Spin crossover phenomena in mixed rare-earth cobaltites

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Motivation

The rare earth cobaltites are widely examined as thermoelectric, catalytic and gas sensor materials. A main feature of such materials is the presence of spin transitions in Co^{3+} ions from low spin (LS, t^6e^0) to immediate (IS, t^5e^1) or high (HS, t^4e^2) states, which are accompanied by magnetic and isolator-metal (IM) transitions, temperatures of which strongly depend on the size of rare earth element.

Results

More than 60 polycrystalline single phase mixed solid solutions with nominal composition $R_{1-x}R`_xCO_3$ ($R$, $R`$ – rare-earth elements) were obtained by solid-state reaction or sol-gel method. Phase purity at the ambient environment of the investigated samples was confirmed by X-ray powder diffraction technique. The La-contained solid solutions are crystallized in two types of symmetry – rhombohedral (space group R-3c) or orthorhombic (space group $Pbnm$), while the rest powders have an orthorhombic structure. A multiphase region in the $R_{1-x}R`_xCO_3$ systems localised within the average ionic radii of R between 1.197 Å and 1.205 Å (fig. 1). Calculated from structural data, the values of average bond lengths reduce with reducing average ionic radii of rare earth elements, while deformation of the perovskite cell increase (fig. 2). Evaluated bandwidth of Co-O-Co overlapping allowed predicting the temperature of diamagnetic-to-paramagnetic phase transition in investigated systems (fig. 3).

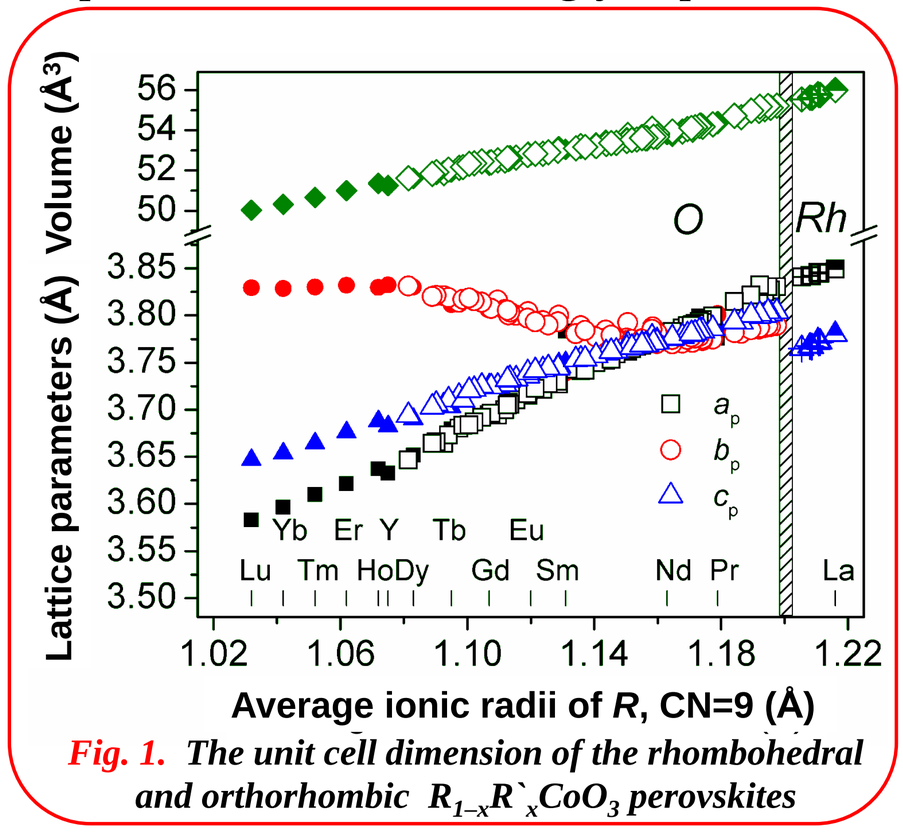

***Fig. 1.** The unit cell dimension of the rhombohedral and orthorhombic $R_{1-x}R`_xCoO_3$ perovskites*

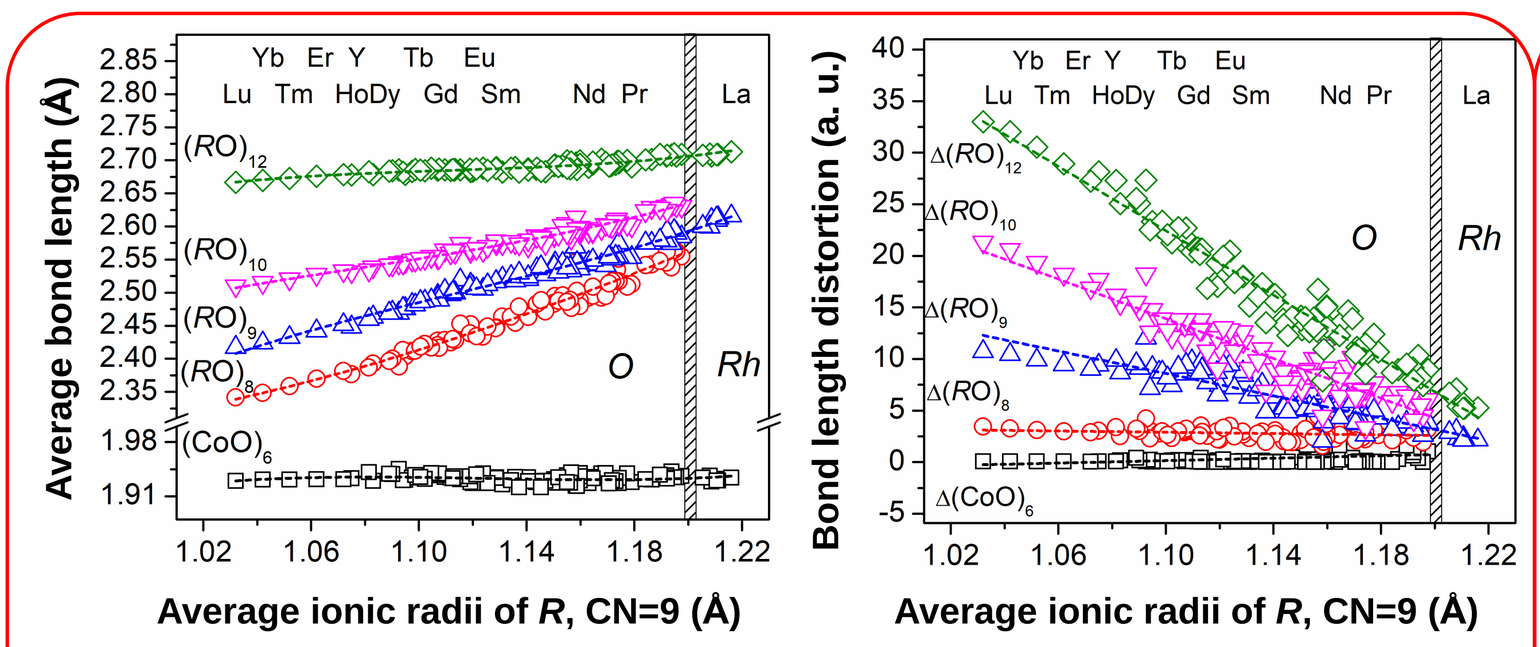

***Fig. 2.** Average bond length and their deformations as a function of the average ionic radius of R cations in the $R_{1-x}R`_xCoO_3$ solid solutions*

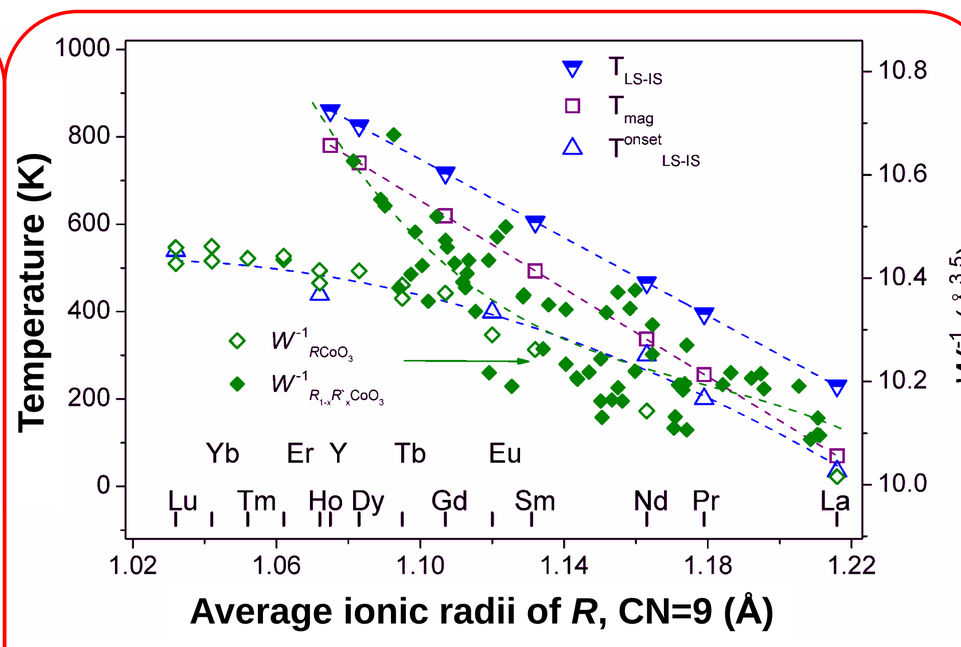

***Fig. 3.** Dependence of orbital overlap of Co^{3+} cations and O^{2-} oxygen anions in the $R_{1-x}R`_xCoO_3$ solid solutions*

The thermal expansion of more than 30 selected solid solutions was studied by X-ray synchrotron powder diffraction technique in the temperature range of 293-1173 K. The structure symmetry remains during a heating in the temperature range investigated, however abnormal thermal expansion behavior was revealed in $R_{1-x}R`_xCO_3$ solid solutions, similar to the "pure" rare earth cobaltites studied early. Additional analysis of valence bond lengths, octahedral tilt angles and perovskite deformation confirm the absence of structural phase transition and the presence of abnormal thermal expansion caused by the spin state transition of Co^{3+} ions.

The magnetic and isolator-metal transition impacts in abnormal thermal expansion manifested in extra maxima on the temperature dependence of the thermal expansion coefficients (**TEC**) (fig. 4). The values of the high-temperature TEC maxima agree well with the temperature of the isolator-metal transition obtained from electro-physical measurements (fig. 5).

Acknowledgment: The work was partially supported by the Ukrainian Ministry of Education and Science (project no. 0121U107736, DB/MODUS).

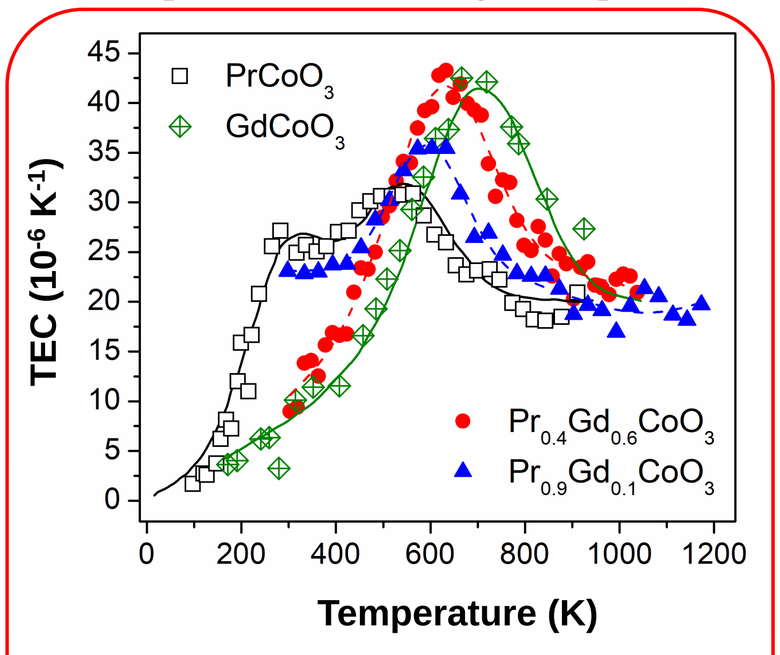

***Fig. 4.** The temperature dependence of TECs of the $PrCoO_3$–$GdCoO_3$ system*

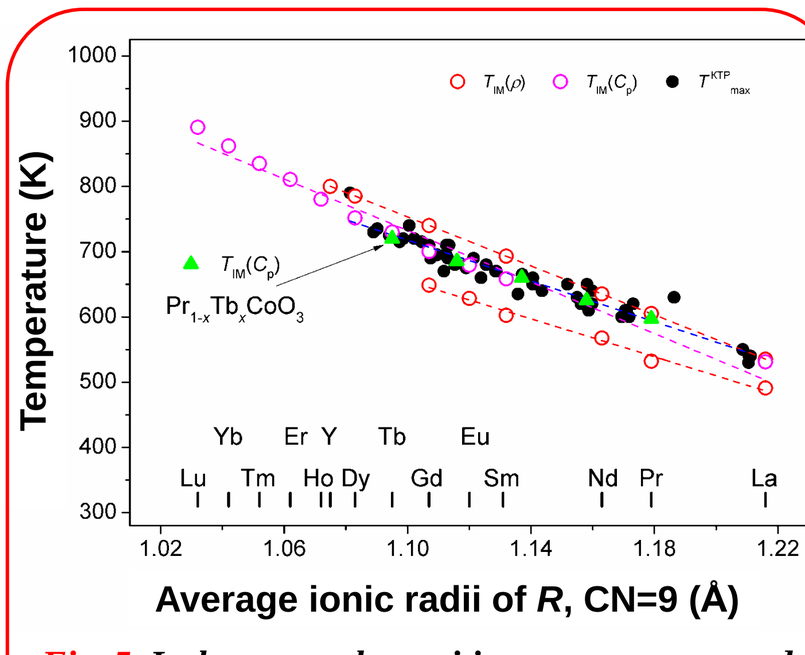

***Fig. 5.** Isolator-metal transition temperatures and TEC maxima as a function of the average ionic radius of R cations*

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