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Preparation of meta-stable phases of barium titanate by Sol-hydrothermal method

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Two low-cost chemical methods of sol–gel and the hydrothermal process have been strategically combined to fabricate barium titanate (BaTiO3) nanopowders. This method was tested for various synthesis temperatures (100 °C to 250 °C) employing barium dichloride (BaCl2) and titanium tetrachloride (TiCl4) as precursors and sodium hydroxide (NaOH) as mineralizer for synthesis of BaTiO3 nanopowders. The as-prepared BaTiO3 powders were investigated for structural characteristics using x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The overall analysis indicates that the hydrothermal conditions create a gentle environment to promote the formation of crystalline phase directly from amorphous phase at the very low processing temperatures investigated. XRD analysis showed phase transitions from cubic - tetragonal - orthorhombic - rhombohedral with increasing synthesis temperature and calculated grain sizes were 34 – 38 nm (using the Scherrer formula). SEM and TEM analysis verified that the BaTiO3 nanopowders synthesized by this method were spherical in shape and about 114 - 170 nm in size. The particle distribution in both SEM and TEM shows that as the reaction temperature increases from 100 °C to 250 °C, the particles agglomerate. Selective area electron diffraction (SAED) shows that the particles are crystalline in nature. The study shows that choosing suitable precursor and optimizing pressure and temperature; different meta-stable (ferroelectric) phases of undoped BaTiO3 nanopowders can be stabilized by the sol-hydrothermal method. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4935645]

I. INTRODUCTION

Barium titanate (BaTiO3) is a perovskite material that possesses superior dielectric properties along with ferroelectric, piezoelectric and electro-optic nature.1,2 It is a promising material for device applications such as ferroelectric, random access memories, optical modulators, switches, wave-guides and multilayer capacitors, micro-electromechanical systems and opto-electronic devices.3–10 In particular, as the levelized cost of solar electricity has plummeted and other intermittent distributed generation technologies become more widespread, electrical storage needs are increasing.11,12 There are many choices for battery technologies, but ultra-capacitors or super capacitors are gaining prominence.13,14 BaTiO3 shows promise as one of these ultra-capacitor materials.15–19

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The crystal structure of BaTiO$_3$ is ABX$_3$. It is usually visualized as simple cubic unit cells with larger cations A located at eight corners, smaller cations B sitting in the body center and oxygen atoms in the face centered location. The first structural study on perovskite was conducted by Goldschmidt et al. in the 1920’s. The cubic perovskite structure can be slightly distorted due to temperature changes, size effects, composition, stress, and strain. Distorted structures have reduced symmetry and have effects on the magnetic and electric properties, which have significant industrial importance. BaTiO$_3$ is the first oxide ferroelectric with a simple crystallographic structure. BaTiO$_3$ and BaTiO$_3$-based materials faces almost all practical demands of electronic industry as being one of the promising ferroelectric, piezoelectric and opto-electronic materials. BaTiO$_3$ undergoes a phase transition at the Curie temperature, which is also called displacement phase transition. Hence the crystal structure of BaTiO$_3$ is dependent on temperature, size, composition, etc. Depending on transition temperatures BaTiO$_3$ has five kinds of crystal systems: hexagonal, cubic, tetragonal, orthorhombic and rhombohedral. The phase transition temperatures are 1432, 130, 5, and -90 °C respectively. These features are studied by Xiao et al., and found that tetragonal phase is stable at room temperature. Among different phases; tetragonal, orthorhombic and rhombohedral are ferroelectric crystals and cubic phase is paraelectric. Hence, for piezoelectric applications, the ferroelectric tetragonal-orthorhombic-rhombohedral phases are the most preferred. Most of the synthesis techniques involve high temperature process. In addition, the paraelectric cubic phase is also observed at room temperature with/without the coexistence of tetragonal phase depending on the synthesis conditions. Moreover, at nano scale different multiphase’s co-existence occur at various temperatures.

The above discussions show that the phase transition of BaTiO$_3$ may be a function of temperature and crystallite size. These variables must be controlled in low-cost industrially scalable processes for BaTiO$_3$ to reach its market potential. Ideally, this process would also be eco-friendly.

To provide such a simple chemical synthesis method, here BaTiO$_3$ is synthesized by the sol-gel hydrothermal method. Hydrothermal synthesis also makes it possible to prepare BaTiO$_3$ powder in a single processing step and does not require elaborate apparatus or expensive reagents. The hydrothermal method is attractive for synthesizing BaTiO$_3$ powder, because the combined effects of solvent, temperature and pressure on the ionic reaction equilibrium can stabilize desirable products, while inhibiting formation of undesirable compounds. The hydrothermal method has been extensively reported on the preparation of BaTiO$_3$ nanopowders by tuning process parameters such as temperature, pH and reaction time. Typical synthesis conditions require temperatures higher than 200 °C for stabilizing tetragonal phase of BaTiO$_3$ and reaction time extends from 10 -15 hours. However, Moreira et al. employing chloride based precursors and microwave assisted hydrothermal method demonstrated stabilization of tetragonal phase at 140 °C and shorter reaction times from 20 – 160 minutes. Fuentes et al., extending the work by employing the sol-hydrothermal method demonstrated synthesis of tetragonal phase with shorter reaction time of 3 hours. Additionally the study established that the grain size of BaTiO$_3$ nanopowders can be reduced by introducing high pressure oxygen atmosphere. In this study, the effect of synthesis temperature providing maximum pressure efficiency was studied. BaTiO$_3$ was prepared at four different temperatures: a) 100 °C, b) 150 °C, c) 200 °C, and d) 250 °C under constant pressure and its phase transitions are studied. The as-prepared powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results are presented and the technical viability of sol-gel hydrothermal synthesis for stabilizing meta-stable phases of BaTiO$_3$ at room-temperature is discussed.

II. EXPERIMENTAL

A. Materials

The materials used in this process were titanium tetrachloride (TiCl$_4$) purchased from Sigma Aldrich, barium dichloride (BaCl$_2$) purchased from Merck, dilute hydrochloric acid, ethanol (99.9 % Channingshuyangyuan), sodium hydroxide (NaOH) purchased from Merck and distilled water.
B. Methods

1.1 ml of TiCl$_4$ was dissolved in 2.3 ml of dilute hydrochloric acid (35 % GR) to form a yellowish solution. Since, TiCl$_4$ oxidizes when exposed to the atmosphere; the mixing of TiCl$_4$ in hydrochloric acid (HCL) was done by keeping both TiCl$_4$ and HCL in an ice bath (temperature was about 1 °C). Then 2.4 gm of BaCl$_2$.2H$_2$O was dissolved in 15 ml of deionized water to form colourless solution. The two solutions were mixed under constant stirring for five minutes with a magnetic stirrer.

13 ml of 6M NaOH was prepared. Then under constant stirring of the mixed solution, the prepared NaOH solution was added drop wise and stirred for 30 minutes, producing a homogenous colloidal barium titanium solution. The colloidal solution was transferred into a 50 ml Teflon-lined autoclave and heated at 100 °C for about 3 hrs in an oven. After 3 hrs it was allowed to cool to room temperature. During the heating, the autoclave was sealed with normal air inside and during the experiment; the pressure reached the equilibrium value for the reaction temperature. At the end of the reaction, the autoclave was naturally cooled to room temperature. The above experiment was repeated for three additional temperatures (150 °C, 200 °C and 250 °C).

The as-formed solid white powder attached to the bottom and inner wall of the Teflon container was collected. The collected BaTiO$_3$ solution was centrifuged. It was washed twice with acetone and ethanol in the spinning vessel to remove remaining ions. The centrifuged sample was dried at 60 °C for 6 hrs in the hot plate.

III. RESULTS AND DISCUSSION

A. Structural studies

The XRD spectrum of barium titanate synthesized for four different temperatures is shown in Fig. 1. The most dominant plane (110) was observed for all the samples. The intensity of the (110) plane vary with temperature and the sample synthesized at 200 °C shows the maximum intensity. There was a continuous increase in intensity up to 200 °C and around 250 °C, the intensity of the peak decreased. The synthesized samples were found to be in crystalline nature along with impurities like barium carbonate (BaCO$_3$). These impurities arise due to the reaction between the reactant species/precursors and mainly dependant on the synthesis conditions. It can be observed from XRD spectra’s (Fig. 1) that the intensity of diffraction peaks corresponding to BaCO$_3$ decreases with increasing temperature meaning the percentage of BaCO$_3$ phase decreases. However, under acidic conditions, BaCO$_3$ can be dissolved.$^{25}$ For sample prepared at 100 °C, the observed corresponding peaks were indexed as cubic lattice (lattice parameter a=b=c) of BaTiO$_3$ (space group Pm3m) and

![FIG. 1. XRD spectra of sol-hydrothermal BaTiO$_3$ prepared at four different temperatures.](image-url)
TABLE I. Structural analysis for (111) crystallographic orientation of BaTiO$_3$ samples synthesized at four different temperatures.

| Sample    | Temperature (°C) | d-spacing | Lattice constant | Grain size | Dislocation density |
|-----------|------------------|-----------|------------------|------------|---------------------|
| BaTiO$_3$(111) | 100             | 2.32156   | 4.02094          | 38         | 0.0006849          |
|           | 150             | 2.31974   | 4.01780          | 35         | 0.0008075          |
|           | 200             | 2.31667   | 4.01247          | 36         | 0.0007859          |
|           | 250             | 2.29836   | 3.98076          | 34         | 0.0008711          |

found in agreement with JCPDS card No. 31-0174. Similar results were reported by Fuentes et al.\textsuperscript{24} However, with increasing synthesis temperature, additional peaks or peak shifts occur. For simplicity, tetragonal phase of BaTiO$_3$ can be considered as distorted cubic structure along [001] crystallographic direction ($a_\text{tetragonal} > a_{\text{cubic}}$ and $a_\text{tetragonal} < a_{\text{cubic}}$) and orthorhombic structure as distorted along [011] face diagonal ($a_\text{orthorhombic} > a_{\text{cubic}}$ and $a_\text{orthorhombic} < a_{\text{cubic}}$) and rhombohedral structure as cubic distorted along [111] body diagonal ($a_\text{rhombohedral} = a_{\text{cubic}}$).\textsuperscript{26}

XRD analysis demonstrates that at all four different synthesis temperatures, BaTiO$_3$ powders are nanostructure in nature and exhibit good crystallinity. Apart from crystalline nature, XRD showed that sample prepared at 100 °C, pseudo-cubic structure preceded the stable room-temperature tetragonal form as the dominating phase. It has been already demonstrated by researchers worldwide that the transition temperature from tetragonal to cubic structure will decrease with decreasing particle size.\textsuperscript{27} The cubic-tetragonal transformation shifts only slightly downward with grain size reduction before being substantially suppressed. The other structural parameters such as d-spacing, lattice constant, grain size and lattice deformation were calculated for (111) crystallographic orientation of BaTiO$_3$ for comparison and summarized in Table I. The Scherrer formula for grain size, D (in nm), is:

$$D = \frac{K\lambda}{\beta_{hlk}\cos\theta}$$  \hspace{1cm} (1)

Where ‘K’ is the shape factor (0.9), and $\lambda$ is the wavelength of X-ray source (Cu K$_{\alpha}$ radiation - 0.154 nm). Particle size estimated from Scherrer formula demonstrated decrease in grain size with increasing temperature. Specifically, average lattice parameter size decreases with phase transition from cubic to rhombohedral crystal structure for BaTiO$_3$, similar observations can be made when the synthesizing temperature was increased indicating the phase transition. Though BaTiO$_3$ powders exhibit multi-phase, Williamson-Hall (W-H) plot analysis can provide an average grain size, as the lattice parameter difference between different crystal structures of BaTiO$_3$ is very small. Mote et al. had proposed that crystallite size calculated using W-H analysis provides good agreement with TEM.\textsuperscript{28} The grain size calculated using W-H plot analysis method was summarized in Table II.\textsuperscript{29} However, three important observations were noted in grain size calculation from W-H analysis: (i) as temperature increases from 100 to 150 °C, there was decrease in grain size, and (ii) further increase in temperature up to 200 °C, there was an increase in grain size and (iii) around 250 °C, there was slight decrease in grain size. For detailed analysis on the phase transitions, enlarged section of the XRD spectra corresponding to (110) and (002) plane of the as-prepared samples were presented to demonstrate additional peaks and peak shifts.

TABLE II. Particle size and strain of BaTiO$_3$ nanocrystalline powders prepared at four different temperatures from XRD.

| Sample | Temperature (°C) | Particle Size (using Debye Scherrer formula) nm | Particle Size (using W-H Plot) nm | Strain (using W-H Plot) |
|--------|------------------|-----------------------------------------------|----------------------------------|-------------------------|
| BaTiO$_3$ | 100             | 32                                            | 66                               | 0.0063                  |
|         | 150             | 25                                            | 36                               | 0.0043                  |
|         | 200             | 25                                            | 150                              | 0.0103                  |
|         | 250             | 26                                            | 55                               | 0.0063                  |
FIG. 2. XRD spectra demonstrating peak shifts of (a) (110) and (b) (200) diffraction plane of BaTiO$_3$ for different synthesis temperatures. The dashed lines are for eye-guidance only.

Figure 2 shows the shift in the (110) and (200) plane for the four sample prepared at different temperatures. Stabilization of tetragonal phase will shift (200) and introduce (002) diffraction peaks at smaller and higher 2$\theta$ angles, respectively. Additionally, c/a ratio of tetragonal phase is characterized by a value $\sim$ 1.010 for bulk BaTiO$_3$ at room temperature. However, c/a ratio decreases with decrease in particle size.\(^{30}\) Similarly, orthorhombic phase should introduce additional peak for (002) diffraction plane at higher 20 angle and shift (200) peak towards smaller 20 angle compared to cubic phase and (002) at smaller angles compared to tetragonal phase. Rhombohedral structure should shift all the diffraction peaks towards smaller 20 angles. From Fig. 2(a) & 2(b), predominant shift of diffraction peaks were observed for samples prepared at 100 – 250 $^\circ$C. For example, the 2$\theta$ position of (110) peak shifts from 31.49$^\circ$-31.82$^\circ$. This variation indicates the possibility of phase transition as temperature increases. No additional peaks at smaller 20 angle were observed for (002) peak, meaning, presence of cubic phase for sample prepared at 100 $^\circ$C. However, (002) and (200) peaks appear (indicated by arrows and labelled as ‘tetra’ in Fig. 2(b)), indicating presence of tetragonal phase along with cubic phase. Increase in synthesis temperature to 150 $^\circ$C, one can observe additional peaks at (110) and (200), meaning stabilization of orthorhombic phase (indicated by arrows and labelled as ‘ortho’ in Fig. 2(b)) in addition to cubic and tetragonal phase. Further increase in temperature, demonstrate only single (110) peak along with (002) and (200) peaks indicating stabilization of orthorhombic phase. At 250 $^\circ$C, the entire diffraction peak shifts towards smaller 20 angles due to stabilization of rhombohedral structure (labelled as ‘rhom’ in Fig. 2(b)).

On the contrary to cubic-tetragonal phase transition, the orthorhombic to tetragonal transformation temperature increases with decrease in particle size and will shift upward slightly before experiencing the same suppression as temperature changes (Ref. 31 and references there-in). The results show that as the temperature increases from 100 $^\circ$C to 200 $^\circ$C, there was a decrease in grain size indicating cubic-tetragonal and cubic-tetragonal-orthorhombic multi-phase stabilization. Recently, Kalyani et al. demonstrated presence of metal-stable orthorhombic BaTiO$_3$ along with tetragonal phase at room-temperature employing neutron powder-diffraction and very high-resolution synchrotron X-ray powder-diffraction.\(^{31}\) Again as temperature increases from 200 $^\circ$C to 250 $^\circ$C there was decrease in grain size indicating phase transition from orthorhombic to rhombohedral phase.\(^{32,33}\) P. Sarrazin et al., demonstrated that BaTiO$_3$ powders synthesized by hydrothermal method demonstrated reduction in lattice parameter upon heating involving loss of water molecules, which induces tension stress state in the material.\(^{34}\)

This transition could also be explained using the strain calculation. Similarly the strain calculated from Williamson Hall plot shows the same change as grain size undergoes with increasing the temperature. The strain was much increased for sample prepared at temperature 150 $^\circ$C indicating phase transition from mixed cubic-tetragonal to cubic-tetragonal-orthorhombic.\(^{21}\) As a result of strain field increasing with synthesis temperature there exist structural transformation of BaTiO$_3$ i.e., mixed cubic-tetragonal-orthorhombic to predominant orthogonal phase and again orthorhombic to rhombohedral phase with further increase in synthesis temperature.
B. SEM Analysis

Further insights into the method of fabricating BaTiO$_3$ can be acquired from SEM analysis. In particle size measurement, microscopy was the only method in which the individual particles were directly observed and measured. Manual or automatic techniques were used for particle size analysis. Manual technique was usually based on the use of a marking device moved along the particle to obtain a linear dimensional measure of the particle added up and divided by the number of particles to get a mean result. Figure 3 shows the SEM images of BaTiO$_3$ synthesized at four different temperatures: a) 100 °C, b) 150 °C, c) 200 °C and d) 250 °C. As can be seen from Fig. 3, the synthesis temperature ranges in the present study, resulted in BaTiO$_3$ particles with a spherical shape. To quantify the uniformity, a particle size distribution (PSD) was obtained, which reflects the statistical result from all sections for each sample. The PSD for samples prepared for four different temperatures was calculated using the aspect ratio method. For each sample about 500 particles were considered. A graph was plotted between the particle size and number of particles expecting a good Gaussian distribution, which provides information about distribution of particles around a particular size.

Figure 4 shows the PSD of BaTiO$_3$ synthesized at four different temperatures. The PSD of sample synthesized at 100 °C shows that, the particles were uniformly distributed above and below an average particle size of 163 nm following a standard Gaussian distribution. Since the Gaussian distribution was a theoretical distribution with finite mean and variance, it can be concluded that the distribution of particles were uniform at 100 °C. The PSD of sample synthesized at 150 °C and 200 °C shows that the particles get highly aggregated around the particle size of 155 nm and 145 nm, respectively. However, the distribution widens with increasing temperature from 100 to 200 °C. Fixing this particle size, the distribution of particles above and below this range was analyzed. The distribution was altered from...
a standard Gaussian. An Ostwald ripening was observed above 145 nm (i.e., small crystals or sol particles dissolve, and redeposit onto larger crystals or sol particles) and the average particle size was estimated to be 155 nm. The PSD of particles synthesized at 250 °C shows that, the particle aggregation around the particle size 116 nm with a Gaussian distribution. From the above distributions, it could be concluded that as reaction temperature increases, the aggregation of particles towards lower particle size was increased. The variation in the PSD might be due to the phase transition as observed in the XRD results.

C. TEM Analysis

The TEM could also yield information such as particle size, size distribution and morphology of the nanopowders, which could be used in comparison with the other methods to gain further insights into the synthesis method. TEM images could also be used to judge whether good dispersion has been achieved or whether agglomeration was present in the system.

Figure 5 shows the TEM images of BaTiO$_3$ synthesized at four different temperatures. From the TEM image, the samples exhibit uniform grain size distribution for all four temperatures. The images confirm that the particles were nearly spherical in shape and the shape of the particles did not change as temperature increases. The PSD was also done for the TEM images, following the same procedure as used for the SEM analysis. Figure 6 shows the PSD of BaTiO$_3$ synthesized at four different temperatures. Over 100 particles were considered in each sample for PSD. The results of particle size distribution of TEM images were similar to SEM. The agglomeration of the particles increases with increasing temperature. The estimated particle sizes for SEM and TEM coincides for sample prepared at 100°C. Only in the case of samples prepared at temperature 150 °C, the size has been reduced to around 114 nm, but for all the other temperatures the particle size was around 170 nm. This variation might be due to the phase transition observed in the XRD results. A similar deviation from Gaussian distribution can be observed from TEM analysis compared to SEM analysis for 150 and 200 °C.
FIG. 5. TEM image (left) and SAED pattern (right) of BaTiO$_3$ synthesized at four different temperatures: a) 100 °C, b) 150 °C, c) 200 °C, and d) 250 °C.

The selected area electron diffraction (SAED) pattern of the sample synthesized at four different temperatures is shown in Fig. 5. As can be seen in Fig. 5, SAED patterns show diffraction rings composed of discrete diffraction spots indicating the polycrystalline nature of the nanopowders. The diffraction rings were formed from region which consists of a large number of randomly oriented crystalline particles. Samples prepared at 100 °C and 200 °C show that the particles were uniformly oriented in the diffraction rings and indicate that the particles have a good crystalline nature. Samples prepared at 150 °C and 250 °C show that the particles were slightly disturbed from its uniform orientation in the diffraction rings. However, they still did not lack the crystalline nature which might be due to the growth methodology. The particle size determined from SEM and TEM results were summarized in Table III, with the maximum percent difference observed to be 31 %. In our results, the particle size determined using W-H plot analysis (Refer Table II) approximately agrees with SEM and TEM results as shown in Table III. This work was promising, as it showed that using this simple low-cost chemical technique and at low temperatures, BaTiO$_3$ could be synthesized at nanoscale with crystalline nature. The phase transition, which alters the magnetic and electric properties of the material and occurs at below-room temperature, can be stabilized at room temperature. Control of these
FIG. 6. Particle Size distribution from TEM analysis of BaTiO$_3$ synthesized at four different temperatures: a) 100 °C, b) 150 °C, c) 200 °C, and d) 250 °C.

TABLE III. Particle size of BaTiO$_3$ prepared at four different temperatures from SEM and TEM analysis.

| Temperature (°C) | Particle size (SEM distribution) nm | Particle size (TEM distribution) nm | Percent Difference (%) |
|-----------------|------------------------------------|------------------------------------|------------------------|
| 100             | 163                                | 153                                | 6                      |
| 150             | 155                                | 114                                | 30                     |
| 200             | 145                                | 171                                | 16                     |
| 250             | 116                                | 159                                | 31                     |

key properties indicates that the sol-gel hydrothermal method is a promising candidate for BaTiO$_3$ nanoparticle synthesis for a wide range of applications in the electronic industries. Since miniaturization of electronic devices has been a vital issue for the future generation, BaTiO$_3$ faces this challenge as it could be synthesized in nano scale with high dielectric constant. Additionally, non-linear optical property of BaTiO$_3$ can be explored from this low temperature process. Since non-linear optics finds numerous applications in the field of telecommunications, optical data storage, energy harvesting etc., along with fundamental research connected to issues like charge transfer, conjugation, polarization and crystallization into non-centro-symmetric lattices.

IV. CONCLUSIONS

The two chemical methods of sol–gel and hydrothermal process have been strategically combined to successfully fabricate the desired crystalline BaTiO$_3$ nano powder. Hydrothermal conditions employing chloride-based precursors and NaOH as a mineralizer created a gentle environment to promote the formation of crystalline phase directly from the amorphous phase at very low processing temperatures of 100 – 250 °C. XRD analysis showed a polyphase including the presence of small amount of impurities like BaCO$_3$. The exhibited peaks could be indexed as cubic (space group Pm3m)
and tetragonal ($P4mm$ space group) lattice of BaTiO$_3$ at synthesis temperature of 100 °C. Further increasing process temperature, stabilized mixed tetragonal-orthorhombic ($Ammm$ space group) phase and pure rhombohedral ($R3m$ space group) phase at 250 °C. From the XRD, the calculated lattice constants were in good agreement with literature and the calculated grain sizes were ~ 35 nm (from the Scherrer formula). SEM and TEM analysis verified that BaTiO$_3$ nanopowders synthesized by these methods were spherical in shape and about 114 – 170 nm. The results indicate that the variation in the PSD might be due to the phase transition as observed from XRD results. SAED shows that for all the four reaction temperatures, the particles possess a crystalline nature, which may be due to the temperature variation along with the concomitant pressure change with temperature. The results of this study show that using this simple low-cost chemical technique and at low temperatures, BaTiO$_3$ could be synthesized at nanoscale with crystalline nature. The phase transition, which alters the magnetic and electric properties of the material, was found to be a function of synthesis temperature and pressure. Control of these key properties indicates that the sol-gel hydrothermal method employing chloride based precursors is a promising candidate for BaTiO$_3$ nanoparticle synthesis for a wide range of applications in the electronic as well as opto-electronic industries.

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