

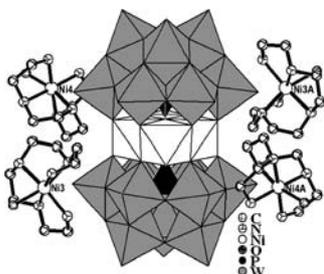
CONTENTS

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Regular Articles

Hydrothermal synthesis and structural characterization of three inorganic–organic composite sandwich-type phosphotungstates

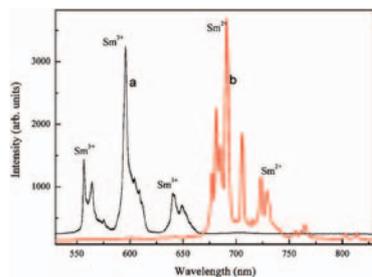
Jun-Wei Zhao, Shou-Tian Zheng and Guo-Yu Yang  
page 3317



Three inorganic–organic composite sandwich-type phosphotungstates  $[\text{Ni}(\text{tapa})(\text{H}_2\text{O})_4]\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2 \cdot 8 \text{H}_2\text{O}$  (1),  $(\text{enH}_2)_3[\text{Ni}_2(\text{H}_2\text{O})_{10}][\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot \text{en} \cdot 8\text{H}_2\text{O}$  (2) and  $(\text{enH}_2)_{10}[\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot 20\text{H}_2\text{O}$  (3) have been hydrothermally synthesized and structurally characterized by IR spectra, elemental analysis, thermogravimetric analysis and magnetic susceptibility. They all contain tetra-*M* sandwiched polyoxoanions  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  ( $M = \text{Ni}^{2+}$  or  $\text{Mn}^{2+}$ ) and nickel-organoamine cations or organoamine cations work as the charge balance ions.

Irradiation-induced reduction and luminescence properties of  $\text{Sm}^{2+}$  doped in  $\text{BaBPO}_5$

Yanlin Huang, Kiwan Jang, Wanxue Zhao, Eunjin Cho, Ho Sueb Lee, Xigang Wang, Dake Qin, Ying Zhang, Chanfang Jiang and Hyo Jin Seo  
page 3325

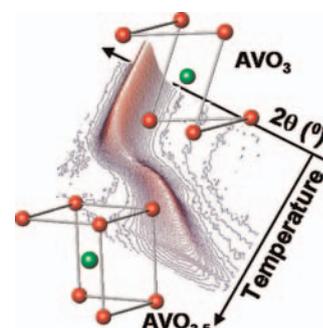


The Sm doped in  $\text{BaBPO}_5$  as-prepared in air contains only  $\text{Sm}^{3+}$  ions and shows its fluorescence bands due to the  $^4\text{G}_{5/2}$  to  $^6\text{H}_{5/2}$ ,  $^6\text{H}_{7/2}$ ,  $^6\text{H}_{9/2}$ , and  $^6\text{H}_{11/2}$  transitions (a) under the excitation of 488 nm  $\text{Ar}^+$ -ion laser. The emission spectra of the samples after X-ray subsequently irradiations are characteristic of  $\text{Sm}^{2+}$  transitions between the energy levels of  $4f^6$  electronic configurations (b). It is found that the conversion of  $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$  is very efficient in  $\text{BaBPO}_5$  hosts after X-ray irradiation.

Regular Articles—Continued

Formation, structure and magnetism of the metastable defect fluorite phases  $\text{AVO}_{3.5+x}$  ( $A = \text{In}, \text{Sc}$ )

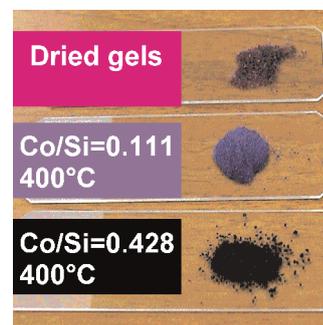
Shahid P. Shafi, Rylan J. Lundgren, Lachlan M.D. Cranswick and Mario Bieringer  
page 3333



Topotactic oxidation of  $\text{AVO}_3$  bixbyite to  $\text{AVO}_{3.5}$  defect fluorite structure followed by in-situ powder X-ray diffraction. The upper structural diagram shows a six coordinated (A/V)- $\text{O}_6$  fragment in bixbyite, the lower structure illustrates the same seven-fold coordinated (A/V)-O, cubic environment in the defect fluorite structure.

Cobalt–silicon mixed oxide nanocomposites by modified sol–gel method

Serena Esposito, Maria Turco, Gianguido Ramis, Giovanni Bagnasco, Pasquale Pernice, Concetta Pagliuca, Maria Bevilacqua and Antonio Aronne  
page 3341



Highly dispersed cobalt–silicon mixed oxide nanocomposites ( $\text{Co}/\text{Si} = 0.111, 0.250$  and  $0.428$ ) were obtained by a modified sol–gel method using almost solely aqueous solutions. The nature of cobalt species and their interactions with the siloxane matrix are strongly depending on both the cobalt loading and the heat treatment. All materials retained high surface areas also after treatments at  $600^\circ\text{C}$  and exhibited surface Lewis acidity.

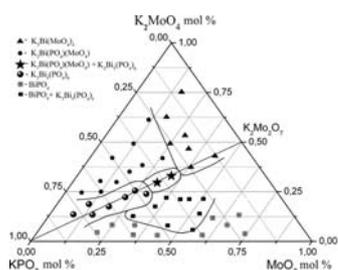
## Phase relations in the system

### $K_2MoO_4$ – $KPO_3$ – $MoO_3$ – $Bi_2O_3$ : A new phosphate

#### $K_3Bi_5(PO_4)_6$

Kateryna V. Terebilenko, Igor V. Zatovsky, Nikolay S. Slobodyanik, Konstantin V. Domasevitch, Denis V. Pushkin, Vyacheslav N. Baumer and Valentina S. Sudavtsova

page 3351

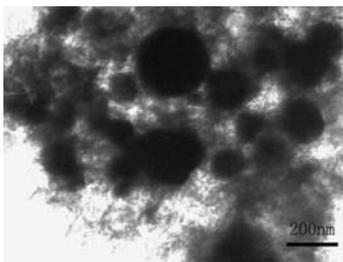


Composition diagram of the  $K_2MoO_4$ – $KPO_3$ – $MoO_3$  system containing 15 mol%  $Bi_2O_3$  with approximate fields of phase formation bismuth phosphates, molybdate and phosphate-molybdate.

## Synthesis and electrochemical performances of amorphous carbon-coated Sn–Sb particles as anode material for lithium-ion batteries

Zhong Wang, Wenhui Tian, Xiaohe Liu, Rong Yang and Xingguo Li

page 3360

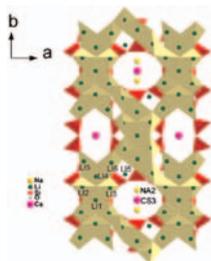


The amorphous carbon coating on the Sn–Sb particles was prepared from aqueous glucose solutions using a hydrothermal method. Because the outer layer carbon of composite materials is loose cotton-like and porous-like, it can accommodate the expansion and contraction of active materials to maintain the stability of the structure, and hinder effectively the aggregation of nano-sized alloy particles.

## Increase of ionic conductivity in the microporous lithosilicate RUB-29 by Na-ion exchange processes

S.-H. Park, A. Senyshyn and C. Paulmann

page 3366

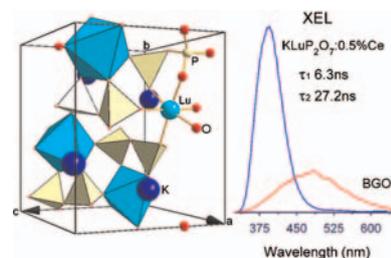


$Li_2O$ -layers formed by edge- and corner-sharing  $LiO_4$ - and  $LiO_3$ -moieties in the zeolite-like lithosilicate RUB-29 provide optimal pathways for conducting  $Li^+$ . The number of empty Li sites in this layer-like configuration could increase via 'simple'  $Na^+$ -exchange processes, promoting fast Li motions.

## Synthesis, structure and X-ray excited luminescence of $Ce^{3+}$ -doped $AREP_2O_7$ -type alkali rare earth diphosphates ( $A = Na, K, Rb, Cs$ ; $RE = Y, Lu$ )

Jun-Lin Yuan, Hui Zhang, Hao-Hong Chen, Xin-Xin Yang, Jing-Tai Zhao and Mu Gu

page 3381

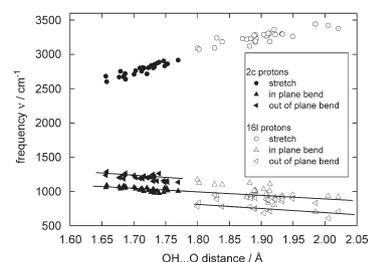


The perspective view of  $KLuP_2O_7$  unit cell. The crystal structures of five  $AREP_2O_7$  diphosphates were obtained from Rietveld refinement. Under the excitation of hard X-ray, the  $Ce^{3+}$ -activated  $AREP_2O_7$  ( $A = Na$ – $Cs$ ;  $RE = Y, Lu$ ) feature strong  $Ce^{3+} 5d-4f$  emission with high light yield (1–2 times of that of  $Bi_4Ge_3O_{12}$ ) and fast decay time within 20–28 ns.

## $Ba_2In_2O_4(OH)_2$ : Proton sites, disorder and vibrational properties

Jean-Raphaël Martinez, Chris E. Mohn, Svein Stølen and Neil L. Allan

page 3388

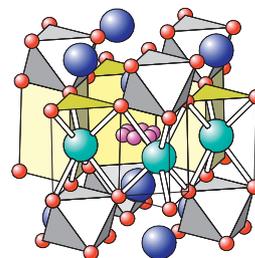


The characteristic O–H vibrational modes of  $Ba_2In_2O_4(OH)_2$  as a function of the  $OH \cdots O$  hydrogen bond length.

## $LnSr_2PtO_{7+\delta}$ ( $Ln = La, Pr, \text{ and } Nd$ ): Three new Pt-containing $[A'_2O_{1+\delta}][A_nB_{n-1}O_{3n}]$ -type hexagonal perovskites

Stefan G. Ebbinghaus, Chasanoglou Erztoument and Ivan Marozau

page 3393



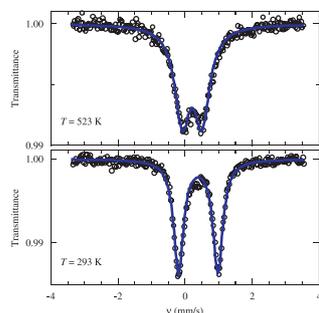
Hexagonal perovskites of the  $[A'_2O_{1+\delta}][A_nB_{n-1}O_{3n}]$  family have so far only been known for the transition metals Mn, Nb, Ru, and Ir. In this paper, three new  $n = 2$  examples containing platinum as  $B$ -type cation are presented. The structure and physical properties of the three title compounds were investigated by XRD Rietveld refinements, thermogravimetry, X-ray absorption spectroscopy, magnetic measurements and optical spectroscopy.

Continued

## Magnetic and Mössbauer studies of 5% Fe-doped BiMnO<sub>3</sub>

Alexei A. Belik, Naoaki Hayashi, Masaki Azuma, Shigetoshi Muranaka, Mikio Takano and Eiji Takayama-Muromachi

page 3401

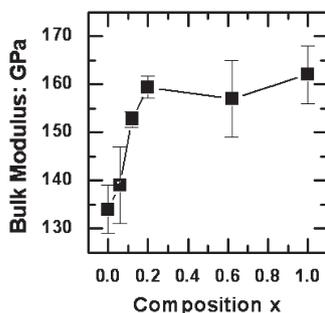


Mössbauer spectra of BiMn<sub>0.95</sub>Fe<sub>0.05</sub>O<sub>3</sub> at 523 and 293 K.

## High-pressure structural evolution of a perovskite solid solution (La<sub>1-x</sub>Nd<sub>x</sub>)GaO<sub>3</sub>

R.J. Angel, J. Zhao, N.L. Ross, C.V. Jakeways, S.A.T. Redfern and M. Berkowski

page 3408

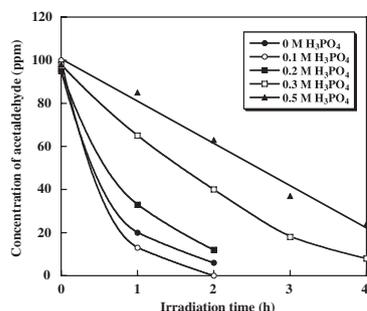


High-pressure structure determinations of six perovskites on the La<sub>1-x</sub>Nd<sub>x</sub>GaO<sub>3</sub> join show that at La-rich compositions the GaO<sub>6</sub> octahedra have much lower bulk moduli, as shown in the figure. This softening of the octahedra drives the high-pressure phase transition from *Pbnm* to *R-3c* structures.

## Effect of electrolysis conditions on photocatalytic activities of the anodized TiO<sub>2</sub> films

Kinji Onoda and Susumu Yoshikawa

page 3425

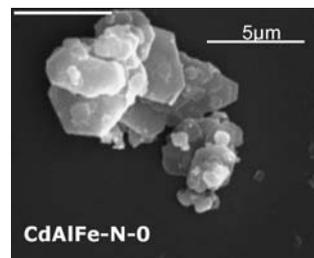


The effect of concentration of H<sub>3</sub>PO<sub>4</sub> on the photocatalytic activity of the anodized TiO<sub>2</sub> films was investigated. The pre-nitrated titanium plates were anodized in electrolyte of 1.5 M H<sub>3</sub>PO<sub>4</sub> and 0.3 M H<sub>2</sub>O<sub>2</sub> with varying H<sub>3</sub>PO<sub>4</sub> concentration in the range from 0 to 0.5 M. The highest photocatalytic activity was obtained at H<sub>3</sub>PO<sub>4</sub> concentration of 0.1 M.

## Synthesis of Cd/(Al+Fe) layered double hydroxides and characterization of the calcination products

M.R. Pérez, C. Barriga, J.M. Fernández, V. Rives and M.A. Ulibarri

page 3434

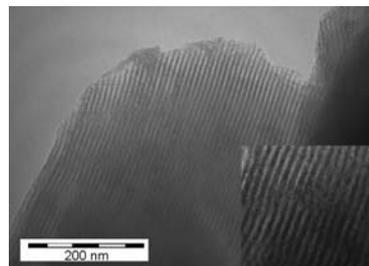


Layered double hydroxides (LDHs) containing Cd(II), Al(III), and Fe(III) in the brucite-like layers with different starting Fe/Al atomic ratios and with nitrate as counteranion have been prepared following the coprecipitation method. An additional Cd(II),Al(III)-LDH sample interlayered with hexacyanoferrate(III) ions has been prepared by ionic exchange. Calcination at 800 °C shows diffraction lines corresponding to CdO and to spinel-type materials.

## Synthesis and characterization of nanoparticulate MnS within the pores of mesoporous silica

Louse Barry, Mark Copley, Justin D. Holmes, David J. Otway, Olga Kazakova and Michael A. Morris

page 3443

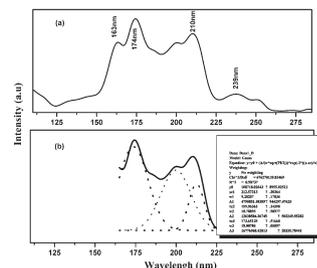


A novel manganese ethylxanthate precursor was used to impregnate the pore network of mesoporous silica and was decomposed to yield MnS particles smaller or equal to the pore size. The particles exhibit all three common polymorphs, demonstrate unexpected ferromagnetism at low temperatures and display a strong luminescence.

## Photoluminescence properties of La(PO<sub>3</sub>)<sub>3</sub>:Tb<sup>3+</sup> under VUV excitation

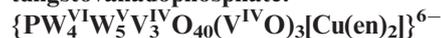
Yuhua Wang and Dan Wang

page 3450



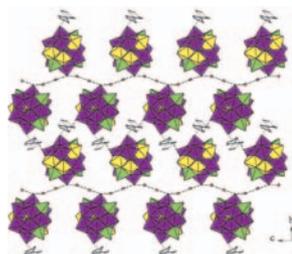
A strongest band around 174 nm, observed in the excitation spectrum of La<sub>0.55</sub>(PO<sub>3</sub>)<sub>3</sub>:Tb<sub>0.45</sub><sup>3+</sup>, indicates that La<sub>0.55</sub>(PO<sub>3</sub>)<sub>3</sub>:Tb<sub>0.45</sub><sup>3+</sup> can efficiently absorb the vacuum ultraviolet (VUV) energy. The band overlapping around 210 nm implies that the excited energy can be efficiently transferred from VUV to UV region. Therefore, La<sub>0.55</sub>(PO<sub>3</sub>)<sub>3</sub>:Tb<sub>0.45</sub><sup>3+</sup> is a promising phosphor in VUV region.

**Hydrothermal synthesis and characterization of the tri-capped and mono-supported pseudo-Keggin-type tungstovanadophosphate:**



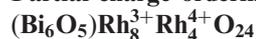
Jian Liu, Jia-Ning Xu, Ya-Bing Liu, Yu-Kun Lu, Jiang-Feng Song, Xiao Zhang, Xiao-Bing Cui, Ji-Qing Xu and Tie-Gang Wang

page 3456



A novel complex  $[Cu(phen)_2]_3\{PW_4^{VI}W_5^{IV}V_3^{IV}O_{40}(V^{IV}O)_3[Cu(en)_2]\} \cdot 4H_2O$ , the first example of tri-capped and mono-supported highly reduced pseudo-Keggin-type tungstovanadophosphate was synthesized under hydrothermal condition. And the heteropolyanions are linked by water dimer and cation  $[Cu(phen)_2]^{2+}$  through the hydrogen bond forming a three-dimensional (3D) supramolecular network. Interestingly, the water dimer and terminal oxygen of the polyanion cluster constitute a beautiful supramolecular helix chain.

**Partial charge ordering in the mixed-valent compound**



H. Mizoguchi, W.J. Marshall, A.P. Ramirez, A.W. Sleight and M.A. Subramanian

page 3463

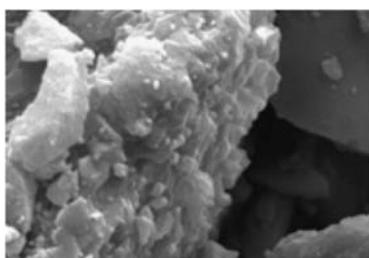


Crystals of the mixed-valent compound  $(Bi_6O_5)Rh_8^{3+}Rh_4^{4+}O_{24}$  show semiconducting properties, and magnetic susceptibility data indicate a localized moment for  $Rh^{4+}$ . Structure refinements at 173 and 296 K show partial charge ordering between  $Rh^{3+}$  and  $Rh^{4+}$ .

**Influence of the morphology and impurities of Ni(OH)<sub>2</sub> on the synthesis of neutral Ni(II)-amino acid complexes**

Vicente Rodríguez-González, Eric Marceau, Michel Che and Claude Pepe

page 3469

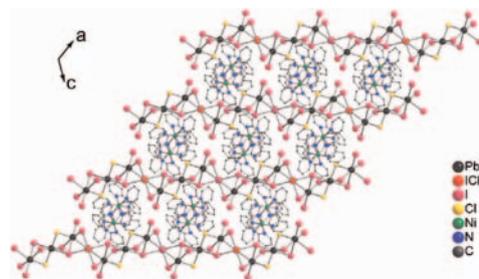


$Ni(OH)_2$  solid precursors can be readily selected on the basis of their defects, themselves stemming from the nickel salt chosen for precipitation, to rapidly synthesize neutral Ni(II)-amino acid complexes by ligand-promoted dissolution.

**Preparation and characterization of a novel hybrid magnetic semiconductor containing rare, one-dimensional mixed-iodide/chloride anion of lead(II)**

Le-Qing Fan, Ji-Huai Wu and Yun-Fang Huang

page 3479

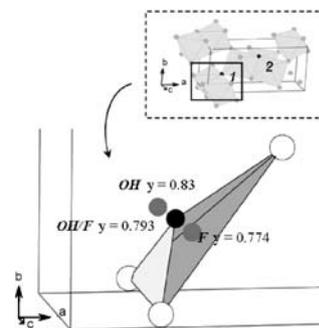


Based upon magnetic metal-organic complex as template, a novel one-dimensional haloplumbate containing mixed-halide anion has been successfully synthesized. Its structural characteristics, optical bandgap, magnetic and thermal properties are reported.

**Structural features of zinc hydroxyfluoride**

H. Serier, M. Gaudon, A. Demourgues and A. Tressaud

page 3485

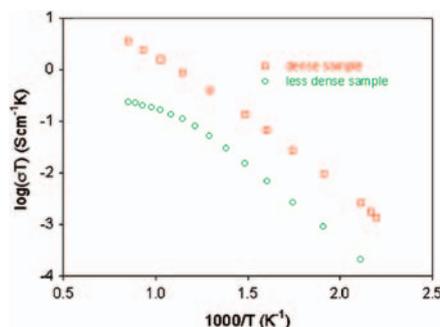


Representation of the splitting of site 1 (black sphere) into two positions (grey spheres) corresponding respectively to the presence of hydroxyl or fluoride ions.

**Conductivity studies of dense yttrium-doped BaZrO<sub>3</sub> sintered at 1325 °C**

Shanwen Tao and John T.S. Irvine

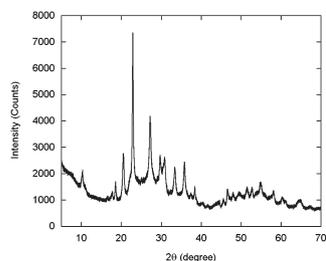
page 3493



Total conductivity of  $BaZr_{0.8}Y_{0.2}O_{3-\delta}$  samples in wet 5%  $H_2/Ar$  with (red) and without (green) addition of 1 wt% ZnO.

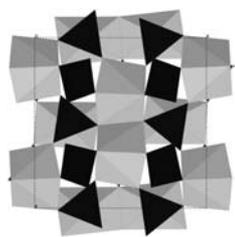
Continued

**Zirconium tungstate hydroxide hydrate revisited: Crystallization dependence on halide and hydronium ions**  
 Julie A. Colin, DeMarco V. Camper, Stacy D. Gates, Monty D. Simon, Karen L. Witker and Cora Lind  
 page 3504



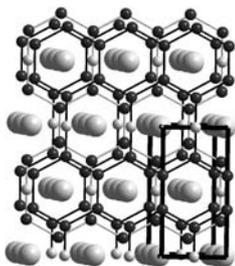
The formation of  $ZrW_2O_7(OH)_2 \cdot 2H_2O$  shows a strong dependence on reaction conditions. Both acid concentration and acid counterion play a significant role in the crystallization. High temperatures, high acid concentrations, and the presence of chloride or bromide ions promote the formation of well-crystallized  $ZrW_2O_7(OH)_2 \cdot 2H_2O$ . For low acid concentrations, a new zirconium tungstate hydrate polymorph is observed.

**Polymorphism in yttrium molybdate  $Y_2Mo_3O_{12}$**   
 Stacy D. Gates and Cora Lind  
 page 3510



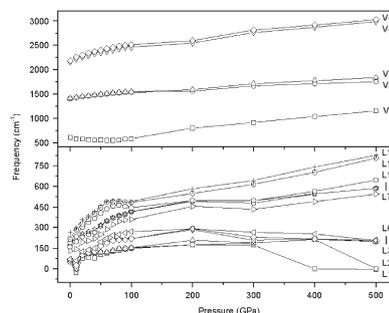
Yttrium molybdate ( $Y_2Mo_3O_{12}$ ) prepared by non-hydrolytic sol-gel chemistry crystallizes in a mixture of orthorhombic polymorphs with different atomic connectivities. The *Pbcn* and *Pba2* phases coexist over a narrow temperature range. Crystallization of the *Pbcn* structure is kinetically favored. The *Pba2* polymorph is the thermodynamically stable phase at low temperatures, and converts to *Pbcn* above 550 °C.

**Ternary rare earth metal boride carbides containing two-dimensional boron-carbon network: The crystal and electronic structure of  $R_2B_4C$  ( $R = Tb, Dy, Ho, Er$ )**  
 Volodymyr Babizhetskyy, Chong Zheng, Hansjürgen Mattausch and Arndt Simon  
 page 3515



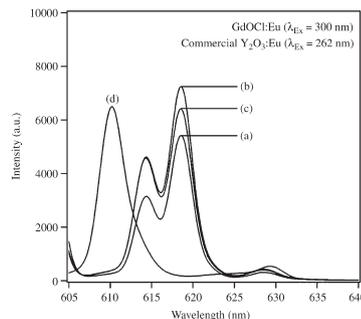
$Dy_2B_4C$  crystallizes a new structure type where planar  $6^3$ -Dy metal atom layers alternate with planar non-metal layers consisting of ribbons of fused  $B_6$  hexagons bridged by carbon atoms. Isostructural analogues with Tb, Ho and Er have also been characterized.

**First-principles study of structural and vibrational properties of crystalline silver azide under high pressure**  
 Weihua Zhu and Heming Xiao  
 page 3521



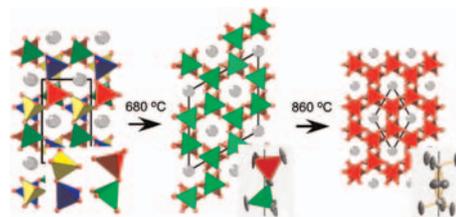
Silver azide attracts scientific and technological interest as an energetic material. There are sufficient difficulties to study it experimentally at extreme conditions due to their explosive nature. This paper presents a detailed first-principles study of the structural and vibrational properties of crystalline silver azide under hydrostatic pressure of 0–500 GPa.

**Morphology-dependent photoluminescence property of red-emitting  $LnOCl:Eu$  ( $Ln = La$  and  $Gd$ )**  
 Seoung-Soo Lee, Ho-In Park, Chung-Hyung Joh and Song-Ho Byeon  
 page 3529



Three different synthetic methods were explored to synthesize  $LnOCl:Eu$  ( $Ln = La$  and  $Gd$ ) phosphors. The application of solvothermal technique was very effective to selectively control the particle shape and consequently to enhance the luminescence intensity if we use an appropriate surfactant material.

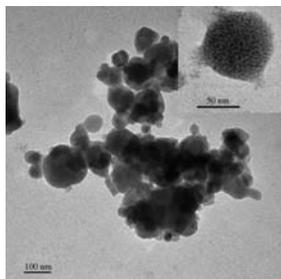
**Transitions between  $P2_1$ ,  $P6_3(\sqrt{3}A)$ , and  $P6_322$  modifications of  $SrAl_2O_4$  by *in situ* high-temperature X-ray and neutron diffraction**  
 Maxim Avdeev, Sergey Yakovlev, Aleksey A. Yaremchenko and Vladislav V. Khartov  
 page 3535



$SrAl_2O_4$  crystal structure evolution through the phase transitions between  $P2_1$ ,  $P6_3(\sqrt{3}A)$ , and  $P6_322$  modifications. Insets show displacements of apical oxygen atoms linking tridymite-type layers.

### Low coercive field and conducting nanocomposite formed by $\text{Fe}_3\text{O}_4$ and poly(thiophene)

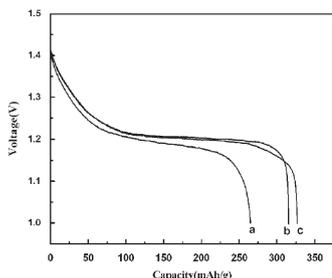
R.A. Silva, M.J.L. Santos, A.W. Rinaldi, A.J.G. Zarbin, M.M. Oliveira, I.A. Santos, L.F. Cótica, A.A. Coelho, A.F. Rubira and E.M. Giroto  
page 3545



TEM image of magnetite/poly(thiophene) nanocomposite.

### Controllable synthesis of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanorods precursor and applications in the synthesis of nickel-based nanostructures

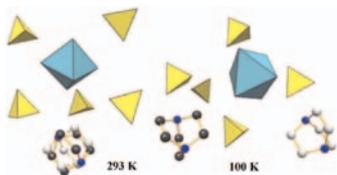
Wei-Guo Tian, Pan-Pan Wang, Ling Ren, Gen-Ban Sun, Ling-Na Sun, Kai Yang, Bing-Qing Wei and Chang-Wen Hu  
page 3551



$\beta$ -Ni(OH)<sub>2</sub> nanorods, NiO sub-microtubes, Ni nanospheres and flower-like nickel complexes were synthesized using the  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  nanorods precursor, which were fabricated via the microemulsion-mediated solvothermal synthesis method. The synthesized  $\beta$ -Ni(OH)<sub>2</sub> nanorods composed of fine nanosheets shown excellent electrochemical performance as an electrode material in rechargeable battery systems.

### Synthesis, crystal structures, phase transition characterization and thermal decomposition of a new dabcodiiium hexaaquairon(II) bis(sulfate):

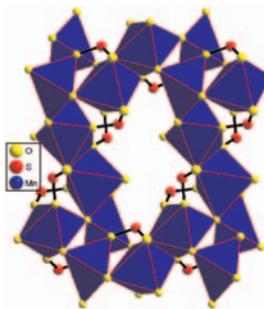
$(\text{C}_6\text{H}_{14}\text{N}_2)[\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2$   
Houcine Naïli, Walid Rekik, Tahar Mhiri and Thierry Bataille  
page 3560



The new dabcodiiium hexaaquairon(II) bis(sulfate),  $(\text{C}_6\text{H}_{14}\text{N}_2)[\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ , was prepared and characterized. It exhibits a supramolecular structure and undergoes a reversible order-disorder phase transition at  $-2.3^\circ\text{C}$ .

### A manganese sulfite with extended metal-oxygen-metal bonds exhibiting hydrogen uptake

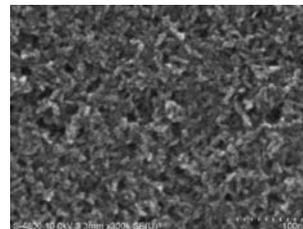
K. Prabhakara Rao, A. Govindaraj and C.N.R. Rao  
page 3571



A three-dimensional manganese sulfite with one-dimensional channels showing selective hydrogen absorption has been synthesized and characterized.

### Preparation and characterization of porous C-modified anatase titania films with visible light catalytic activity

Yi Xie, Xiujian Zhao, Yunxia Chen, Qingnan Zhao and Qihua Yuan  
page 3576

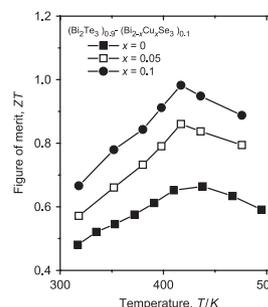


Carbon modifying not only produces homogeneous worm-like structure with uniform pores, but also extends the absorbance spectra of the as-prepared titania films into visible region.

## Rapid Communications

### Thermoelectric properties of Cu-doped n-type $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Cu}_x\text{Se}_3)_{0.1}$ ( $x=0-0.2$ ) alloys

J.L. Cui, L.D. Mao, W. Yang, X.B. Xu, D.Y. Chen and W.J. Xiu  
page 3583



After Cu-doping with  $x=0.1$ , the highest ZT value of 0.98 is obtained at 417 K, which is about 0.32 and 0.12 higher than those of Cu-free  $\text{Bi}_2\text{Se}_3\text{Te}_{2.7}$  and the Ag-doped alloys  $(\text{Bi}_2\text{Te}_3)_{0.9}-(\text{Bi}_{2-x}\text{Ag}_x\text{Se}_3)_{0.1}$  ( $x=0.4$ ), respectively.

Continued

**Fabrications of some kinds of 2-D frameworks consisting of nanosized polyoxomolybdate anion  $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}$  via condensation processes**

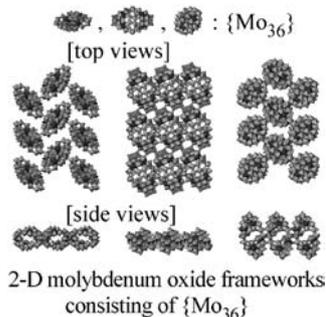
Kazuo Eda, Yuichi Iriki, Kenjiro Kawamura, Takeshi Ikuki and Masahiko Hayashi  
page 3588

**Author Index for Volume 180**

**Page 3594**

**Cumulative Keyword Index**

**Page 3602**



The image shows a variety of 2-D molybdenum oxide frameworks consisting of nanosized polyoxometalate anion  $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}$  ( $\{\text{Mo}_{36}\}$ ), obtained by our fabrication techniques. The variations are expected to provide diversity in physical properties of the frameworks.

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