# Strategic Buffer Layer Development for YBCO Coated Conductors

Mariappan Paranthaman, Tolga Aytug, Kyunghoon Kim, Eliot D. Specht, and Lee Heatherly

***Abstract*—We have developed a simplified buffer layer architecture for the rolling-assisted biaxially textured substrates (RABiTS) template approach. The overall purpose of this research is to enable potentially a low-cost, high throughput and high yield manufacturing processes for buffer fabrication and to gain fundamental understanding of the growth of buffer layers for RABiTS templates. This understanding is critical to the development of a reliable, robust, and long-length manufacturing process for second generation wires. In this study, efforts are being made to either reduce the number of vacuum deposited layers or to replace one or more of these vacuum deposited layers with a solution based layer. We have chosen $Gd_2O_3 - ZrO_2$ system as a potential barrier layer for this study. We have deposited epitaxial Gadolinia Stabilized Zirconia (GSZ) ($Zr_{1-x}Gd_xOy$; $x = 0$–$1$) films on 30-nm thick e-beam evaporated $Y_2O_3$ seeded Ni-W (3 at. %) (Ni-3W) substrates using a metal-organic decomposition (MOD) process. Detailed X-ray studies indicated that all of the MOD-GSZ layers were cube textured and both in-plane and out-of-plane lattice parameters increases linearly with increasing the Gd content. We have also developed process conditions for reactively sputter deposited epitaxial $Gd_2Zr_2O_7$ (Gadolinium Zirconium Oxide (GZO); $Zr_{1-x}Gd_xO_y$ $(x = 0.5)$) films on the e-beam evaporated $Y_2O_3/Ni - 3W$ substrates. YBCO films with a critical current density $J_c$ of $2.14 \times 10^6$ $A/cm^2$ and $1.4 \times 10^6$ $A/cm^2$ at 77 K and self-field were grown on the newly developed architectures of $Gd_2Zr_2O_7/Y_2O_3/Ni - 3W$ and $Zr_{1-x}Gd_xO_y$ $(x = 0.2)/Y_2O_3/Ni - 3W$ substrates, respectively using a pulsed laser deposition (PLD) process. This work promises a route for producing cost-effective simplified buffer architectures for the RABiTS-based YBCO coated conductors.**

***Index Terms*—Buffer layers, metal organic deposition, reactive sputtering, transport property measurements, YBCO coated conductors.**

## I. Introduction

THE focus of this research is to conduct a fundamental research in the area of buffer layer development. The results of this project provide new insights and suggest new methods to improve buffer fabrication. The main purpose of this research is to gain a fundamental understanding of the growth of buffer layers for RABiTS based templates. This understanding is critical to the development of a reliable, robust, long-length manufacturing process for second generation (2G) wires. The current RABiTS architecture used by American Superconductor consists of a starting template of biaxially textured Ni-W (5 at. %) with a seed layer of 75-nm thick $Y_2O_3$, a barrier layer of 75-nm thick YSZ, and a cap layer of 75-nm thick $CeO_2$ [1]–[4]. In this architecture, all the buffers have been deposited by reactive sputtering. To reduce the initial investment cost for buying 2G pilot-scale production equipment, it is essential to either reduce the number of buffer layers or to replace some of the sputtered buffer layers with a solution deposited counterparts. By reducing the number of buffer layers and without compromising the wire performance, the throughput and reliability of the 2G wire will increase and the associated production cost will decrease. Moreover, use of a wet-chemical solution approach such as metal-organic decomposition (MOD) method offers a significant potential cost advantage over the physical vapor deposition (PVD) process. In addition, solution approach is more amenable to grow complex oxides and combines a faster deposition rate, rapid crystallizing potential, and inexpensive equipment with almost 100% materials utilization. A slot-die coating process has been chosen to scale up solution buffer layers. However, for optimization of the process conditions for short samples, a spin coating technique was used.

Recently, a $Gd_2Zr_2O_7$ (GZO) buffer layer with a pseudocubic lattice parameter of 3.72 Å has been deposited by using the ion-beam assisted deposition (IBAD) process, a vacuum-based approach for biaxially textured template fabrication [5]. In addition, GZO films have also been used as a multi-functional buffer layer in a simplified RABiTS approach [6]–[8]. Alternatively, $Zr_{1-x}Gd_xO_y$ $(0.18 \leq x \leq 0.62)$ has been widely investigated as good oxygen conductors due to the presence of oxygen ion vacancies in its structure as well as its ionic conductivity [9], [10]. As x (Gd) increases, structure changes from monoclinic to fluorite, pyrochlore and then to simple cubic-type structures. Hence, it is essential to assess the solution deposition method for depositing $Gd_2O_3 - ZrO_2$ films on the RABiTS template. In this work, we have investigated the feasibility of $Gd_2O_3 - ZrO_2$ system as a potential multi-functional buffer layer for coated conductors. We have successfully demonstrated the growth of epitaxial $Zr_{1-x}Gd_xO_y$ $(x = 0$–$1)$ (Gadolinia Stabilized Zirconia: GSZ) thin films on the e-beam evaporated $Y_2O_3/Ni - 3W$ substrates using MOD approach. In addition, we have also developed process conditions for the reactive sputtered $Gd_2Zr_2O_7$ [$Zr_{1-x}Gd_xO_y$ $(x = 0.5)$] thin films. Here we report our results obtained on the YBCO films deposited on the simplified architecture of $GSZ/Y_2O_3/Ni - 3W$.

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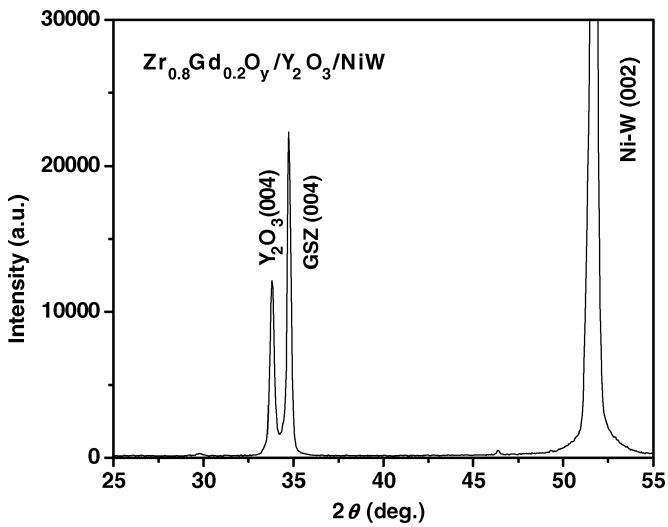


Fig. 1. Typical $\theta - 2\theta$ scans for 60 nm thick $Zr_{1-x}Gd_xO_y$ (x = 0.2) (GSZ: Gadolinia Stabilized Zirconia) films grown on 30 nm thick e-beam $Y_2O_3/Ni-3W$ substrates using metal-organic decomposition. GSZ film has a preferred $c$-axis orientation.

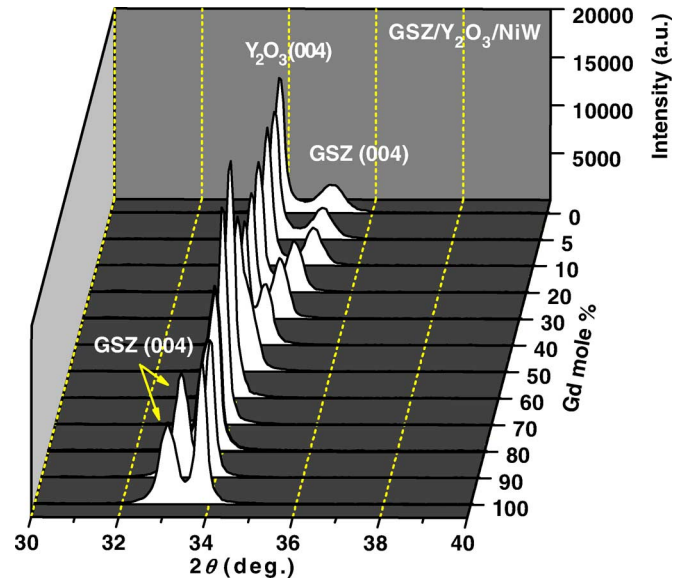


Fig. 2. Typical $\theta - 2\theta$ scans for 30 nm thick $Zr_{1-x}Gd_xO_y$ (x = 0–1) (GSZ: Gadolinia Stabilized Zirconia) films grown on 30 nm thick e-beam $Y_2O_3/Ni-3W$ substrates using metal-organic decomposition. All the GSZ films have a preferred $c$-axis orientation.

## II. Experimental Procedure

Biaxially textured Ni-W (3 at. %) substrates were typically 1 cm wide and 50 $\mu$m thick. Electron beam evaporation was used to deposit $Y_2O_3$ seeds. It is well established that $Y_2O_3$ seed layers improve the degree of texture relative to the underlying substrate [3]. The MOD GSZ solution was prepared from the purified gadolinium acetate by first dissolving it in acetic acid and then mixing with stoichiometric amount of zirconium acetylacetonate (acac) (Alfa) while continuously stirring at room temperature. The final volume was adjusted to 10 ml to produce a 0.25 M cation precursor solution. The coatings were done using spin-coating on 1 cm wide $Y_2O_3/Ni-3W$ substrates at 2000 rpm for 30 s followed by direct heating to the crystallization temperature of 1100°C for 30 min in a reducing atmosphere of forming gas $(Ar + 4\%\ H_2)$. Typically, a 20 nm thick crystallized GSZ film was deposited in a single coat. For reactive sputtering, a 2″ circular Gd:Zr (each 50%) alloy target was used. Depositions were carried out under 5–10 mTorr of Argon with a mixture of $10^{-5}$ Torr of water vapor.

The YBCO films were then deposited by pulsed laser deposition (PLD) at 780°C in 200 mTorr oxygen with an average energy density of 2 $J/cm^2/pulse$. Following deposition, the films were annealed under 550 Torr oxygen during cool down. Typical YBCO thickness was 0.2 $\mu$m. The films were then prepared for current density measurements by depositing silver for current and voltage leads, followed by oxygen annealing at 500°C for 1 h. The samples were characterized for crystal structure, phase purity, and texture by using x-ray diffraction (XRD). Electrical transport properties of the composite structures were evaluated by a standard four-probe technique. Values of $J_c$ were assigned at a 1 $\mu V/cm$ criterion.

## III. Results and Discussion

Typical $\theta - 2\theta$ XRD patterns for three-coat (60 nm-thick) $Zr_{1-x}Gd_xOy$ (x = 0.2) films grown on 30 nm thick e-beam $Y_2O_3/Ni-3W$ substrates using MOD approach is shown in Fig. 1. GSZ film has a preferred c-axis orientation. There is no GSZ (222) phase present in this sample. In addition, we have also successfully grown MOD $Zr_{1-x}Gd_xO_y$ films for the entire range of x = 0–1 on 30 nm thick e-beam $Y_2O_3/Ni-3W$ substrates. Typical $\theta - 2\theta$ scans for single-coat 20 nm thick $Zr_{1-x}Gd_xO_y$ (x = 0–1) films grown on 30 nm thick e-beam $Y_2O_3/Ni-3W$ substrates using MOD approach are shown in Fig. 2. All the GSZ films have a preferred c-axis orientation. The position of GSZ (004) peak shifts towards lower $2\theta$ values due to the increase in the lattice parameter with increase in Gd content. Detailed XRD results from $\omega$ and $\phi$ scans revealed good epitaxial texturing. The full width at half maximum (FWHM) values for all the GSZ films are reported in Table I. Note that GSZ texture is comparable to that of the underlying $Y_2O_3$ seed layer.

TABLE I
X-Ray Texture Data for 20 nm Thick $Zr_{1-x}Gd_xO_y$ (x = 0–1) (GSZ: Gadolinia Stabilized Zirconia) Films Grown on 30 nm Thick E-Beam $Y_2O_3/Ni-3W$ Substrates Using a Metal-Organic Decomposition Process

| Sample Zr1-xGdxOy/ $Y_2O_3$/Ni-3W | GSZ (004) FWHM Phi=0 (deg.) | GSZ (004) FWHM Phi=90(deg.) | GSZ (222) (deg.) |
|---|---|---|---|
| X (Gd) = 0 | 3.5 | 5.1 | 5.8 |
| X (Gd) = 0.05 | 4 | 5.9 | 5.9 |
| X (Gd) = 0.1 | 3.7 | 4.8 | 5.6 |
| X (Gd) = 0.2 | 3.5 | 5 | 5.8 |
| X (Gd) = 0.3 | 3.5 | 5 | 6 |
| X (Gd) = 0.4 | 3.5 | 5.4 | 6 |
| X (Gd) = 0.5 | 3.3 | 5.2 | 6.2 |
| X (Gd) = 0.6 | 3.5 | 5.1 | 6 |
| X (Gd) = 0.7 | 3.7 | 5.2 | 6.1 |
| X (Gd) = 0.8 | 3.4 | 5 | 5.7 |
| X (Gd) = 0.9 | 3.7 | 5.4 | 5.6 |
| X (Gd) = 1.0 | 3.4 | 5.3 | 5.5 |

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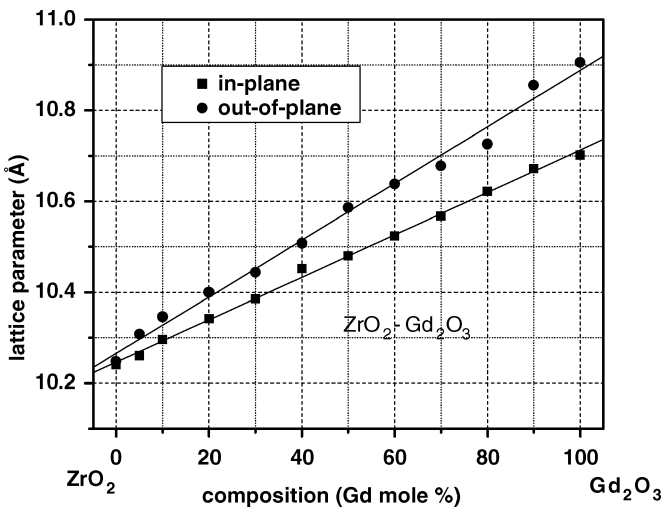


Fig. 3. Both in-plane and out-of-plane texture data for 30 nm thick $Zr_{1-x}Gd_xO_y$ (x = 0–1) (GSZ: Gadolinia Stabilized Zirconia) films grown on 30 nm thick e-beam $Y_2O_3/Ni-3W$ substrates using MOD approach. All the GSZ films have been indexed as a pseudo-cubic structure.

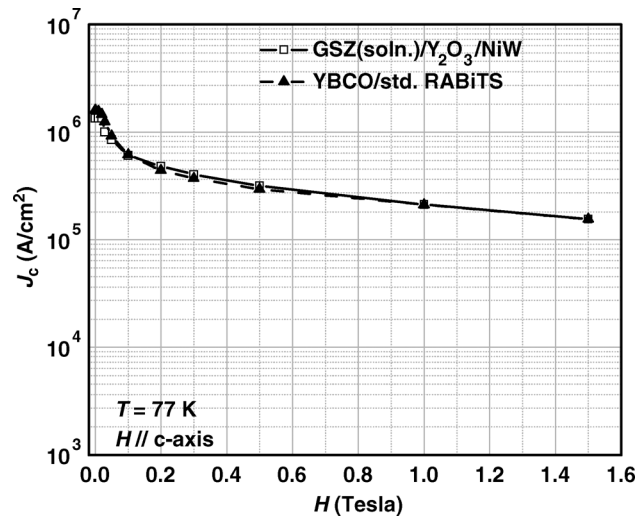


Fig. 4. Magnetic field dependence of $J_c$ for a 0.2 $\mu$m thick YBCO film grown on a 60 nm thick $Zr_{1-x}Gd_xO_y$ (x = 0.2)/30 nm thick e-beam $Y_2O_3/Ni-3W$. For comparison, a typical data for PLD-YBCO (0.35 $\mu$m-thick) on the standard RABiTS (sputtered $CeO_2$/sputtered YSZ/e-beam $Y_2O_3/Ni-3W$) architecture is also shown. Similar self-field $J_c$ of 1.4 $MA/cm^2$ at $H \| c$; 77 K was achieved on both samples.

Fig. 3 shows the change in both the in-plane and out-of-plane lattice parameters for 30 nm thick GSZ over the entire range of x = 0–1. Irrespective of the composition, all GSZ films have been indexed as a pseudo-cubic structure, unlike the bulk phase diagram data where monoclinic $ZrO_2$ phase was observed in the composition range of x = 0–0.1. This may be attributed to the high processing temperatures used for the growth of GSZ layers at which the GSZ layers could interact with the underlying $Y_2O_3$ seeds and possibly form a cubic structure, i.e., yttrium doped GSZ. It is clear from the figure that the lattice parameter of GSZ layers increases linearly with increase in Gd content. This increase is due to the replacement of smaller $Zr^{4+}$ ions with larger $Gd^{3+}$ ions. By choosing proper Gd composition, one can tailor the lattice parameters of GSZ to match them with those of the substrate or YBCO.

The performance of the MOD GSZ buffer layers was evaluated by depositing PLD YBCO films. A typical $J_c$ (self-field) of $1.4 \times 10^6$ $A/cm^2$ at 77 K is obtained for a 0.2 $\mu$m thick YBCO films on $Zr_{1-x}Gd_xO_y$ (x = 0.2)/$Y_2O_3$/Ni − W, which reflects performance comparable to those obtained on standard vacuum-based three-layer $CeO_2/YSZ/Y_2O_3$ buffer architectures (as shown in Fig. 4). This demonstrates the use of two-layer buffer architecture as a possible alternate in RABiTS template. Based on these results we have also successfully deposited $Zr_{1-x}Gd_xO_y$ (x = 0.5) ($Gd_2Zr_2O_7$: GZO) films using reactive sputtering. Typical $\theta - 2\theta$ XRD pattern for a 200 nm thick GZO film grown on a 30 nm thick e-beam $Y_2O_3/Ni-3W$ substrate shows good $c$-axis texture (Fig. 5). The full width at half maximum (FWHM) values for Ni-W (002), $Y_2O_3$ (004), and GZO (004) are 6°, 4.2°, and 3.9°, and those of Ni-W (111), $Y_2O_3$ (222), and GZO (222) are 6.7°, 6.8°, and 5.7°, respectively. Note the significant improvement in the out-of-plane texture compared to the underlying Ni-W substrate.

The performance of the reactively sputtered GZO buffer layers was evaluated by depositing PLD YBCO films. A self-field $J_c$ (77 K) of $2.14 \times 10^6$ $A/cm^2$ is obtained for a 0.2 $\mu$m thick YBCO film on the GZO/$Y_2O_3$/Ni − W substrate (Fig. 6). All these observations clearly underscore the strong viability of MOD and reactive sputtered GSZ layers for the development of simplified coated conductor architectures with reduced cost and high-performance.

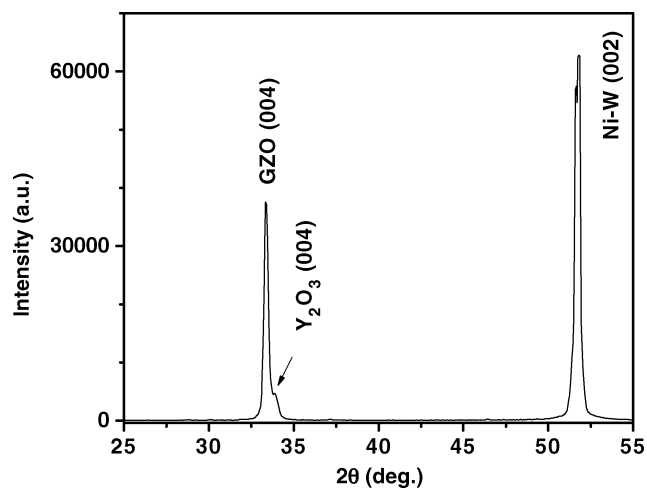


Fig. 5. Typical $\theta - 2\theta$ scans for a 200 nm thick $Zr_{1-x}Gd_xO_y$ (x = 0.5) (GZO: Gadolinium Zirconium Oxide) film grown on a 30 nm thick $Y_2O_3/Ni-W$ substrate using reactive sputtering.

## IV. Summary

In summary, we have demonstrated a simplified RABiTS buffer architecture using MOD based GSZ and reactively sputtered GZO films. We have investigated the epitaxial growth of MOD based $Zr_{1-x}Gd_xO_y$ (x = 0–1) (GSZ: Gadolinia Stabilized Zirconia) films on $Y_2O_3$/NiW substrates. In addition, we have developed process conditions for the epitaxial growth of reactively sputter deposited GZO films on $Y_2O_3$ seeds. The $J_c$ performance of YBCO films on both GSZ and GZO films are found to be comparable to those attained on the standard

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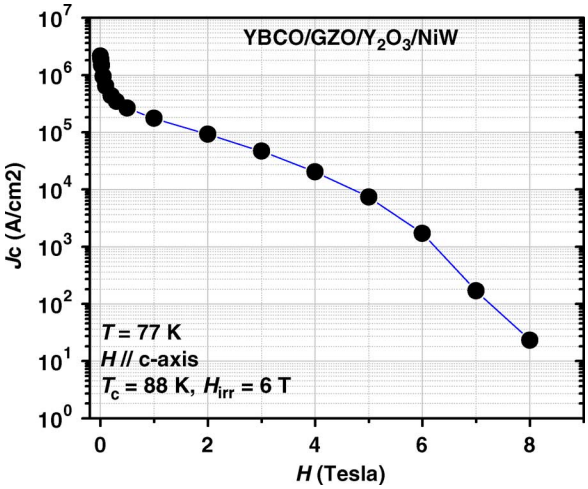


Fig. 6. The field dependence of $J_c$ for 0.2 $\mu$m thick PLD-YBCO film grown on a 200 nm thick $Zr_{1-x}Gd_xO_y$ $(x = 0.5)$ (GZO: Gadolinium Zirconium Oxide)/30 nm thick e-beam $Y_2O_3/Ni-W$ substrate. The superconducting critical temperature $T_c$ of the sample is 88 K and demonstrates self-field $J_c$ of $2.14 \times 10^6$ $A/cm^2$ at $H \| c$; 77 K.

three layer RABiTS buffer architecture. Finally, this work may open a pathway for the fabrication of more efficient, robust and lower cost second generation HTS coated conductors.

## REFERENCES

[1] M. P. Paranthaman, "Superconductor wires," in *McGraw-Hill 2006 Yearbook of Science and Technology*. New York: McGraw-Hill, 2006, pp. 319–322.

[2] M. P. Paranthaman and T. Izumi, Eds., "High-performance YBCO-coated superconductor wires," *MRS Bulletin*, vol. 29, pp. 533–536, 2004.

[3] A. Goyal, M. Paranthaman, and U. Schoop, "The RABiTS approach: Using rolling-assisted biaxially textured substrates for high-performance YBCO superconductors," *MRS Bulletin*, vol. 29, pp. 552–561, Aug. 2004.

[4] M. W. Rupich, D. T. Verebelyi, W. Zhang, T. Kodenkandath, and X. Li, "Metalorganic deposition of YBCO films for second-generation high-temperature superconductor wires," *MRS Bulletin*, vol. 29, pp. 572–578, 2004.

[5] Y. Iijima, K. Kakimoto, Y. Yamada, T. Izumi, T. Saitoh, and Y. Shiohara, "Research and development of biaxially textured IBAD-GZO templates for coated superconductors," *MRS Bulletin*, vol. 29, pp. 564–571, 2004.

[6] T. Aytug, M. Paranthaman, K. J. Leonard, H. Y. Zhai, M. S. Bhuiyan, E. A. Payzant, A. Goyal, S. Sathyamurthy, D. B. Beach, P. M. Martin, D. K. Christen, X. Li, T. Kodenkandath, U. Schoop, M. W. Rupich, H. E. Smith, T. Haugan, and P. N. Barnes, "Assessment of chemical solution synthesis and properties of $Gd_2Zr_2O_7$ thin films as buffer layers for second-generation high-temperature superconductor wires," *J. Mater. Res.*, vol. 20, pp. 2988–2996, 2005.

[7] R. N. Bhattacharya and S. Phok, "Electrodeposited $Gd_2Zr_2O_7$ and $Gd_2O_3$ buffer layers for $YBa_2Cu_3O_{7-\delta}$ superconductors," *J. Electr. Mater.*, vol. 36, pp. 1275–1278, 2007.

[8] Y. X. Zhou, X. Zhang, H. Fang, P. T. Putman, and K. Salama, "Development of single solution buffer layers on textured Ni substrates for HTS coated conductors," *IEEE Trans. Appl. Supercond.*, vol. 15, pp. 2711–2714, 2005.

[9] J. Wang, H. Otobe, A. Nakamura, and M. Takeda, "Correlation of crystal structures with electric field gradients in the fluorite- and pyrochlore-type compounds in the $Gd_2O_3 - ZrO_2$ system," *J. Solid State Chem.*, vol. 176, pp. 105–110, 2003.

[10] V. Grover and A. K. Tyagi, "Phase relation studies in the $CeO_2 - Gd_2O_3 - ZrO_2$ system," *J. Solid State Chem.*, vol. 177, pp. 4197–4204, 2004.

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