Utilization of Traveling Solvent Floating Zone Method in the Growth of BaTi$_2$O$_5$ Crystal

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移動溶融帯法を用いた BaTi$_2$O$_5$ 単結晶の育成

ABSTRACT

BaTi$_2$O$_5$ has been shown to have highly anisotropic properties that are of interest in both research and industry. We will detail the application of an empirical new phase diagram for BaO-TiO$_2$ system, an in-depth description of the steps used to make each of the ceramics used in each experiment, a record of the utilization of the Floating Zone (FZ), Traveling Solvent Floating Zone (TSFZ), and Ceramic Feed Crystal Seed (CFCS) methods for growing BaTi$_2$O$_5$ crystals, and finally, some miscellaneous techniques relating to other aspects of the research. In addition to the description of the steps used to make each of the ceramics, tables consisting of the actual experimental details will also be given.

［Keywords : BaTi$_2$O$_5$, Crystal growth, Floating Zone Method, Traveling Solvent Floating Zone Method］

1. New Phase Diagram

BaTi$_2$O$_5$ is a very promising material for use in dielectric and piezoelectric devices operating at high temperatures [1,2]. The purpose of this research is to increase crystal size from what has been previously reported [1,3,4]. More specifically, the goal is to grow large sized single crystals. However, the stable BaTi$_2$O$_5$ formation region presented by Takashi Goto in an empirical BaO-TiO$_2$ phase diagram is very narrow [5], as shown by a shaded area in Fig. 1. According to the phase diagram, the liquid-phase line for BaTi$_2$O$_5$ is not flat, showing an incongruent melt. This would mean that a regular Floating Zone crystal growth technique would not be feasible. Using a Traveling Solvent Floating Zone crystal growth technique is thought to be a solution to overcome this problem. The phase diagram in Fig. 1 was utilized to determine the BaCO$_3$/TiO$_2$ ratio composition range and the best possible ceramic compositions. The composition ratio determines not only the melting temperature of the ceramic, but also the likelihood of formation of BaTi$_2$O$_5$ after cooling. However, since the region is so small, and the diagram is an empirical one, the accuracy of the diagram must be approached with caution.
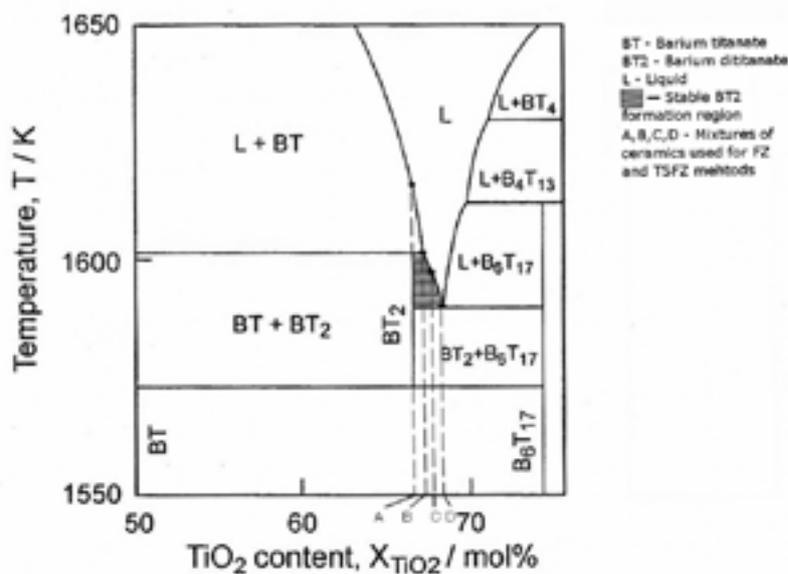

Fig. 1 New phase diagram as proposed by T. Goto in [5]

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2. Preparation of Ceramics

$BaCO_3$ (99.9% - Kanto Chemical) and TiO_2 (99.98% - Mitsuwa Pure Chemical) powders were used for growth of BaTi$_2$O$_5$ single crystals. The raw chemicals were weighed before and after evaporation of water, after that they were mixed. The mixed powders were also weighted before and after calcinations. The Table 1 lists the particular mixtures that were of interest: A, B and C mixture designated in Fig. 1. Due to time constraints, D mixture was not used but could be used in the future to aid verification of the new phase diagram.

Table 1 － Ceramic composition report

Ratio (BaCO$_3$:TiO$_2$)	Pre:Post Evap. Wt. (BaCO$_3$)	Pre:Post Evap. Wt. (TiO$_2$)	Final Wt (BaCO$_3$:TiO$_2$)	Post mix wt.	Post Calcine Wt.	Designation in Fig. 1
1.00 : 2.00	11.0322g : 11.0272g	8.7632g : 8.7669g	9.8769g : 7.9983g	17.7521g	17.0312g	A
1.00 : 2.09	9.8144g : 9.8004g	8.3227g : 8.3116g	9.4423g : 7.9980g	17.3813g	16.6404g	C
1.00 : 2.00	10.1103g : 10.1285g	8.1419g : 8.1341g	9.8768g : 7.9979g	17.8118g	17.0689g	A
1.00 : 2.06	9.6927g : 9.6431g	8.2673g : 8.2421g	9.5806g : 7.9981g	17.5420g	16.6770g	B
1.00 : 2.00*	10.0142g : 9.8769g	8.2160g : 8.2046g	9.8769g : 7.9980g	17.8240g	17.2591g	A
1.00 : 2.00	10.2145g : 10.1807g	8.2145g : 8.2070g	9.8769g : 7.9980g	17.7861g	17.5770g	A
1.00 : 2.09*	9.8476g : 9.8401g	8.3061g : 8.3022g	9.4425g : 7.9983g	16.1678g	15.4478g	C

* These samples were not packed correctly and were possibly contaminated during the firing and final baking process.

We summarize the general recipe for making a particular ceramic as follows:

1. Determine the ratio of $BaCO_3$ to TiO_2. In order to make BaTi$_2$O$_5$, the ratio starts at 1:2 and is theoretically still viable until 1.00 : 2.18 as shown in the phase diagram in Fig. 1.
2. Weigh the powders using an electronic force balance. Results are shown in Table 1.
3. Evaporate the H_2O from the samples by baking at 100-150 ℃ for 1+ hrs. This was done in a box furnace. The time varied from sample to sample as it seemed that the powders absorbed a negligible amount of H_2O and thus did not need to be heated for evaporation for long.
4. Record the post-evaporation weight of the powders, and proceed to reduce the powder's weight to the amount required to achieve the pre-determined ratio.
5. Mix powders together for 1 hr using an agate mortar. This was done in the automatic mixer, but can also be done by hand.
6. Weigh the powder post-mixing.
7. Calcine the powder for 8 hr. at 800 ℃ . This was performed in a flux furnace. The ramp-up and ramp-down times should both be 2 hrs.
8. Weigh the post-calcined powder.
9. Mix powder for 1 hr. The purpose of this mixing is to make the powder fine. If the powder is not made fine by the mixer (or whatever apparatus being used), then it will be necessary to manually crush the powder in order to produce good ceramics.
10. Pack the powder into rubber tubes（see Fig. 2）. In order to produce longer ceramics, it is necessary that the powder be packed tightly. The best method to accomplish this is to only add about half of a teaspoon of powder to the tube, press the powder until it is firm, then palpitate the powder for 5-15 seconds. Caution should be used while pounding the powder, as the rubber tube is easily damaged.
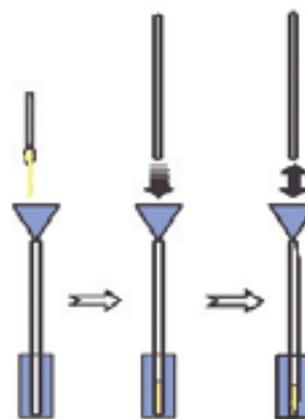

Fig. 2 － Depiction of packing

11. Evacuate the air from the powder using some type of compressor pump for 20+ minutes. This also varied from sample to sample, but the optimum amount of time for evacuation seemed to hover around 30 min.

12. Apply 2.0-2.3 tons of hydrostatic pressure for 10+ min (see Fig. 3). The purpose of the hydrostatic pressure is to pack the powder tightly enough that it stays in the form of a rod. For most applications, a longer rod is more desirable than a shorter rod, but the powder rod nearly always breaks into segments upon removal from the rubber tube. The optimum time for hydrostatic pressure is around 35 min.

13. Remove the powder rod from the rubber tube. This is best accomplished by gently laying the rubber tube on a table, cutting both ends of the rubber tube near the edges of the powder rod using scissors, and cutting the rubber tube with a small pair of scissors where the blade is held nearly parallel with the powder at all times.

14. Fire the powder rod for 2 hr. at 1150 ℃ This step is best done in the tube furnace. The ramp-up and ramp-down time should both be 6 hr.

15. Fire the ceramic rod for 12 hr. at 1300 ℃ again. This step is also performed in the tube furnace. The purpose is to increase the density of the ceramic that is necessary to maintain a good floating zone. The ramp-up time should be 8 hr. and the ramp down time should be 6 hr.
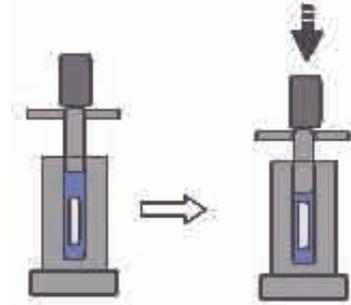
16. Measure the density of the ceramics.

Fig. 3 － Hydrostatic press

Here are tables containing all the details of the ceramics made during the summer internship:

Table 2 － Ceramic ratio chart

Designation	TiO$_2$ (%)	BaCO$_3$:TiO$_2$	Average Density (g/cm^3)
A	66.6667%	1.00 : 2.00	3.0249
B	67.3333%	1.00 : 2.06	3.0821
C	67.6667%	1.00 : 2.09	2.7727
D	68.5556%	1.00 : 2.18	N/A

Table 3 － Crystal growth report: Red － Ceramic Feed Crystal Feed, Blue － Floating Zone/Double Floating Zone and Green － Traveling Solvent Floating Zone

Date	Nomen	Ceramic Comp.	Method	Power (%)	Mirror Rate (mm/hr)	Top/Bottom rot. Rate (rpm)	Feed Rate (mm/hr)	O$_2$ Flow Rate (L/S)	Crystal Form.?
06/11/2007	FZ-1	A	FZ	39.40%	18.69	20/20	0.00	0.5	Success
06/19/2007	FZ-2	Ba$_{0.8}$Ca$_{0.2}$TiO$_3$	FZ	47.3%~46.7%	8.00	25/25	0.00	0.5	Failure
06/21/2007	FZ-3	C	FZ	38.5%~39.1%	8.50	15/20	0.00	0.5	Success
06/22/2007	FZ-4	C	FZ	38.5%~39.1%	8.50	15/20~20/20	6.50	0.5	Success
06/27/2007	DFZ-1	C	DFZ*	39.1%~38.6%	5.00	20/20	0.00	0.5	Success
06/28/2007	TSFZ-1	ACA	TSFZ	38.5%~38.0%	5.00	20/20	0.00	1.5 -> 0.5	Success
06/29/2007	TSFZ-2	ACA	TSFZ	38.1%~37.9%	5.00	20/20	4.50	1.2 -> 0.5	Success
07/02/2007	FZ-5	B	FZ	38.30%	8.50	20/20~25/25	5.00	0.5	Success
07/03/2007	TSFZ-3	ABA	TSFZ	38.3%~37.5%	6.00	20/20	0.00	0.5	Success
07/04/2007	CFCS-1	B	CFCS	41.0%~38.3%	10.00	13./10	0.00	0.5	Failure
07/05/2007	TSFZ-4	ABA	TSFZ	38.3%~38.1%	15.00	25/25	0.00	1.0	Success
07/11/2007	CFCS-2	A	CFCS	48.0%~37.1%	5.00	20/20	0.00	0.5	Success
07/12/2007	CFCS-3	B	CFCS	42.5%~37.9%	6.50	20/20	0.00	0.5	Success
07/17/2007	TSFZ-5	ACA	TSFZ	39.0%~37.8%	5.00	20/20	0.00	0.5	Success
07/17/2007	TSFZ-6	ACA	TSFZ	39.0%~38.1%	2.50	20/20	0.00	0.5	Success
07/18/2007	TSFZ-7	ABCA	TSFZ	39.0%~38.2%	6.00	25/25	0.00	0.5	Success

* DFZ refers to Double Floating Zone in which the floating zone method was performed on the same ceramic twice.

3. Crystal Growth

The next three sections contain pictures of the crystals formed from those methods. The pictures are all given designations from Table 3. The apparatus employed was an infrared radiation convergence-type heater with 4 halogen lamps as the radiation source (Crystal System Inc. 4000-H).

3.1   Floating Zone Method

Crystals in this section were grown using Floating Zone (FZ) method, which consists of moving a molten zone through two counter-spinning BaTi$_2$O$_5$ ceramics of the same composition. In general, the FZ method should not work when the liquid-phase line is not flat (incongruent melt) like BaTi$_2$O$_5$ formation in Fig. 1. However, this method had been performed for BaTi$_2$O$_5$ numerous times by different research groups with success. The grown-crystals were small needle-like crystals that averaged 1-4mm is length and 1-2mm is diameter. At the time of writing this report, there had not been any reported usage of the new phase diagram to determine the compositions of the ceramics (Fig. 1). The standard BaCO$_3$/TiO$_2$ ratio is 1:2. Below is a depiction of the FZ method (Fig. 4).
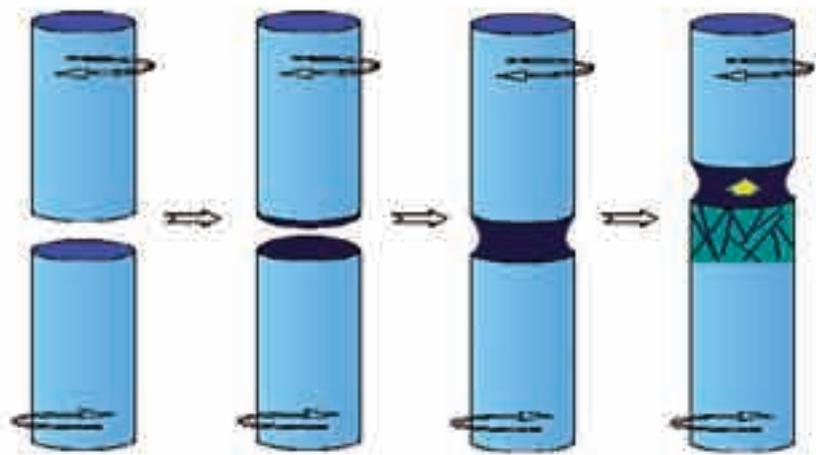

Fig. 4 — Floating Zone crystal growth method

FZ-1 — Crystals

FZ-3 — Crystals
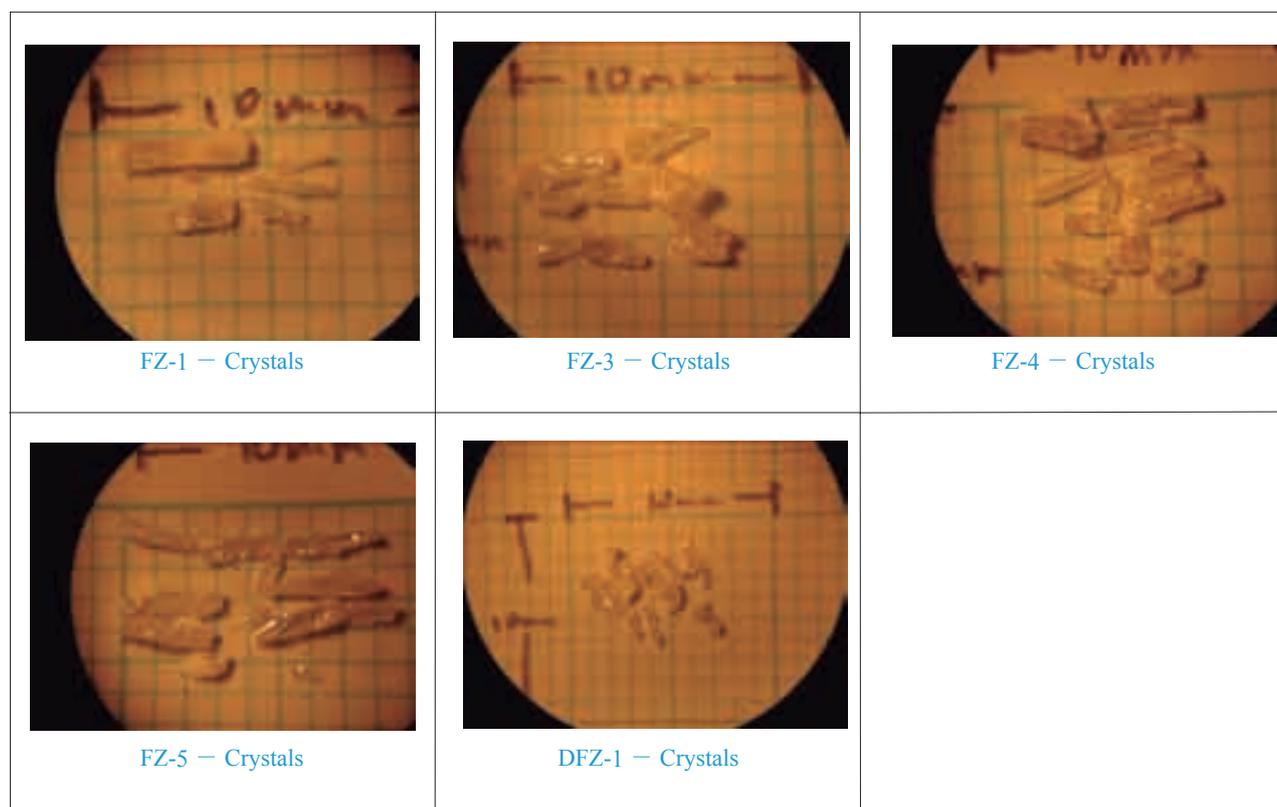
FZ-4 — Crystals

FZ-5 — Crystals

DFZ-1 — Crystals

Photo. 1 — Pictures of crystals grown using FZ method

3.2 Traveling Solvent Floating Zone Method

Crystals in this section were grown using the Traveling Solvent Floating Zone (TSFZ) method. The TSFZ technique was used because the liquid-phase line in the $BaTi_2O_5$ formation region is not flat (see Fig. 1). However, in this case the stable region is small enough that crystal formation is possible even with the regular floating zone method. So, in this instance, the primary difference between the FZ and TSFZ methods is that ceramics with different compositions are used. The primary feed and seed ceramics are both of the same composition. A section of ceramic differing in composition from the feed/seed is initially attached to the seed rod, combined with the feed rod using a zone melt, and then used as a starter feed for the regular FZ method. The process is explained more clearly in the depiction below (Fig. 5).
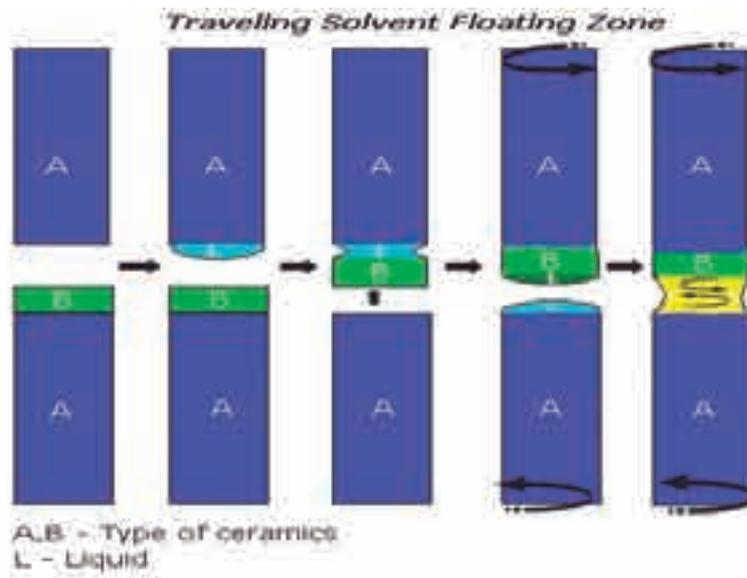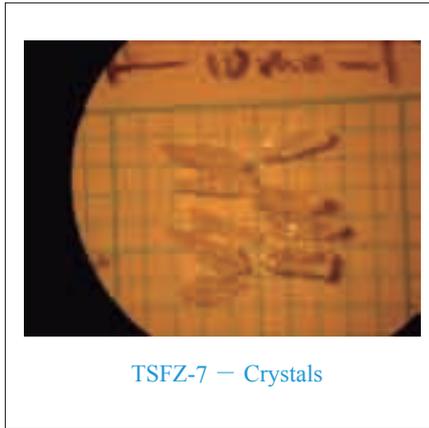

Fig. 5 — Depiction of Traveling Solvent Floating Zone technique

TSFZ-1 — Crystals

TSFZ-2 — Crystals

TSFZ-3 — Crystals

TSFZ-4 — Crystals

TSFZ-5 — Crystals

TSFZ-6 — Crystals

TSFZ-7 − Crystals

**Photo. 2** − Pictures of crystals grown using TSFZ method

3.3 Ceramic Feed Crystal Seed Method

This method is a first. The concept of Ceramic Feed Crystal Seed (CFCS) is a combination of FZ and Top-seeded Crystal Growth methods. A single or poly- crystal is used as a seed, and a ceramic rod for the feed. A small molten zone is created in the same manner as regular FZ, and the temperature of the melting zone is lowered so that the crystal and liquid can be combined in the molten zone without significantly damaging the crystal. After combination, the process is essentially the FZ method.

This method was very difficult to apply successfully as melting the feed ceramic required higher temperatures than what was required in a normal FZ application. The higher temperature either caused the ceramic to melt too quickly resulting in a large zone which was infeasible for combination with the crystal, or it would cause the crystal to melt when it approached the molten. Also, the thickness of the ceramic affected the stability of the melted zone. It seemed a thicker ceramic would, at least initially, produce too much liquid BaTi$_2$O$_5$ so that when bubbles destabilized in the melted zone, the molten zone liquid would drip over the edges of the seed crystal. The most effective technique to prevent the collapse of the zone seemed to be very careful maintenance of the molten zone temperature and relatively thin ceramics (less than 0.5 cm in diameter). The depiction below explains the process (Fig. 6).
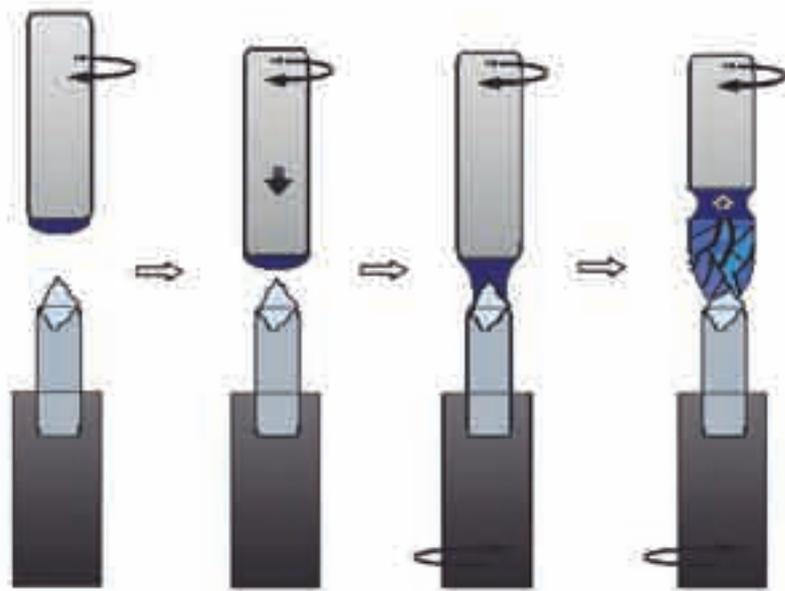
Fig. 6 − CFCS crystal growth method. Notice that the sample has already been melted at the beginning of the depiction

| CFCS-2 – Crystals | CFCS-3 – Crystals | CFCS – Setup |
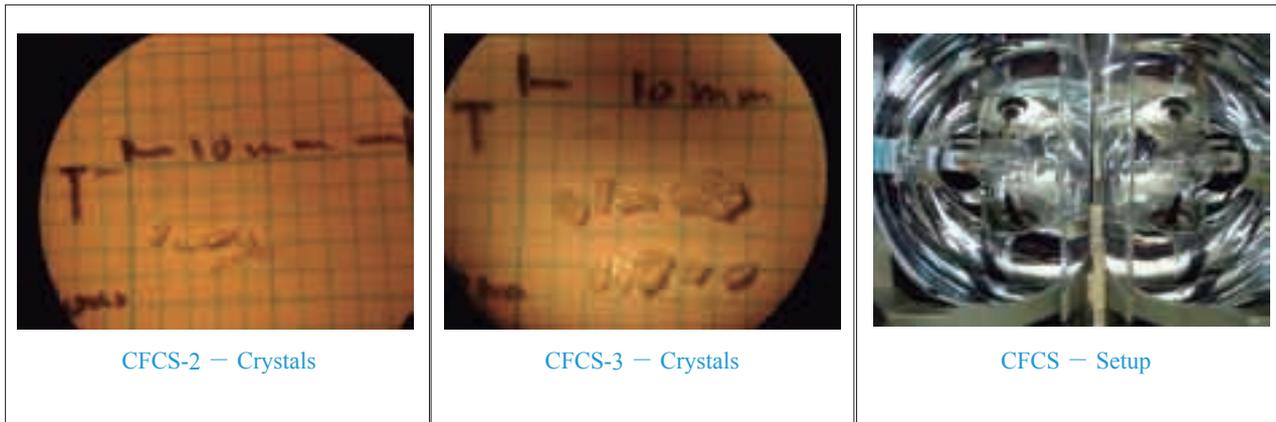
Photo. 3 – Pictures of crystal grown by CFCS method.

4. Miscellaneous Techniques

4.1 TSFZ Ceramic Stacking

The TSFZ method requires the use of ceramics that do not have the same composition. In order to accomplish this task, the ceramics must be stacked in some manner that allows them to be easily movable from the seed ceramic to the feed ceramic. Initially, this was accomplished by gluing the solvent ceramic to the feed ceramic (solvent ceramic - ceramic that differs in composition for the primary feed/seed ceramics). Because glue is used, a high O_2 flow rate is initially required to ensure the glue does not contaminate the experiment after it evaporates at low temperatures. However, this presents a significant problem. Once the glue evaporates, the solvent ceramic is only held in place by its own balance, and the high O_2 flow rate can easily cause the ceramic to become unstable and fall. In order to remedy this, a new stacking technique was developed that does not require the use of glue, and can be applied to stack multiple solvent layers reliably. The stacking technique is essentially drilling a small hole into a supporting ceramic; usually this is the seed ceramic. A part of the solvent ceramic is then fashioned into the shape of a stub that fits snuggly into the small hole. As long as the fit is not too snug, the solvent ceramic can be easily detached to the feed ceramic as depicted in the TSFZ section, and will not require a high oxygen flow. In addition, the setup is stable enough that the solvent ceramic will not fall unless significantly bumped. The depiction below explains the setup (Fig. 7).
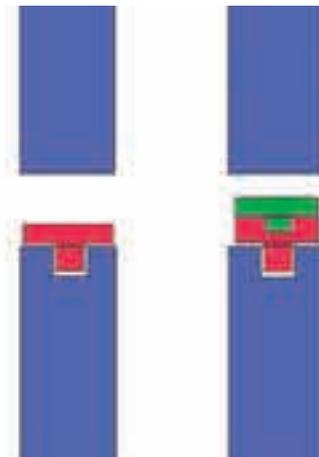
4.2 CFCS Sample Preparation

The CFCS technique requires a special seed setup because it requires that a single or poly-crystal be the only object in contact with the molten zone initially. The crystal is placed into a small platinum tube that has been embedded into some type of support base. In all cases up to this point, the support base has been a ceramic. The concept is similar to that of the TSFZ stacking technique: a hole with the diameter of the copper tube is drilled into the center of the support ceramic so that 0.5~2.0 cm of the platinum tube is in the supporting ceramic. A crystal is then placed into the platinum tube. Ideally, a crystal that has a diameter slightly larger than the platinum tube at some near-midway point in its structure should be used.

Fig. 7 – Cut-away of ceramics from TSFZ method

4.3 Pacifying O_2 Deficiencies

After performing the FZ, TSFZ, or CFCS methods, it was common for the crystallized sample to have O_2 deficiencies near the feed/seed interface. The primary cause for the O_2 deficiencies is cooling the sample too fast. In order to pacify the deficiencies, the sample was placed into the tube furnace and pacified at 1000℃ for 5 hr. with a very low O_2 flow throughout the entire process. The steps below explain the process.

1. Place sample in ceramic boat in the center of the tube furnace.
2. Start very low O_2 flow.
3. Keep the sample at 1000℃ for 5 hr. in O_2 gas flow. The ramp up and ramp down times are 6 hr. each.

4.4 Method for Taking out the Crystals

Taking out the crystals from the crystallized ceramic is probably the most important aspect of the entire experimental process. Before this newer method was introduced, recovering crystals consisted of crushing the crystallized ceramic into small chunks with a blunt object. This is counterproductive to the goal of this research (to recover large sized crystals) because crushing the crystals ceramic almost certainly crushed many of the crystals, large and small. The newer method is more time consuming, but preserves more of the crystals in the process. The process consists of splitting the ceramic along the growth direction of the crystallized ceramic, and using tweezers to both break the smaller chunks and pick apart the ceramics so that crystals are preserved. The process below gives an outline of what should be followed when recovering the crystals from the ceramics.

1. Stabilize the ceramic in a mixing bowl with the growth direction facing upwards (See Fig. 8). Usually, the feed/seed interface part of the ceramic has a small depression. This is the part of the ceramic that should be facing upwards.
2. Stabilize the sharp end of a thin, long, sharp object into the top of the ceramic.
3. Hammer gently on the sharp object until the ceramic splits. If the resulting chunks are still large, and there is not a large are of crystals visible, this process should be repeated until the chunks are not overly large. Large meaning comparable to the size of the un-split ceramic.
4. Use tweezers to pick apart the chunks until they are on par with the crystal sizes. Focus on only one section at a time, and whenever there are crystals visible, place the crystals aside in a container of some sort. It is also advisable to occasionally hammer gently on tweezers that can be firmly placed on the smaller chunks.
5. Place the crystals in a container of some sort. Do not place the crystals in wax paper and fold them as was done prior to this method. Fold the wax paper almost certainly crushes some of the crystals. If the crystals are to be placed in the wax paper, the paper should be folded very carefully as to not damage any of the crystals.
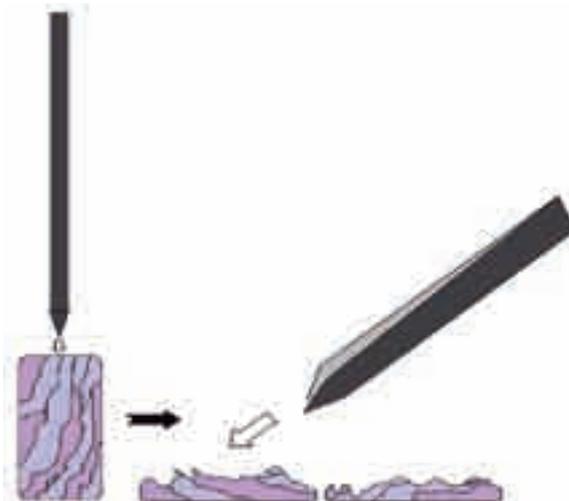

Fig. 8 － Visualization of steps 2 and 4

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