.; Ewing, R.C. Structure and properties of rare earth silicates with the apatite structure at high pressure. *Phys. Chem. Miner.* **2013**, *40*, 817–825. [CrossRef]
- 22. Kobayashi, K.; Sakka, Y. Rudimental research progress of rare-earth silicate oxyapatites: Their identification as a new compound until discovery of their oxygen ion conductivity. *J. Ceram. Soc. Jpn.* **2014**, *122*, 649–663. [CrossRef]
- 23. Ptáček, P. Rare-earth Element-bearing Apatites and Oxyapatites. In *Apatites and Their Synthetic Analogues*; IntechOpen: Rijeka, Croatia, 2016; Chapter 5. [CrossRef]
- 24. Lazarev, A.N.; Tenisheva, T.F.; Bondar, I.A.; Koroleva, L.N. The structure of rare earth pyrosilicates. *Russ. Chem. Bull.* **1962**, *11*, 514–516. [CrossRef]
- 25. Felsche, J.; Hirsiger, W. The polymorphs of the rare-earth pyrosilicates R.E.₂Si₂O₇, [R.E.: La, Ce, Pr, Nd, Sm]. *J. Less-Common Met.* **1969**, *18*, 131–137. [CrossRef]
- 26. Smolin, Y.I.; Shepelev, Y.F. The crystal structures of the rare earth pyrosilicates. *Acta Cryst.* **1970**, *B26*, 484–492. [CrossRef]
- 27. Felsche, J. Polymorphism and crystal data of the rare-earth disilicates of type R.E.₂Si₂O₇. J. Less-Common Met. **1970**, 21, 1–14. [CrossRef]
- Chen, P.; Zhou, Y.; He, J.; Jiang, W.; Li, J.; Ni, H.; Zhang, Q.; Lin, L. On the Crystal Chemistry of RE₂Si₂O₇: Revisited Structures, Group–Subgroup Relationship, and Insights of Ce³⁺-Activated Radioluminescence. *Chem. Mater.* 2023, 35, 2635–2646. [CrossRef]
- Müller-Bunz, H.; Schleid, T. Über die Oxidsilicate M₂O[SiO₄] der schweren Lanthanoide (M = Dy-Lu) im A-Typ. Z. Anorg. Allg. Chem. 1999, 625, 613–618. [CrossRef]
- 30. Wang, J.; Tian, S.; Li, G.; Liao, F.; Jing, X. Preparation and X-ray characterization of low-temperature phases of R₂SiO₅ (R = rare earth elements). *Mater. Res. Bull.* **2001**, *36*, 1855–1861. [CrossRef]
- 31. Rey-García, F.; Costa, F.M.; Zaldo, C. Laser floating zone growth of Yb, or Nd, doped (Lu_{0.3}Gd_{0.7})₂SiO₅ oxyorthosilicate single-crystal rods with efficient laser performance. *J. Mater. Chem. C* 2020, *8*, 2065–2073. [CrossRef]

- 32. Phanon, D.; Černý, R. Crystal Structure of the B-type Dierbium Oxide ortho-Oxosilicate Er₂O[SiO₄]. *Z. Anorg. Allg. Chem.* **2008**, 634, 1833–1835. [CrossRef]
- 33. Ryba-Romanowski, W.; Strzęp, A.; Lisiecki, R.; Berkowski, M.; Rodriguez-Rodriguez, H.; Martin, I. Effect of substitution of lutetium by gadolinium on emission characteristics of $(Lu_xGd_{1-x})_2SiO_5$: Sm³⁺ single crystals. *Opt. Mater. Express* **2014**, *4*,739–752. [CrossRef]
- Seminko, V.; Maksimchuk, P.; Bespalova, I.; Malyukin, Y. Different Roles of Ce³⁺ Optical Centers in Oxyorthosilicate Nanocrystals at X-ray and UV Excitation. *Crystals* 2019, 9, 114. [CrossRef]
- 35. Ren, X.; Tian, Z.; Zhang, J.; Wang, J. Equiatomic quaternary (Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})₂SiO₅ silicate: A perspective multifunctional thermal and environmental barrier coating material. *Scr. Mater.* **2019**, *168*, 47–50. [CrossRef]
- Sukhanov, A.; Likerov, R.; Eremina, R.; Yatsyk, I.; Gavrilova, T.; Tarasov, V.; Zavartsev, Y.; Kutovoi, S. Crystal environment of impurity Nd³⁺ ion in yttrium and scandium orthosilicate crystals. *J. Magn. Reson.* 2018, 295, 12–16. [CrossRef]
- 37. Sun, Z.; Li, M.; Zhou, Y. Thermal properties of single-phase Y₂SiO₅. J. Eur. Ceram. Soc. 2009, 29, 551–557. [CrossRef]
- Belt, R.F.; Catalano, J.A. Single Crystal Growth of Cerium Doped Rare Earth Silicates. In Advanced Solid State Lasers; Optica Publishing Group: Washington, DC, USA, 1986; p. ThA2. [CrossRef]
- 39. Utsu, T.; Akiyama, S. Growth and applications of Gd₂SiO₅: Ce scintillators. J. Cryst. Growth **1991**, 109, 385–391. [CrossRef]
- 40. Tanaka, M.; Hara, K.; Kim, S.; Kondo, K.; Takano, H.; Kobayashi, M.; Ishibashi, H.; Kurashige, K.; Susa, K.; Ishii, M. Applications of cerium-doped gadolinium silicate Gd₂SiO₅:Ce scintillator to calorimeters in high-radiation environment. *Nucl. Instrum. Methods* **1998**, 404, 283–294. [CrossRef]
- Leonyuk, N.I.; Belokoneva, E.L.; Bocelli, G.; Righi, L.; Shvanskii, E.V.; Henrykhson, R.V.; Kulman, N.V.; Kozhbakhteeva, D.E. Crystal Growth and Structural Refinements of the Y₂SiO₅, Y₂Si₂O₇ and LaBSiO₅ Single Crystals. *Cryst. Res. Technol.* 1999, 34, 1175–1182. [CrossRef]
- Campos, S.; Petit, J.; Viana, B.; Jandl, S.; Vivien, D.; Ferrand, B. Spectroscopic investigation of the laser materials Yb³⁺:RE₂SiO₅, RE = Y, Sc, Lu. In *Solid State Lasers and Amplifiers*; Sennaroglu, A., Fujimoto, J.G., Pollock, C.R., Eds.; International Society for Optics and Photonics, SPIE: Bellingham, WA, USA, 2004; Volume 5460, pp. 335–343. [CrossRef]
- Lee, W.G.; Lee, D.H.; Kim, Y.K.; Kim, J.K.; Park, J.W. Growth and Characteristics of Gd₂SiO₅ Crystal Doped Ce³⁺. J. Nucl. Sci. Technol. 2008, 45, 572–574. [CrossRef]
- 44. Xu, X.; Xu, W.; Cheng, Y.; Li, D.; Cheng, S.; Wu, F.; Zhao, Z.; Zhou, G.; Xu, J. Investigation on upconversion luminescence in Yb³⁺/Er³⁺-codoped Gd₂SiO₅ single crystal. *Phys. Status Solidi A* **2010**, 207, 432–435. [CrossRef]
- 45. Liu, L.; Wang, C.; Zhang, D.; Zhang, Q.; Ning, K.; Wang, J.; Sun, X. Dielectric Relaxations and Phase Transition in Laser Crystals Gd₂SiO₅ and Yb-Doped Gd₂SiO₅. *J. Am. Ceram. Soc.* **2014**, *97*, 1823–1828. [CrossRef]
- Iskhakova, L.D.; Ilyukhin, A.B.; Kutovoi, S.A.; Vlasov, V.I.; Zavartsev, Y.D.; Tarasov, V.F.; Eremina, R.M. The crystal structure of new quantum memory-storage material Sc_{1.368}Y_{0.632}SiO₅. *Acta Cryst.* 2019, *C75*, 1202–1207. [CrossRef]
- 47. Jobbitt, N.L.; Wells, J.P.R.; Reid, M.F.; Longdell, J.J. Raman heterodyne determination of the magnetic anisotropy for the ground and optically excited states of Y₂SiO₅ doped with Sm³⁺. *Phys. Rev. B* **2021**, *103*, 205114. [CrossRef]
- Buisson, G.; Michel, C. Serie isomorphe d'orthosilicates (T₂SiO₅) et d'orthogermanates (T₂GeO₅) de terres rares. *Mat. Res. Bull.* 1968, 3, 193–197. [CrossRef]
- 49. Wanklyn, B.M.; Wondre, F.R.; Ansell, G.B.; Davison, W. New rare earth silicate crystals: Dy₂MoSi₂Al₄O₁₆, compounds in the systems R₂O₃-SiO₂-PbO, and a new form of R₂SiO₅. *J. Mater. Sci* **1975**, *10*, 1494–1500. [CrossRef]
- 50. Maqsood, A. Single crystal preparation of the rare earth oxyorthosilicates R₂SiO₅ (R = Er, Ho, Dy) by a flux method. *J. Mater. Sci. Lett.* **1984**, *3*, 65–67. [CrossRef]
- 51. Novoselov, A.; Ogino, H.; Yoshikawa, A.; Nikl, M.; Pejchal, J.; Mares, J.; Beitlerova, A.; D'Ambrosio, C.; Fukuda, T. Study on crystal growth and luminescence properties of Pr-doped RE₂SiO₅ (RE = Y, Lu). *J. Cryst. Growth* **2006**, *287*, 309–312. [CrossRef]
- Xue, Z.; Chen, L.; Zhao, S.; Yang, F.; An, R.; Wang, L.; Sun, Y.Y.; Feng, H.; Ding, D. Enhancement of Scintillation Properties of LYSO:Ce Crystals by Al Codoping. *Cryst. Growth Des.* 2023, 23, 4562–4570. [CrossRef]
- 53. Gao, M.; Zhang, P.; Luo, L.; Guo, R.; Wang, Y. Structural and optical characterization of Gd₂SiO₅:Tb³⁺ crystal obtained by optical floating zone method. *Optik* **2021**, 225, 165814. [CrossRef]
- 54. Nair, H.S.; DeLazzer, T.; Reeder, T.; Sikorski, A.; Hester, G.; Ross, K.A. Crystal Growth of Quantum Magnets in the Rare-Earth Pyrosilicate Family R₂Si₂O₇ (R = Yb, Er) Using the Optical Floating Zone Method. *Crystals* **2019**, *9*, 196. [CrossRef]
- 55. Ciomaga Hatnean, M.; Petrenko, O.A.; Lees, M.R.; Orton, T.E.; Balakrishnan, G. Optical Floating Zone Crystal Growth of Rare-Earth Disilicates, *R*₂Si₂O₇ (*R* = Er, Ho, and Tm). *Cryst. Growth Des.* **2020**, *20*, 6636–6648. [CrossRef]
- 56. De La Fuente, G.F.; Black, L.R.; Andrauskas, D.M.; Verdún, H.R. Growth of Nd-doped rare earth silicates by the laser floating zone method. *Solid State Ionics* **1989**, 32–33, 494–505. [CrossRef]
- Rey-García, F.; Sedrine, N.B.; Soares, M.R.; Fernandes, A.J.S.; Lopes, A.B.; Ferreira, N.M.; Monteiro, T.; Costa, F.M. Structural and optical characterization of Gd₂SiO₅ crystalline fibres obtained by laser floating zone. *Opt. Mater. Express* 2017, 7, 868–879. [CrossRef]
- 58. Rey-García, F.; Rodrigues, J.; Fernandes, A.J.S.; Soares, M.R.; Monteiro, T.; Costa, F.M. (Lu_{0.3}Gd_{0.7})₂SiO₅:Y³⁺ single crystals grown by the laser floating zone method: Structural and optical studies. *CrystEngComm* **2018**, *20*, 7386–7394. [CrossRef]

- 59. Rey-García, F.; Sedrine, N.B.; Fernandes, A.; Monteiro, T.; Costa, F. Shifting Lu₂SiO₅ crystal to eutectic structure by laser floating zone. *J. Eur. Ceram. Soc.* **2018**, *38*, 2059–2067. [CrossRef]
- 60. Rey-García, F.; Bao-Varela, C.; Costa, F.M. Laser floating zone: General overview focusing on the oxyorthosilicates growth. In *Synthesis Methods and Crystallization*; Marzouki, R., Ed.; IntechOpen: Rijeka, Croatia, 2019; Chapter 6. [CrossRef]
- 61. Rey-García, F.; Fernandes, A.; Costa, F. Influence of Lu content on $(Lu_xGd_{1-x})_2SiO_5$ oxyorthosilicates grown by Laser Floating Zone: Structural studies and transparency. *Mat. Res. Bull.* **2019**, *112*, 413–419. [CrossRef]
- 62. Ciomaga Hatnean, V.C.; Pui, A.; Simonov, A.; Ciomaga Hatnean, M. Materials Discovery Laboratory, Department of Materials, ETH Zurich, Switzerland. 2023, *manuscript in preparation*.
- 63. Mos, Y.M.; Vermeulen, A.C.; Buisman, C.J.; Weijma, J. X-ray Diffraction of Iron Containing Samples: The Importance of a Suitable Configuration. *Geomicrobiol. J.* 2018, 35, 511–517. [CrossRef]
- 64. Rao, S.G.; Shu, R.; Boyd, R.; Greczynski, G.; le Febvrier, A.; Eklund, P. Phase formation and structural evolution of multicomponent (CrFeCo)_{1-v}N_v films. *Surf. Coat. Technol* **2021**, 412, 127059. [CrossRef]
- 65. Rodríguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. *Phys. B Condens. Matter* **1993**, *192*, 55–69. [CrossRef]
- 66. CrysAlis PRO. Agilent; Agilent Technologies Ltd.: Yarnton, Oxfordshire, England, UK, 2014.
- 67. Sheldrick, G.M. A short history of SHELX. Acta Cryst. 2008, A64, 112–122. [CrossRef]
- 68. Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Cryst. 2015, C71, 3–8. [CrossRef]
- 69. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *OLEX2*: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [CrossRef]
- 70. Koohpayeh, S.; Fort, D.; Bradshaw, A.; Abell, J. Thermal characterization of an optical floating zone furnace: A direct link with controllable growth parameters. *J. Cryst. Growth* **2009**, *311*, 2513–2518. [CrossRef]
- 71. Koohpayeh, S.; Fort, D.; Abell, J. The optical floating zone technique: A review of experimental procedures with special reference to oxides. *Prog. Cryst. Growth Charact. Mater.* **2008**, *54*, 121–137. [CrossRef]
- Dabkowska, H.A.; Dabkowski, A.B. Crystal Growth of Oxides by Optical Floating Zone Technique. In Springer Handbook of Crystal Growth; Dhanaraj, G., Byrappa, K., Prasad, V., Dudley, M., Eds.; Springer: Berlin/Heidelberg, Germany, 2010; pp. 367–391. [CrossRef]
- 73. Pierre, P.D.S.S. A Note on the Melting Point of Titanium Dioxide. J. Am. Ceram. Soc. 1952, 35, 188. [CrossRef]
- 74. Tian, Z.; Zheng, L.; Wang, J.; Wan, P.; Li, J.; Wang, J. Theoretical and experimental determination of the major thermo-mechanical properties of RE₂SiO₅ (RE = Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) for environmental and thermal barrier coating applications. *J. Eur. Ceram. Soc.* **2016**, *36*, 189–202. [CrossRef]
- Li, Y.; Luo, Y.; Tian, Z.; Wang, J.; Wang, J. Theoretical exploration of the abnormal trend in lattice thermal conductivity for monosilicates RE₂SiO₅ (RE = Dy, Ho, Er, Tm, Yb and Lu). *J. Eur. Ceram. Soc.* 2018, *38*, 3539–3546. [CrossRef]
- 76. Tian, Z.; Zheng, L.; Hu, W.; Sun, L.; Zhang, J.; Wang, J. Tunable properties of (Ho_xY_{1-x})₂SiO₅ as damage self-monitoring environmental/thermal barrier coating candidates. *Sci. Rep.* **2019**, *9*, 415. [CrossRef]
- 77. Tian, Z.; Zhang, J.; Zhang, T.; Ren, X.; Hu, W.; Zheng, L.; Wang, J. Towards thermal barrier coating application for rare earth silicates RE₂SiO₅ (RE = La, Nd, Sm, Eu, and Gd). *J. Eur. Ceram. Soc.* **2019**, *39*, 1463–1476. [CrossRef]
- Zhong, X.; Zhu, T.; Niu, Y.; Zhou, H.; Zhang, L.; Zhang, X.; Li, Q.; Zheng, X. Effect of microstructure evolution and crystal structure on thermal properties for plasma-sprayed RE₂SiO₅ (RE = Gd, Y, Er) environmental barrier coatings. *J. Mater. Sci. Technol.* 2021, *85*, 141–151. [CrossRef]
- Chen, Z.; Tian, Z.; Zheng, L.; Ming, K.; Ren, X.; Wang, J.; Li, B. (Ho_{0.25}Lu_{0.25}Yb_{0.25}Eu_{0.25})₂SiO₅ high-entropy ceramic with low thermal conductivity, tunable thermal expansion coefficient, and excellent resistance to CMAS corrosion. *J. Adv. Ceram.* 2022, *11*, 1279–1293. [CrossRef]
- 80. Shannon, R.D.; Prewitt, C.T. Effective ionic radii in oxides and fluorides. Acta Cryst. 1969, B25, 925–946. [CrossRef]
- Momma, K.; Izumi, F. VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data. J. Appl. Cryst. 2011, 44, 1272–1276. [CrossRef]
- 82. Brese, N.E.; O'Keeffe, M. Bond-valence parameters for solids. Acta Cryst. 1991, B47, 192–197. [CrossRef]
- 83. Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* **2015**, *48*, 3–10. [CrossRef] [PubMed]
- 84. Ciomaga Hatnean, M.; Decorse, C.; Lees, M.R.; Petrenko, O.A.; Balakrishnan, G. Zirconate Pyrochlore Frustrated Magnets: Crystal Growth by the Floating Zone Technique. *Crystals* **2016**, *6*, 79. [CrossRef]
- 85. Sibille, R.; Lhotel, E.; Ciomaga Hatnean, M.; Nilsen, G.J.; Ehlers, G.; Cervellino, A.; Ressouche, E.; Frontzek, M.; Zaharko, O.; Pomjakushin, V.; et al. Coulomb spin liquid in anion-disordered pyrochlore Tb₂Hf₂O₇. *Nat. Commun.* **2017**, *8*, 892. [CrossRef]

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