

s12.m34.p11 **Alkali Ion Disorder in  $(\text{Na,Li})_2\text{FeTi}(\text{PO}_4)_3$  and  $\text{Na}_2\text{FeZr}(\text{PO}_4)_3$  NASICON Phases by Neutron Diffraction.** M. Sommariva, M. Catti, and A. Comotti, *Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via Cozzi 53, 20125 Milano, Italy. E-mail: marco.sommariva@mater.unimib.it*

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NASICON materials are crystalline phosphates of transition metals Me and alkali atoms A, according to the formula  $\text{A}_x\text{M}_y(\text{PO}_4)_3$ , which display a high mobility of the  $\text{A}^+$  ion, and are thus promising materials for applications as solid state electrolytes and electrodes in microbatteries. The structural characterization of the mobile ion environment, and of its bonding interactions with the neighbouring atoms, is essential to understand the mechanisms of ionic conduction in these phases. We have been investigating a number of NASICON compounds by high-resolution neutron powder diffraction at variable temperature (HRPD time-of-flight diffractometer at the ISIS Facility, Rutherford Appleton Laboratory, U.K.; resolution  $\Delta d/d \approx 4 \times 10^{-4}$ ). By use of Rietveld refinements coupled with difference Fourier maps, multiple disorder effects involving the alkali ions in the large M1 and M2 cavities of the NASICON framework can be detected [1,2].

The structures of the  $\text{Na}_2\text{FeTi}(\text{PO}_4)_3$  and  $\text{Na}_2\text{FeZr}(\text{PO}_4)_3$  phases are presented here, together with preliminary results for the partially lithium-exchanged FeTi compound. The two sodium materials were synthesized by solid state reactions. Rietveld refinements converged to  $R_p$  factors of 0.068 and 0.094 (space group R-3c, Z=6) for the two above phases, respectively. In the  $\text{Na}_2\text{FeTi}(\text{PO}_4)_3$  case ( $a=8.59665(3)$ ,  $c=21.7137(1)$  Å), half of Na (Na1) was located within the M1 and half (Na2) within the M2 cavity; however, about 40% of Na1 lies exactly on the (0,0,0) site with -3 symmetry, but the remaining part is disordered in an off-centre position. Further, also Na2 is slightly displaced from the centre of the M2 hollow at (2/3,0,1/4), attaining a disordered configuration. Such results are at variance with the fully ordered structural model previously reported for the same compound [3]. A different situation was observed in  $\text{Na}_2\text{FeZr}(\text{PO}_4)_3$  ( $a=8.76828(4)$ ,  $c=22.2706(2)$  Å), where only 0.64 atoms per formula unit lie on the M1 site, and 1.36 atoms per f.u. are distributed between the M2 site and a disordered position also located within the M2 cavity but significantly off-centre. Lithium exchange was performed in water solution on  $\text{Na}_2\text{FeTi}(\text{PO}_4)_3$ , and the product was studied by neutron diffraction. Occupancy refinements and difference Fourier syntheses indicate that about 50% of sodium was actually exchanged. Preliminary results of the structural analysis show that the symmetry lowers from R-3c to R-3, consistent with what reported in [3]; sodium occupies the M1 sites in an orderly way, whereas lithium goes into the M2 cavity on a disordered position similar to that observed in  $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$  [2]. Models of ionic mobility and diffusion pathways can be proposed on the basis of the disorder found.

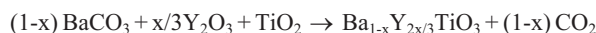
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s12.m34.p12 **Ferroelectric Behavior in Perovskite Ceramics of Composition  $\text{Ba}_{1-x}\text{Y}_{2x/3}\text{TiO}_3$ .** K. Taibi<sup>a</sup>, C. Abdellaoui<sup>a</sup>, A. Guehria-Laidoudi<sup>a</sup>, A. Simon<sup>b</sup> and J. Ravez<sup>b</sup>, <sup>a</sup>Faculté de Chimie, U.S.T.H.B., BP 32 El-Alia, Bab-Ezzouar, Alger, Algérie, <sup>b</sup>I.C.M.C.B.-C.N.R.S., 87 avenue du D' A. Schweitzer, 33608 Pessac, France. E-mail: taibikamelz@yahoo.fr

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A large number of perovskite materials exhibit a ferroelectric behavior. Depending on the composition, these materials can be divided in two classes: classical ferroelectric or relaxor one. The ferroelectric relaxor materials exhibit a large range of interesting properties resulting from the intricate ordered/disordered nanostructures and the formation of local polar nanodomains [1, 2]. To usual applications, relaxor materials are of great interest both for device application and in the fundamental understanding of ferroelectric systems. Relaxor materials actually used are lead-based ceramics i.e  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN),  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PZT)...). The latter's present a disadvantage due to the toxicity and volatility of PbO. The actual evolution of research is oriented to environment-friendly application. In this way, the present work concerns a new lead-free compositions of non-stoichiometric perovskite derived from the well known  $\text{BaTiO}_3$ .

The various composition were obtained from  $\text{BaCO}_3$ ,  $\text{TiO}_2$  and  $\text{Y}_2\text{O}_3$  by solid state synthesis according to the following reaction:



The limits of solid solution have been determined on the basis of room temperature X-ray diffraction analysis. Owing to the fact that the dielectric properties of the ceramics are strongly affected by a number of dependent factors like grain size, densification and porosity, microstructural studies of some selected compositions have been undertaken. The microstructures are investigated by scanning electron microscopy for ceramic with composition  $0.025 \leq x \leq 0.10$  sintered at different temperatures between 1200 and 1400°C.

Dielectric measurements are performed on ceramic disks. For all samples, the temperature and frequency variations of the real part of permittivity are investigated. The results are discussed and compared to previous work concerning  $\text{Ba}_{1-x}\text{A}_{2x/3}\text{TiO}_3$  compositions where La and Bi are in the dodecahedral sites (A)[3, 4]. These materials has showed conventional properties for composition close to  $\text{BaTiO}_3$  and relaxor behavior for  $x \geq 0.15$ .

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