

[o.m2.p9] New oxyfluoride lead-free ferroelectric relaxors in the BaTiO₃-BaZrO₃-BaLiF₃ system. A. Kerfah*, K. Taïbi*, A. Guehria-Laïdoudi* and A. Simon**, J. Ravez**. * Laboratoire de Cristallographie Appliquée, Institut de Chimie, U.S.T.H.B., B.P 32 El-Alia, Bab-Ezzouar, Alger, ALGERIE. ** I.C.M.C.B.-C.N.R.S., Avenue du docteur A. Schweitzer, 33608 Pessac, Cedex FRANCE.

Keyword: relaxor ferroelectric, lead-free ceramics.

The perovskite oxides with compositions very close to BaTiO₃ are well known and constitute a large family of classical ferroelectric. Otherwise, the relaxor behaviour, in perovskites, mainly occurs in lead-based compositions (PMN, PSN, PIN...) with more than one type of ion occupying the equivalent 6-coordination number crystallographic site [1]. Research is now progress to obtain such lead-free ceramics wich could be relaxors at temperature close to 300 K. Lead-free compositions could be of great interest applications since they are environment-friendly.

The present study concerns oxyfluoride compositions relatively close to BaTiO₃ in the ternary system BaTiO₃-BaZrO₃-BaLiF₃. Final compositions are obtained from BaTiO₃, BaZrO₃ and BaLiF₃ according to the following starting mixture:



Selected compositions correspond to $0 \leq x \leq 0.4$ and $y=0.25, 0.50$ and 0.75 respectively. Powders are pressed into disks (8 mm in diameter, 1 mm thick) and sintered at 1250° C for 4 h in platinum sealed tubes under dry argon in order to avoid hydrolisis at high temperature.

X-ray powder diffraction studies has allowed to determine the room symmetry and limits of the perovskite solid solution domains.

Dielectric measurements were performed on ceramic disks after deposition of gold electrodes on the circular faces of ceramics by cathoding sputtering. ϵ' and ϵ'' were determined under helium as a function of both temperature (77– 450 K) and frequency (10^2 – 2.10^5 Hz) using a Wayne-Kerr6425 component analyser.

This study of ceramics with a composition inside the BaTiO₃-BaZrO₃-BaLiF₃ diagram shows a large solid solution domain relatively close to BaTiO₃ with a derived perovskite structure. The ferroelectric behaviour is of a classical type for compositions close to BaTiO₃. Two relaxor type regions occur when they derivate from BaTiO₃. These results are related to ionic substitution and chemical bonding. The relaxor properties are related to electrical charge heterogeneities. Some of these compositions could prove valuable (dielectric for capacitors, actuators) because they are without lead, thus environment-friendly. A spontaneous classical ferroelectric - relaxor ferroelectric transition has now been evidenced in lead free relaxors. All the compositions studied could be also of interest due to the fact that oxyfluoride ceramics can be sintered at lower temperature than oxides.

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[o.m2.p10] Charge ordering in the layered perovskites LnBaCo₂O₅ (Ln=Ho,Tb). E. Suard¹, F. Fauth², V. Caignaert³, I. Mirebeau⁴, G. Baldinozzi⁵, ¹Institut Laue Langevin, Av. des Martyrs, F-38042 Grenoble, ²Swiss Light Source (SLS), Paul Scherrer Institute, CH-5232 Villigen PSI, ³Laboratoire CRISMAT-ISMRA, Bd du M^l JUIN, F-14050 CAEN, ⁴Laboratoire Léon Brillouin, CE-Saclay, F-91191 Gif sur Yvette, ⁵Laboratoire SPMS, CNRS-Ecole Centrale de Paris, 92295 Châtenay-Malabry Cedex, France.

Keywords: neutron diffraction, charge ordering, phase transition.

In the ordered oxygen deficient perovskite HoBaCo₂O₅, we have observed by neutron powder diffraction two structural phase transitions at 350K and 210K, corresponding to the occurrence of magnetism and long-range charge ordering, respectively [1]. In the paramagnetic domain (T_N≈350K), the crystal structure is tetragonal with P4/mmm space group and derives from the perovskite structure. Cell parameters are $a=b=a_p$, $c=2a_p$ where a_p is the cell parameter of the cubic perovskite. The structure is described with an alternate stacking of holmium and barium layers along c direction, and rows of CoO₅ pyramids as in YBaCuFeO₅ structure [2]. When cooling down, a magnetic moment appears on the Co sites resulting in an AF structure with a propagation vector $k=(\frac{1}{2} \frac{1}{2} 0)$. The Co spins point along a crystallographic direction in the ab plane and therefore induce an orthorhombic distortion of the nuclear structure. In the temperature range $210K < T < 350K$, the space group is Pmmm. For $T < 210K$, we have observed a doubling of the cell in the b direction and solved the nuclear structure in the Pmmb space group, leading to the existence of two different sites for the Co atoms. It is interpreted by a long-range charge ordering of the Co²⁺/Co³⁺ cations over these two sites, which also induces a perturbation in the magnetic ordering due to the existence of two magnetic sublattices with Co²⁺ HS and Co³⁺ HS. The observed magnetic moments $\mu_{Co^{3+}}=3.7\mu_B$ and $\mu_{Co^{2+}}=2.7\mu_B$, which give $1\mu_B$ difference between the two sites are in perfect agreement with this model. Both transitions have been confirmed by DSC, electron microscopy and resistivity measurements. Moreover, in a recent paper on YBaCo₂O₅, the authors observe an associated spin state transition with the charge-ordering. Nothing in our present data indicates such a spin transition, but the model will be discussed.

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[3] T. Vogt, P.M. Woodward, P. Karen, B.A. Hunter, P. Henning and A.R. Moodenbaugh, *Phys. Rev. Lett.* 84, 2969, (2000).