

Review of physical properties of NASICON materials for use in sodium batteries

M. Guin, F. Tietz, H.P. Buchkremer

Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung IEK-1, Jülich, Germany

The structure, compositional diversity and ionic conductivity of Na⁺ ion-conducting NASICON materials are reviewed in order to correlate the lattice parameters and specific crystal structure data with the sodium mobility and the activation energy.

Correlation structure / ionic conductivity:

General formula of a sodium NASICON material:



Extensive study for approximately 150 compositions:

- Introduction of a geometrical parameter: the effective ionic radius r_{eff}

$$r_{\text{eff}} = \frac{x \times r_{\text{M}^{\text{II}}} + y \times r_{\text{M}^{\text{III}}} + (2-x-y) \times r_{\text{M}^{\text{IV}}}}{2}$$

- Illustration of an optimal size for M^{II}, M^{III} and M^{IV}, $r_{\text{eff}} \approx r_{\text{Zr}^{\text{IV}}} = 0,72 \text{ \AA}$
- Impact of the amount of Na per formula on the conductivity.
- Importance of the substitution of P with Si

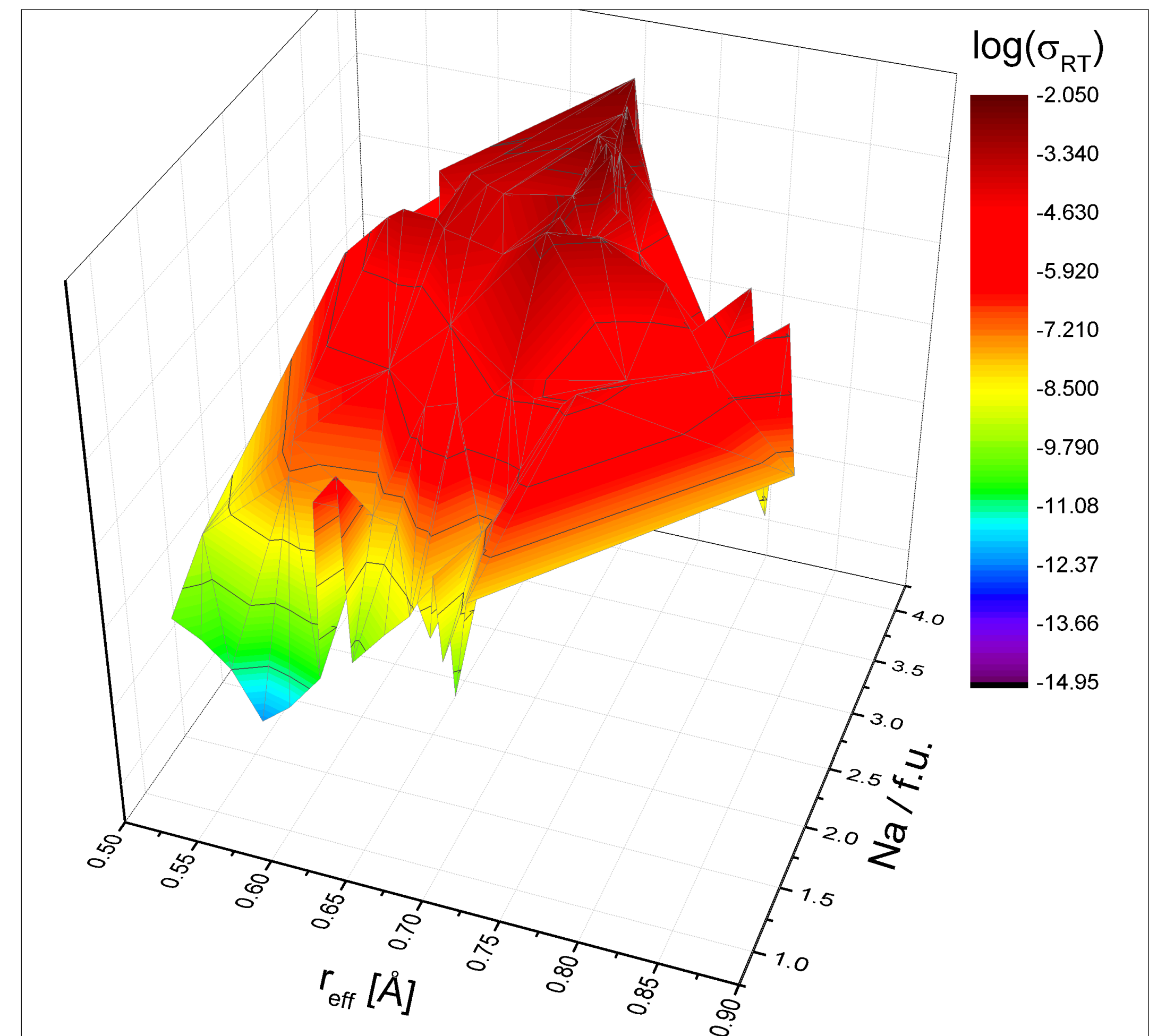


Figure 1: $\log(\sigma_{\text{RT}})$ as a function of the Na content per formula and the effective ionic radius of the cations in $\text{Na}_{1+2x+y}\text{M}^{\text{II}}_x\text{M}^{\text{III}}_y\text{M}^{\text{IV}}_{2-x-y}(\text{SiO}_4)_z(\text{PO}_4)_{3-z}$.

Bottleneck for Na⁺ conduction, correlation with the activation energy:

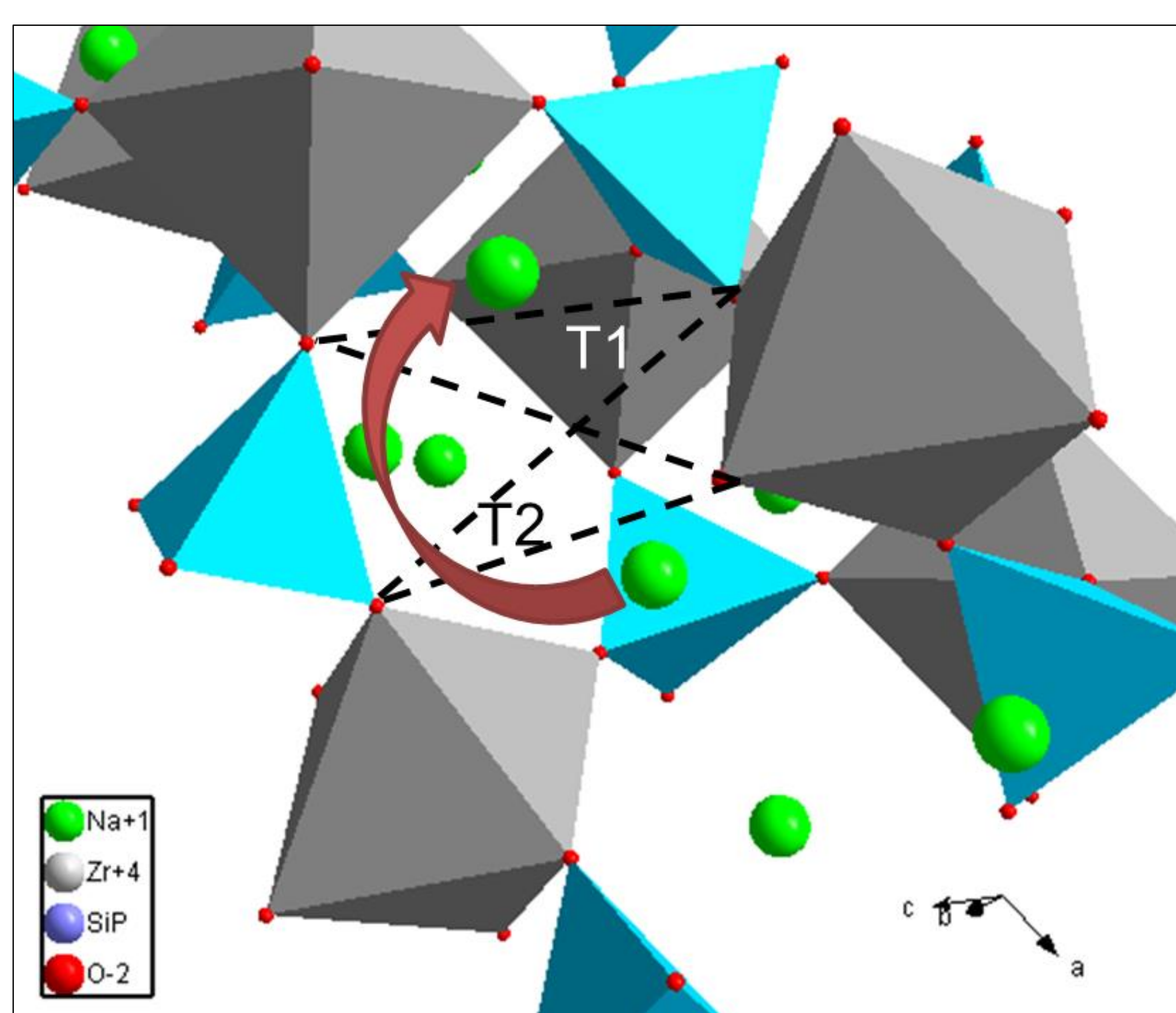


Figure 2: representation of the geometric bottleneck for the Na⁺ conduction and the path of Na⁺ ion hopping in $\text{Na}_3\text{Zr}_2(\text{SiO}_4)_2(\text{PO}_4)$

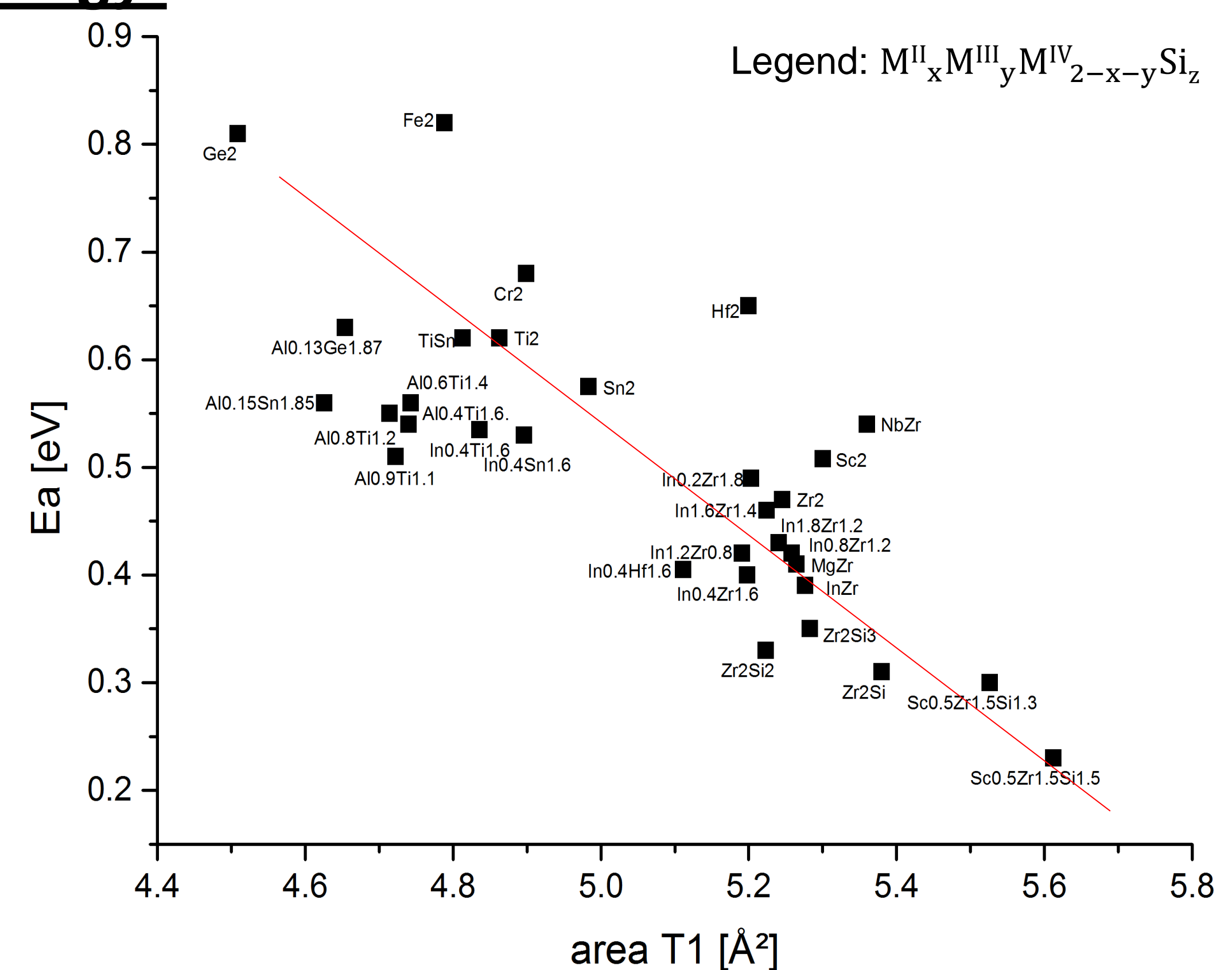


Figure 3: Influence of the area T1 on the activation energy for different NASICON materials

Factors influencing the bottleneck for the Na⁺ conduction:

- Size of the cations M^{II}, M^{III}, M^{IV} (r_{eff})
- Presence of Si in the formula

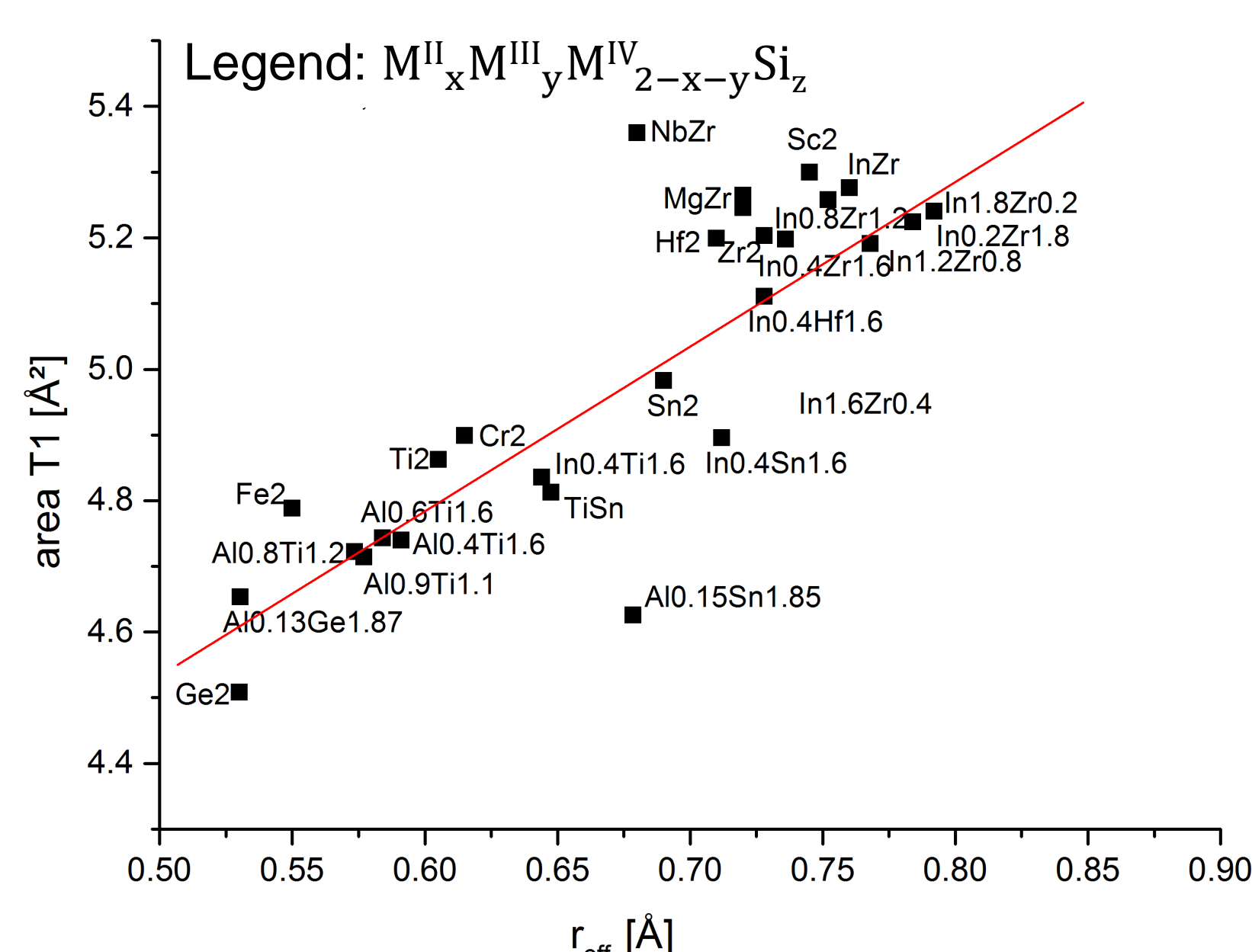


Figure 4: Influence of r_{eff} on the area T1

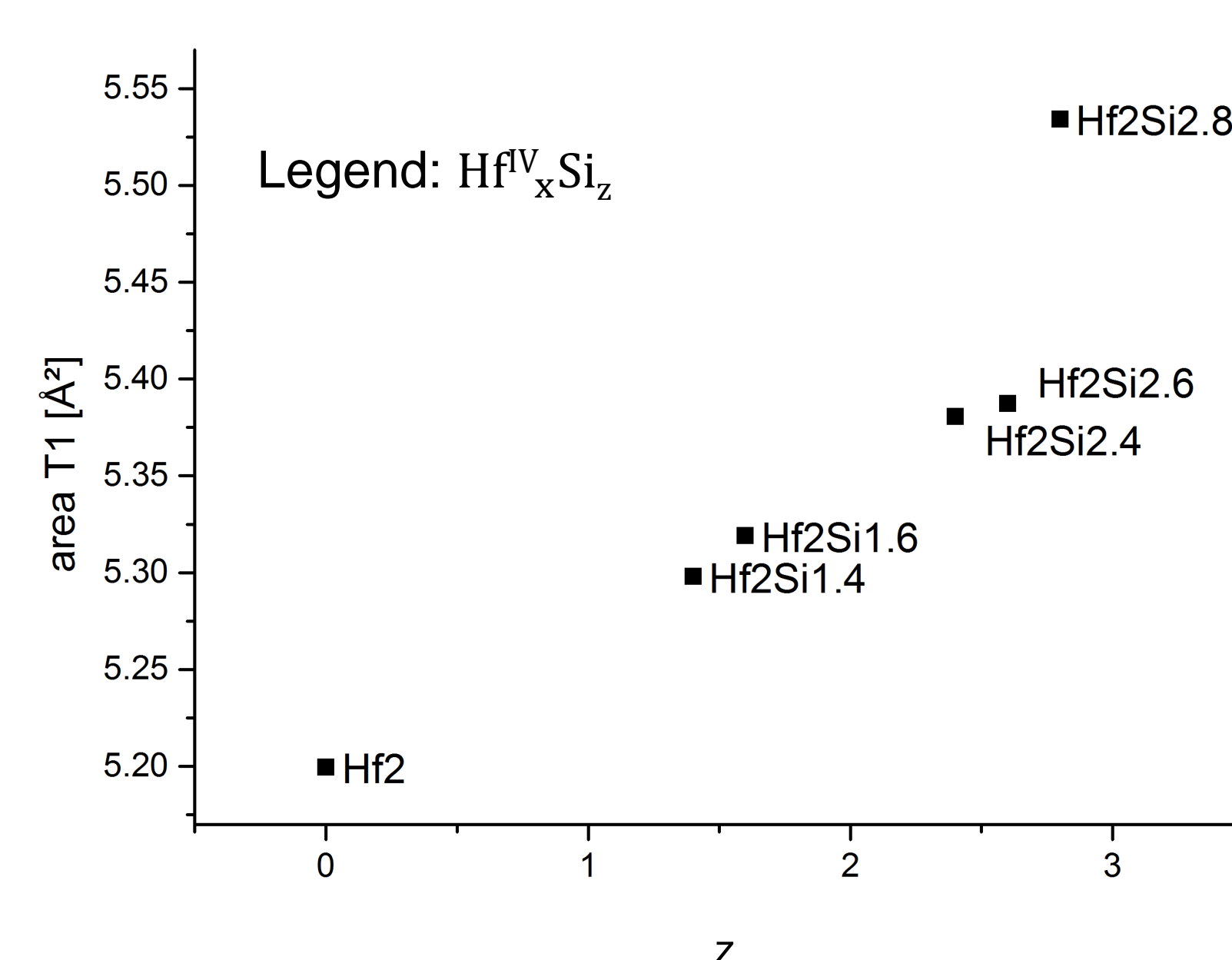


Figure 5: Influence of the amount of Si per formula on the area T1 (example of Hf-based NASICON. Vogel, E.M. et al. Solid State Ionics, 1984. 14: p. 1-6.)

The activation energy is correlated to the geometric bottleneck for the Na⁺ conductivity, the area T1, which increases with the size of the cations M^{II}, M^{III} and M^{IV} and the presence of Si in the formula. The existence of an optimal size for M^{II}, M^{III} and M^{IV}, $r_{\text{eff}} \approx r_{\text{Zr}^{\text{IV}}} = 0,72 \text{ \AA}$ can not be explained only by a geometrical parameter.