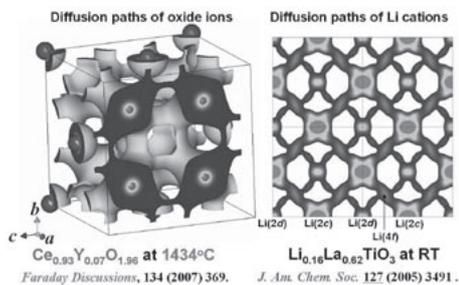


(La<sub>0.8</sub>Sr<sub>0.2</sub>)(Ga<sub>0.8</sub>Mg<sub>0.15</sub>Co<sub>0.05</sub>)O<sub>2.8</sub> [CPL380(2003)391], CeO<sub>2</sub> [APL84(2004)526], Bi<sub>1.4</sub>Yb<sub>0.6</sub>O<sub>3</sub> [APL87(2005)221909], Ce<sub>0.93</sub>Y<sub>0.07</sub>O<sub>1.96</sub> [Farad.Discuss.134(2007)369], and La<sub>0.64</sub>(Ti<sub>0.92</sub>Nb<sub>0.08</sub>)O<sub>3</sub> [Chem.Mater.19(2007)32604], Y<sub>0.79</sub>Ta<sub>0.21</sub>O<sub>1.72</sub> [ChemMater19(2007)3539], La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3</sub> [JApplCryst40(2007)1166], (La<sub>0.6</sub>Sr<sub>0.4</sub>)(Co<sub>0.8</sub>Fe<sub>0.2</sub>)O<sub>3-x</sub> [SolStIon179(2008)1939], (Pr<sub>0.9</sub>La<sub>0.1</sub>)<sub>2</sub>(Ni<sub>0.74</sub>Cu<sub>0.21</sub>Ga<sub>0.05</sub>)O<sub>4+x</sub> [JACS139(2008)2662], La<sub>0.62</sub>Li<sub>0.16</sub>TiO<sub>3</sub> [JACS127(2005)3491] and CuLi [JMaterChem16(2006)4393] (Figure). It was found that the disorder and path depend on the crystal structure.



Keywords: neutron and X-ray diffractometry, *in-situ* powder diffraction, ionic conductors

**P11.13.81**

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**Short-range to long-range order structure change of Mg-Fe alloys**

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We performed structure analysis of Mg-Fe alloy system prepared by mechanical alloying. For Mg concentrations up to about 15 mol%, mechanical alloying can produce single-phase bcc alloys. By using the conventional average structure analysis and X-ray pair-distribution function method, we can bridge the long-range and short-range order structure of Mg-Fe alloys. The substituted Mg atoms arranged randomly in the low-Mg composition, but Mg atoms came to have the order structure as the Mg composition increases. It can explain this new finding as a kind of short-range order to long-range order phase transition.

Keywords: Mg-Fe, mechanical alloying, pair-distribution function

**P11.13.82**

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**Development of a new type of Li-battery materials based on the milarite-family**

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Over the last three decades, enormous efforts have been devoted to advance Li-ion based batteries by exploiting a variety of electrode and electrolyte materials [1]. However, demands for lighter and

smaller batteries exceed the dimension offered by the modern technology. In this respect, it is try-worthy continuing to develop new battery materials. The milarite-family (A<sub>2</sub>B<sub>2</sub>C[T(II)<sub>3</sub>T(I)<sub>12</sub>O<sub>30</sub>): A = Sn<sup>4+</sup>, Ti<sup>4+</sup>, Zr, Al, Fe<sup>3+</sup>, ...; B = Na, H<sub>2</sub>O; C = Na, K; T(I) = Si, Al; T(II) = Li, Be, Mg, ... [2, 3] is a highly interesting candidate due to: 1) the presence of short pathways available for conducting Li; 2) the presence of a crystal-chemical basis for the formation of solid-solutions and defect-engineering; 3) a high thermal stability up to 1200 K. In fact, our recent studies showed ionic conductivity in Li-bearing milarite-type minerals, sogdianite and sugilite, for the first time [4, 5]. The ionic conductivity in sogdianite could be assigned to site exchange processes of Li between T(II) and A sites parallel to the (001)-plane at elevated temperatures. Interestingly, the ionic conductivity in this topology is proportional to the amount of Na cations at B sites [5]. These Na cations may play a relevant multiple role, as carrying and transferring charges for the negative-charged framework [Li<sub>3</sub>Si<sub>12</sub>O<sub>30</sub>]<sup>9-</sup>. Here, the state of the art development of Li-Na-bearing milarite-type Li-battery materials will be presented.

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Keywords: ionic conductors, milarite, sogdianite

**P11.13.83**

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**Optimization of energy parameters indemnification of impurity levels in lead and bismuth**

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In impurity semiconductors except for the impurity giving the basic carriers of a charge, there are compensating impurities. Usually for their characteristic the measure of indemnification is entered and properties of semiconductors in a wide interval of a degree of indemnification are investigated. Influence of indemnification on properties of alloys is expressed that in the forbidden zone there are additional resolved power levels. Indemnification influences dispersion of carriers of a charge. These two factors strongly change such characteristics, as concentration and mobility of carriers of a charge (including electro-conductivity and thermoelectromotive of semiconductors). Influence of indemnification on properties of chalcogenides of bismuth and lead is investigated. Crystals PbTe-PbCl<sub>2</sub>-B and Bi<sub>2</sub>Te<sub>3</sub> <CdCl<sub>2</sub>-B with low concentration of the hole carriers of current. The measured and calculated parameters (electro-conductivity, thermoelectromotive, concentration of carriers of current testify the strong compensating influence of boron. Adjusting with complex impurity (PbCl<sub>2</sub>-B) and (CdCl<sub>2</sub>-B) it was possible to receive a set of samples with concentration of the hole carriers down to P=6,2-1017 cm<sup>-2</sup>. The reason of strong indemnification is, on seen, linkage of vacancies of lead in complexes with ions of chlorine (in case PbS and PbTe). In Bi<sub>2</sub>Te<sub>3</sub>, strong p-type influence of boron results in indemnification of donor levels of chlorine.

Keywords: electro-conductivity, thermoelectromotive, impurities

### P11.13.84

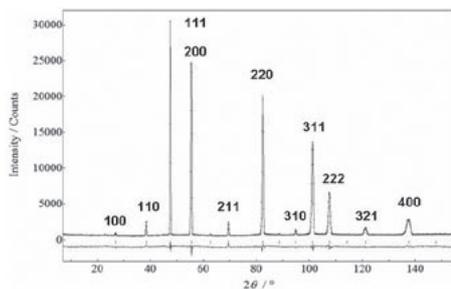
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#### Structural investigation of the cubic perovskite-type doped lanthanum cobaltite $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$

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Lanthanum strontium cobaltites,  $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$ , which have a perovskite-type structure, are promising electrode materials for solid oxide fuel cells (SOFCs). The purpose of the present study is to investigate the crystal structure of the cubic Pm-3m perovskite-type  $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$  at room temperature and at high temperature by neutron diffraction. Neutron diffraction data were collected in air by a diffractometer HERMES with a 150 multi-detector system. A furnace with  $\text{MoSi}_2$  heaters was placed on the sample table, and used for neutron diffraction measurements at high temperatures (J. Am. Ceram. Soc. 85 (2002) 2925). The experimental data were analyzed assuming the cubic perovskite-type structure by Rietveld method. La and Ba atoms were placed at the special position 1b  $1/2, 1/2, 1/2$  of the Pm-3m symmetry. Co and O atoms were put at the 1a 0, 0, 0 and 3d  $1/2, 0, 0$  sites, respectively. The calculated profile agreed well with the observed one taken at room temperature (Figure). The refined crystal structure of  $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$  is similar with that of cubic  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-x}$  at 1531K reported in our previous work [J. Appl. Crystallogr., 40 (2007) 1166].



Keywords: neutron diffraction, solid oxide fuel cells, perovskite-type structure

### P11.13.85

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#### Synchrotron XRD and EXAFS studies on nanocrystalline $\text{ZrO}_2\text{-CaO}$ solid solutions

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The crystal structure and the local atomic order of a series of nanocrystalline  $\text{ZrO}_2\text{-CaO}$  solid solutions with varying CaO content were studied by synchrotron radiation X-ray powder diffraction and extended X-ray absorption fine structure (EXAFS) spectroscopy. These samples were synthesized by a pH-controlled nitrate-glycine gel-combustion process. For CaO contents up to 8 mol%, the  $t''$ -

form of the tetragonal phase ( $c/a > 1$ ) was identified, whereas, for 10 and 12 mol% CaO, the  $t''$ -form ( $c/a = 1$ ; oxygen anions displaced from their ideal positions in the cubic phase) was detected. Finally, the cubic phase was observed for solid solutions with CaO content of 14 mol% CaO or higher. Thus, the  $t''/t''$  and  $t''/\text{cubic}$  compositional boundaries were determined to be at  $(9 \pm 1)$  and  $(13 \pm 1)$  mol% CaO, respectively. EXAFS study demonstrated that this transition is related to a tetragonal-to-cubic symmetry change of the first oxygen coordination shell around Zr atoms.

Keywords: zirconia, XAFS, synchrotron X-ray diffraction

### P11.13.87

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#### Novel long period structures in hydrogen storage $\text{La}_x\text{Y}_{1-x}\text{Ni}_{3.8}$ compounds

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A series of  $(\text{La},\text{Y})\text{Ni}_z$  ( $3 < z < 4$ ) alloy compounds show polymorphic block-stacking superstructures. These structures can be interpreted as rhombohedral stacking sequence of ABC (3R-type) and hexagonal stacking sequence of AB (2H-type), where the structural unit is composed of  $\text{LaNi}_5$  (Haücke phase) and  $\text{YNi}_2$  (Laves phase, C15) type structures at unit-cell scale. In this presentation, we describe the differences of local chemistry between non-reacted and after gaseous- $\text{H}_2$  reacted  $(\text{La},\text{Y})\text{Ni}_z$  ( $3 < z < 4$ ) compounds through the direct observation by Z-contrast scanning transmission electron microscopy (STEM). All of  $(\text{La}_x\text{Y}_{1-x})\text{Ni}_{3.8}$  ( $x=0.4, 0.5, 0.6$ ) superstructures annealed at 1023K for 14 days are identified as 5:19R-type (3R) [1] based on electron diffraction analysis. Interestingly, for all the images there appear Z-contrast modulations at nanometer scales, which become significant for the  $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{3.8}$ . These directly represent local chemical fluctuations, namely the occurrence of La-rich/Y-rich chemical domains in these alloys: that is to say, 'chemical mosaicism'. STEM image of  $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{3.8}$  reacted with 2MPa hydrogen shows disappearance of 'chemical mosaicism', and to transform a novel long period Y-ordered 9R superstructure with c-length approximately 167Å. On the basis of Z-contrast analysis, we find that the novel structure contains Y-hydride layers, whose structure is well interpreted by referring structure local atomic configurations within  $\text{YH}_3$  compound.

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Keywords: hydride compounds, STEM, chemical domain structure

### P11.13.88

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#### Structural investigation of the Ba doped $\text{LaInO}_3$

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A high ionic conductor Ba doped lanthanum indium oxide was investigated by synchrotron powder diffraction and transmission