



MARTENZITNI PRIJELAZI U MOLEKULSKIM KRISTALIMA

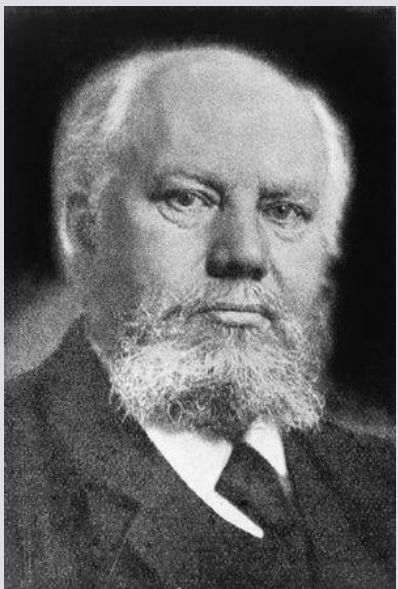
Kemijski seminar I

Izrađeno prema radu: S. Kyu Park and Y. Diao, *Chem. Soc. Rev.*, 2020., **49**, 8287-8314.

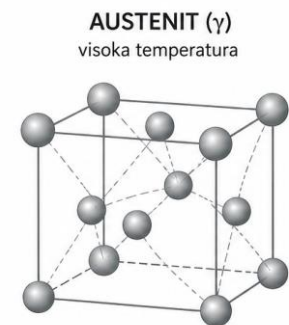
Božena Tokić

20.05.2026.

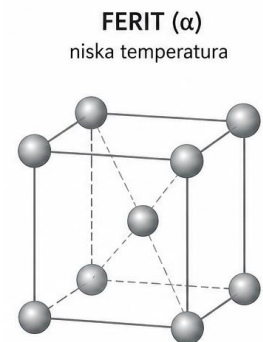
MARTENZITNI PRIJELAZI



Adolf Martens

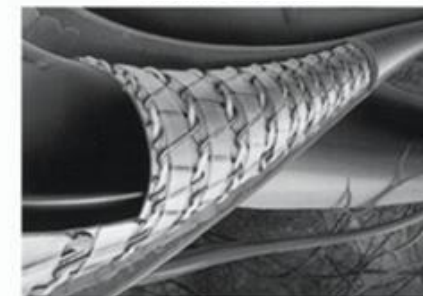


Plošno centrirana kubična kocka

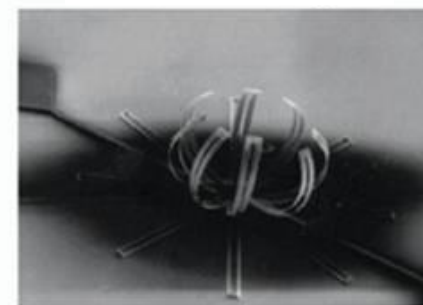


Volumno centrirana kubična kocka

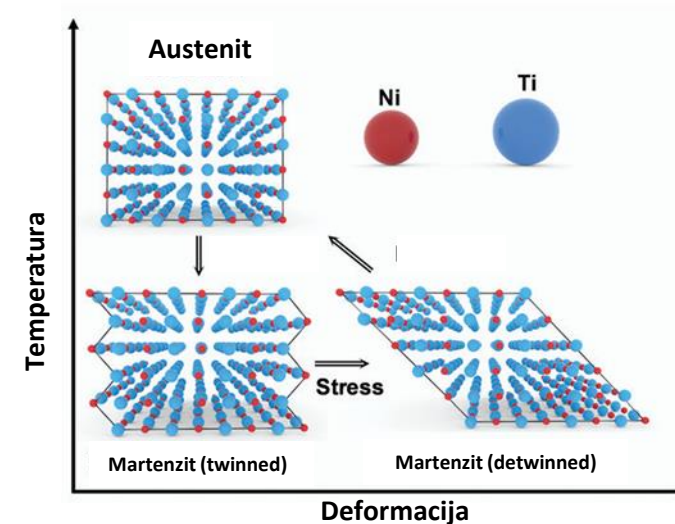
NiTi Stent



Mikro ovojnice



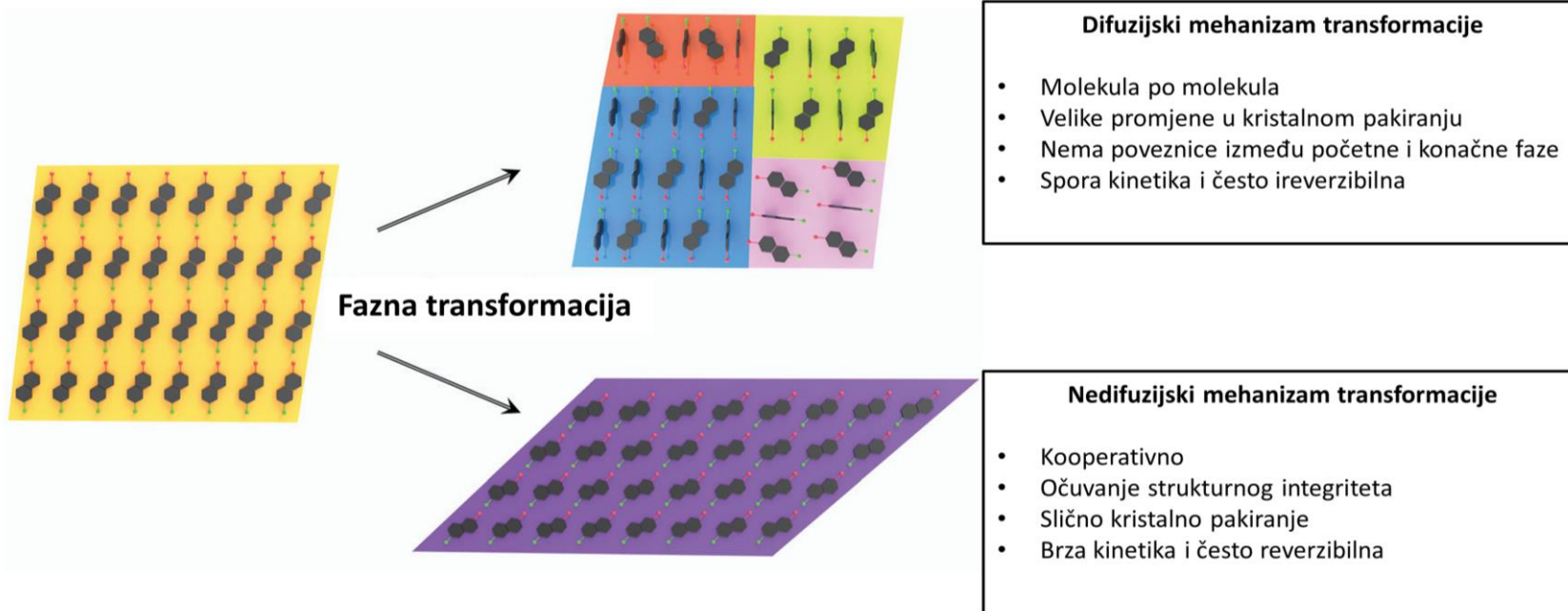
- Difuzijski neovisni fazni prijelazi prvog reda
- Brza i koordinirana promjena kristalne strukture bez dugodosežne difuzije atoma.
- Kolektivni pomaka atoma
- Deformacija kristalne rešetke



D. Kalish and M. Cohen, *Mater Sci. Eng*, 1970, **6**, 156-166.

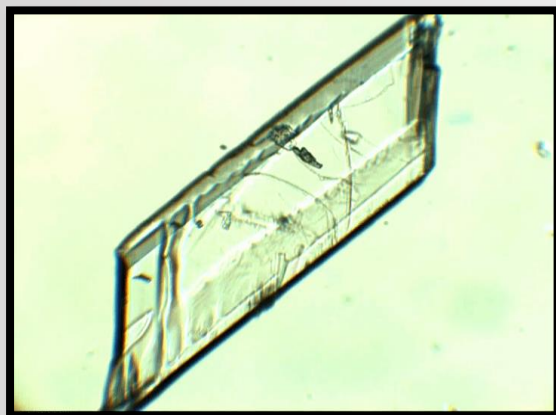
W. J. Buehler and F. E. Wang, *Ocean Eng.*, 1968, **1**, 105-120.

Difuzijski mehanizam vs martenzitni prijelazi



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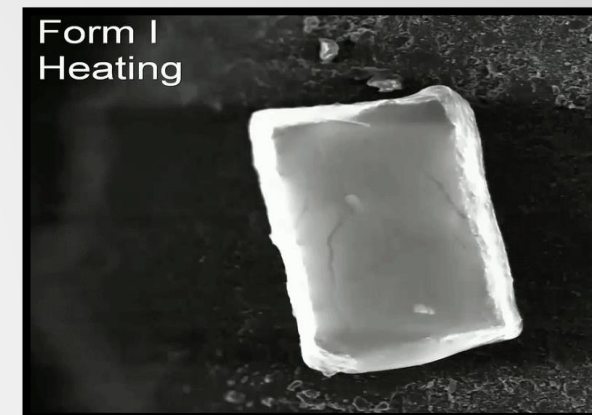
Molekulski kristali pokazuju martenzitne prijelaze povezane s termoelastičnim i superelastičnim svojstvima, termoodskočnim te "shape-memory" efektom.



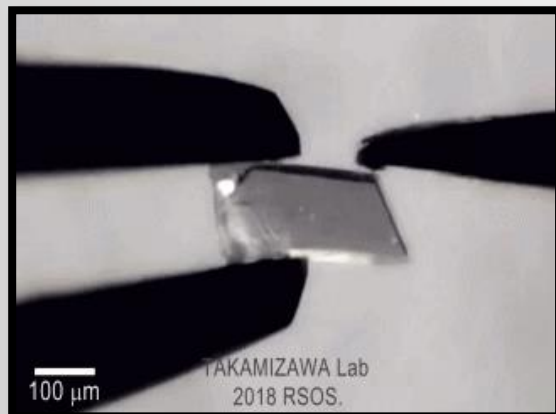
D.P.Karothu, J. Weston, I. T. Desta and P. Naumov, *J. Am. Chem. Soc.*, 2016, **138**, 13298–13306.



S. C. Sahoo, S. B. Sinha, M. S. Kiran, U. Ramamurty, A. F. Dericioglu, C. M. Reddy and P. Naumov, *J. Am. Chem. Soc.*, 2013, **135**, 13843–13850.



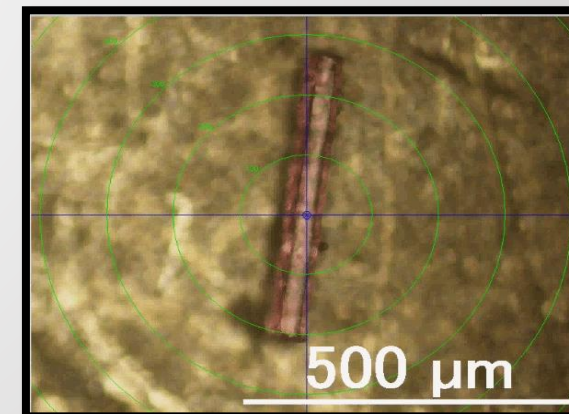
A. Colin-Molina, D. P. Karothu, M. J. Jellen, R. A. Toscano, M. A. Garcia-Garibay, P. Naumov and B. Rodriguez-Molina, *Matter*, 2019, **1**, 1033–1046.



S. Takamizawa, Y. Takasaki, T. Sasaki and N. Ozaki, *Nat. Commun.*, 2018, **9**, 3984.



S. Takamizawa and Y. Miyamoto, *Angew. Chem., Int. Ed.*, 2014, **53**, 6970–6973.

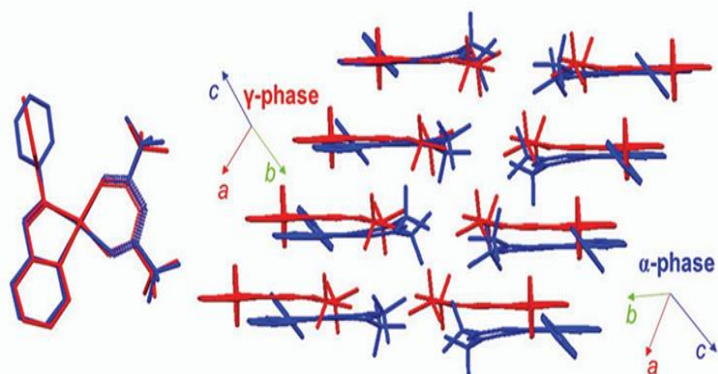


Z. S. Yao, M. Mito, T. Kamachi, Y. Shiota, K. Yoshizawa, N. Azuma, Y. Miyazaki, K. Takahashi, K. Zhang, T. Nakanishi, S. Kang, S. Kanegawa and O. Sato, *Nat. Chem.*, 2014, **6**, 1079–1083.

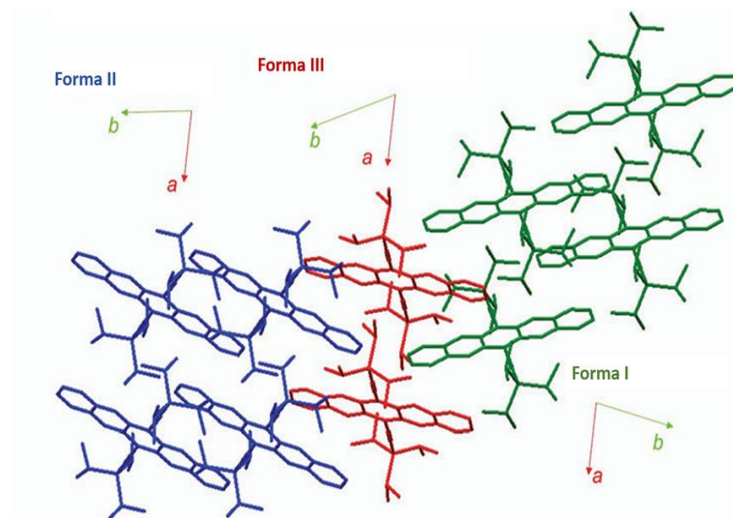
Klasifikacija Martenzitnih prijelaza u molekulskim kristalima

(Klasifikacija prema dominantnom mehanizmu molekuskog pomaka koji pokreće transformaciju)

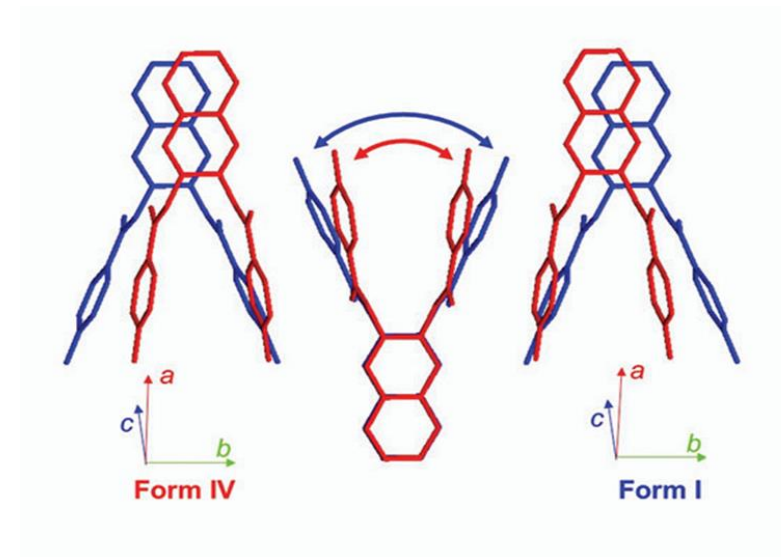
MOLEKULSKO KLIZANJE



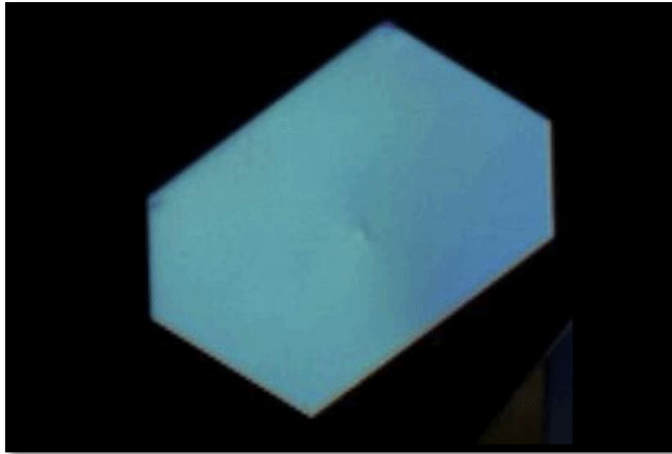
ROTACIJE MOLEKULE



KONFORMACIJSKE PROMJENE



TERMOELASTIČNOST



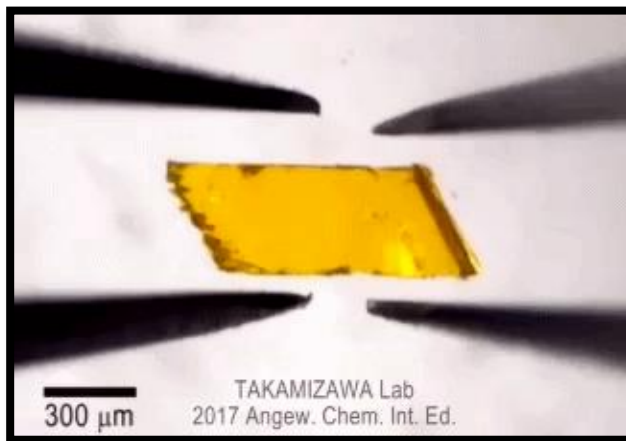
H. Chung, D. Dudenko, F. Zhang, G. D'Avino, C. Ruzie', A. Richard, G. Schweicher, J. Cornil, D. Beljonne, Y. Geerts and Y. Diao, *Nat. Commun.*, 2018, 9, 278.

SUPERELASTIČNOST



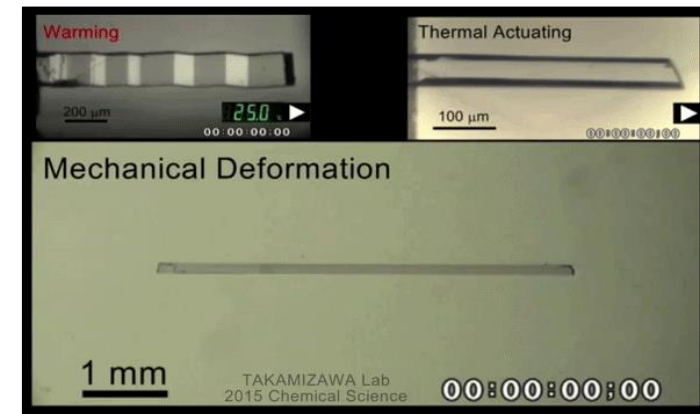
S. Takamizawa and Y. Takasaki, *Angew. Chem.*, 2015, 54, 4815–4817.

FEROELASTIČNOST



S. Takamizawa and Y. Takasaki, *Angew. Chem., Int. Ed.*, 2015, 54, 4815–4817.

“SHAPE-MEMORY” EFEKT



S. Takamizawa and Y. Takasaki, *Chem. Sci.*, 2016, 7, 1527–1534.

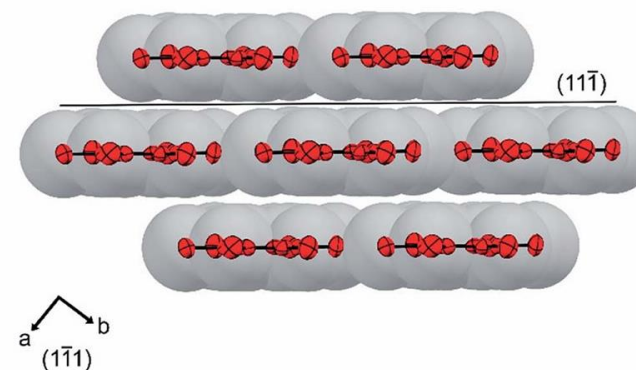
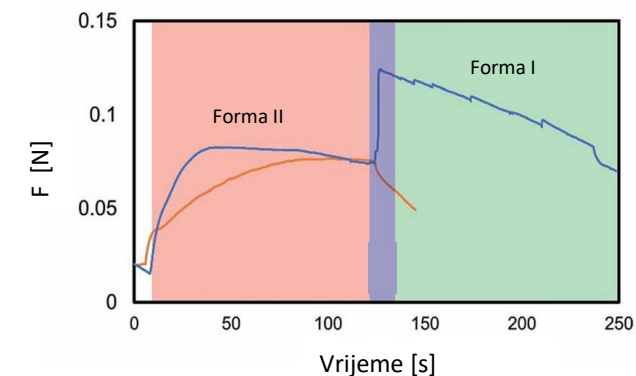
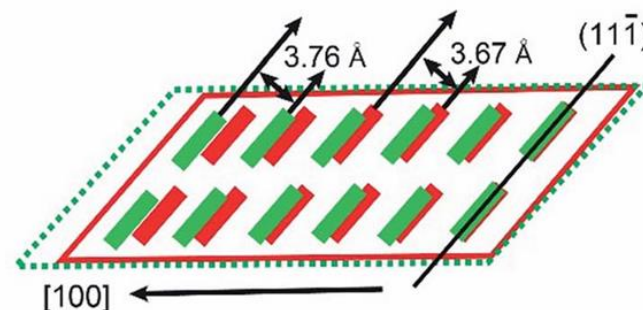
Heksametilbenzen (HMB)

- Struktura sadržava paralelno pomaknute π interakcije
- Prijelaz iz forme II u formu I na 382–385 K
- Dolazi do promjene kristalnog pakiranja (triklinski \rightarrow ortorombski)
- Strukturna promjena pripisuje se klizanju molekula duž fazne fronte (odnosno granice prijelaza), koja je paralelna molekulskoj π -ravnini

Forma II

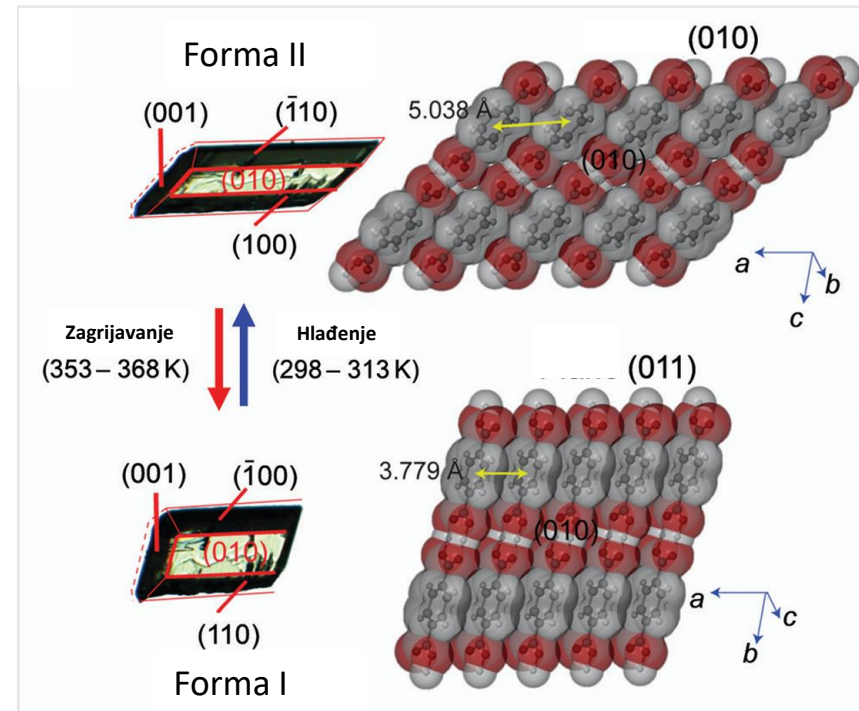
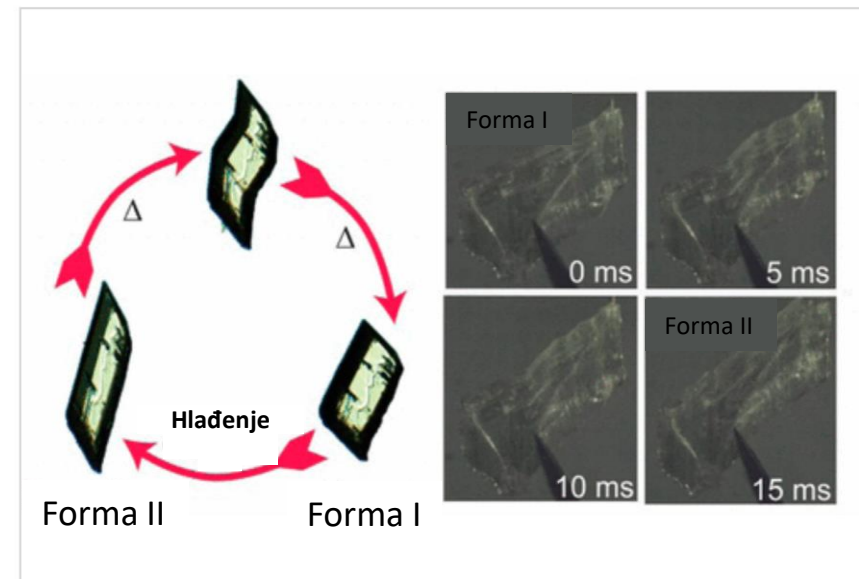


Forma I



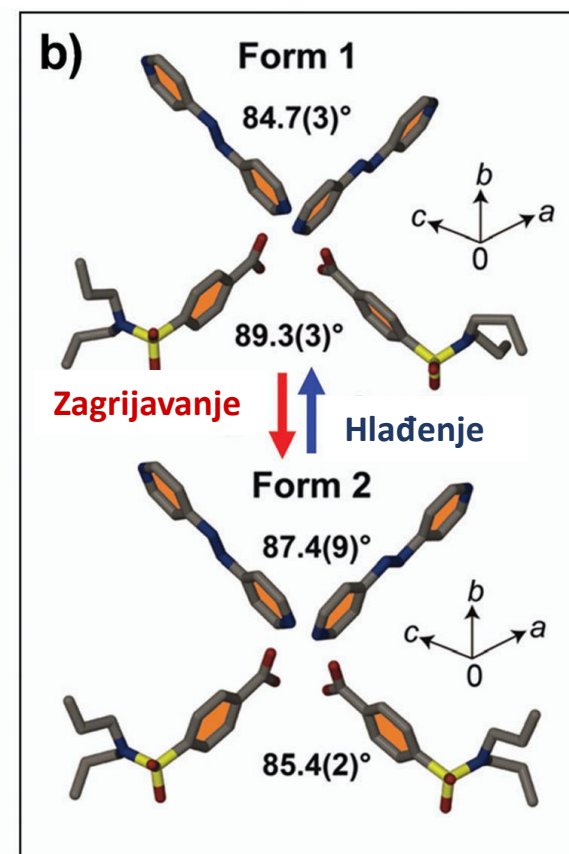
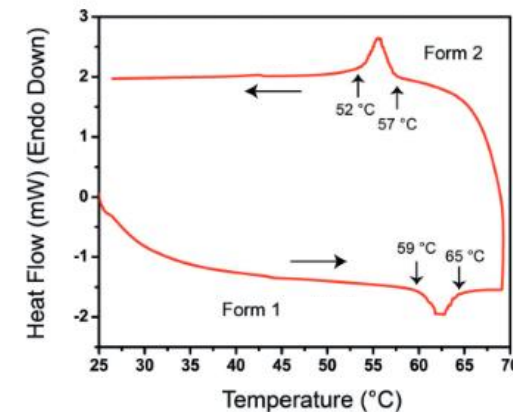
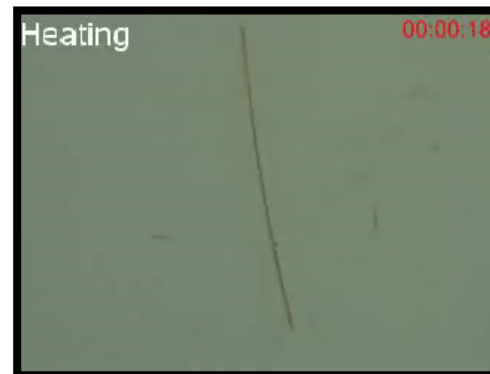
Tereftalna kiselina

- Značajno skraćivanje osi kristala (26%) prilikom polimornog prijelaza
- Mehanizam molekuskog klizanja
- Dolazi do promjene u pakiranju, različite udaljenosti slojeva i kuteva
- Mehaničkim poticajem moguć je prijelaz iz I u II – termoodskočni efekt
- Plastična deformabilnost te funkcija memorije oblika



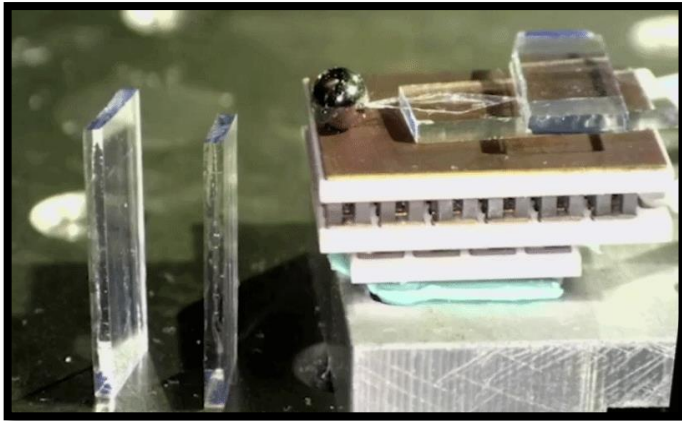
Kokristal probenecida i 4,4'-azopiridina

- Prilikom zagrijavanja dolazi do prelaske iz forme I u formu II;
- Mehanizam molekuskog klizanja;
- Izražen termoodskočni efekt
- Struktura oblika II u sve strukturne motive pristune u formi I, uz male promjene u kutovima
- Autori pripisuju reverzibilno uvijanje kristala neujednačenim naprezanjima koja nastaju tijekom faznog prijelaza.



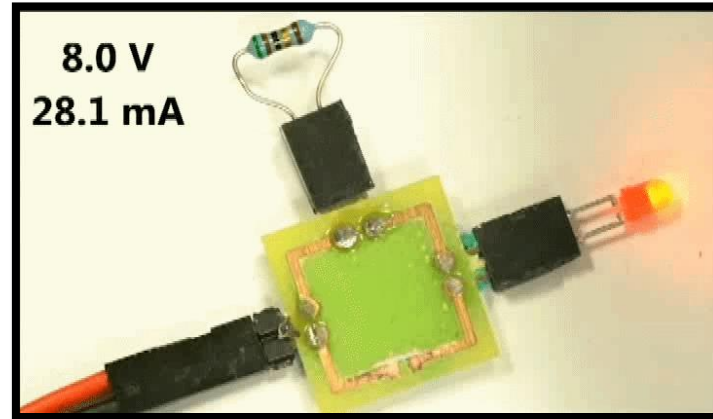
POTENCIJALNE PRIMJENE MOLEKULSKIH MARTENZITNIH MATERIJALA

LAGANI AKTUATORI



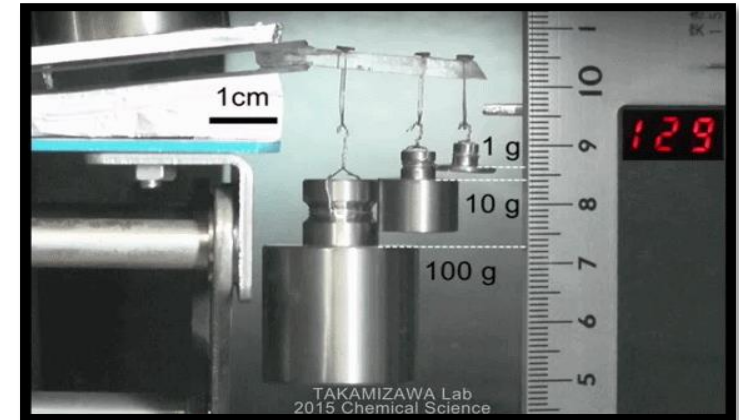
L. Li, P. Commins, M. B. Al-Handawi, D. P. Karothu, J. M. Halabi, S. Schramm, J. Weston, R. Rezgui and P. Naumov, *Chem. Sci.*, 2019, **10**, 7327–7332

ELEKTRIČNI OSIGURAČI



A. Khalil, E. Ahmed and P. Naumov, *Chem. Commun.*, 2017, **53**, 8470–8473.

TERMOMEHANIČKE DIZALICE



S. Takamizawa and Y. Takasaki, *Chem. Sci.*, 2016, **7**, 1527–1534.

FLEKSIBILNA ELEKTRONIKA

ELEKTRONIKA S MEMORIJOM FUNKCIJE I OBLIKA

MEMBRANE ZA KONTROLU PROTOKA PLINA

SMJERNICE ZA DIZAJN MOLEKULSKIH MARTENZITA:

I. POSTOJANJE RAVNINA POGODNIH ZA KLIZANJE

II. MOGUĆNOST AKTIVIRANJA DINAMIČKOG
GIBANJA SUPSTITUENATA ILI CIJELE MOLEKULE

III. UVOĐENJE TORZIJSKI FLEKSIBILNIH
FUNKCIONALNIH SKUPINA

IV. PRISUTNOST ZAJEDNIČKE OSI ROTACIJE KOJA
OMOGUĆUJE USMJERENU KOOPERATIVNU
ROTACIJU MOLEKULA

HVALA NA PAŽNJI!