Er^{3+} doped tellurite glass films through sputtering

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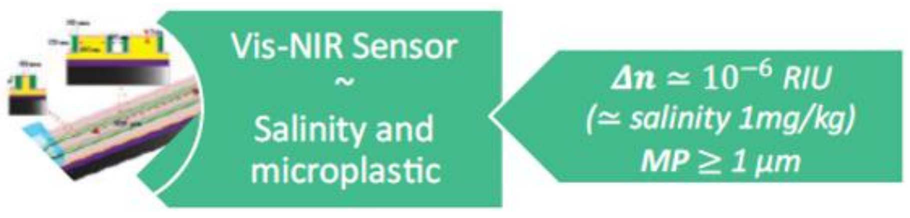
In collaboration with

Introduction

Growing global issue to address environmental water pollution → Increase in regulations and in demand for improved water quality monitoring solutions.

About IBAIA project (https://ibaia.eu/): Development of innovative optimally functionalized sensor modules, one of them being for microplastics and salinity.

Goal of IBAIA project: Monitoring a wider range of water quality parameters in comparison to existing solutions and provide a one-size-fits-all solution for waterbody quality detection. Contributing to European Green deal objectives.



Interest of study

- Use of Erbium (Er^{3+}) doped oxide glass waveguide with high refractive index for the sensing.

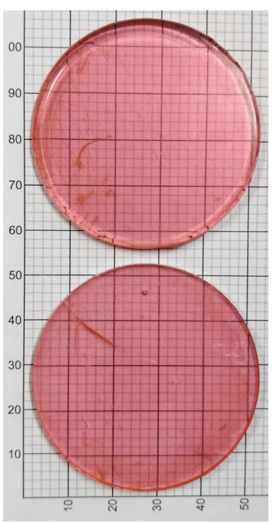
Goal: **To study the feasibility to deposit tellurite glasses doped with Er^{3+} into films using sputtering.**

Film deposition

Target preparation:

- Glass composition: 68.25 TeO_2 - 19.5 ZnO - 9.75 X - 2.5 Er_2O_3 (in mol%) with X = BaO (**TeBa**), Bi_2O_3 (**TeBi**), Na_2O (**TeNa**)*.
- Standard melt-quench technique: Melting at 775 °C for 40 minutes & annealing at around T_g for 6 hours.

Sputtering targets

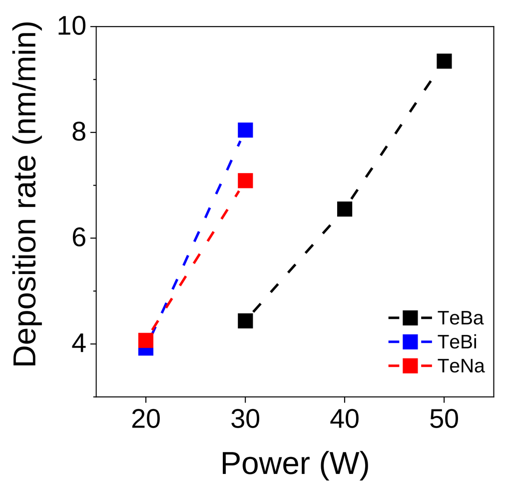


Film deposition using radio-frequency (rf) magnetron sputtering parameters for thickness of ≈ 700 nm — 1 μm.

- Power: 20 W to 50 W in 10 W increment.
- Argon-Oxygen gas flow ratio: 40:10 sccm (fixed for all depositions).
- Target to substrate distance: 50 mm (fixed for all depositions, vertical). Substrate rotated at 5 rpm.
- Overall pressure: 0.5 Pa (fixed for all depositions).
- Substrate(s): c-Si <100>, BK7 glass, SiO_2/Si.

Highest deposition rate for the TeBi composition followed by TeNa and TeBa.

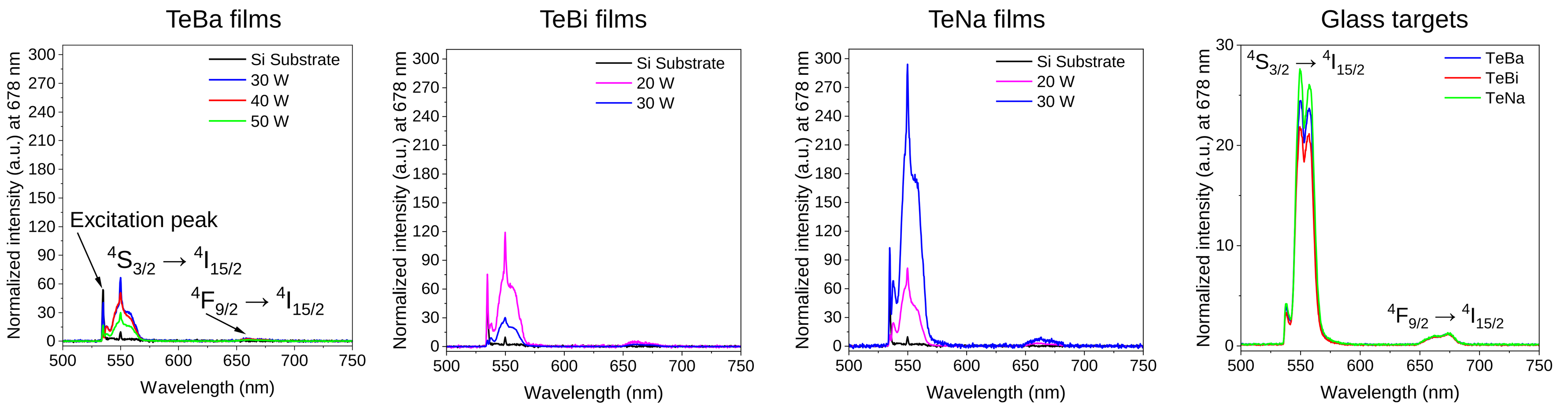
Power vs Deposition rate



Film characterization #1

Normalized emission spectra in the visible (λ_{exc} = 532 nm)

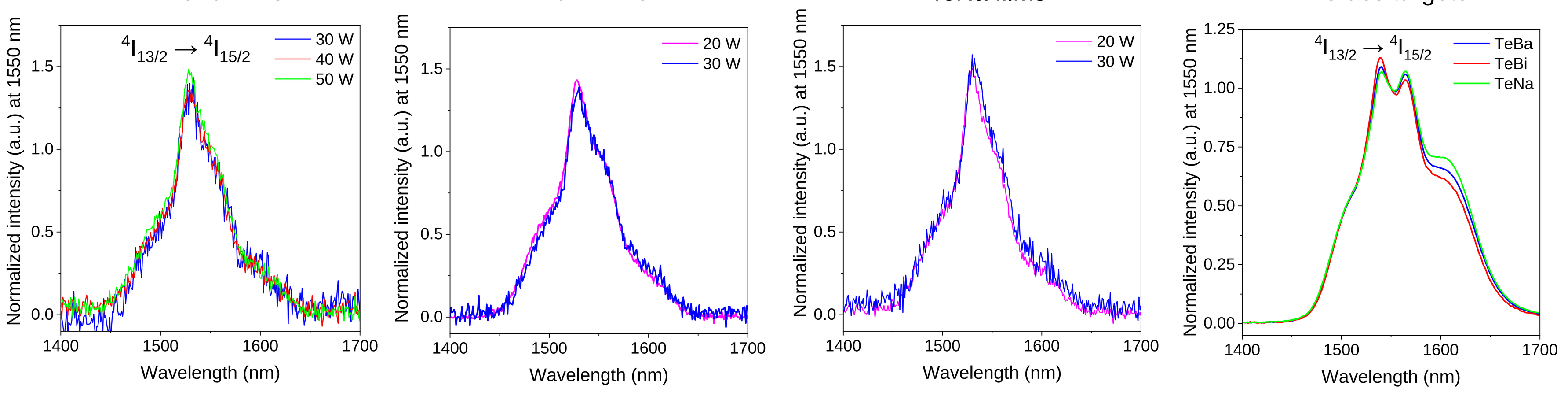
TeBa films · TeBi films · TeNa films · Glass targets



- Typical emission bands of Er^{3+} detected from the films but with changes in the shape of the emission after deposition.
- Sputtering power displays no trend in up-conversion intensity for all compositions.
- TeNa composition exhibits highest up-conversion intensity as seen in the bulk glasses*.

Normalized emission spectra in NIR (λ_{exc} = 808 nm)

TeBa films · TeBi films · TeNa films · Glass targets



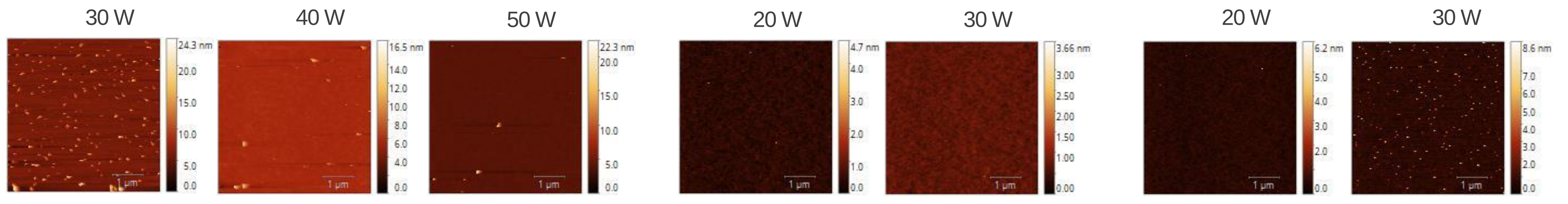
- As seen in the visible emission spectra, no significant change in the shape of the NIR emission band between films and with different powers BUT different shape compared to target glasses.

→ Er^{3+} confirmed in the film but changes in the Er^{3+} sites suspected to occur during film deposition.

Topography and ageing

AFM images (5x5 μm²) on as deposited films

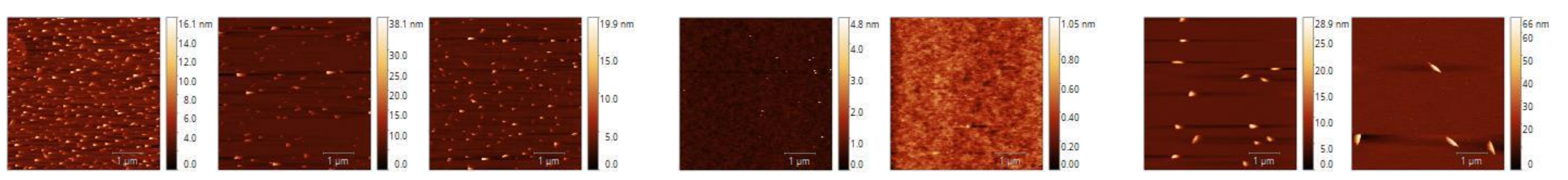
TeBa films (30 W, 40 W, 50 W) · TeBi films (20 W, 30 W) · TeNa films (20 W, 30 W)



TeBa: R_{sq} = 1.25 (± 0.1) nm; R_{sq} = 0.3 (± 0.1) nm; R_{sq} = 0.4 (± 0.1) nm — TeBi: R_{sq} = 0.1 (± 0.1) nm; R_{sq} = 0.1 (± 0.1) nm — TeNa: R_{sq} = 0.1 (± 0.1) nm; R_{sq} = 0.4 (± 0.1) nm

- Highest roughness. For the TeBa films with increase in power → Decrease in surface roughness.
- Low roughness for the TeBi and TeNa films.

AFM images measured 8 months after deposition (ageing)



TeBa: R_{sq} = 2.5 (± 0.1) nm; R_{sq} = 1.5 (± 0.1) nm; R_{sq} = 1.2 (± 0.1) nm — TeBi: R_{sq} = 0.1 (± 0.1) nm; R_{sq} = 0.1 (± 0.1) nm — TeNa: R_{sq} = 1.5 (± 0.1) nm; R_{sq} = 1.5 (± 0.1) nm

- Noticeable increase in roughness for TeBa and TeNa films overtime maybe due to oxidation or crystallization, subject to further analysis.
- **TeBi film is the most stable overtime.**

Film characterization #2

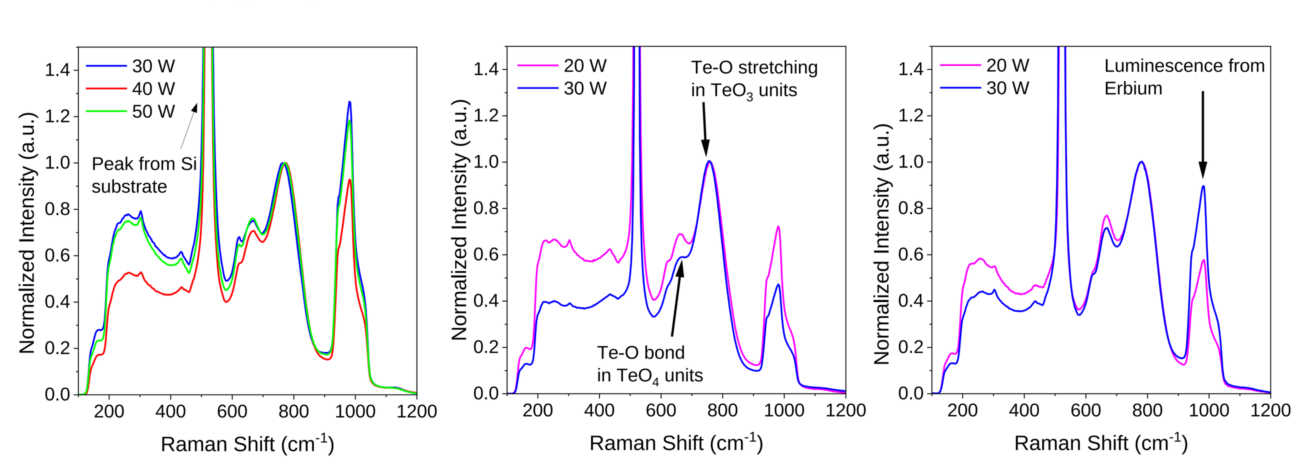
SEM/EDS composition analysis of the targets and films (± 1 at%)

Material	Oxygen (O)	Tellurium (Te)	Zinc (Zn)	Erbium (Er)	Barium (Ba)	Total
Target TeBa	62	25	8	2	3	100
30 W	66	15	10	3	6	100
40 W	66	17	9	2	6	100
50 W	65	18	9	2	6	100
					Bismuth (Bi)	
Target TeBi	**63**	**22**	**7**	**2**	**6**	**100**
20 W	67	17	7	1	8	100
30 W	67	15	7	1	10	100
					Sodium (Na)	
Target TeNa	**59**	**24**	**6**	**2**	**9**	**100**
20 W	63	21	6	1	9	100
30 W	62	21	6	2	9	100

- Deposition leads to an increase in the amount of Barium and Bismuth at the expense of Tellurium.
- Power does not have a strong impact on the film composition.
- **TeNa film has the closest stoichiometric composition to bulk target.**

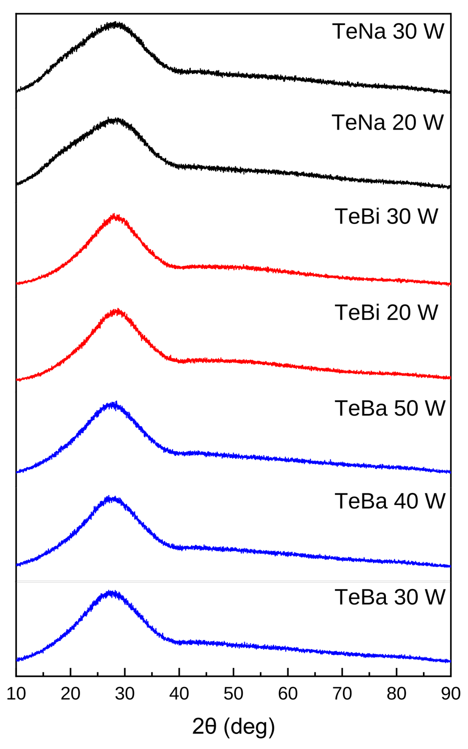
Normalized Raman spectra (λ_{exc} = 404 nm)

TeBa films · TeBi films · TeNa films



- Film(s) structure made of TeO_4 and TeO_3/TeO_{3+1} units.
- As reported in bulk glasses*, lowest intensity of TeO_4 band from TeBi films → Most depolymerized network for the TeBi films.
- Increase in power → Decrease in TeO_4 compared to TeO_3/TeO_{3+1} → depolymerization of the tellurite network.

XRD pattern of the films



No sharp peaks → Amorphous deposited films.

Transmittance spectra of the film

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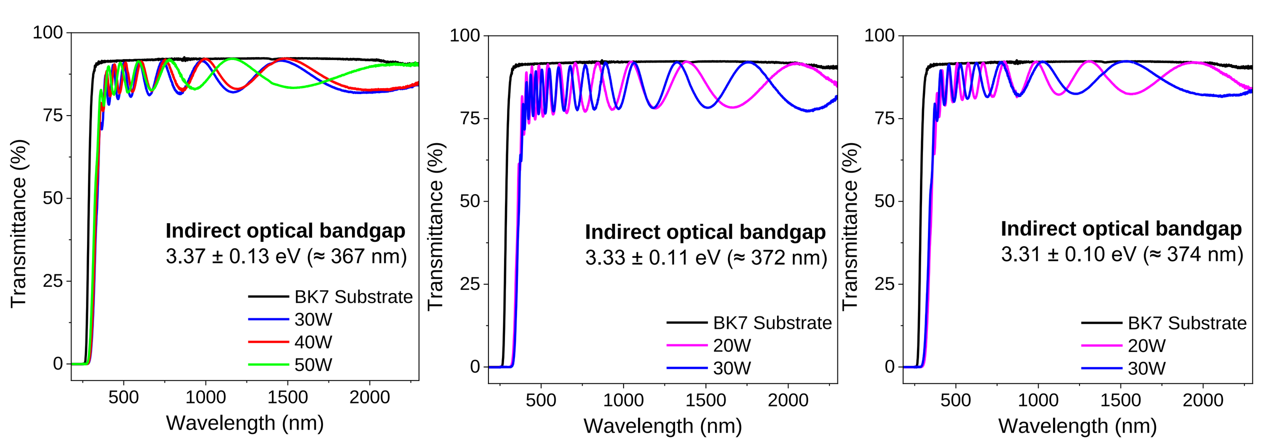
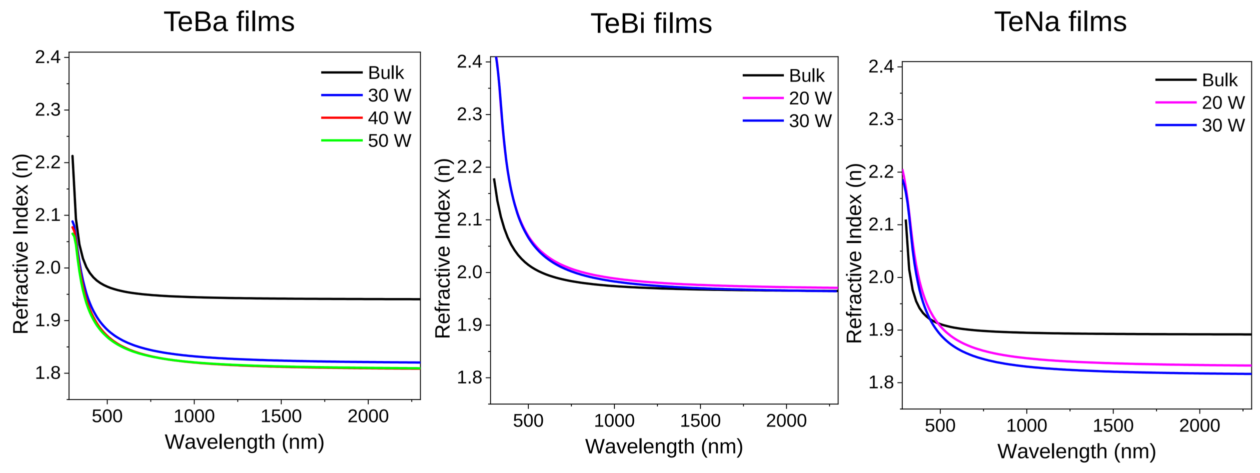


- Transmittance till UV-Visible wavelength.
- Interference maxima of transmission intensities reaching 90%, equal to that of the BK7 substrate.
- Bandgap values of respective glass compositions do not change with sputtering power.
- **TeBa has the highest band gap close to UV-Visible edge. TeBi and TeNa display bandgap values close to each other within uncertainty limits.**

Refractive index dispersion

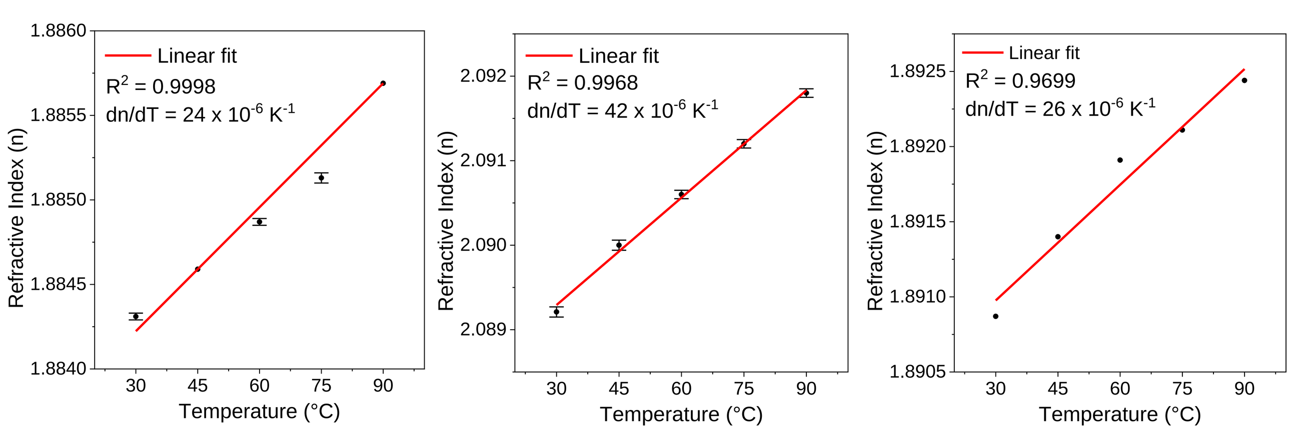
TeBa films · TeBi films · TeNa films



- **TeBi film composition has the highest refractive index (most depolymerized network with larger amount of NBO's), closer to the refractive index of the target (lower Te content but larger Bi content).**
- TeBa and TeNa have lower refractive index than the target due to lower Te content.

Thermo-Optic coefficient in Transverse Electric (TE) mode at 532nm

TeBa films · TeBi films · TeNa films



- **TeBi film has the largest dn/dT.**

CONCLUSION

Film deposition has a noticeable impact on the glass composition and on the structural, optical, and spectroscopic properties.

✓ Possible to deposit transparent amorphous doped tellurite films using radio-frequency (rf) magnetron sputtering.
✓ Changes in the glass composition after film deposition, especially lower Te content leading to film with lower refractive index than the target for the TeBa and TeNa compositions.
✓ Visible and NIR Emissions observed from the films, confirming the presence of Er^{3+} in the films BUT film deposition process is suspected to change the Er^{3+} sites.

TeBi film has the highest refractive index and dn/dT and is the most chemically stable film overtime.

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References:
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