o.m2.o3 Structures and phase transitions of Elpasolite type perovkites – Any connections with relaxor compounds ? Ph. Sciau*, M. Bonin[$], *CEMES-CNRS, BP 4347, 38055 Toulouse, France, [$]Université de Lausanne, Institut de Cristallographie, 1015 Dorigny, Suisse.
Keywords: perovskites.

In the general family of lead-based perovskites, various compounds have been synthesized by substituing two species of cation in the B site leading to the general formula $PbB'_{1/2}B''_{1/2}O_3$. Following the nature of the B-cations, ordering may occur, giving rise to different structural characteristics and to various very selective physical properties. Partially or fully disordered compounds exhibit diffuse transitions and/or relaxor behavior which are adequate for technological applications (capacitors, actuators, …). The totally ordered perovskites have the elpasolite type structure and present shaper transitions with a phase sequence strongly depending on the cations involved. Several of these compounds are the end member of solid-solutions with relaxor behavior and industrial applications. Then it is very important to understand the ferroic phase transitions.

The principal caracteristics of non cubic phases of these elpasolite type compounds are rewieved. All these phases have an antiferroelectric dominant behavior. Different type of superstructures (commensurate or incommensurate) are observed but the main distortion is very often tetragonal. Only the incommensurate phase of Pb_2MgTeO_6 have a rhomboedral symmetry which is also the symmetry of relaxor compounds. In pseudo tetragonal symmetry two types of commensurate modulation are found in relation to the B cation charges. The structure Pb_2MgWO_6 can be considered as a protopype of the first type and seems only to concern the $Pb_2B^{2+}B'^{6+}O_6$ compounds. It is characterised by two modulation wavevectors and the atomic shifts from the cubic positions can be described by the sum of modulations associated with the lattice vibrational modes Σ_3 and X_{10}. The second type is observed for the $Pb_2B^{3+}B',^{5+}O_6$ compounds as for example Pb_2YbNbO_6 or Pb_2YbTaO_6. It is characterised by only one modulation wavevectors and the Pb shifts should be along the [110] cubic direction and not along [100] as for Pb_2MgWO_6. These phase transitions are analysed on the basis of Landau theory.

The thermal motion of Pb-atoms, large in cubic phase, reaches a normal value in the pseudo tetragonal phase. In contrast, in the rhombohedral phases the thermal ellipsoid remains abnormally large down to the low temperatures. This point is discussed in relation to the relaxor behavior.

o.m2.o4 Evidence of Charge Transfer in $YBa_2Fe_3O_8$ from a Bond Valence Analysis of the Structure. I. Natali Sora, A. Santoro, and Q. Huang, *Nat'l Inst. of Stds. and Tech. 100 Bureau Dr. Stop 8562, Gaithersburg, MD 20899-8562, USA.*
Keywords: structure of $YBa_2Fe_3O_8$, charge transfer, bond valence analysis.

The Structure of $YBa_2Fe_3O_8$ has been studied with the bond valence method in an attempt to explain the bond valence sum anomalies observed for the Y and Ba atoms. The results of this analysis show that such anomalies are not entirely due to geometrical constraints imposed by symmetry, since it is possible to generate a model of the structure more relaxed than the experimental configuration, without violating the space group conditions and the bonding scheme of the atoms. A comparison between the bond distance of the relaxed model and those of the experimental structure suggests that the atomic configuration observed experimentally is consistent with a charge transfer that tends to equalize the oxidation states of the two crystallographically independent iron atoms. This conclusion is corroborated by bond valence calculations and by the similarities between $YBa_2Fe_3O_8$ and the 123 copper superconductor, in which charge transfer between the two copper atoms has been demonstrated by Brown [J. Solid State Chem. 90, 155(1991)].