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Paper

New Precision Contouring Process of Lanthanum Hexaboride (LaB_6) Crystals Used for Electron Guns

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電子銃用ランタンヘキサボライド（LaB_6）の新しい精密尖端加工

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Ultra-precision processing technique is indispensable for the production of high-quality tip to a desired shape from a LaB_6 single crystal chip which recently emerged as a cathode material for electron guns. This report describes a high-precision, high-quality tip processing method of LaB_6, and evaluates the electron emission characteristics of various electron guns manufactured for this experiment. A new polishing method was designed implementing a taper processing method, and applied to the finishing process with the combination of a hard plastic disk polisher and slurry in which ultra-fine particles are suspended. As a result, this new polishing method was proved to produce a strain-free mirror surface tip as small as 2 μm radius. Desired tip radius was also obtained applying the elastic polisher. Several tips of LaB_6 crystals have been processed accordingly using new method to an apical angle of $\theta=90°$ at the radius of curvature (R) of 10, 100 μm and ∞ (flat tip) each, and incorporated into the Vogel-type electron guns in order to understand various electron characteristics. This experiment confirmed that the smaller R is, the higher the brightness becomes, and the larger R is, the spot-shape becomes larger.

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1. Introduction

The performance of the electron beam exposure apparatus in the ULSI device fabrication process is very much dependent on that of the electron gun which generates electrons. Hereupon, LaB_6 single crystals have emerged as a primary material as a cathode.[1)] Currently extensive studies on the relative materials and processing methods have been progressing worldwide aiming at the development of high-brightness, long life and high performance cathodes.

When a LaB_6 single crystal is used as a cathode, the shape of its tip turns to be one of the most important parameters for the structure of an electron gun. However, there are still many unknown points about LaB_6 concerning the distribution of the emission current from the tip and its age-deterioration and the vacuum stability, which has forced the shape of LaB_6 crystals to be determined by trial and error in accordance with the purpose and specifications of each equipment.[2)]

Therefore, it is a vital necessity to develop a technique to process the tips of LaB_6 crystals to a high quality and desired shape. In this experiment, a method to process LaB_6 single crystals to a high-quality and desired shape is studied employing the conventional ultra-precision processing method for crystal substrates. Several LaB_6 crystals finished with this processing method were assembled into the electron guns to enable us to investigate their characteristics.

2. Contouring method of LaB_6 single crystals to be assembled into electron guns

2.1 Requirements for LaB_6 single crystals and electron guns

LaB_6 single crystals are grown mainly by either alumina flux method or floating zone method which was improved recently and gives the single crystals significantly improved purity and low dislocation.[3)]

Since the thermocouple emission is related to both temperature and work function, the materials suitable for a cathode are those that have low work function as a cathode, and high temperature resistance.[1)] Due to its structural properties, LaB_6 single crystal is given unique characteristics and outstanding thermocouple emission, and supported not only by its low work function but also by the high-melting point (1500°C) as well as by the high hardness (microhardness: 2770 kg/mm^2). LaB_6 single crystals have been widely recognized as one of the best high density electron sources currently available for practical use.[1)] The characteristics of LaB_6 is shown in Table 1.

In order to use LaB_6 single crystals as a cathode featuring superior characteristics, the tip of the cathode should be processed to a certain shape without damaging the surface. Also important is the right selection of a crystalline plane, since, depending on the axial orientation of the crystal, some planes are apt to generate electrons, and others have low work functions.[4)] In this study, we pay attention to the shape of the tips while selecting an orientation ⟨100⟩ to have the tip constituted of the plane (100), since ⟨100⟩ is easy to generate electrons and stable even at high temperatures. The tip point and its neighboring conical surface should be mirror-finished in order to uniformly stabilize the electrons generated from the conical side.[4)]

In general the brightness is high when the tip of the cathode is sharp, while if the radius of the tip curvature is large, the distribution of the thermocouple emission intensity is known good.[3)] Here, a strong desire has emerged to

Table 1. Characteristics of Lanthanum Hexaboride (LaB_6)

Molecular weight	203.78	
Boron content	31.83%	
Structure	Crystal structure Lattice constant	Cubic a = 0.4154nm(4.154Å)
Density	X-ray method Pycnometer system	4.721 g/cm^3 4.61 g/cm^3
Heat	Heat of formation Latent heat of evaporation	112 Kcal/mole 169 Kcal/mole
Thermal characteristics	Melting point Thermal conductivity Thermal expansion (25-1000℃)	over 2400℃ 0.114 cal/cm. sec,℃ 5.75 x 10^{-6}/℃
Electric characteristics	Specific resistivity (room temp.)	15 $\mu\Omega$cm at 20℃
Optical characteristics	Incident rate (λ=655 μm) Color	0.7 purplish red
Mechanical characteristics	Hardness Bending strength	2770 kg/mm^2 12.85 kg/cm^2
Thermocouple emission	Work function Richardson constant	2.66 eV 29 A/cm^2・℃^{2}

establish a technique to process LaB_6 single crystal tips to a high precision, high quality shape.

2.2 Current situations of processing methods of LaB_6 single crystals

Currently available tip contouring methods of LaB_6 single crystals are as follows:

(1) A method to produce a mirror-surface tip using a metal disk and diamond abrasives after the taper grinding with a diamond grinding stone,[5]

(2) A method to apply etching to the crystal after the taper grinding,[5]

(3) Electrolytic polishing.[2]

The method (1), that is an application of the processing technique of record needles, contours the tips to a radius of 2–5 μm, which, however, leaves damages to the layers during the processing. The method (2) removes damaged layers, whereas it presents problems in the reliability of the shape accuracy and reproducibility. The method (3) is to perform electrolytic polishing with the solutions mixed with, for example, 30% of phosphoric acid, 20% of glycerin and 50% of water.[2] The application of its polishing is limited only to certain crystal orientation planes, besides its shape accuracy is not satisfactory.

No other scientific articles on the technique to apply to LaB_6 crystals have been published. Although the ion sputtering method which was used for the diamond tip machining by Miyamoto and Taniguchi can also be applied to this tip contouring process of LaB_6 single crystals at a radius of below 1 μm,[6] its processing efficiency still remains low and therefore found inapplicable.

2.3 LaB_6 crystal machining and its method

LaB_6 crystals dissolve in oxidant acid such as nitrate, but not in hydrochloric or dilute sulfuric acid. It is mechanically very hard with micro-hardness of 2770 kg/mm^2. Because of the cleaving nature of LaB_6 crystals with the cleavage plane (100), careful attention should be given during processing to prevent generation of cracks and high pressure along cleavage.

Since LaB_6 is chemically stable and mechanically strong, it requires rough machining (premachining) using a diamond grinding stone. During the finishing, the crystal is polished to a damage-free, mirror-surface, for which a polishing method using colloidal silica is considered effective.[7] However, its processing condition can not be applied as it is to the LaB_6 tip contouring in view of extremely high precision required. Consequently, since the conventional elastic polisher is not suitable for sharpening the tips of LaB_6 single crystals, a hard plastic wheel-type polisher was chosen in this study.

Figure 1 shows a flow chart of the contouring process of LaB_6 crystals. The LaB_6 crystal chips are inserted into the holes of a jig and bonded with low viscosity adhesives (instantaneous adhesives). By inclining the LaB_6 crystal chip by half the desired angle (θ) of the tip ($\theta/2$), taper-grinding is performed while having the jig auto-rotating and at the same time reciprocating within the width of the grinding stone.

In the finishing process, chips are polished with colloidal silica using a wheel-type hard plastic polisher (ϕ 120 × 10^w mm) instead of the grinding stone employed in the rough machining process. This method is called "polishing with tapering," for which making the cutting depth small is important.

The polishing with tapering can make the radius of curvature of the tip large by forcing the rotating tip against the elastic polisher (e.g., artificial leather) for a certain period of time.

Upon completion of the polishing, scrub-cleaning with pure water is performed in order to remove residual slurries. The LaB_6 crystal chips are detached from the fixing jig and further cleaning is done with an ultrasonic wave in acetone and pure water.

LaB_6 crystal chips used in this experiment and experimental conditions of each process are shown in Table 2.

During the finishing process with the tapering method, over 20 μm was removed by polishing for the removal of the damaged layers induced by the rough machining. The cutting depth (Δx) was set to 1 μm/30 s in the initial stage, and later, polishing without cutting was carried out for a few minutes in the final stage, which is equivalent to the spark-out in the grinding, in order to make the radius of the tip as small as possible. Assuming that a whole chip of a LaB_6 crystal is buried in the plastic polisher by the depth of $\Delta x = 1$ μm, the tip must be processed to the R of as small as 2 μm pursuant to the equation $R \fallingdotseq 2\Delta x$.

3. Contouring processing of LaB_6 crystal chips and a trial manufacture of electron guns

3.1 Results of contouring processing of LaB_6 crystal chips

Figure 2 shows the tips of LaB_6 crystal chips (photos by scanning electron microscopy (SEM)) which were taper-ground (premachining) with the grinding stones of resinoid bond diamond, D#400 and D#1000. Processed with a D#

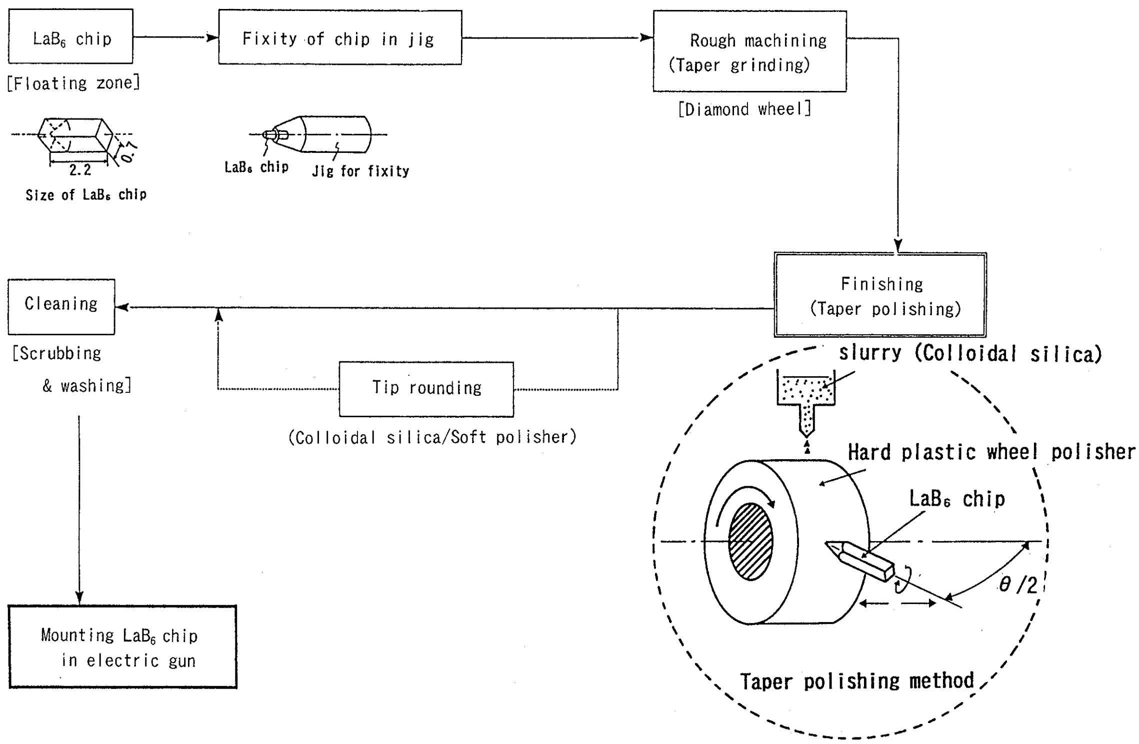


Fig. 1. Flow chart of a tip-shape processing of LaB_6 single crystal chips.

Table 2. Samples and Conditions for Each Process

Sample	LaB_6 single crystal (100) by a floating zone method (chip size : 0.75 x 0.6 x 2.2 mm)			
Item \ Process	① Rough machining	② Finishing	③ Tip rounding	④ Cleaning
Tool	Resinoid bond wheel (D#400, D#1000)	Hard type plastic wheel polisher (ϕ 120 x 10mm)	Artificial leather polisher	1st: scrubbing with pure water 2nd: washing with organic detergent (ultrasonic cleaning)
Revolution	1000rpm	1000rpm	1000rpm	
Slurry	water	colloidal silica	colloidal silica	
Fixed jig (sample) Inclination (θ/2) Revolution Depth of cut	45° 400rpm 1 μm/s	45° 400rpm about 1 μm/30s	45° 400rpm about 1 μm/60s	

400 grinding stone, the surface irregularities produced by crushing became large, while with a D#1000 grinding stone, the surface was found smoother although deep irregularities were still partially observed. The top views of the processed tips reveal that when ground with a D#1000 grinding stone, small cavities are crowded along a diagonal line as shown in Fig. 3. A large number of these directional small cavities on the surface are not conspicuous as far as irregularities of the processed surface are large. The exact cause of this phenomenon is not yet known. However, in view of the certain way of appearance, the polishing is not likely a cause of such phenomenon, but it can be considered a kind of the structural defects produced during the formation of crystals.

In the trial manufacturing, a D#1000 grinding stone (resinoid bond) that is considered advantageous in achieving smoothness was chosen for rough processing.

Figure 4 shows an example of the tips finished with a hard plastic wheel type polisher using colloidal silica in which oxide fine powders (10–20 nm SiO_2) are suspended. Surfaces processed by this method proved to be very smooth without generating defects like scratches. The radius of the curvature obtained by this polishing method with tapering was below 2 μm, making the tip very sharp. The angle of the tip (θ) was within 0.5° with respect to the set-up angle of 90° according to the observation by the magnified projector.

Using etching method (etchant: dilute HNO_3 solution), the processed surface was examined further in order to detect any defect induced by the processing. However, the result showed a complete absence of such defect, which allows us to confirm that this processing method provides

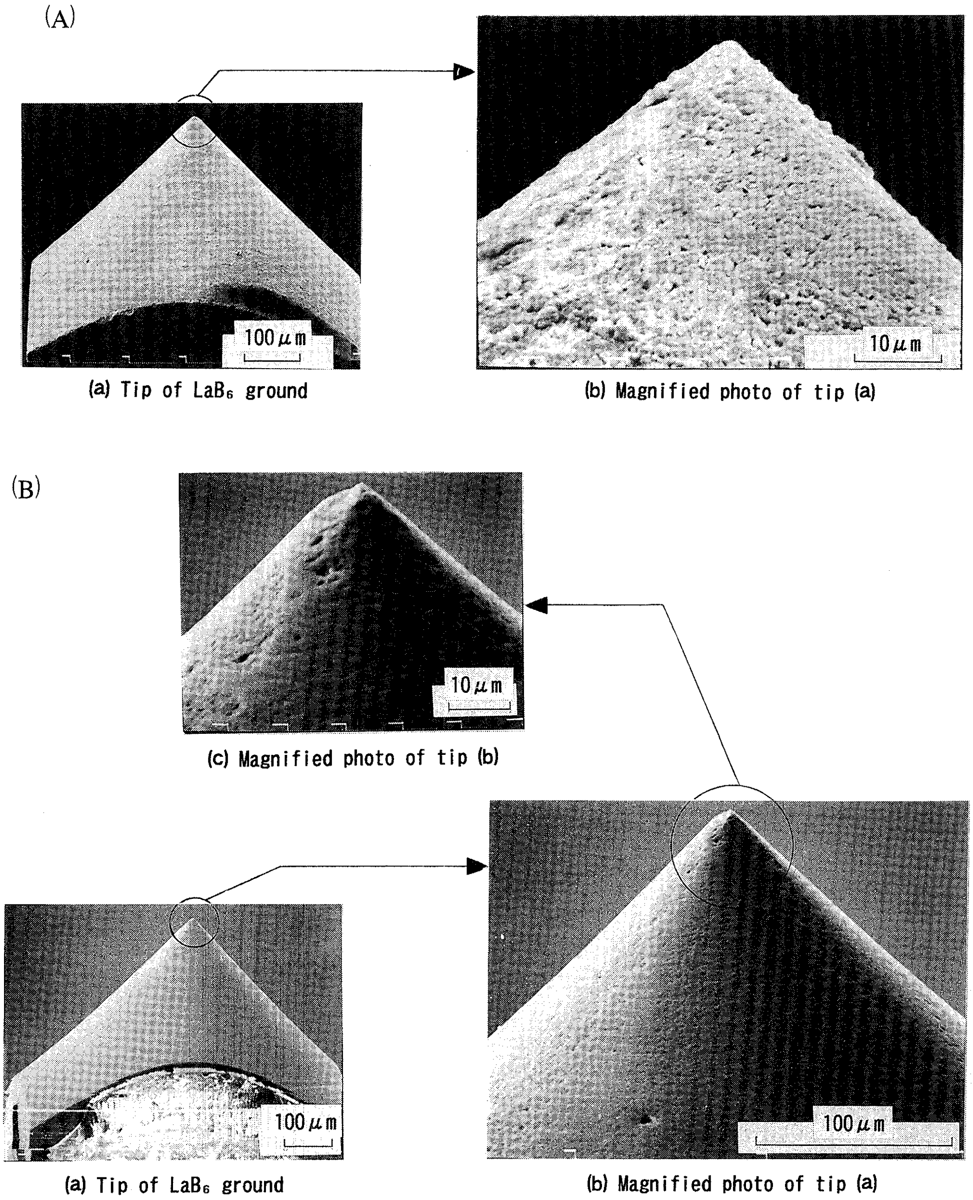


Fig. 2. Tips of LaB_6 ground by taper grinding method.
(A) Tip of LaB_6, ground with a diamond (#400) wheel.
(B) Tip of LaB_6, ground with a diamond (#1000) wheel.

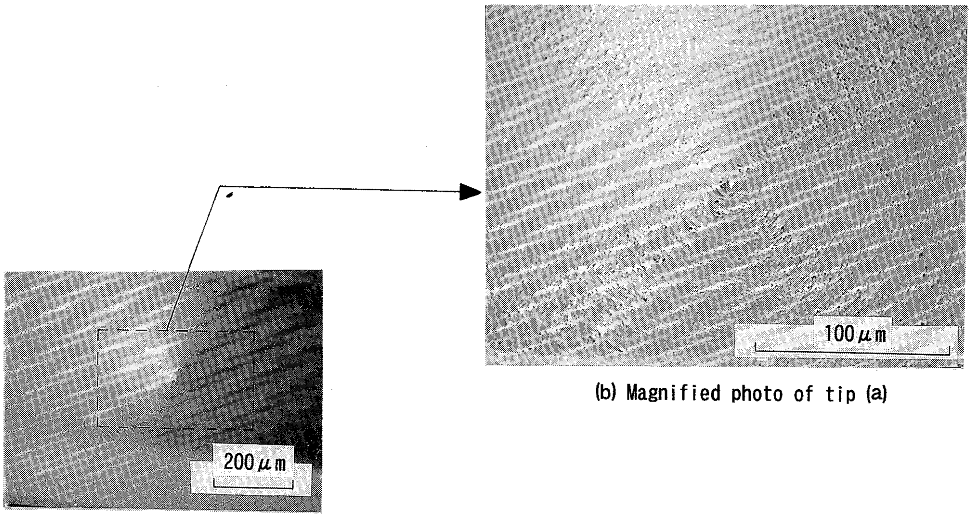
excellent quality to the surfaces.

Figure 5 shows the surface conditions processed in accordance with the processing flow (see Fig. 1) excluding the first-stage cleaning (scrub-cleaning with pure water), while Fig. 4 shows the conditions of the surface to which the first-stage cleaning was applied. These comparative figures confirm the effectiveness of the scrub-cleaning with pure water.

The LaB_6 crystals processed as mentioned previously were further processed to make the tip round using a colloidal silica slurry and a soft artificial leather. Two SEM photos are shown in Fig. 6, with the tips processed to $R=10\,\mu m$ and $R=100\,\mu m$, respectively. Same as Fig. 4, the processed surfaces are found very smooth. Good reproducibility of the tip round processing can be obtained by the processing time control. For example, the time needed to process the tips to $R=10$ and $100\,\mu m$ was 0.2 and 0.3 min, respectively.

Figure 7 shows an example of the LaB_6 crystal chip whose tip was contoured to flat ($R=\infty$, flat area: $\phi 200\,\mu m$) after the finish machining (R=below $2\,\mu m$). This is made by cutting a given depth, fixing a sample holding jig perpendicular to the lateral side of the outer edge of the tool (hard plastic wheel type polisher). This is called "tip-flattening process." However, as seen in Fig. 7(a), the edge of the tip flattened by the hard plastic wheel type polisher became sharp, which is not desirable for an electron gun, since, if used as a cathode, it is vulnerable to emit electrons from the sharp area of the edge. Therefore, in order to make the outer edge smoothly round, the tip in Fig. 7(a) was then chamfered as shown in Fig. 7(b) using the artificial leather polisher.

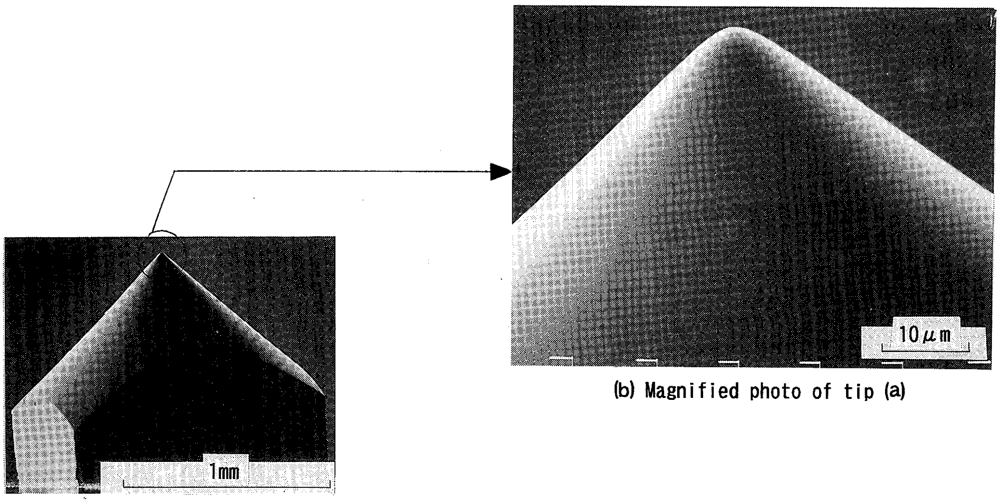
As described above, the tip can be processed to a damage-free, mirror surface with the R below $2\,\mu m$ by polishing with tapering, applying the combination of colloidal slurry and a hard plastic polisher. The tip angle (θ) can be determined to a desired one by changing the inclining set angle of $\theta/2$ of the sample-fixing jig against the polisher. Furthermore, it is confirmed that the tips are processed to a desired radius of curvature, R, by the tip flatten-



(b) Magnified photo of tip (a)

(a) Tip of LaB_6 ground

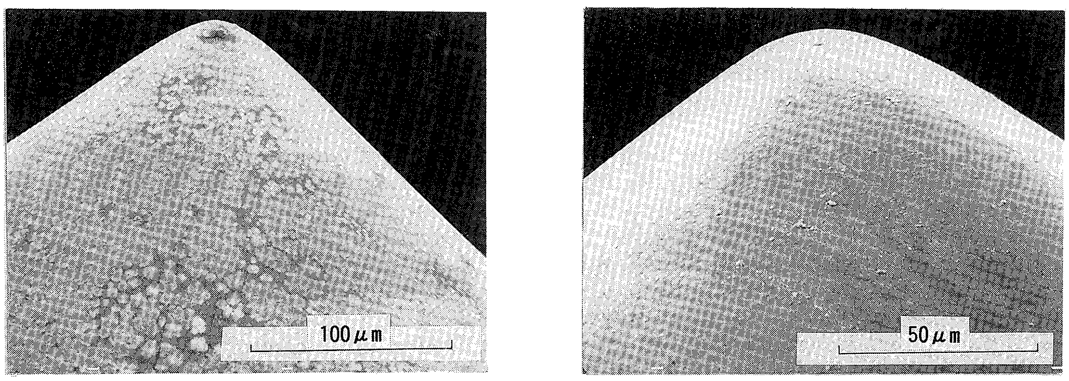
Fig. 3. Tip of LaB_6 crystal, processed with a diamond (#1000) wheel (top view).



(b) Magnified photo of tip (a)

(a) Tip of LaB_6 polished

Fig. 4. An example of LaB_6 crystal tip, finished with a combination of colloidal silica slurry and hard type plastic wheel polisher (radius of curvature of the tip, $R<2\ \mu m$).

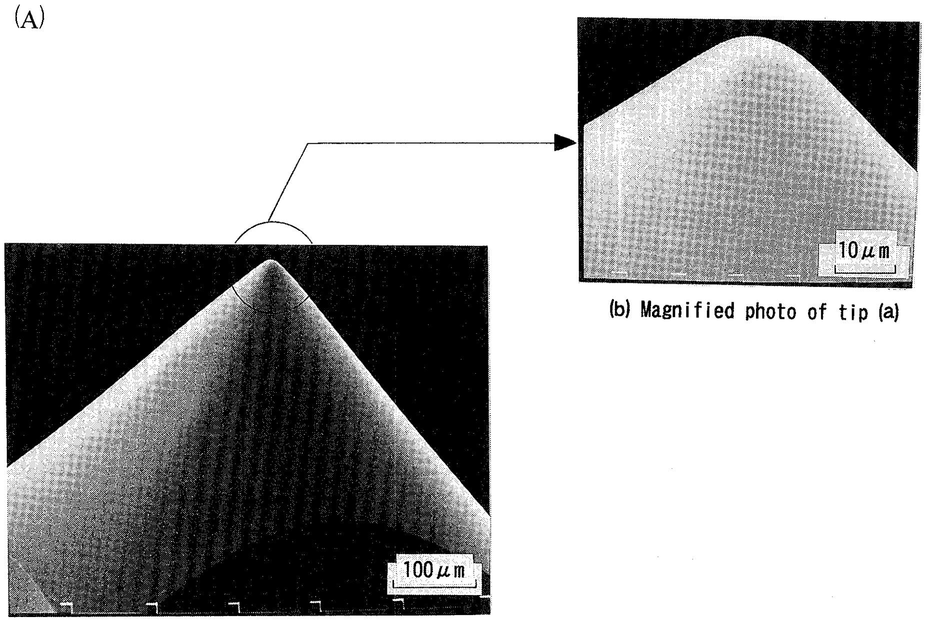


(a) Stains caused by colloidal silica slurry

(b) Deposits of gelled slurry

Fig. 5. Tip of LaB_6 crystal, finished with a colloidal silica slurry without the first cleaning (scrubbing).

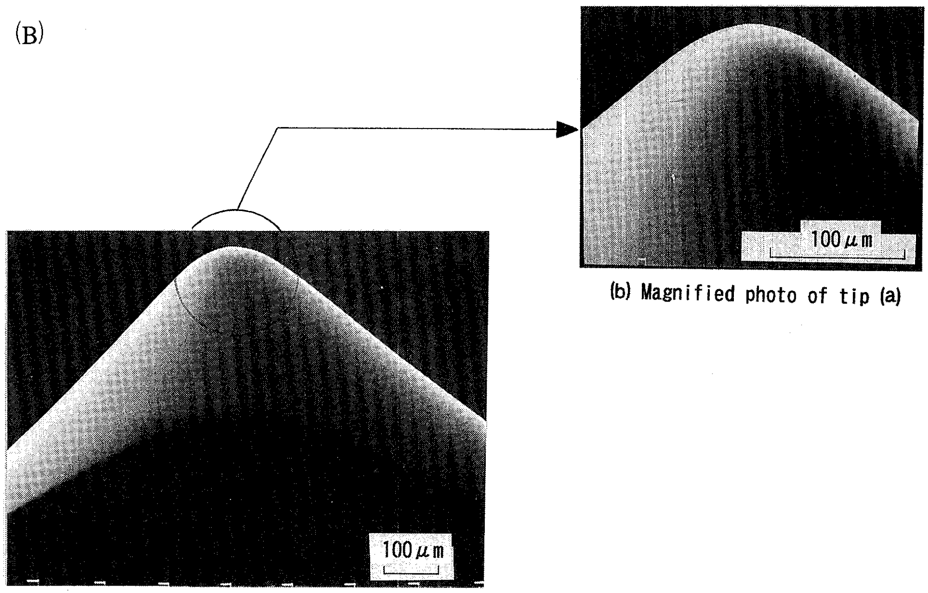
(A)



(a) Tip of LaB_6 polished

(b) Magnified photo of tip (a)

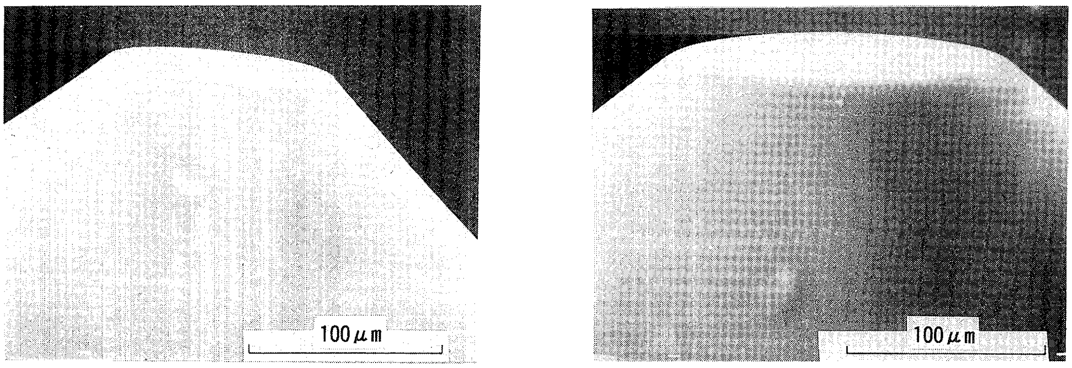
(B)



(a) Tip of LaB_6 polished

(b) Magnified photo of tip (a)

Fig. 6. LaB_6 tips finished to various radius of curvature by a new taper polishing method.
(A) An example of LaB_6 crystal tip, finished to a radius of curvature, $R=10$ μm.
(B) An example of LaB_6 crystal tip, finished to a radius of curvature, $R=100$ μm.



(a) Flat machining of tip by a hard plastic wheel polisher

(b) Chamfering by polishing using an elastic polisher

Fig. 7. Tips of LaB_6 crystal, polished to flat shape ($R=\infty$).

ing process or the tip round-chamfering process (using an elastic polisher).

3.2 Electron emission characteristics of Vogel-type electron guns with LaB_6 chip

LaB_6 chips (orientation ⟨100⟩, tip angle $\theta=90°$, dimensions $0.75\times0.6\times(2.3\text{–}2.1)$ mm) with three different radius of the curvature of the tips (①$R=10\ \mu$m, ②$R=100\ \mu$m and ③$R=\infty$ (flat area ϕ 200 μm, tip chamfered to round) were mounted on the prototype electron guns to investigate the spot-shapes of the uniform beam. The Vogel-structure was adopted to these electron guns. A LaB_6 chip mounted inside the Vogel-type electron gun is illustrated in Fig. 8.

The electron gun was incorporated inside the vacuum chamber of 3×10^{-5} Pa, and temperatures at several points of the electron gun were taken directly by a pyrometer (magnification; ×50) through the observation window made of fused quartz.

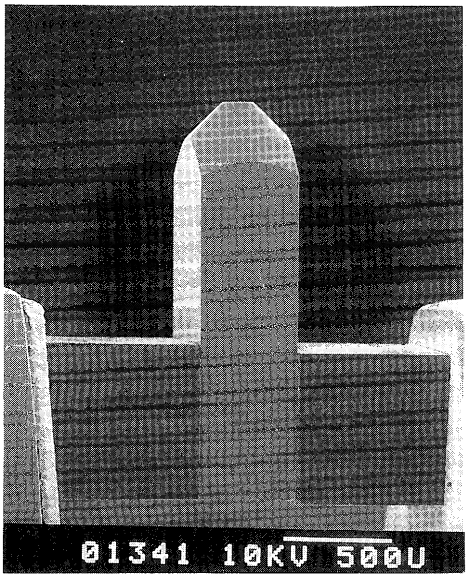


Fig. 8. An example of LaB_6 crystal mounted inside the Vogel-type electric gun (LaB_6 crystal: flat shape tip).

The characteristics of the current vs. temperature of several electron guns with integrated LaB_6 crystals are given in Fig. 9 showing similar results among them. However, each respective gun showed certain difference in the temperatures taken in itself from the tip of the LaB_6 chip (where marked ©) to heat generator (graphite/Ⓐ) and joint area of the LaB_6 chip Ⓑ.

In the next the results of the spot shapes and its profiles taken when electrons were emitted at the vacuum of 3×10^{-5} Pa and accelerating voltage of 20 kV are described.

Figure 10 shows the spot shapes formed by the electron guns and their profiles that correspond to their intensity distributions. The spot-shapes grew larger as the radius of the curvature R of the tips became large. It was prominent in particular when $R=\infty$. This means that a wide range of temperatures (over 95% of the beam diameters in the intensity distribution profile) are applicable. The tip of $R=\infty$ (tip is flat) is expected to be used as a cathode for the electron beam exposure. On the other hand, LaB_6 crystal chips with small R are expected to be applied as a cathode to SEM and analyzer which require high brightness and small spot diameter.

Figure 11 is an external view of the Vogel-type electron gun with the LaB_6 crystal finished with the processing method specified in the present study.

4. Conclusion

The tip-shape and surface quality of LaB_6 cathode have become essential parameters for the performance of electron guns. This research is based on and developed from the results achieved along the conventional processing methods. Since the finishing method affects directly the radiation characteristics of electrons, we have specially devised for a finishing process a new polishing technique with tapering, using a colloidal silica slurry in which ultrafine particles are suspended and a hard plastic wheel-type polisher.

Smooth, strain-free, mirror surface polishing was suc-

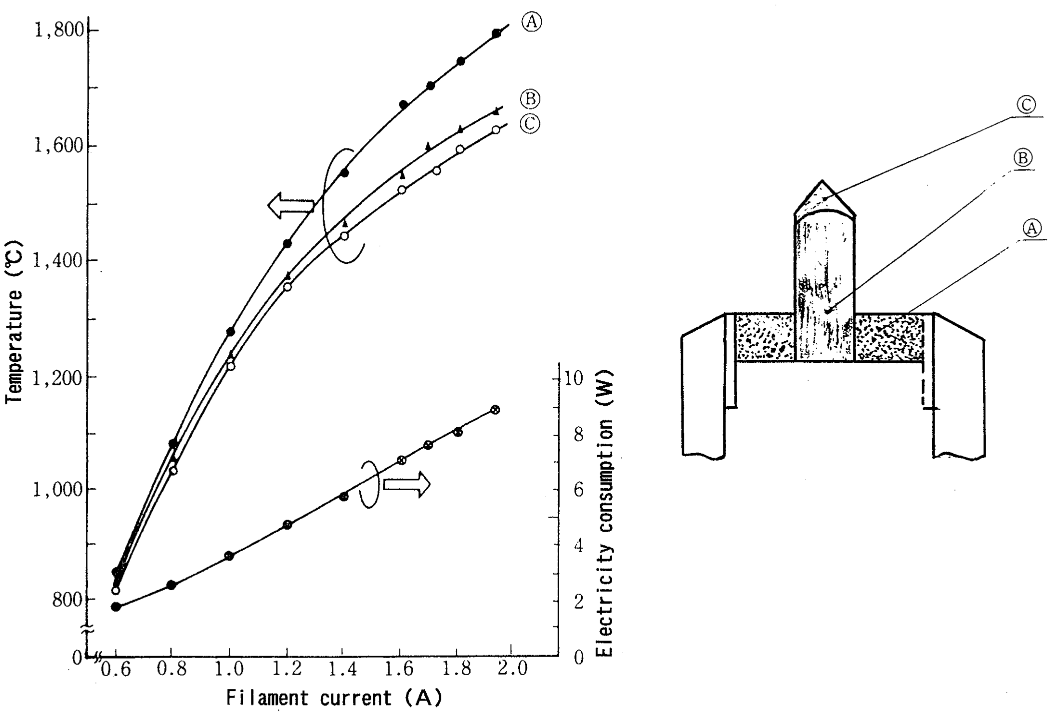
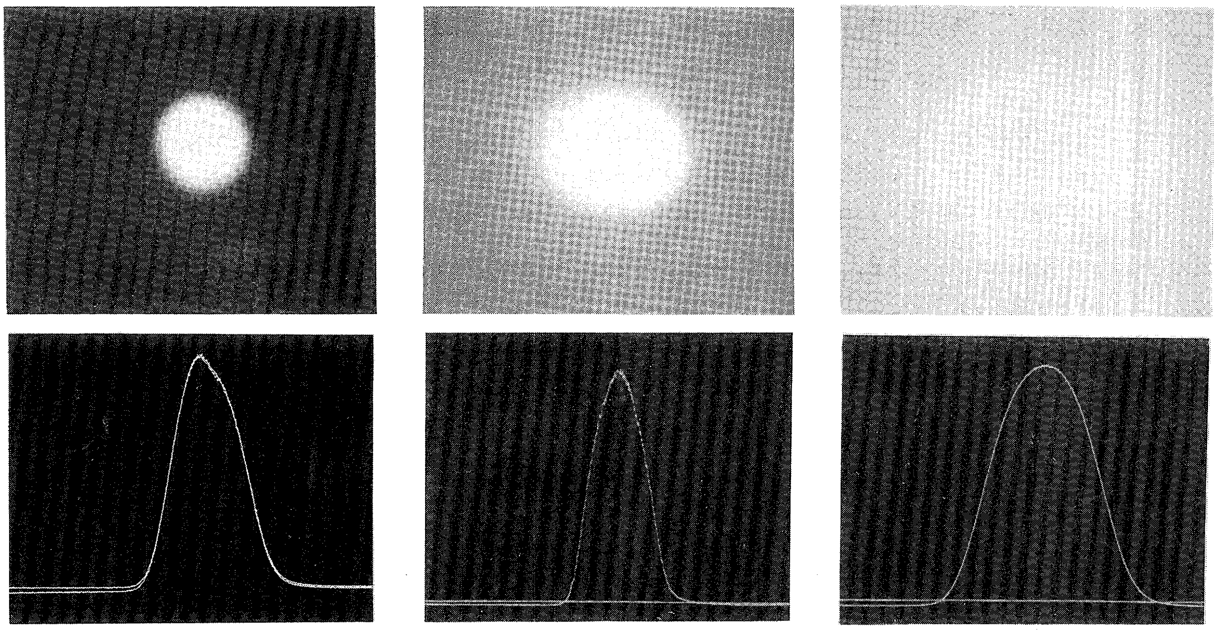


Fig. 9. Characteristics of the current and temperature of electric guns ($R=100\ \mu$m).



(a) R=10 μm (b) R=100 μm (c) R=∞ (Flat shape) (Flat part: φ200 μm)

Fig. 10. Beam spot patterns and intensity profiles by the Vogel-type electric gun, with the LaB_6 crystal chips finished to various shapes (LaB_6 crystal: ⟨100⟩, tip angle $\theta=90°$, R: radius of curvature of tip).

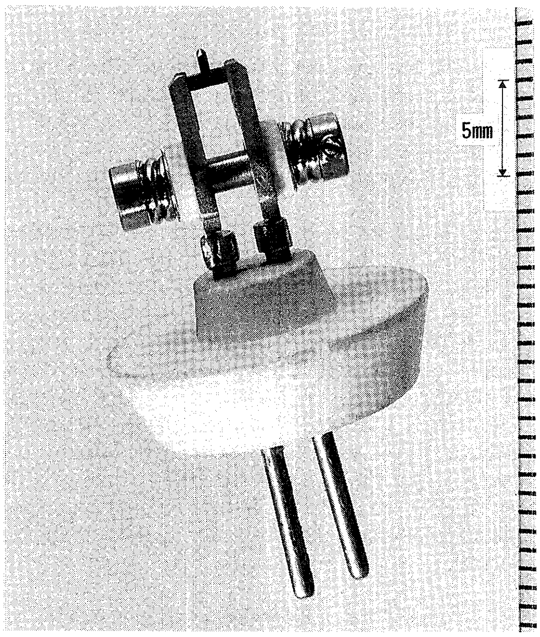


Fig. 11. Photo of a Vogel-type electric gun with the LaB_6 crystal chips processed in the present research.

cessfully realized by using this technique at as small as 2 μm radius of curvature. Processing to a desired tip-angle θ also becomes possible by inclining the sample by $\theta/2$ with respect to the lateral side of the polisher. Furthermore, it has been confirmed that the tips of a desired radius of curvature can be obtained if processing is done as specified by using an elastic polisher. Such tips were then mounted on the Vogel-type electron gun. It proved that the smaller R is, the higher the luminance becomes, and as the R increases, the spot-shape also enlarges, making the applicable range of the intensity become wider.

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