by large plasmon–phonon interactions with anomalous temperature shifts of the resonance frequencies. Substitution of arsenic in $CoAs_3$ by small amounts of phosphorus or antimony results in an additional short-waved mode at 362 and 342 cm^{-1}, respectively, which can be assigned to an internal vibration of the four-membered anionic rings not allowed in the binary skutterudites. The infrared spectra of the ordered ternary skutterudites $MGe_{1.5}Y_{1.5}$ (M = Co, Ir) show a large number of the total of 64 ir-allowed lattice modes, whereas the spectra of the rhodium compounds are mainly of the free carrier type. $RhGe_{1.5}S_{1.5}$ and the firstly obtained $RhGe_{1.5}Se_{1.5}$ exhibit small deviations from the formerly claimed pseudocubic cell. The lattice constants (space group $R3$) are $a = 828.2(1)$ pm, $\alpha = 89.85(1)°$ and $a = 854.6(1)$ pm, $\alpha = 89.86(1)°$, respectively.

Monoclinic–Trigonal Transition in Some $M^{I}_{3}M'^{III}(XO_4)_3$ Compounds: The High-Temperature Form of $(NH_4)_3In(SO_4)_3$. B. Jolibois, G. Laplace, F. Abraham,* and G. Nowogrocki. Universite des Sciences et Techniques de Lille, B.P. 36, 59655 Villeneuve d'Ascq Cedex, France. The high-temperature form of $(NH_4)_3In(SO_4)_3$ is rhombohedral, $R3c$, with $a = 15.531$ (12), $c = 9.163$ (8) Å, $Z = 6$. The structure was solved to $R = 0.023$ for 570 independent reflections measured at about 140°C. The structure is built up of $[In(SO_4)_3]_\infty$ columns extending along the c axis and composed of InO_6 octahedra and SO_4 tetrahedra linked together; this arrangement is very similar to that found in the low-temperature form. To explain the transition mechanism, existence of an intermediate phase of point symmetry $\bar{3}m$ is postulated. This phase would be the prototypic structure of the possibly ferroelastic low-temperature modification which can apparently exist only with non-spherical monovalent cations.

Lithium Substituted Cobalt Oxide Spinels $Li_xM_{1-x}Co_2O_4$ ($M = Co^{2+}, Zn^{2+}$; $0 \leq x \leq 0.4$). N. K. Appandairajan, B. Viswanathan,* and J. Gopalakrishnan, Department of Chemistry, Indian Institute of Technology, Madras 600 036, India. Substitution of Li^+ into Co_3O_4 and $ZnCo_2O_4$ gives rise to the solid solution series $Li_xM_{1-x}Co_2O_4$ ($M = Co^{2+}$ or Zn^{2+}) having the spinel structure up to $x = 0.4$. X-Ray diffraction intensities show that the spinel solid solutions are likely to have the following cation distribution: $(Co^{2+})_t[Li^{+}_{x}Co^{3+}_{2-3x}Co^{4+}_{2x}]_0O_4$ and $(Zn^{2+}_{1-x}Co^{2+}_{x})_t[Li^{+}_{x}Co^{3+}_{2-3x}Co^{4+}_{2x}]_0O_4$. Electrical resistivity and Seebeck coefficient data indicate that the electron transport in these systems occurs by a small polaron hopping mechanism.

X-Ray Study of Hg_2Cl_2–Br_2 and $HgCl_2$–$HgBr_2$ Reactions in Solid State. S. Mehdi* and S. M. Ansari. X-Ray Division, Regional Research Laboratory, Hyderabad 500 009, Andhra Pradesh, India. The reactions (i) $Hg_2Cl_2(s) + Br_2(g)$ and (ii) $HgCl_2(s) + HgBr_2(s)$ have been investigated by an X-ray method. Both the reactions yield two forms of the mixed halide HgClBr designated as α-HgClBr and β-HgClBr. The cell parameters of the two are as follows: *α-HgClBr:* $a = 6.196$ Å, $b = 13.12$ Å, $c = 4.37$ Å, $Z = 4$, $\rho = 5.91$ g/cm^3. The powder pattern and cell parameters are similar to that of $HgCl_2$. Therefore it is probable that the chlorine atoms, in the linear halogen–Hg–halogen molecules of $HgCl_2$ structure have been replaced by bromines, and since the radius of bromine atom is larger than that of chlorine, the lattice is larger in this case. *β-HgClBr:* $a = 6.78$, $b = 13.175$ Å, $c = 4.17$ Å, $Z = 4$, $\rho = 5.40$ g/cm^3. These parameters are the same as those reported in the literature for β-$Hg(ClBr)_2$, and its X-ray powder pattern is similar to $HgCl_2$. Therefore this phase also has linear halogen–Hg–halogen molecules but the distribution of Cl and Br atoms is perhaps random. Heating the products (i) and (ii) up to the melting point increases the amount of α-phase and decreases the β-phase, whereas crystallisation increases the β-phase. DTA study has supported the X-ray findings.

Reduction of the Titanium Niobium Oxides. I. $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$. S. K. E. Forghany and J. S. Anderson,* Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia. Reduction of the titanium–niobium oxides follows a common pattern. TiO_2 is eliminated, to form a new phase richer in titanium than the original compound, and Nb(IV) replaces Ti(IV) in the original block structure, which is thereby enriched in niobium. With $TiNb_2O_7$, the second phase is a TiO_2–NbO_2 solid solution, with the rutile structure, initially with a high titanium content, in equilibrium with a solid solution of composition Me_3O_7, isostructural with $TiNb_2O_7$. At log P_{O_2} (atm) about -9.0 this reaches the limiting composition $Ti_{0.72}Nb_{2.28}O_7$, in equilibrium with $Ti_{0.56}Nb_{0.44}O_2$. The Me_3O_7 block structure then transforms into the $Me_{12}O_{29}$ block structure ($Ti_2Nb_{10}O_{29}$–$Nb_{12}O_{29}$ solid solution), which rapidly increases in niobium content as reduction continues. Reduction of $Ti_2Nb_{10}O_{29}$ at oxygen fugacities above log P_{O_2} (atm) $= -9.0$ forms the Me_3O_7 phase as the titanium-rich phase. At log $P_{O_2} = -9.0$, and a composition about $Ti_{1.6}Nb_{10.4}O_{29}$, the rutile