method to obtain accurate lattice parameters. The Meissner effect was also measured to determine the T_c. The change in the lattice parameter of $Ba_{0.6}K_{0.4}BiO_3$ could be detected at T_c, which can be attributed to the spontaneous strain in the superconducting phase. We can conclude that this phenomenon is common to all superconductors.

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Keywords: spontaneous strain, superconductors, phenomenological theory

P08.06.39

Charge ordering, isosymmetrical phase transitions and magnetic properties of mixed valence vanadates

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The mixed valence vanadates $MV^{3+}V_3^{4+}O_8$ (M=Yb, Y, Lu) are structurally related to $CaFe_2O_4$ and are build of a framework of VO_6-octahedra [1,2]. Two different phases (α and β), which differ only in the arrangement of the trivalent M-cations, are known. Their similarity favours the occurrence of polytypism. The magnetic susceptibility shows anomalies for the β-phases at ≈185 K (YbV_4O_8, [3]) and 190 K (YV_4O_8, [2]), respectively. For the α-phases, the anomalies occur below 100 K. Powder and single crystal diffraction as well as specific heat studies confirm the existance of first order isosymmetrical structural phase transitions. While above the phase transition the bond valence sums indicate no clear charge separation of the tri- and tetravalent V-ions, below the transition temperature a complete charge ordering is observed. The magnetic transitions can be understood assuming that the Curie-Weiss type d-electrons of the vanadium cations in the high temperature phases separate at the phase transition into d-electrons, which maintain their Curie-Weiss character and others, which lose their spin moment. The unusual complete charge ordering can thus be attributed not only to Coulomb repulsion between the cations, but also to possible spin gap formation [3]. Lattice parameter of the α-phase show a clear domain size effect: for samples with large domain sizes (≥ 100 Å) they show a smooth behaviour down to the phase transition temperature (65 K), while for samples with small domain sizes (≤ 40 Å) they are influenced by phase transition in the β-phase (180 K).

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Keywords: isosymmetrical phase transition, charge order, composit crystal

P08.06.40

Neutron diffraction study of quantum effects on structural phase transition in quartz

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A phenomenological theory describes the temperature dependences of the order parameter Q, which is atomic shifts in displacive structural phase transition, and of strain e, which is coupled to Q, near a phase transition. We can describe their temperature dependences at low temperature if we use the quantum expansion of a potential [1]. We carried out the X-ray structure analysis of quartz, which shows a structural phase transition at approximately 850K, at various temperatures between 298 and 1126K using a single crystal [2]. The atomic shift of Si and the change in the strain were shown to obey the classical phenomenological theory. Recently, Romero and Salje have carried out a precise X-ray lattice parameter measurement of quartz in the temperature range of 30-300K [3]. They showed that the strain obeys the quantum phenomenological theory with a characteristic temperature of 187K. Direct evaluation of the quantum phenomenological theory by measuring the order parameter in the entire temperature range is required to verify the effectiveness of the theory. We carried out the structure analysis of quartz by powder neutron diffraction at several temperatures in the temperature range of 10-250K. Powder neutron diffraction patterns were obtained using a high-resolution powder diffractometer with 64 detectors. The diffraction patterns were analyzed by the Rietveld method. Squares of the shift of the Si atom along the a-direction and the strain were found to show the proportional dependence of each other in the entire temperature region. The effectiveness of the theory was directly verified by the atomic shift.

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Keywords: quartz, structure analysis, quantum expansion of Landau potential

P08.06.41

Effect of temperature and pressure on the crystal structure of NaV_6O_{11}

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Since the discovery of its anomalous resistivity and ferrimagnetism, NaV_6O_{11} received wide interest. Its structure ($P6_3/mmc$, Z = 2) consists of hcp layers of O and Na atoms. $V(1)O_6$ octahedra form a Kagome; lattice, while $V(2)O_6$ octahedra form a face-sharing dimer. $V(3)$ cations are five-fold coordinated to oxygen. The compound shows two structural phase transitions at 243K ($P6_3/mmc$ ---

$P6_3mc$) and 80K ($P6_3mc$ --- $Cmc2_1$). In the $P6_3mc$ phase, the V(1)O$_6$ octahedra form trimers with a regular triangular shape, below 80K they distort into isosceles triangles [1]. Below 64.2K, NaV_6O_{11} exhibits a uniaxial magnetic anisotropy [2]. We performed low-temperature (down to 8 K at 10^{-4} GPa) and high-pressure (up to 8.06 GPa at 298 K) powder and single-crystal x-ray diffraction in the home laboratory and at different synchrotron sources and could confirm the stability of the $Cmc2_1$ phase from 80 to 8 K. The high pressure data show that the hexagonal lattice is stable at least to 8.06 GPa at T = 298 K. The refinement of the single-crystal data based on symmetry mode analysis indicates the $P6_3/mmc$ --- $P6_3mc$ phase transition below 1 GPa. The volume of the V(1)O$_6$ octahedron is almost independent of the pressure. The V(2)O$_6$ octahedron expands, while the V(3)O$_5$ polyhedron shrinks on compression. In addition, the V(2)-V(2) distance shrinks. These observations indicate possible pressure-induced electron transfer from the V(3) to the V(2) cations. Symmetry mode analysis may serve as an aid for the restricted refinement of diffraction data with a small reflection-to-parameter ratio. As high-pressure data generally suffer from this problem, the potential of this method will be explored.

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Keywords: phase transitions, mixed-valence transition-metal compounds, high-pressure crystallography

P08.06.42

A study of the octahedral tilting / cooperative Jahn-Teller transition in (Sr$_{0.8}$Ce$_{0.2}$)MnO$_3$

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Previous room temperature measurements on the system $(Sr^{2+}_{1-x}Ce^{3+}_x)$$(Mn^{4+}_{1-x}Mn^{3+}_x)O^{2-}_3$ have shown a Jahn-Teller distortion of the MnO$_6$ octahedron that is significant at x=0.1 (10% of the active Mn^{3+} ion) but diminishes, somewhat unexpectedly, as the concentration of Mn^{3+} is increased [1]. We have explored the effect further through comparative variable temperature diffraction studies on $(Sr^{2+}_{0.8}Ce^{3+}_{0.2})$$(Mn^{4+}_{0.8}Mn^{3+}_{0.2})O^{2-}_3$ and $(Sr^{2+}_{0.8}Ce^{3+}_{0.2})(Mn^{4+}_{0.8}Co^{3+}_{0.2})O^{2-}_3$ - the former contains a JT active ion (Mn^{3+}) whereas the latter does not. Both compounds show a transition from a cubic structure in Pm-$3m$ (no tilting) to a tetragonal structure in $I4/mcm$ (with tilting) at about 400℃ - this transition appears to be of tricritical form. The tilt angle and its temperature dependence are the same in each case. There is no evidence for a separate cooperative JT transition in the title compound - the effect of the JT is simply to lead to elongation of the MnO$_6$ octahedra below the transition observed. The reason that the JT distortion appears to diminish with increasing (Mn^{3+}) concentration is not yet understood.

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Keywords: perovskite, phase transition, Jahn-Teller

P08.06.43

Direct atomic scale observation of photoinduced isomerization of realgar to pararealgar

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The reaction mechanism underlying the photoinduced linkage isomerization of discrete arsenic-sulfur clusters in the realgar form of tetraarsenic tetrasulfide (alpha-As$_4$S$_4$) to its pararealgar form was studied on a natural specimen of the mineral with in situ single-crystal X-ray photodiffraction [1]. The technique provided direct atomic-resolution evidence of formation of intermediate As$_4$S$_5$ phase in which half of the realgar molecule is retained in its envelope-type conformation, while the other half is transformed by effective switching of positions of one sulfur and one arsenic atom. The initiation and propagation stages of the process are studied under light and dark conditions, during and after photoexcitation with polychromatic visible light. In the light reaction stage, the interatomic and cell parameters averaged over the crystal volume and photoexcitation time remain almost unchanged. The residual electron density features are indicative for formation of a small amount of As$_4$S$_5$ clusters, which at this stage do not affect the overall crystalline order. In the dark reaction stage, a set of self-sustainable autocatalytic reactions results in strong and nearly isotropic expansion of the unit cell. The structure in the dark stage represents direct evidence of formation of pararealgar which was obtained in yield of about 5% in the single-crystal of realgar. The cell expansion is due to increased mole ratio of clusters of pararealgar relative to realgar and to increased intercluster separation. Due to lattice incompatibility, a higher content of the product results in progressive decrease of crystal quality.

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Keywords: X-ray diffraction, realgar and pararealgar, photochemistry

P08.06.44

Characterization of large nano-polycrystalline diamond synthesized by direct conversion of graphite

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High-purity nano-polycrystalline diamond (NPD) up to 5 mm in diameter and 8 mm in thickness with no cracks or contaminations has been successfully synthesized through direct conversion from graphite under a pressure of 15 GPa and a temperature of 2300 ℃. A high-purity isotropic graphite rod was used as the starting material. The HPHT condition was generated with a large-sized Kawai-type multi anvil apparatus. The NPD obtained by this method was found to have a light brownish color and are highly transparent. The brownish color is ascribed to a continuous absorption similar to that of natural brown diamond crystal. TEM observations and XRD analyses revealed that the NPD consists of nano-diamond particles (<100 nm)

P8