Phase transition in Gd₃RuO₇ and Tb₃RuO₇ at elevated temperatures

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The ordered oxygen-deficient fluorite-type compounds, Gd₃RuO₇ and Tb₃RuO₇, undergoes a structural phase transition between the P₂₁nb and Cmcm modifications at elevated temperatures. This paper describes the phase transition from a structural point of view, based on the high-temperature single-crystal X-ray and electron diffraction studies. The transition is characterized by an additional tilt about the c axis that occurs in the low-temperature modification for half of the RuO₆ octahedra in association with a reduction of apparent coordination number from 6+2 to 7 for one-third of Gd atoms. Dimerization of the Ru array along the [−RuO₆−] zigzagging chain occurs below the transition temperature, which provides a folding effect on the chain. The folding tendency of the chain explains geometrically an expansion of the b-length and a compression of the c-length near 382 K on cooling and vice versa on heating. One of the crystallographically independent Gd atoms in the high-temperature Cmcm modification is statically or dynamically distributed between two positions located very close with each other. The disordered distribution of the Gd atom in the high-temperature modification is presumably correlated with the octahedral tilts about the c axis, resulting in the experimental observation of the extremely prolate atomic displacement ellipsoid for the O1 atom in the cis position along the chain. The in situ electron diffraction experiments and changes of cell dimensions suggested a possible existence of an incommensurately modulated intermediate phase between the high- and low-temperature modifications.

Keywords: defect fluorite, phase transition, single-crystal study

Cation order/disorder and local structures in alkaline earth pyrochlores

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Materials that form the A₂₋ₓBₓO₄₋ₓ pyrochlore structure have various applications including use as catalysts, fuel cells, piezoelectrics, ferroelectric devices and ferro-magnets; have a wide range of electrical and ionic conductivities, including metallic, semi and super; can be used in nuclear-waste immobilisation due to radiation toughness, and have ion exchange properties. The degree of disorder of the A-cation is important and may play the major role in the effectiveness of these materials ion exchange properties; and contribute to the high relative permittivities displayed by (Bi₂Zn)(Zn,Nb)₂O₇. Previous Neutron and X-ray diffraction studies suggest that the disorder involves displacement of the A-cation along the six <112> or <110> directions. Our observation of diffuse scattering in electron diffraction patterns of CsTi₀.₅W₁.₅O₆ pyrochlores suggests there are strong local correlations among the disordered ions. Movement of O at 48f away from 0.375 reduces the interaction between the two networks and so may increase the amount of disorder of the A-cation. The structures of the defect pyrochlores Aₓ₋ₓ₁W₁ₓO₇ where A= K, Rb or Cs have been investigated using an array of advanced structural probes; X-ray and neutron diffraction methods, NMR spectroscopy as well as the ab-initio modeling using VASP. The structures do not show a simple correlation between the radius of the A-type cation and the cubic lattice parameter. Our structural studies suggest that this may reflect the degree of local disorder of the A-cation. The results of these studies will be presented in this presentation.

Keywords: oxides, neutron powder diffractometry, X-ray diffraction crystallography

Icosahedral quasilattices generated by inflation rules

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