REVIEW ON CRYSTALLIZATION OF RARE EARTH METALS THROUGH CZOCHRALSKI METHOD

Vinay Chintala[1], Sivaprasad Rao Sajja[2], Jyothi Thati[3]*

ABSTRACT: -

This paper reviews the various topics regarding crystal growth, concentrating on developments in particular zones. This paper includes mainly four sections "The Czochralski Method 90 years after Jan Czochralski's invention, Growth and Characterization of SrI2 doped with Eu crystals fabricated using the Czochralski method, Rare earth crystals under Pulling growth technique, Rare Earth Elements and Intermetallic Compounds."

The first section explores the instabilities of the Czochralski method, a seminal strategy for Crystal growth. It explains its recent applications and its impact on crystal growth. The second section focuses on the Growth and Characterization of SrI2: Eu crystals using the Czochralski method. It describes the fabrication process, Crystal quality impacted by the Key parameters, and the spectroscopic properties of SrI2: Eu crystals. The third section focused on rare earth elements and Intermetallic compounds, pointing to their importance in crystal growth research. This section explores the unique properties and the applications of Rare earth elements, shedding light on their intermetallic compounds and their part in advancing materials science. The final section explores the pulling growth technique for growing rare earth single crystals. It analyzes the standards and applications of this technique, including its capability to produce high-quality crystals with desirable properties. Later advancements and progressions within the pulling growth technique are also examined here. This review paper provides an overview of significant topics in crystal growth, including the historical context, recent developments, challenges, and potential future directions in multiple areas.

Keywords: Czochralski method, Crystal growth technique, rare earth crystals, energy resolution, solid scintillation detectors, sintering process, pulling growth technique, Czochralski Pulling growth technique, micro-pulling down growth, Rare earth single crystals.

[1,2,3]*Department of Chemical Engineering, University College of Technology (A), Osmania University, Hyderabad Telangana -500007

***Corresponding Author: -** Jyothi Thati
*Email: kattajyothi@gmail.com

DOI: 10.53555/ecb/2023.12.Si13.214

1. INTRODUCTION:-

Jan Czochralski invented the Czochralski technique of growing single crystals from a melt 90 years ago [1]. This technique has become the most used method for dropping bulk single crystals, particularly semiconductor and optic crystals utilized in electronics and optics diligence. The Cz technique involves melting the feed material in a gauntlet with a freestanding liquid face and warming the melt using opposition or radio-frequency heaters. A seed crystal is dipped into the melt and sluggishly boosted while whirling, permitting the crystallization of a new crystal portion at the seed interface. The periphery of the crystal is regulated by conforming the heating power, pulling rate, and gyration rate. Four ways, including optical reflection and imaging, are utilized for periphery detection and regulator.

Although the Cz technique may feel simple, it requires sophisticated specialized knowledge and attention to grow large, high-quality single crystals suitable for industrial operations. Understanding the physicochemical relations and optimizing the process through computer simulation is pivotal. This paper aims to present the current condition of development and scientific knowledge about the Cz technique and discuss compulsory advancements for measuring up production and enhancing crystal quality. Achieving these advancements requires a deep analysis of heat and species transport mechanisms that impact process stability and crystal performance. Numerical simulation modeling has proved to be a necessary tool for understanding the Czochralski process. There is an increasing demand for low-cost sensors for prompt and dependable detection of radioactive isotopes. While semiconductor radiation sensors offer high energy resolution, their cost hinders wide practical use. The Laser Intensity, despite their lower energy resolution, presents a potentially more affordable volition. The commercially available halide scintillators contain NaI: Tl, CsI: Tl, and LaBr3: Ce. Advanced production ways such as the modified Czochralski- Kyropoulos [2] technology give the low-cost and high-yield product of NaI: Tl and CsI: Tl crystals. Still, the energy resolution of NaI Tl is roughly 6.5% at 662 keV [3], with limited volume for significant enhancement. Recent progress in raw material purification has led to the preface of bright Eu2+ unravel Alkali earth halide scintillation accouterments with energy resolutions within the range of 2.5% to 4% at 662 keV [4]. Despite several reports on the Alkali earth halite growth, there has been limited progress in developing large-scale crystal growth technologies to reduce production costs. Although moisture is to acclimatize conventional growth methods to halides, similar to SrI2: Eu, marketable sensors are still limited to a periphery of 2 inches [5]. Industrial-scale product for SrI2: Eu has not been achieved, despite its roughly 50-year development history. The study presents an essential approach concentrated on Czochralski growth and characterization of SrI2: Eu crystals with diameters up to 50 mm. Phase transition is an effective process for converting mass in materials formation. Crystallization is a phase transition from gas or liquid to a liquid state, involving the transition phase from disordered arrangement to ordered arrangements. Nucleation and crystal growth stages determine the crystallographic structure, shape, and quality [6]. Different growth Techniques, similar to Czochralski (Cz) and micro-pulling down methods, have been developed for Single crystal growth. The Czochralski technique has been essential for growing single crystals of semiconductors, essence, mariners, and synthetic gemstones. The Size control methods, similar to importing the increased crystal, are used in Cz growth. Micro-pulling down growth techniques are utilized for growing single crystal fibers [7,8]. Rare earth single crystals evaluated for their luminescence properties used in laser and scintillation operations. Rare earth crystal fibers join the advantages of single crystals and fiber lasers. Recent advancements in pulling techniques for rare earth single crystal growth include a fast growth parameter design grounded on chemical cling theory and progress in rare earth crystal fibers using the micro-pulling down growth method.

2. CHALLENGES IN THE CZOCHRALSKI GROWTH PROCESS:-

The growth of certain oxide materials using the Czochralski (Cz) method is limited to the instabilities caused by complex and emphatically non-linear radiative heat transfer conditions. These growth instabilities can ascribe to several factors:

1. Most oxide crystals have low thermal conductivity, constraining their capacity to disseminate heat effectively during growth.
2. Radiative heat transfer inside the crystal and melt is unique and contributes to growth instabilities.
3. The optical properties, which influence radiative heat transfer, strongly depend on the wavelength transmitted through the media.
4. The doping level of the crystal impacts its optical properties and, consequently, the radiative heat transfer.
5. The radiative heat transfer conditions, especially the viewing factors, change significantly over time during the Czochralski

growth process due to the changing geometry of the growing crystal.

These challenges and incorporating these factors 1-5 into oxide growth modeling pose the most prominent obstacle. Besides, modeling is further intricate by the lack of precise material parameters for considering temperature-dependent optical properties and doping levels, particularly at high temperatures (up to 2000°C). In any case, a recent advance has been made in recreating the Czochralski growth of oxide crystals whereas considering these phenomena. Figure 1 illustrates an example simulation of the change of a convex to a concave interface shape during the Czochralski growth of YVO4 crystals, considered efficiently by Tsukada [9]. Another significant disturbance in Czochralsk's development is the event of spiral growth, exemplified by three occasions in Figure 2. By numerically simulating the flow field within the melt, the authors found that this instability can be assigned a bifurcation. Based on these investigations, they were recently able to avoid the spiral growth of DyScO3 for the first time (shown in Fig. 3) [11]. Regardless of the challenges examined earlier, The Czochralski technique is employed worldwide to grow a wide range of oxide and halide crystals with exceptional properties. Due to space restrictions, only some illustrations as shown in Figures 3 and 4. For a comprehensive review of the growth and characterization of technologically significant oxide crystals, readers are encouraged to refer to the review article by Lal et al. [13].

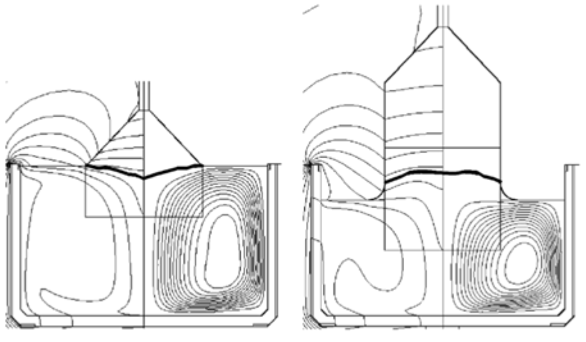


Fig. 1. Computing the interface conversion in yttrium orthovanadate (YVO4) crystals grown by the Czochralski method (with Photonic Materials). [9]

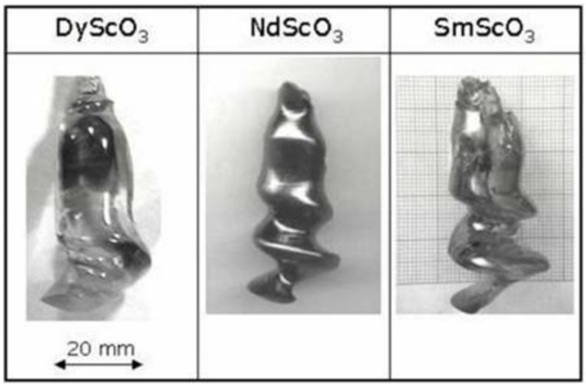


Fig. 2. Rare earth scan-date crystals and their spiral formation in Czochralski growth. [10]

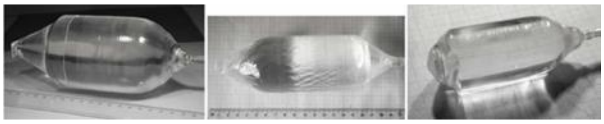


Fig. 3. Oxide crystals grown by the Czochralski method at IKZ Berlin [11]: Sapphire (left), LiAlO2 (middle), and DyScO3 (right) with c, [100], and [110] orientations respectively.

Fig. 4. Czochralski method for growing CaF2 crystal with 200 mm diameter. [12]

3. EXPERIMENTAL RESULT ON SrI2:Eu CRSTALS:-

The Czochralski method is to be used to fabricate and characterize SrI2: Eu crystals:

The following course of action, outlined in [14], was used for incorporating the Strontium Iodide using Eu crystal with a normality (N) of 4. In this process, the pH of water has maintained below 6. On the other hand, EuI2 raw material with a normality of 4 was synthesized by reacting Eu2O3 with NH4I. The concentration of Eu2+ within the material was around 0.5 atomic percent, and the concentration of Eu2+ crystals is to be determined by titrimetric analysis.

To assess the energy resolution beneath irradiation with 662 keV, γ-quanta from the 137 Cs isotope, amplitude spectra were measured using a set-up portrayed in [15]. The set-up utilized an R1307 PMT with a bias voltage of 690V and a shaping time of 12 µs. Pulsed X-ray decay measurements were conducted using the same light collection system, in addition to the Hamamatsu N5084 light-excited X-ray tube working at 30 kV as the irradiation source. The tubing was optically excited using a Hamamatsu PLP-10 picosecond light pulser. Different radioactive sources having energies ranging from 31 to 1274 keV, were employed for this reason. Detailed data regarding these computations can be found in the outline [16].

CRYSTAL GROWTH:-

The Czochralski growth crystals exhibited good uniformity of light yield and energy resolution. When 662 keV γ-quanta energized them, detectors from different crystal parts had a high energy resolution of 3.6±0.1%, as shown in Fig. 5. Surprisingly, this high energy resolution was achieved even with weak Eu-doping whereas, Bridgman-grown crystals required a concentration of around five atomic percent of Eu to achieve comparable results. It suggests the potential to maintain a very high energy resolution in SrI2: Eu, even with a significant decrease within the concentration of the expensive EuI2 activator [17,18]. The lower Eu2+ concentration makes a difference in anticipating solid self-absorption in largesize crystals. The improved quality of raw materials likely contributes to the high energy resolution in Czochralski growth crystals. Likewise, The Czochralski method's advantages, such as better uniformity of Eu distribution due to efficient melt mixing and easier control of the crystallization interface, support a high energy resolution. By reducing the activator concentration, as depicted in Figure 6, the rationale for further reducing Eu concentrations dependent on the observed faster scintillation decay time. Decay constant values obtained from experimental data are in according to the previous findings and affirm the reduction of self-absorption phenomena in the weakly doped crystal [19]. An extra benefit of SrI2: Eu crystals is their exceptional proportionality between light yield and excitation energy. A comparison of Czochralski growth and Bridgman growth crystals in Fig. 7 reveals similar trends in the light yield variation [16], with fluctuations inside ±5% relative to the light yield at 662 keV excitations. The Czochralski growth crystal maintains this outstanding nonproportionality behavior.

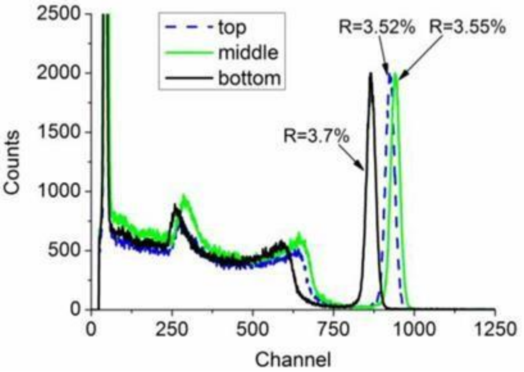


Fig. 5. Various parts of a Cz-grown strontium iodide crystal triggered by europium and their amplitude spectra as scintillation detectors. [17,18]

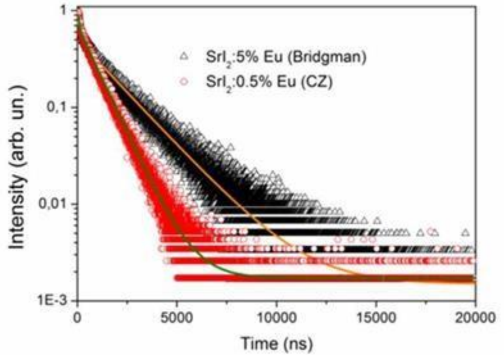


Fig. 6. Decay curves of X-ray energized crystals from Bridgman and Cz growth techniques. [19]

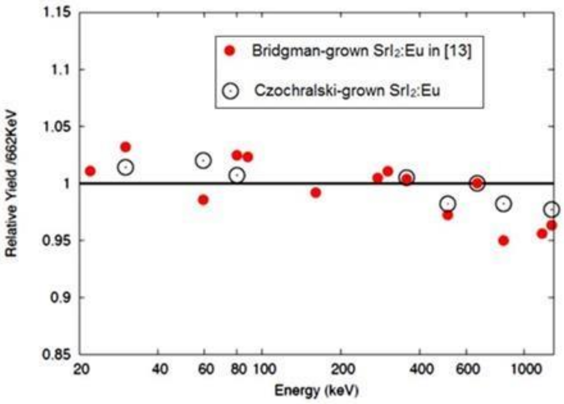


Fig. 7. Cz-grown vs. Bridgman-grown SrI2:Eu: non-proportionality by various radioactive sources normalized by 662 keV light yield. [16]

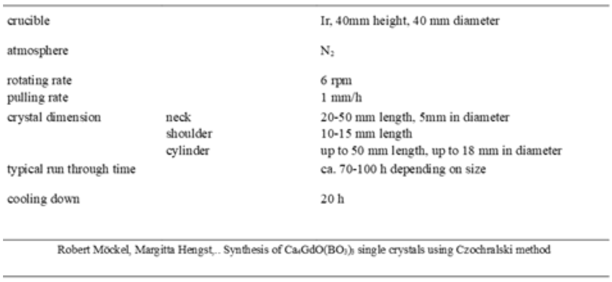
4. CRYSTAL GROWTH AND CHARACTERIZATION of Ca4GdO(BO3)3 & XRD ANALYSIS :-

The sintering process utilized parameters mentioned in Table 1, and XRD measurements confirmed the purity of the resulting material as Ca4GdO(BO3)3. The measured weight loss during sintering slightly exceeded the theoretical value (26.2 wt.% vs. 25.66 wt.%), likely due to water loss from adsorbed B2O3[21], compensated by an excess. DSC measurements supported this finding, disproving the suggested evaporation of B2O3.

Crystals with cylindrical shapes, up to 18 mm in diameter and 50 mm in length, were grown in both the [010] and [001] directions (Fig.8 a and b, respectively). These crystals were generally defectfree, transparent, colorless, and non-hygroscopic. Growth in the c-direction has been more challenging compared to the b-direction. Cleavage occurred along [201] and [010], as previously reported [20]. Single crystals grown in the c-axis direction had smooth surfaces with radial cross-sections and few growth striations, while the b-direction exhibited a rhomboidal shape with partial growth striations. The crystal faces (201) and (101) were considerable, while the (100)-faces mostly disappeared due to their fast growth [22].

Rhomboidal features also appeared on [001] grown crystals, particularly in the shoulder regions, sometimes protruding up to 1-2 mm from the surface (Fig.9). Asymmetric growth occurred in the [010] direction, likely due to differences in lattice constants and growth velocities.

Table 1. Crystal growth parameters



crucible		Ir, 40mm height, 40 mm diameter
atmosphere		N_2
rotating rate		6 rpm
pulling rate		1 mm/h
crystal dimension	neck	20-50 mm length, 5mm in diameter
	shoulder	10-15 mm length
	cylinder	up to 50 mm length, up to 18 mm in diameter
typical run through time		ca. 70-100 h depending on size
cooling down		20 h

Robert Möckel, Margitta Hengst,.. Synthesis of $Ca_4GdO(BO_3)_3$ single crystals using Czochralski method

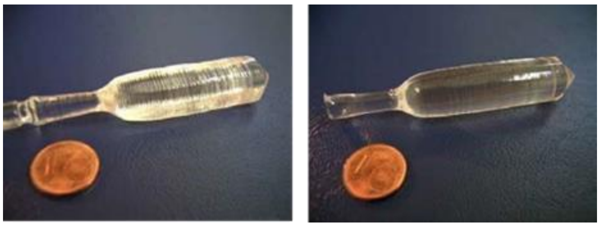


Fig. 8. Crystals are grown in (a) b-direction and (b) c-direction.

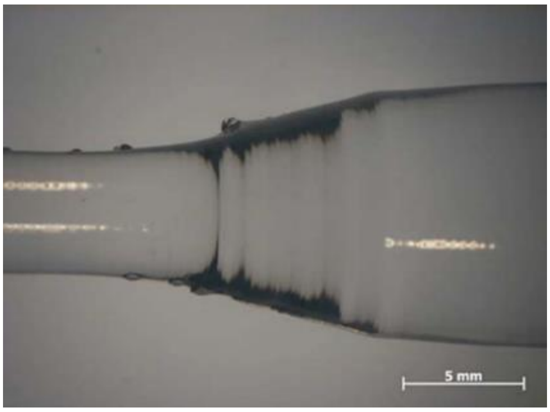


Fig. 9. [001]-grown crystal and inherent outgrowth features [20].

5. RARE EARTH ELEMENTS AND INTERMETALLIC COMPOUNDS:-

The most widely used and rewarding method for growing liquid-solid single crystals of rare earth elements and intermetallic compounds is the Czochralski technique. Figure.10 shows the essential features. The melt contains some forms of the crucible, hot or cold, which is ideally hemispherical to encourage thorough mixing.

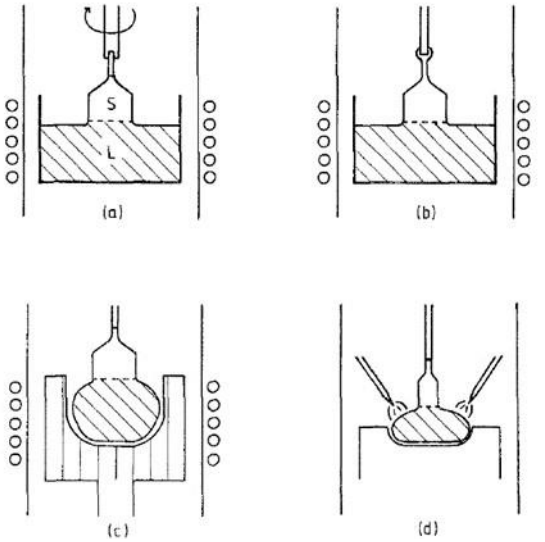


Fig. 10. Schematic diagram of the Czochralski technique: (a) hot crucible seeded growth; (b) necking random growth; (c) cold crucible induction heating; and (d) cold crucible tri-arc heating.[23,24]

This method involves pulling a crystal from the melt by establishing a solid-liquid interface using a seed rod. The shape and size of the crystals are to be determined by the power input to the melt and the extraction rate. Rotation of the crucible and seed rod sometimes is used to ensure thorough mixing and minimize thermal gradients. The Czochralski technique offers advantages such as precise control of the solid-liquid interface, visual observation of its interface, and lack of physical constraint on the growing crystal. If a single crystal isn't available for a seed rod, a polycrystalline rod or a W or Mo rod can be used. A singleorientation grain is to grow from a polycrystalline matrix by reducing the diameter of the solidified material and then increasing it again. The size of the crystal varied by manipulating the diameter, limited by the size of a crucible shown in Fig.11. Both hot and cold crucible versions of the Czochralski technique operate in high vacuum or inert gas conditions[23,24]. This method can produce crystals with a high degree of perfection but requires precise temperature and growth rate control to avoid fluctuations that could be affected the crystal quality. The shape and position of the solid-liquid interface are crucial for successful growth.

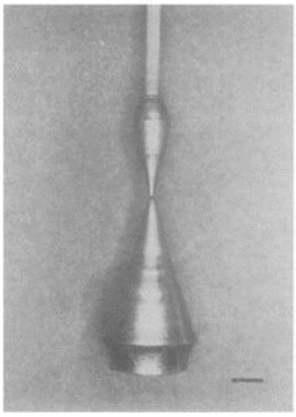


Fig.11. From a tungsten crucible, an RAI_2 boule was grown using a tungsten pull rod.[25]

Various crucible materials have been used, with W being the important choice due to its lower solubility character. Induction-heated W crucibles employ for crystal growth of rare earth intermetallic compounds, with good results in terms of crystal quality. Cold crucibles have been used either employing Hukin-type designs or tri-arc furnaces. Tri-arc melting has found wide applications for materials preparation and single-crystal growth. It has been successful in the growing crystals of various intermetallic compounds, including those of the R2Fe14B series. Overall, the Czochralski technique, whether using hot or cold crucibles, has proven effective in growing single crystals of rare earth elements and intermetallic compounds, offering control over crystal quality and size.

6. PULLING GROWTH TECHNIQUE TOWARDS RARE EARTH SINGLE CRYSTALS:-

The process of developing a crystal fiber using the micro-pulling down method, as shown in Fig.12.The raw materials for melt are pulled down from a crucible through a capillary tube, forming a thin molten zone known as the Meniscus. The crystal grows under specific temperatures and pulling-down rate conditions. The micro-pulling down technique offers advantages such as faster growth and the ability to shape the crystal [26]. This technique has gained attention for mass production compared to other methods.

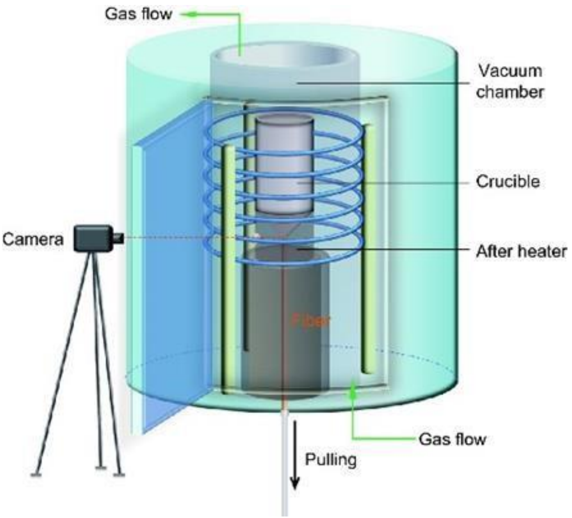


Fig. 12. A schematic of the micro-pulling down the furnace and the process of growing crystal fiber. (color online).[26]

Rare earth crystal fibers exhibit a unique crystallographic structure, high aspect ratio, and large specific surface area similar to glass fibers. They combine the advantages of traditional single-crystal lasers and fiber lasers, including exceptional optical & thermal properties and high laser conversion efficiency. Research on rare earth crystal optical fibers divides into two approaches: one influenced by traditional glass fiber lasers and the other proposing an intermediate transition between bulk solid-state lasers and fiber lasers. Various research groups, such as Maxwell's team and Harrington's research group, form significant contributions to this field. Notably, Rutgers University and Shasta Crystals has grown single crystal optical fibers by using the laser heating pedestal method [27,28], achieving stable growth of rare earth-doped YAG fibers. The United States Army Research Laboratory outlined the first optical waveguide laser output using single crystal fiber. Delen-et-al conducted continuous laser studies using different crystal fibers [29], demonstrating high output power and efficiency [30,31]. The micro-pulling down growth process involves complex melt flow and heat transfer, influenced by convection, surface tension, and temperature gradients. The maximum pulling rate approximation theory and thermal equilibrium at the growing interface are essential considerations. Recent non-steady state calculations have explored factors affecting micro-pulling down growth and proposed techniques to improve dopant concentration distribution in YAG crystals [32,33].

REFERENCES:-

1. J. Czochralski, Z. Phys. Chemie 92, 219 (1918).

2. A Gektin, V. Goriletskiy, B. Zaslavskiy, "Continuous growth of large halide scintillation crystals", in Crystal Growth Technology. From Fundamentals and Simulation to Large-Scale Production, H.J. Scheel and P. Capper Eds., Weinheim, Germany, Wiley-VCH Verlag GmbH, 2008, pp. 351–379.
3. N. Shiran, A. Gektin, Y. Boyarintseva, S. Vasyukov, A. Boyarintsev, V. Pedash, S. Tkachenko, O. Zelenskaya, and D. Zosim, "Modification of NaI crystal scintillation properties by Eu-doping", Opt. Mater., vol. 32, Iss. 10, pp. 1345-1348, Aug. 2010, doi:10.1016/j.optmat.2010.04.014.
4. E. Rowe, E. Tupitsyn, B. Wiggins, P. Bhattacharya, L. Matei, M. Groza, V. Buliga, A. Burger, P. Beck, N. Cherepy, and S. Payne, "Double Salts Iodide Scintillators: Cesium Barium Iodide, Cesium Calcium Iodide, and Barium Bromine Iodide", Cryst. Res. Technol., vol. 48, Iss. 4, pp. 227–235, Apr 2013, doi:10.1002/crat.201300010.
5. A. Yoshikawa, Y. Yokota, K. Kamada et.al. "Development and melt growth of novel scintillating halide crystals", Opt. Mater., In Press, doi:10.1016/j.optmat.2017.03.043
6. Whittaker M L, Smeets P J M, Asayesh-Ardakani H, et al. Multi-step crystallization of barium carbonate: rapid interconversion of amorphous and crystalline precursors. Angew Chem Int Ed, 2017, 56:
7. Hu Q, Jia Z, Veronesi S, et al. Crystal growth and optimization of Pr: CaGdAlO4 by the flux-Czochralski method. CrystEngComm, 2018, 20: 590–596
8. Kononets V, Benamara O, Patton G, et al. Growth of Ce-doped LGSO fiber-shaped crystals by the micro pulling down technique. J Cryst Growth, 2015, 412: 95–102
9. T. Tsukuda, M. Kobayashi, and C. Jing, J. Cryst. Growth 303, 150 (2007).
10. R. Uecker, H. Wilke, D. G. Schlom, B. Velickov, P. Reiche, A. Polity, M. Bernhagen, and M. Rossberg, J.Cryst. Growth 295, 84 (2006).
11. R. Uecker and H. Wilke, (private communication 2007).
12. Tokuyama Corp. Ltd. (unpublished).
13. K. Lal, R. V. A. Murthy, A. Choubey, and N. Goswami, in Crystal Growth Technology, K. Byrappa and T. Ohachi (Eds.), Springer Series in Materials Processing (2002) pp. 387-417.
14. N. Rebrova, V. Cherginets, T. Ponomarenko et.al., "Scintillation materials based on BaxSr1-xI2:Eu solid solutions", Func. Mater., vol. 16, no. 4, pp. 501-504, Dec. 2009
15. E. Galenin, V. Baumer, I. Gerasymov, S. Tkachenko, O. Sidletskiy, "Characterization of bismuth germanate crystals grown by EFG method", Cryst. Res. Technol., vol. 50, no. 2, pp. 150–154, Jan. 2015,doi:10.1002/crat.201400237
16. S. Lam, S.E. Swider, A. Datta, S. Motakef, "The influence of cation impurities on the Scintillation Performance of SrI2(Eu)", IEEE Trans. Nucl. Sci., vol. 62, no 6, pp. 3397-3404, Dec. 2015,doi:10.1109/TNS.2015.2496800.
17. R.H. Bartram, L.A. Kappers, D.S. Hamilton et.al., "Suppression of afterglow in CsI: Tl by codoping with Eu2+ II. Theoretical model." Nucl. Instr. Meth. Phys. Res. A., vol. 558, Iss. 2, pp. 458–467, March. 2006, doi: 10.1016/j.nima.2005.11.051.
18. N. Shiran, A. Gektin, S. Vasyukov et.al., "Afterglow suppression in CsI crystal by Eu2+ doping", Func. Mater., vol. 18, no. 4, pp. 438-441, Oct. 2011.
19. J. Glodo, E. V. van Loef, N. J. Cherepy, S. A. Payne, and K. S. Shah, "Concentration Effects in Eu Doped SrI2", IEEE Trans. Nucl. Sci., vol. 57, no. 3, pp. 1228-1232, June 2010, doi:10.1109/TNS.2009.2036352.
20. Aka, G., Kahn-Harari, A., Vivien, D., Bénitez, J.-M., Salin, F. and Godard, J. (1996): A new non-linear and neodymium laser self-frequency doubling crystal with congruent melting: Ca4GdO(BO3)3 (GdCOB). European Journal of Solid State and Inorganic Chemistry, 33:727–736
21. Cohen-Adad, M., Aloui-Lebbou, O., Goutaudier, C., Panczer, G., Dujardin, C., Pedrini,C. Florian, P., Massiot, D., Gerard, F. and Kappenstein, C. (2000): Gadolinium and Yttrium Borates: Thermal Behaviour and Structural Considerations. Journal of Solid State Chemistry, 154:204–213
22. Zhang, S., Cheng, Z., Zhou, G., Sun, Y., Hou, X., Liu, X., Han, J., Shao, Z., and Chen, H. (2000): Growth and properties of (Cr3+, Nd3+) doped GdCa4O(BO3)3 crystals.Progress in Crystal Growth and Characterization of Materials, 40:81–88 23. Rutter, J.W., 1968, in: Techniques of Metals Research, Vol. 1, ed. R.F. Bunshah (Wiley, New York) p. 923.
24. Laudise, R.A., 1970, Growth of Single Crystals (Prentice-Hall, Englewood Cliffs, NJ).

25. Beyss, M., J.M. Welter and T, Kaiser, 1980, J. Cryst. Growth 50, 419.
26. Sugiyama M, Yokota Y, Fujimoto Y, et al. Dopant segregation in rare earth doped lutetium aluminum garnet single crystals grown by the micro-pulling down method. J Cryst Growth, 2012, 352: 110–114
27. Harrington J A. Single-crystal fiber optics: A review. Proc SPIE, 2014,8959: 895902
28. Mu X, Meissner S, Meissner H. Laser diode pumped high-efficiency Yb: YAG crystalline fiber waveguide lasers. Proc SPIE, 2015, 9342:934209
29. Delen X, Aubourg A, Deyra L, et al. Single crystal fiber for laser sources. Solid State Lasers XXV: Technology and Devices. Proc SPIE,2015, 9342: 934202
30. Deyra L, Martial I, Didierjean J, et al. 3 W, 300 µJ, 25 ns pulsed 473 nm blue laser based on actively Q-switched Nd: YAG single-crystal fiber oscillator at 946 nm. Opt, Lett, 2013, 38: 3013–3016
31. Délen X, Piehler S, Didierjean J, et al. 250 W single-crystal fiber Yb: YAG laser. Opt Lett, 2012, 37: 2898–2900
32. Zeng Z, Qiao L, Liu Y, et al. Numerical study on the radial dopant distribution in micro-pulling-down crystal growth. J Cryst Growth,2016, 434: 110–115
33. Samanta G, Yeckel A, Daggolu P, et al. Analysis of limits for sapphire growth in a micro-pulling-down system. J Cryst Growth, 2011, 335:148–159