Doping-induced structural phenomena in Pb-based relaxors

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Perovskite-type relaxor ferroelectrics are among the key materials in modern solid-state science due to their outstanding dielectric, electro-optic, and electro-elastic properties, which are the basis of a number of technological applications including information storage and processing. The unique physical properties of relaxors are related to their local structure, which strongly deviates from the global, average structure. Here we report on the relationship between the observed phonon anomalies and the local atomic arrangements in Pb-based perovskite-type relaxors studied by synchrotron X-ray diffraction and polarized Raman spectroscopy of representative lead scandium tantalate/niobate single-crystal compounds. It is shown that the development of ferroic species and ferroelectric state on cooling can be followed by analysing quantitatively the intensity ratios of the Raman scattering arising from the corresponding local structural distortions [1]. The degree of B-site doping can control the size of ferroelectric domains. Different types of local structural changes occur upon A-site doping, depending on the ionic radius of doping element, its valence and affinity to form stereochemically active lone-pair electrons.

References

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Variation in natural mercury isotopic ratios of coal formations

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High precision mercury (Hg) stable isotope measurements of coal offer a new tool to investigate inputs of Hg to the atmosphere from coal combustion. Mercury was quantitatively isolated from coal by combustion and trapping in a $KMnO_4$ solution. Mercury isotopic measurements were determined by cold vapor multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). Instrumental mass bias was corrected using an internal thallium standard and concentration-matched sample-standard bracketing. Mercury isotopic variations are reported here in delta notation ($\delta^{202}Hg/^{198}Hg$) and referenced to the NIST SRM 3133 Hg standard. Sample and standard replicates had an external 2σ standard deviation of $< \pm0.2‰$ for $\delta^{202}Hg$ (Blum and Bergquist, 2007).

Coal samples were analyzed from across the USA that ranged in rank from lignite to bituminous and in age from Eocene (~55 Ma) to Pennsylvanian (~300 Ma). The $\delta^{202}Hg$ of these samples ranged from -0.98 to -2.27 ‰. A positive correlation was observed between calorific value of coal (BTU lb^{-1}) and $\delta^{202}Hg$ values for coals ($p < 0.05$, $R^2 = 0.89$) (Figure 1). One interpretation of this trend is that the Hg isotopic composition of coal shifts towards isotopically heavier values with increased metamorphism due to preferential volatilization of isotopically lighter Hg.

We also observed mass independent fractionation (MIF) in these coal samples with $\Delta^{201}Hg$ and $\Delta^{199}Hg$ (Blum and Bergquist, 2007) ranging from –0.1 to –0.3 ‰, which we suggest may be caused by photochemical reduction of Hg prior to deposition in coal. Analyses of Hg ores and refined Hg do not show MIF and thus may be isotopically distinguishable from coals (Smith *et al*., 2005). Our results suggest that Hg isotopic ratios of coal formations could aid in source apportionment of coal combustion emissions of Hg and lead to a better understanding of the global Hg cycle.

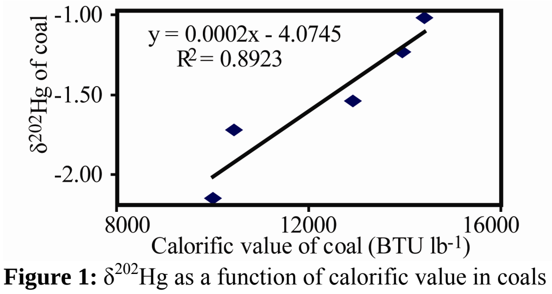

Figure 1: $\delta^{202}Hg$ as a function of calorific value in coals

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