

DEFECT-FLUORITE OXIDES: Ln (Eu AND Gd)-MÖSSBAUER SPECTROSCOPIC STUDY COUPLED WITH NEW DEFECT-CRYSTAL-CHEMISTRY MODEL

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Defect-fluorite (DF) oxides as a generic term of various grossly oxygen-deficient oxygen-vacancy (V_O) type $M_{1-y}Ln_yO_{2-y/2}(V_{Oy/2})$ solid solutions (ss) formed between parent fluorite (F) MO_2 ($M^{4+} = Zr, Hf, Ce, Th, U, Np$ and Pu etc) and its V_O -ordered superstructure, lanthanide (Ln) and light-Ln C-type $LnO_{1.5}$ ($Ln^{3+} = La-Lu, Y, Sc, In$ etc), have been the object of enormous research efforts for over these several decades due to their technological importance in nuclear, ceramic and electrochemical etc areas. Yet, much has remained elusive till now as to their detailed defect (V_O)-related local structure and its correlations with many key defect properties such as oxygen conductivity ($\sigma(\text{ion})$), radiation tolerance, catalytic ability and phase and structural stability etc. To serve this purpose in these years we have been engaged in their combined Ln (Eu and Gd)-Mössbauer and XRD lattice-parameter ($a_0(\text{ss})$) studies [1-5], lately extending them to ^{170}Yb -Mössbauer, EXAFS and Y-MAS-NMR etc studies.

One basic controversy of such defect-structure study has been; albeit classified as the same DF oxides, whether those based on larger M^{4+} s (Ce, Th, U, Np, Pu and Am etc) which themselves adopt F structure and those based on smaller M^{4+} s (Zr and Hf) which are first stabilized into F structure by $LnO_{1.5} \rightarrow Zr(Hf)O_2$ doping, the both have either mutually 'different or similar' local structure. Our ^{151}Eu -Mössbauer study of $M_{1-y}Ln_yO_{2-y/2}$ ($M^{4+} = Ce, Th, U, Zr$ and Hf) (Fig. 1 [1]) has given a clear answer to this controversy: Based on the well-known near inversely-proportional $IS(\text{Eu}^{3+})-(\text{Eu}^{3+}-O)$ bond-length (BL) relationship, these data decisively reveal that:

(i)The parent F-based $M^{4+}=\text{Ce}$ and Th have a naïve (but non-random) 'disordered DF-type' local structure in which both $BL(\text{Eu}^{3+}-O)$ s decrease smoothly and similarly due to the steady oxygen coordination number (CN) decrease about Eu^{3+} from ~ 7.5 at $y=0$ to 6 at $y=1.0$.

(ii)The stabilized zirconia (SZ) and stabilized hafnia (SH) ($M^{4+}=\text{Zr}$ and Hf) the both have a sharp $BL(\text{Eu}^{3+}-O)$ maximum, that of the SH with the shorter $a_0(\text{ss})$ being even longer than that of the SZ with the longer $a_0(\text{ss})$. Such characteristic $IS(\text{Eu}^{3+})$ behavior of SZ and SH is entirely different from that of the above parent-F-based systems, and is almost a first direct experimental evidence that SZs and SHs have basically the same intermediate ordered pyrochlore (P $Zr(Hf)_2Eu_2O_7$ at $y=0.50$)-based strongly anisotropic local structure extending to either the $y < 0.50$ or > 0.50 region retaining its short-range (local) P-type ordering, and thus the both have the longest $BL(\text{Eu}^{3+}-O)$ at $y=0.50$ at which the most highly-ordered and the most-

dilated near-ideally P-type $\text{Eu}-8O^{2-}$ (CN=8) coordination structure is realized. Making these findings a major incentive, one of the authors (A.N) has recently proposed a new defect-crystal-chemistry (DCC) $a_0(\text{ss})$ model for parent-F-type $M^{4+}=\text{Ce}$ and Th [2-4] which can provide not only a novel possibly unified picture of their non-Vegardianity and non-random defect structure as closely coupled two sides of 'distortion-dilation' phenomenon of C-type $LnO_{1.5}$ but also a new consistent description of their detailed mutually non-randomly coordinated cation-anion concentration variations and also of their intriguing $\alpha(\text{ion})$ maximum behavior in low y ($< 0.10-0.20$) range.

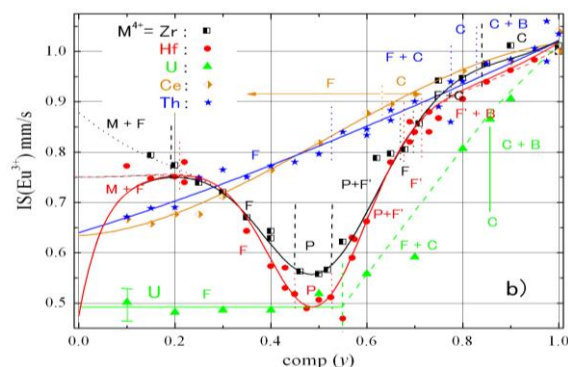


Figure 1. ^{151}Eu -Mössbauer Isomer-shift (IS) vs. composition (y) plot in the $M_{1-y}Ln_yO_{2-y/2}(V_{Oy/2})$ ($M^{4+}=\text{Ce, Th, U, Zr}$ and Hf)

We are now trying to extend this DCC $a_0(\text{ss})$ model to the more complex SZs and SHs involving the intermediate P (or δ)-type ordering and hence its-based extra distortion-dilation effect [5]. In the present talk, this ongoing efforts of our group, being in progress by piecing together their reported various $a_0(\text{ss})$, local-structure, $\alpha(\text{ion})$ and thermodynamic etc data with our own latest ^{155}Gd -Mössbauer, EXAFS and Y-MAS-NMR etc data obtained for several of them, will be described and discussed, in pursuit for the more global understanding of the whole DF oxides, either parent F- or stabilized P-type.

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