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Rationalization of the influence of the chemical bonds on the radiation tolerance of compounds related to the M_7O_{12} oxygen-deficient fluorite system.

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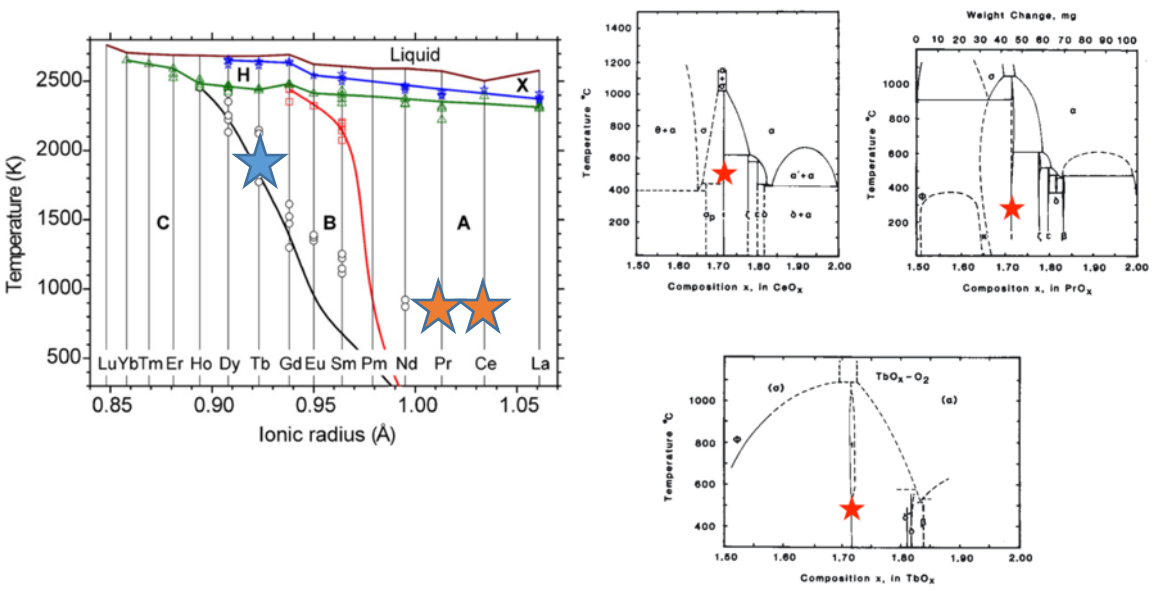
Outline

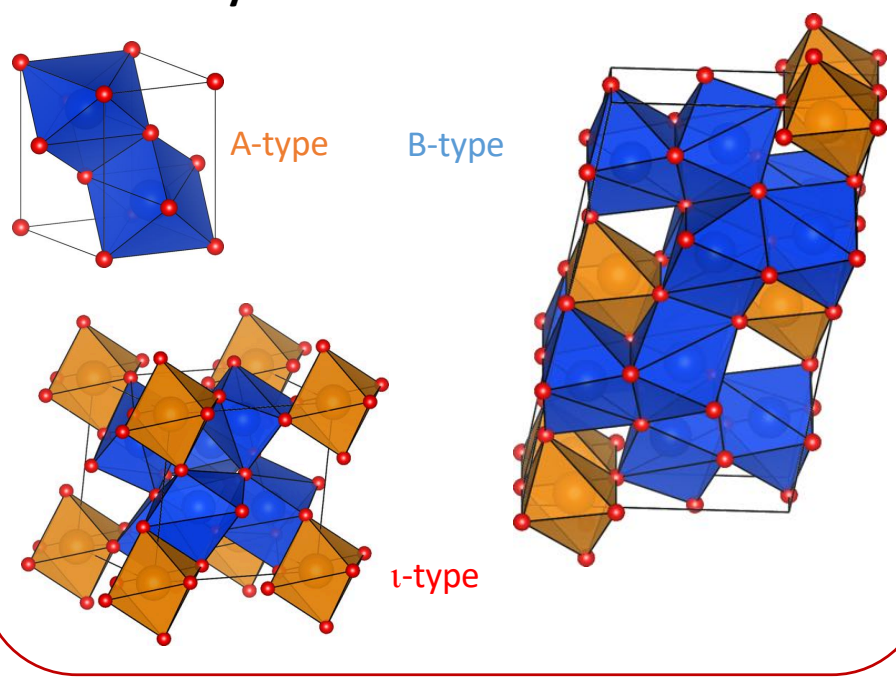
Cerium, praseodymium, and terbium stand out among other rare-earth systems because they exhibit two possible oxidation states that produce a series of anion deficient phases that are fluorite-related and have a generic formula Ln_nO_{2n-2}. Since the seminal works of Eyring, and the valuable contributions of many other scientists, many of the occurring phases were determined using scattering techniques. It was then possible to propose a paradigm for the particular oxygen vacancy order that is observed in most of these phases We would like to discuss how the structural characteristics of these systems can affect their radiation tolerance. In this contribution, we analyze using Bader's analysis the charge density and the chemical bonds of the A-type, B-type, and the ι phase, which corresponds to the generic compound formula with *n*=7. Then we try to correlate these results with irradiation experiments on simple lanthanide oxides and with the behavior of the broad family of δ phases that are pseudo-binary compounds with generic formulas A_6BO_{12} or $A_4B_3O_{12}$ that share many structural features.

Polymorphic and morphotropic transformations



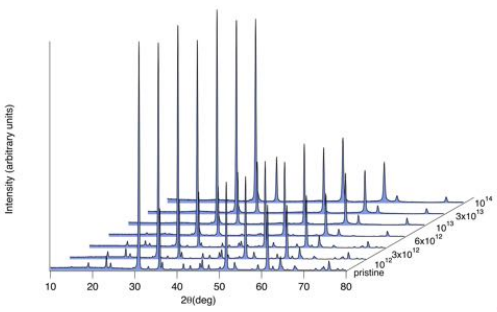
As *d*-electrons in many transition-metal oxides, the *f*-electrons play an important role for the transport properties in rare-earth oxides. We investigate how the local environments change the charge density in various reference structures. It is common belief (e.g. CeO_2) that in LnO_2 4 valence electrons nominally leave the lanthanide atoms and transfer into the *p*-bands of two oxygen atoms while in Ln_2O_3 *f*-electron localization occurs. The O vacancy formation process involves the localization of 2 electrons into *f*-level traps onto two lanthanide atoms. This implies a strong correlation between formation, migration, and ordering of virtual Ln^{III}-vacancy complexes [1,2].

Polyhedra and structural blocks

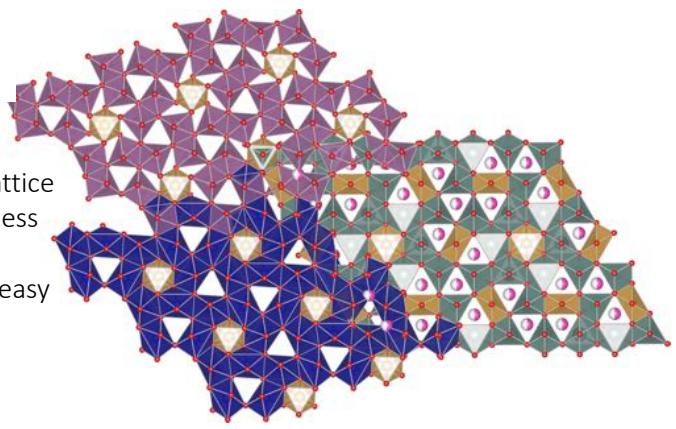


'Heating' up quickly with Swift Heavy Ion irradiation …

Fast amorphization was induced in a few A_2O_3 compounds irradiated by Swift Heavy Ions and a dependence on cation ionic radius was claimed [4] but differences among their electronic configurations (Eu^{III} can reduce, Nd^{III} cannot, and Mn is a compound with only *d*-states) still leave this matter about the influence of cation radii open.



The pseudobinary compounds $RE_3B^{IV}{}_4O_{12}$ with δ phase structure (isostructural to the ι phase Ln_7O_{12}) exhibit excellent radiation resistance

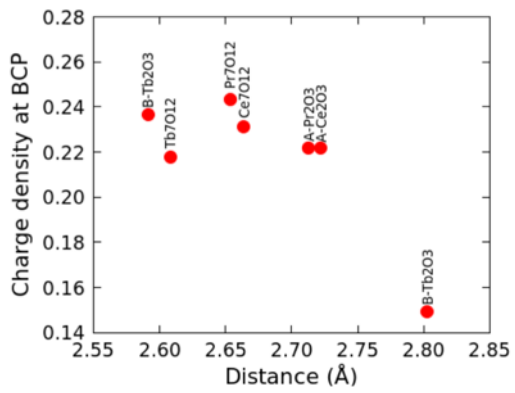


Lack of cation selectivity and the easy reorganization mechanism of the anion sublattice seem essential [5]. In this respect, the weakness of the 7th bond of the polyhedra of the ι structures seems a critical ingredient for the easy rearrangement of the anion sublattice as the diffusion barriers are known to be low.

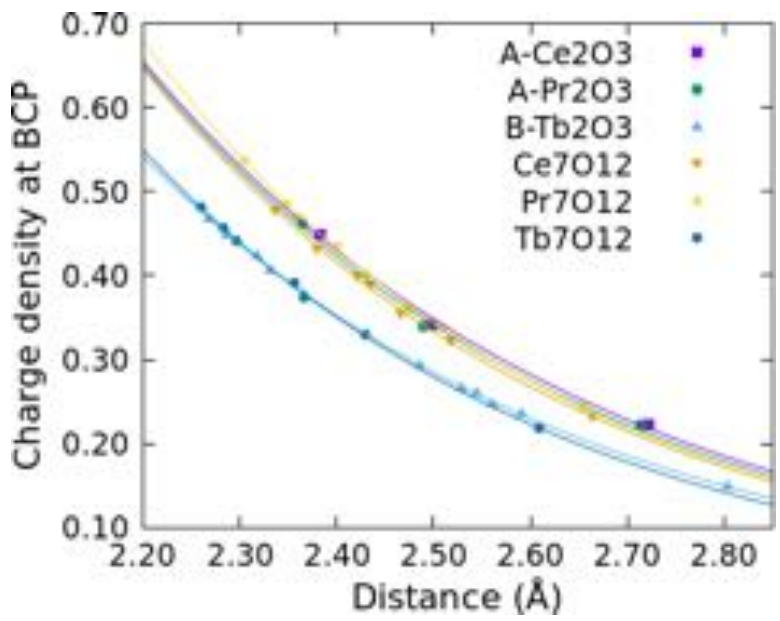
On the other hand, ordered δ phase structures ($RE_6B^{VI}O_{12}$) can experience higher migration entalpies because of the cation selectivity and this justifies the easy amorphization of these compounds [6].

Topologigal charges and bond strength [3]

Results of the AIM Bader analysis and bond covalency character according to the Bader-Essen rules.



Larger charges at the BCPs are representative of shared contributions among the atoms.



The predicted strength of the 7th bond (and of all bonds) is significantly weaker in Tb-based compounds.

Conclusion

The existence of a cation ordering temperature T_{co} tells us that below some energy per site E_{co} the space bifurcates into regions corresponding to different "solutions," and that as we go lower and lower in energy (or temperature) the space breaks up even more. This gives us a clear reason why reorganizing is hard: If we are in the wrong region, we have to cross an ordering energy and entropy barrier that is very high to achieve a more stable state. This also motivates a thorough study of the radiation behavior of non-stoichiometric lanthanides as their properties are still largely unknown but the absence of cation selectivity simplifies the overall problem.

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