Lithium niobate: from single crystals to nanocrystals

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Abstract: LiNbO$_3$ single crystals were first grown more than 50 years ago. Since that time thousands of papers have been published dealing with their outstanding ferroelectric, acoustic, nonlinear optical, holographic etc. properties and demonstrating their countless realized or potential applications. It was about 25 years ago, when the first stoichiometric LiNbO$_3$ crystals gave a new impulse to the never-ending investigations. Different applications require different undoped or doped systems of bulk, thin film, or nanocrystal forms. In the present talk I’ll show two examples, (i) incorporation of dopants into stoichiometric crystals, and (ii) properties of LiNbO$_3$ nanocrystals prepared by high-energy ball-milling. Dopants are generally used to tailor the crystal properties for a given application. To understand the effect of dopants the substitution site in the crystal have to be known. Our IR absorption studies unambiguously showed that for the di-, tri-, and tetravalent cations a threshold concentration exists above which the dopants partially substitute at Nb sites, while below it they can be found on Li sites. Nano-crystalline LiNbO$_3$ was prepared from single crystals by the high-energy ball-milling technique. During milling the material suffered partial reduction that lead to the formation of bipolarons and polarons yielding gray color together with Li$_2$O segregation on the open surfaces. Upon high temperature oxidation a LiNb$_3$O$_8$ shell was formed. The particle size of the nano-crystals were determined by dynamic light scattering (DLS) and scanning electron microscopic (SEM) methods.

Keywords: lithium niobate; single crystal; nanocrystal;
OUTLINE

i) Dopant sites in stoichiometric LiNbO$_3$ single crystals
   - Stoichiometric vs. congruent LiNbO$_3$ (SLN ↔ CLN)
   - Hydroxyl ions in SLN
   - Optical damage resistant (ODR) ions
   - Rare-earth (RE) ions
   - Transition metal (TM) ions (Fe$^{3+}$, Cr$^{3+}$, Ti$^{4+}$)

ii) Mechanochemical reactions of LiNbO$_3$ induced by high-energy ball-milling
   - Lithium niobate nanocrystals
   - High-energy ball-milling (dry and wet grinding)
   - Particle and grain size reduction
   - Phase transformation and chemical reaction
   - Structure characterization (X-ray, Raman, reflection spectroscopy, coulometric titration, electron microscopy)
i) Stoichiometric vs. congruent LiNbO$_3$

Phase diagram, crystal growth

LiNbO$_3$ melts congruently grown by the Czochralski method

- 48.4 mol% Li$_2$O
- 51.6 mol% Nb$_2$O$_5$
- Li/Nb $\approx$ 0.94
- Li$_{1.5z}$Nb$_{1+z}$O$_3$ ($z \approx 0.01$)

Stoichiometric crystals grown by the HTTSSG method from K$_2$O flux

- K/Nb = 0.31, Li/Nb = 1 in the flux
- K $\approx$ 0, Li/Nb $\approx$ 1 in the crystal
- LiNbO$_3$ ($z \approx 0$)

i) Stoichiometric vs. congruent LiNbO$_3$

**OH$^-$ absorption band**

OH$^-$ ions are probes of the defect structure in LiNbO$_3$

**Congruent (Li/Nb $\approx$ 0.94)**
Li$_{1.5z}$Nb$_{1+z}$O$_3$ ($z \approx 0.01$)
$
u_{\text{max}} \approx 3484$ cm$^{-1}$

**Stoichiometric (Li/Nb $\approx$ 1)**
LiNbO$_3$ ($z \approx 0$)
$
u_{\text{max}} = 3466$ cm$^{-1}$

Stretching vibration of OH$^-$ ions in LiNbO$_3$

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i) Dopant ions in LiNbO$_3$

- Transition metal (TM) ions: $\text{Fe}^{2+/3+}$, $\text{Mn}^{2+}$, $\text{Cu}^{+}/^{2+}$, $\text{Ni}^{2+}$, $\text{Cr}^{3+}$, $\text{Ti}^{4+}$, etc.
  - Increase the photorefractive sensitivity utilized in holographic recording
  - Surface layer diffused Ti$^{4+}$ is used in optical waveguides
- Optical damage resistant (ODR) ions: $\text{Mg}^{2+}$, $\text{Zn}^{2+}$, $\text{Sc}^{3+}$, $\text{In}^{3+}$, $\text{Hf}^{4+}$, $\text{Zr}^{4+}$, $\text{Sn}^{4+}$
  - ODR ions above a threshold concentration suppress the photorefractive damage
  - The threshold concentration depends on the valence state of the dopant and the composition of LN (much lower for stoichiometric LN).
- Rare earth ions: $\text{Pr}^{3+}$, $\text{Nd}^{3+}$, $\text{Dy}^{3+}$, $\text{Er}^{3+}$, $\text{Yb}^{3+}$, ...
  - Laser active dopants, 4f - 4f transitions
  - Quantum Information Processing (QIP), Quantum Optics
i) Threshold concentration of ODR dopants

Below threshold $M^{n+} \rightarrow Li^+$ for $n = 2, 3, 4$ reducing the number of $Nb_{Li}$

Above threshold $M^{n+} \rightarrow Li^+$ and $Nb^{5+}$ no $Nb_{Li}$ ions are left in the crystal

Congruent LiNbO$_3$ ($Li_{1-5z}Nb_{1+z}O_3$ ($z \approx 0.01$), $Nb_{Li} \approx 0.01$)

Stoichiometric LiNbO$_3$ ($Li_{1-5z}Nb_{1+z}O_3$ ($z \approx 0$), $Nb_{Li} \approx 0$)

No excess Nb – no $Nb_{Li}$ $C_{th} \approx 0$ mol%

Experimentally – almost fulfilled

• for $Mg^{2+}$ $C_{th} \approx 0.2$ mol% in sLN $\ll C_{th} \approx 5$ mol% in cLN

• for $Zr^{4+}$ $C_{th} \approx 0.09$ mol% in sLN $\ll C_{th} \approx 2$ mol% in cLN

The OH$^-$ absorption spectrum is one of the best indicator of the threshold effect


i) Hydroxyl ions in ODR ion doped SLN

i) Hydroxyl ions in ODR ion doped SLN

Stronger attractive forces for the protons in $M_{\text{Nb}^{2+}}$ - OH$^-$ than in $M_{\text{Nb}^{5+}}$ - OH$^-$.

L. Kovács, Zs. Szaller, K. Lengyel, G. Corradi: Hydroxyl ions in stoichiometric LiNbO$_3$ crystals doped with optical damage resistant ions, Optical Materials, 37, 55-58, 2014.
i) Hydroxyl ions in ODR ion doped SLN

θ is the angle between the O–H bond and the oxygen plane perpendicular to the c axis.

i) Hydroxyl ions in ODR ion doped SLN

- The new OH\(^{-}\) band is present if \(C_{M^{n+}}\) is above the threshold.
- OH\(^{-}\) is close to \(M^{n+}\).
- Above threshold \(M^{n+}\) at least partially occupies Nb site.

\[M^{n+}_{\text{Nb}} - \text{OH}^{-}\]

i) Dopants in stoichiometric LiNbO$_3$

The defect model

$M^{n+}_{Nb} - OH^-$

based on the „threshold effect” is valid for all ODR ions.

It should also work for $M^{n+} = RE^{n+}$ and $TM^{n+}$ ions!
i) Hydroxyl ions in RE$^{3+}$-doped SLN

- Above a threshold Er concentration a new OH$^-$ band appears at $\approx$3488 cm$^{-1}$
- New OH$^-$ bands appear for other RE$^{3+}$ ions as well

i) RE$^{3+}$ ions in stoichiometric LiNbO$_3$

- RE$^{3+}$ ions fit into the incorporation model of ODR ions

i) $\text{TM}^{n+}$ ions in stoichiometric LiNbO$_3$

$\text{Ti}^{4+}$, $\text{Fe}^{3+}$, $\text{Fe}^{3+}+\text{Ti}^{4+}$ and $\text{Cr}^{3+}$ doped SLN crystals were grown by the HTTSSG and Czochralski methods.

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Conc. in solution [mol%]</th>
<th>Conc. in crystal [mol%]</th>
<th>OH$^-$ band [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe 0.06 Ti 0</td>
<td>Fe - Ti -</td>
<td>Fe - Ti -</td>
</tr>
<tr>
<td></td>
<td>Fe 0.06 Ti 0</td>
<td>Fe - Ti -</td>
<td>Fe - Ti -</td>
</tr>
<tr>
<td></td>
<td>Fe 0.5 Ti 0</td>
<td>Fe - Ti -</td>
<td>Fe - Ti -</td>
</tr>
<tr>
<td>2</td>
<td>0 0.012</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td>0 0.06</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td>0 0.12</td>
<td>- 0.077</td>
<td>- 3485</td>
</tr>
<tr>
<td>3</td>
<td>0.012 0.012</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td>0.06 0.012</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td>0.12 0.12</td>
<td>0.068 0.069</td>
<td>3502vw 3485</td>
</tr>
<tr>
<td></td>
<td>0.24 0.12</td>
<td>0.13 0.048</td>
<td>3502w 3485</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Growth method</th>
<th>Cr conc. in solution/melt [mol%]</th>
<th>Cr–OH band [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>HTTSSG</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HTTSSG</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Czochralski</td>
<td>0.5</td>
<td>3502</td>
</tr>
</tbody>
</table>

i) OH\(^-\) ions in Fe\(^{3+}\)- and Ti\(^{4+}\)-doped SLN

- Above a threshold concentration of the TM\(^{n+}\) dopants, new OH\(^-\) absorption bands appear in SLN crystals

L. Kovács, L. Kocsor, É. Tichy-Rács, K. Lengyel, L. Bencs, and G. Corradi: Hydroxyl ion probing transition metal dopants occupying Nb sites in stoichiometric LiNbO\(_3\), *Optical Materials Express*, 9, 4506-4516, 2019.
i) Hydroxyl ions in Cr$^{3+}$-doped SLN

- In the inhomogeneous bottom part of Cr-doped SLN a number of narrow overlapping OH$^{-}$ bands appeared due to Cr – OH centres with different defect environments

- Due to the composition change (becoming more stoichiometric) a single OH$^{-}$ band appears at 3502 cm$^{-1}$ at the bottom part of the Czochralski-grown crystal similarly to the Fe-doped SLN

i) TM$^{n+}$ ions in stoichiometric LiNbO$_3$

- The higher the valence state of the dopant, the lower the OH$^-$ vibrational frequency and the closer the O–H bond direction to the oxygen plane.
- The observed trend is valid for all dopants studied so far.

i) $M^{n+}$ ions in LiNbO$_3$ – Summary

- The IR absorption spectra of the OH$^-$ stretching vibration have been investigated in stoichiometric LiNbO$_3$ doped with $M^{n+}$ (ODR$^{n+}$, RE$^{3+}$, TM$^{n+}$) ions.
- Above a threshold $M^{n+}$ dopant concentration new OH$^-$ absorption bands appear due to the presence of $M^{n+}$–OH$^-$ type defects in the crystals. In the $M^{n+}$–OH$^-$ complex the dopant substitutes Nb site.
- It has been reaffirmed that OH$^-$ ions are excellent probes of the defect structure in LiNbO$_3$ crystals.
ii) Mechanochemical reactions of LiNbO$_3$ induced by high-energy ball-milling

- Lithium niobate nanocrystals
- High-energy ball-milling (dry and wet grinding)
- Particle and grain size reduction
- Phase transformation and chemical reaction
- Structure characterization (X-ray, Raman, reflection spectroscopy, coulometric titration, electron microscopy)
ii) LiNbO$_3$ nanocrystals

- Can be used e.g. in
  - Nonlinear optics – as harmonic nanoparticles (HNP) in nano-biophotonics
  - Quantum optics – rare-earth doped LN as single photon source
- Can be prepared by
  - „Bottom up“ method
    - Mechanochemical calcination (grinding + heat treatment)
    - Wet chemical, sol-gel, hydrothermal, combustion, etc.
  - „Top down“ method
    - High-energy ball-milling (dry and wet grinding) for particle and grain size reduction
      - Shaker mill – Spex mixer mill
      - Planetary mill – Fritsch Pulverisette
    - Etching
### ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

<table>
<thead>
<tr>
<th>#</th>
<th>Vial</th>
<th>Ball</th>
<th>Time (h)</th>
<th>Number of balls</th>
<th>Ball-to-powder mass ratio</th>
<th>Ball-to-powder volume ratio</th>
<th>Sample quantity (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-5</td>
<td>Stainless steel</td>
<td>11 mm 5.5 g</td>
<td>5</td>
<td>2</td>
<td>3.8 : 1</td>
<td>2.2 : 1</td>
<td>2.9</td>
</tr>
<tr>
<td>ALO-5</td>
<td>Alumina</td>
<td>12.5 mm 4.2 g</td>
<td>5</td>
<td>2</td>
<td>3.8 : 1</td>
<td>4.4 : 1</td>
<td>2.2</td>
</tr>
<tr>
<td>ALO-20</td>
<td>Alumina</td>
<td>11 mm 4.2 g</td>
<td>20</td>
<td>2</td>
<td>3.8 : 1</td>
<td>1.2 : 1</td>
<td>5.65</td>
</tr>
<tr>
<td>TC-5</td>
<td>Tungsten carbide</td>
<td>11 mm 10.7 g</td>
<td>5</td>
<td>2</td>
<td>3.8 : 1</td>
<td></td>
<td>5.65</td>
</tr>
</tbody>
</table>

**ii) High-energy ball-milling**

Dry grinding in SPEX shaker mill

![Particle size distribution](image)

<table>
<thead>
<tr>
<th>#</th>
<th>Resulting particle diameter (nm)</th>
<th>Resulting grain diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DLS</td>
<td>XRD</td>
</tr>
<tr>
<td>SS-5</td>
<td>190, (800)</td>
<td>55±18</td>
</tr>
<tr>
<td>ALO-5</td>
<td>700</td>
<td>63±21</td>
</tr>
<tr>
<td>ALO-20</td>
<td>700</td>
<td>37±2</td>
</tr>
<tr>
<td>TC-5</td>
<td>500</td>
<td>51±6</td>
</tr>
</tbody>
</table>

Particle diameter distributions of the ground samples in different vials determined by the Dynamic Light Scattering (DLS) method

Particle and grain sizes of samples ground in different vials

ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

Sample coloration

- **Al** was detected in the sample ground in *alumina* vial
- No **Fe** and **W** were detected in samples ground in *stainless steel* and *tungsten carbide* vials, respectively
- The coloration is not related to contamination

Energy-dispersive X-ray spectroscopy

ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

The series of samples ground in different vials with subsequent heat treatments underwent a change concerning the oxidation state of niobium during the grinding process. Annealing treatments in oxidative or non-oxidative atmospheres was applied for restoring or modifying the oxidation state of niobium in the ground samples.

L. Kocsor, L. Péter, G. Corradi, Z. Kis, J. Gubicza and L. Kovács: Mechanochemical reactions of lithium niobate induced by high energy ball-milling, Crystals, 9, 334/1-14, 2019.
ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

X-ray diffraction

Diffraction patterns of LN ground in **stainless steel** (a) and **alumina** (b) vials

The unmarked peaks are the reflections of LiNbO$_3$

- As-ground samples – broad peaks – small grain size
- Heat-treatment results in narrower diffraction lines due to increased grain sizes
- LiNb$_3$O$_8$ phase appeared in annealed samples

\[ 3 \text{LiNbO}_3 = \text{LiNb}_3\text{O}_8 + \text{Li}_2\text{O} \]

ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

Raman spectroscopy

Raman spectra of ground and heat-treated samples ball-milled for 5 h in stainless steel (a), and in tungsten carbide vial (b)

L. Kocsor, L. Péter, G. Corradi, Z. Kis, J. Gubicza and L. Kovács: Mechanochemical reactions of lithium niobate induced by high energy ball-milling, Crystals, 9, 334/1-14, 2019.
ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

Optical reflection measurements

Optical reflection spectra of samples ball-milled in different vials (a) and of ground and heat-treated samples ball-milled in stainless steel vial (b)

L. Kocsor, L. Péter, G. Corradi, Z. Kis, J. Gubicza and L. Kovács: Mechanochemical reactions of lithium niobate induced by high energy ball-milling, Crystals, 9, 334/1-14, 2019.
ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

- Congruent LiNbO$_3$ crystals:
  - Li$_{1.5x}$Nb$_{1+x}$O$_3$, x≈0.01
  - Nb$_{Li}^{4+}$: small polaron
  - Nb$_{Li}^{4+}$ - Nb$_{Nb}^{4+}$: bipolaron

- Ball-milling
  
  \[
  2\text{LiNbO}_3 \rightarrow \text{Nb}_{Nb}^{4+} + \text{Nb}_{Li}^{4+} + 3\text{O}_2^- + 2e^- + \text{Li}_2\text{O} \uparrow + \text{O}_2 \uparrow
  \]

- Oxidation

  \[
  \text{LiNbO}_3 + \text{Nb}_{Nb}^{4+} + \text{Nb}_{Li}^{4+} + 3\text{O}_2^- + 2e^- + \text{O}_2 \rightarrow \text{LiNb}_3\text{O}_8
  \]

ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

Quantitative determination of the degree of decomposition during ball-milling

- Coulometric titration \( m_{OX} = MQ/2F \)
  - \( M \): molar weight of Li_2O
  - \( Q \): charge passed until the equivalence point
  - \( F \): Faraday-constant (96485 C/mol)
  - 2: the hydrolysis of 1 mol of Li_2O results in 2 mols of hydroxide ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>100w_{ox} (weight%)</th>
<th>Mean particle radius, DLS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALO-20</td>
<td>0.97±0.05</td>
<td>350</td>
</tr>
<tr>
<td>TC-5</td>
<td>1.05±0.10</td>
<td>250</td>
</tr>
<tr>
<td>SS-5</td>
<td>1.52±0.21</td>
<td>95</td>
</tr>
</tbody>
</table>

The measured Li_2O mass ratios \( w_{ox} \) expressed as weight percent of the as-ground powder.

ii) High-energy ball-milling

Dry grinding in SPEX shaker mill

Estimation of the thickness of the LiNb\textsubscript{3}O\textsubscript{8} layer

- Assumptions
  - Uniform spherical LN particles of unmodified composition
  - Uniformly thick LiNb\textsubscript{3}O\textsubscript{8} layer
  - \(d\ll R\)

\[
\begin{align*}
  w_{\text{OX}} &= \frac{m_{\text{LTN}} M_{\text{OX}}}{m_{\text{LN}} + m_{\text{LTN}} \left( 1 + \frac{M_{\text{OX}}}{M_{\text{LTN}}} \right)} \quad \text{weight ratio of Li}_2\text{O in the ground material} \\
  d_{\text{LTN}} &\approx \frac{R}{3 \rho_{\text{LTN}}} M_{\text{LTN}} \omega_{\text{OX}} \quad \text{and} \quad d_{\text{OX}} \approx \frac{\rho_{\text{LTN}} M_{\text{OX}}}{\rho_{\text{OX}} M_{\text{LTN}}} d_{\text{LTN}} \approx \frac{d_{\text{LTN}}}{5.6}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>100(w_{\text{OX}}) (weight%)</th>
<th>Mean particle radius, DLS (nm)</th>
<th>Mean grain radius, XRD (nm)</th>
<th>(d_{\text{LTN}}) LiNb\textsubscript{3}O\textsubscript{8} shell thickness (nm)</th>
<th>(d_{\text{OX}}) Li\textsubscript{2}O shell thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALO-20</td>
<td>0.97(\pm)0.05</td>
<td>350</td>
<td>18.5</td>
<td>14.6</td>
<td>2.6</td>
</tr>
<tr>
<td>TC-5</td>
<td>1.05(\pm)0.10</td>
<td>250</td>
<td>25.5</td>
<td>11.3</td>
<td>2.0</td>
</tr>
<tr>
<td>SS-5</td>
<td>1.52(\pm)0.21</td>
<td>95</td>
<td>27.5</td>
<td>6.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

L. Kocsor, L. Péter, G. Corradi, Z. Kis, J. Gubicza and L. Kovács: Mechanochemical reactions of lithium niobate induced by high energy ball-milling, Crystals, 9, 334/1-14, 2019.
ii) High-energy ball-milling
Dry and wet grinding in Fritsch planetary mill

Recent results

<table>
<thead>
<tr>
<th></th>
<th>Vial / Ball</th>
<th>RPM</th>
<th>Time</th>
<th>Solvent</th>
<th>Ball size / quantity</th>
<th>Sample quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRY</td>
<td>ZrO$_2$</td>
<td>1100</td>
<td>10x1 min</td>
<td>-</td>
<td>0.5-3 mm / 70 g</td>
<td>5 g</td>
</tr>
<tr>
<td>WET</td>
<td>ZrO$_2$</td>
<td>1100</td>
<td>10x1 min</td>
<td>10 ml water</td>
<td>0.1-3 mm / 70 g</td>
<td>5 g</td>
</tr>
</tbody>
</table>
ii) High-energy ball-milling

Dry and wet grinding in Fritsch planetary mill

Recent results

Size distribution measured by Dynamic Light Scattering (DLS)
ii) High-energy ball-milling

Dry grinding in Fritsch planetary mill

Recent results

Scanning electron microscopy (SEM) images of the LiNbO$_3$ particles
ii) High-energy ball-milling
Wet grinding in Fritsch planetary mill

Recent results

The material (Zr) of the vial/ball is present in the particles measured by EDAX
ii) High-energy ball-milling
Dry grinding in Fritsch planetary mill

Recent results

Dopants (Tm and Yb) planned to use in single photon source are present in the particles
ii) High-energy ball-milling – Summary

- Nano-LN (10-50 nm particle size) has been successfully prepared by high-energy ball-milling.
- During the milling process the material suffers partial reduction interpreted by polaron/bipolaron formation.
- Li$_2$O loss and LiNb$_3$O$_8$ formation was observed in the outer shell of the particles.
- These findings provide a comprehensive explanation of the physicochemical behaviour of the system during grinding and annealings.
- RE$^{3+}$-doped nano-LN has been successfully prepared for single photon source.
Conclusions

• LiNbO$_3$ either in single crystal or in nanocrystalline form is one of the most versatile materials for optical applications

• The study of both intrinsic and extrinsic defects affecting the properties of LN may provide new results for future applications
Acknowledgment

NATIONAL RESEARCH, DEVELOPMENT AND INNOVATION Office
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MOMENTUM OF INNOVATION

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