

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 $M\text{Ge}_{1.5}\text{Y}_{1.5}$ ($M = \text{Co}, \text{Ir}$) 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. $\text{RhGe}_{1.5}\text{S}_{1.5}$ and the firstly obtained $\text{RhGe}_{1.5}\text{Se}_{1.5}$ exhibit small deviations from the formerly claimed pseudocubic cell. The lattice constants (space group $R\bar{3}$) are $a = 828.2(1)$ pm, $\alpha = 89.85(1)^\circ$ and $a = 854.6(1)$ pm, $\alpha = 89.86(1)^\circ$, respectively.

Monoclinic-Trigonal Transition in Some $M_3M'^3(\text{XO}_4)_3$ Compounds: The High-Temperature Form of $(\text{NH}_4)_3\text{In}(\text{SO}_4)_3$. 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 $(\text{NH}_4)_3\text{In}(\text{SO}_4)_3$ is rhombohedral, $R\bar{3}c$, 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 $[\text{In}(\text{SO}_4)_3]_\infty$ 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 Spinel $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}^{2+}, \text{Zn}^{2+}; 0 \leq x \leq 0.4$). 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 $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}^{2+}$ 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: $(\text{Co}^{2+})_1[\text{Li}_x^{2+}\text{Co}_{2-3x}^{2+}\text{Co}_{2x}^{2+}]_0\text{O}_4$ and $(\text{Zn}^{2+})_1[\text{Li}_x^{2+}\text{Co}_{2-3x}^{2+}\text{Co}_{2x}^{2+}]_0\text{O}_4$. 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 $\text{Hg}_2\text{Cl}_2\text{-Br}_2$ and $\text{HgCl}_2\text{-HgBr}_2$ 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) $\text{Hg}_2\text{Cl}_2(\text{s}) + \text{Br}_2(\text{g})$ and (ii) $\text{HgCl}_2(\text{s}) + \text{HgBr}_2(\text{s})$ have been investigated by an X-ray method. Both the reactions yield two forms of the mixed halide HgClBr designated as $\alpha\text{-HgClBr}$ and $\beta\text{-HgClBr}$. The cell parameters of the two are as follows: $\alpha\text{-HgClBr}$: $a = 6.196$ Å, $b = 13.12$ Å, $c = 4.37$ Å, $Z = 4$, $\rho = 5.91$ g/cm³. 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. $\beta\text{-HgClBr}$: $a = 6.78$, $b = 13.175$ Å, $c = 4.17$ Å, $Z = 4$, $\rho = 5.40$ g/cm³. These parameters are the same as those reported in the literature for $\beta\text{-Hg}(\text{ClBr})_2$, 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 $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. 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 $\text{TiO}_2\text{-NbO}_2$ 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 $\log P_{\text{O}_2}$ (atm) about -9.0 this reaches the limiting composition $\text{Ti}_{0.72}\text{Nb}_{2.28}\text{O}_7$, in equilibrium with $\text{Ti}_{0.56}\text{Nb}_{0.44}\text{O}_2$. The Me_3O_7 block structure then transforms into the $\text{Me}_{12}\text{O}_{29}$ block structure ($\text{Ti}_2\text{Nb}_{10}\text{O}_{29}\text{-Nb}_{12}\text{O}_{29}$ solid solution), which rapidly increases in niobium content as reduction continues. Reduction of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ at oxygen fugacities above $\log P_{\text{O}_2}$ (atm) = -9.0 forms the Me_3O_7 phase as the titanium-rich phase. At $\log P_{\text{O}_2} = -9.0$, and a composition about $\text{Ti}_{1.6}\text{Nb}_{10.4}\text{O}_{29}$, the rutile