Multiferroic properties in β - $R_2(MoO_4)_3$ predicted from symmetry

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 β - $R_2(MoO_4)_3$ (R: rare earth) undergoes the first-order phase transition above 400 K with the symmetrical change from $P\bar{4}2_1m$ (phase I) to Pba2 (phase II). The material shows ferroelectric below phase transition temperature (T_C), and extremely small spontaneous polarization appears along c axis. Dielectric permittivity varies from the Currie-Weiss's law and no precursory phenomenon is observed above T_C . Crystal structure is constructed by two types of MoO₄ layers and four R exist between the layers. Small lattice strain about 3/100 Å in phase II is inverted by external stress showing ferroelastic. Characteristic domain structure including anti-phase boundaries is observed in phase II A thermodynamic free energy for zone-boundary system has been proposed by group theoretical calculation, and the symmetrical change is explained by a two-dimensional real-representation, which unitary transformed from complex-conjugate representations (CCRs). A soft optical mode has been observed at the zone-boundary, M-point, by inelastic neutron scattering; therefore, the phase transition is classified both improper-ferroelectric and -ferroelastic type.

Recently, magnetic properties of β -Tb₂(MoO₄)₃ have been reported. The saturation magnetic moment depends on the direction of magnetic field showing magnetic anisotropy. Furthermore, magneto-electric switching has been observed. The electric polarization induced above threshold magnetic field, 100 kOe, along [100] direction while no switching has been observed for [110] direction. These results indicate that some magnetic mechanism exist, which close relate to ferro-electricity and -elasticity; and remind us of that the symmetrical change is based on the CCRs. In this study, the author reexamined the symmetrical change, and applied the CCRs to crystal structure. Furthermore, the author investigated the crystal filed splitting from change of point group at R^{3+} site.

From the group theoretical analysis, it is proved that CCRs, M_5 and M_6 , account for the symmetrical change. Real part of both representations derives an alternative rotational displacement of MoO₄ tetrahedra, which corresponds to the soft mode. Freezing of the mode changes the arrangement of oxygen atoms around R^{3+} , and tilts the crystal filed from 8.5° in phase I to 27.1° and 20.3° in phase II from the *c*. Site symmetry at R^{3+} changes from *m* to 1. By operating the CCRs, a magnetic structure in Fig. 1 is obtained. Two R^{3+} atoms that have canting magnetic moments make a dimer and two kinds of dimer exist. Both kinds of dimer induce negative dipole moment by Dzyaloshinski-Moriya interaction, although each magnetic moment is inverted. From the differences of initial magnetic moments, four kinds of the magnetic structure are

obtained and those correspond to magnetic and ferroelectric domains. Two of them are composed of the same dimers showing the same dipole while the magnetic moments are inversed. It demonstrates that the anti-phase boundary in phase II is that between magnetic domains.

Grand state of Tb³⁺, ⁷F₆ (13-ply), is reduced as $A_{1u}+A_{2u}+E_u+T_{1u}+2T_{2u}$ under the crystal filed in O_h . Grand state is A_{1u} in Tb³⁺ and shows non-magnetism. The states are splitting with lowering the symmetry; all of states are described by one-dimensional representations in C_{2v} . The A_{1u} state degenerates again with $|\pm 4>$ in the site symmetry for phase I and II, *m* and 1, respectively; and shows magnetism. Quantized axis in phase I is perpendicular to *m* and flips to the direction of crystal field in phase II.

