quantum interference device) magnetometer, as a function of temperature for a SrRuO₃ film of thickness 1000 Å (Fig. 5). The magnetization is reported in units of Bohr magnetons $(\mu_{\rm B})$ per Ru atom. The saturation moment is roughly 1.05 μ_B , a value that is consistent with the literature. The ferromagnetic transition is significantly broadened in such a high field; low-field measurements indicate a T_{Curie} of about 140 K, slightly lower than that reported for bulk (25) and single-crystal (14) material, 150 to 160 K. The large field is required to obtain saturation owing to the large anisotropy energy, $\sim 10^6$ to 10^7 erg/cm³, reported for this material. It has been reported that CaRuO3 orders antiferromagnetically with a T_{Curie} of ~110 K (14), but we were unable to resolve any transition in our films. This result is consistent with the lack of any inflection in the resistivity curve and may indicate the absence of long-range order. This result is also consistent with the Mossbauer data (26), which give no evidence for antiferromagnetic ordering in CaRuO₃. The unique magnetic properties of these thin films offer new opportunities for studying superconductivity through model experiments.

We have already prepared epitaxial heterostructures with high- T_c superconductors $(YBa_2Cu_3O_7/Sr_{1-x}Ca_xRuO_3)$ (27). These heterostructures are structurally and electrically as good as the individual single-layer thin films on SrTiO₃(100) substrates. We have also fabricated epitaxial ferroelectric heterostructures with a ferroelectric material $[SrRuO_3/Pb(Zr_{0.52}Ti_{0.48})O_3/SrRuO_3]$. These heterostructures have a high crystalline quality and clean interfaces as revealed by x-ray diffraction, RBS, and cross-sectional transmission electron microscopy. The ferroelectric layers exhibit superior fatigue and retention characteristics over 10¹⁰ cycles at 20 kHz and 10 V with a large remnant polarization $(27 \ \mu C/cm^2)$ (27). These multilayer structures can be used for the fabrication of superconducting, ferroelectric, magneto-optic, and electro-optic devices (27).

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Open Framework Structures Based on Se_x^{2-} Fragments: Synthesis of $(Ph_4P)[M(Se_6)_2]$ (M = Ga, In, TI) in Molten $(Ph_4P)_2Se_x$

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Polychalcogenide compounds with open polymeric frameworks are rare, and they represent a class of compounds in which microporosity might be achieved. Microporous frameworks that are not oxide-based are now attracting interest because of the combination of catalytic and electronic properties they may simultaneously possess. Three new compounds that may be forerunners to such materials have been discovered and are reported here. The reaction of gallium (Ga), indium (In), and thallium (TI) metal with $(Ph_4P)_2Se_5$ (Ph, phenyl) and an excess of elemental selenium (Se) in a sealed, evacuated Pyrex tube at 200°C yielded small red crystals of (Ph4P)[Ga(Se6)2] (I), (Ph4P)[In(Se6)2] (II), and $(Ph_4P)[TI(Se_6)_2]$ (III), respectively. The $[M(Se_6)_2]^-$ (M = Ga, In, TI) ions form a two-dimensional, open framework filled with Ph_4P^+ ions. The $[M(Se_6)_2]_n^{-n}$ structure consists of tetrahedral M³⁺ centers and bridging Se₆²⁻ ligands, leading to an extended structure in two dimensions. These layers stack perfectly one on top of the other giving rise to one-dimensional channels running down the c axis that are filled with $Ph_{A}P^{+}$ cations. These cations are situated in the layers, as opposed to between the layers, and the whole structure can be viewed as a template. Compound II shows remarkable thermal stability and melts congruently at 242°C. Upon cooling to room temperature it gives a glassy phase that recrystallizes upon subsequent heating to 160°C.

 ${f T}$ here is an increasing interest in new and unusual synthetic conditions that may help stabilize new compounds with novel structural frameworks and interesting physical properties that are not possible by conventional techniques. Soluble and solid-state metal chalcogenides are undergoing intense investigation owing to their interesting electrical (1, 2), optical (3, 4), and catalytic properties (5), as well as their unusual structural features (6-23). Conventionally, syntheses of molecular metal polychalcogenides take place in solution at ambient temperature (6-12), whereas syntheses of solid-state metal chalcogenides are performed at temperatures higher than 500°C (13-16). In the past few years, fluxes of molten alkali metal polychalcogenides (17-20) have been used as reaction media to synthesize novel solid-state materials in the relatively low-temperature regime of 150°

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to 500°C. Recently, we have shown that the hydrothermal technique represents another direction for the synthesis of some exotic materials made of metal polychalcogenides (21-23). Given the enormous utility of microporous oxides (such as zeolites) in chemical technology and the corresponding prominence of metal chalcogenides in electronic applications, it is worthwhile to envision materials that combine the useful properties of both into one new class of microporous chalcogenides. Although such materials have not been reported to exist, a few publications have made reference to this concept (24, 25). To extend this work and obtain solids with large organic cations in their lattice, we undertook a synthetic approach using the reactive $(Ph_4P)_2Se_x$ in molten form as a reaction media to incorporate the organic cations as templates in order to stabilize open, anionic, metal-polyselenide frameworks. Herein we report the synthesis, structural characterization, and thermal properties of three isostructural compounds, $(Ph_4P)[Ga(Se_6)_2]$ (I), $(Ph_4P)[In(Se_6)_2]$ (II),

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Fig. 1. (A) View of single unit cell of $(Ph_4P)[M(Se_6)_2]$ lying in crystallographic *a–b* plane, and (B) view of the layers perpendicular to *c* axis. Shaded circles, M atoms; crossed circles, Se atoms; filled circles, P atoms; open circles, C atoms.

and $(Ph_4P)[Tl(Se_6)_2]$ (III), that exhibit an unusual and open layered framework.

The reaction of 0.028 g (0.402 mmol) of Ga, 0.200 g (0.186 mmol) of $(Ph_4P)_2Se_5$, and 0.236 g (2.989 mmol) of elemental Se in a sealed, evacuated Pyrex tube at 200°C for 2 days produced small red cubic crystals of $(Ph_4P)[Ga(Se_6)_2]$ (I) in 60% yield. Similar reactions with In and Tl yielded $(Ph_4P)[In(Se_6)_2]$ (II) and $(Ph_4P)[Tl(Se_6)_2]$ (III) (26) in almost quantitative yields. The reaction occurs in molten $(Ph_4P)_2Se_x$ and the products crystallize at the isotherm tem-

perature, making the crystallization independent of the cooling rate. This is a redox reaction in which the metal is oxidized as $\operatorname{Se}_{x}^{2-}$ is reduced, forming smaller $\operatorname{Se}_{x}^{2-}$ fragments that bind to the M³⁺ center. The reactions are

$$Ph_4P)_2Se_5 + nSe \rightarrow$$

$$(Ph_4P)_2Se_x (x = n + 5)$$
(1)

 $2M + (Ph_4P)_2Se_x \rightarrow$

C

$$2(Ph_4P)[M(Se_6)_2] + (Ph_4P)_2Se_y$$
 (2)

where M = Ga, In, and Tl.

The $(Ph_4P)_2Se_x$ melt serves as a solvent and as the reactant. We isolated the products by removing any unreacted $(Ph_4P)_2Se_x$ with acetonitrile and washing them with ether. These compounds are insoluble in all common organic solvents and are stable with regard to hydrolysis in degassed water. Compound II can also be synthesized hydrothermally (27). The structures were determined by single-crystal x-ray diffraction analysis, and the homogeneity of the products was confirmed by comparison of the observed and calculated powder x-ray diffraction patterns (28).

Single-crystal x-ray diffraction analysis reveals that compounds I, II, and III are isostructural (29) and composed of a unique $[M(Se_6)_2]_n^{n-}$ two-dimensional framework polymer (Fig. 1, A and B). If we consider each Se₆²⁻ chain to be a single, hypothetical atom, the structure of $[M(Se_6)_2]_n^{n-}$ can be thought to be derived from HgI₂, in which M occupies the Hg site and Se₆²⁻ occupies the I site. (30). The anions are polymeric and composed of tetrahedral M³⁺ centers coordinated by four Se₆²⁻ ligands. There is good precedent for the tetrahedral coordination geometry of group IIIA metals in their M³⁺ oxidation state with selenide ligands, for example, $[In_3Se_3(Se_4)_3]^{5-}$ (31), $[In_2Se_2(Se_4)_2]^{2-}$ (31), $[GaSe_2]^-$ (12), $[Ga_6Se_{14}]^{10-}$ (12), $[InSe_2]^-$ (32, 33), $[In_2Se_5]^{4-}$ (34), and $[In_4Se_{10}]^{8-}$ (12). The M–Se bond distances for I, II, and III,



Fig. 3. (A) Differential scanning calorimetry data for $(Ph_4P)[In(Se_6)_2]$ showing the first heating and cooling cycle. Heat is absorbed at 242°C as the material melts but is not released by means of crystallization upon cooling slowly (5°C per minute). Cooling rates as low as 0.1°C per minute gave similar results. (B) Data for subsequent heating (5°C per minute) showing the crystallization of $(Ph_4P)[In(Se_6)_2]$ at 165°C followed by melting at 242°C. The onset of the exothermic peak is at ~135°C.

given in Table 1, increase from Ga to Tl, as expected.

Each Se₆²⁻ ligand bridges two M³⁺ centers by means of their terminal Se atoms. The Se₆²⁻ chains have a helical conformation and lie along the crystallographic *a* and *b* axes. This unique bridging mode leads to an extended, anionic, twodimensional open framework in the *a*-*b* plane (Fig. 2A). The layers are held together by van der Waals forces and the average interlayer spacing is ~7.63 Å.





Fig. 2. (A) View of $[M(Se_6)_2]_n^n$ layers in a-b plane, and (B) stereoview of the unit cell down the c axis, Ph_4P^+ cations omitted.

Fig. 4. X-ray diffraction patterns of $(Ph_4P)[In(Se_6)_2]$ (II): curve A, single crystals; curve B, material treated at 300°C and cooled (glassy state); and curve C, material after heating to 170°C (recrystallization).



Table 1. Bond distances (in angstroms) and bond angles (in degrees) of the anion $[M(Se_6)_2]_n^{n-}$ (M = Ga, In, TI). Errors are noted in parentheses.

Bonds (see Fig. 1A)	(Ph ₄ P)Ga(Se ₆) ₂	(Ph ₄ P)In(Se ₆) ₂	(Ph ₄ P)TI(Se ₆) ₂
	Distand	Ce	
M–Se(1)	2.409 (4)	2.576 (5)	2.639 (2)
Se(1)–Se(2) Se(2)–Se(3) Se(3)–Se(3) Se–Se (mean)	2.341 (6) 2.340 (6) 2.367 (9) 2.349 (12)	2.353 (7) 2.337 (7) 2.350 (10) 2.347 (15)	2.334 (3) 2.341 (3) 2.360 (4) 2.345 (10)
	Anale	9	
Se(1)–M–Se(1) Se(1)–M–Se(1)	107.3 (1) 113.9 (2)	107.9 (1) 112.7 (1)	108.6 (1) 111.3 (1)
M–Se(1)–Se(2) Se(1)–Se(2)–Se(3) Se(2)–Se(3)–Se(3)	98.1 (2) 106.2 (2) 110.8 (2)	96.7 (2) 106.9 (3) 110.4 (2)	96.2 (1) 106.6 (1) 110.2 (1)

Fig. 5. (A) Absorption spectrum of glassy films of (Ph₄P)[In(Se₆)₂]. The inset is a plot of square root of absorption versus energy, showing a linear relation and suggesting an indirect band gap of ~1.4 eV. (B) Absorption spectrum of polycrystalline $(Ph_4P)[In(Se_6)_2]$. We calculated the absorption data from reflectance data using the Kubelka-Munk (35-37) function: $\alpha/S = (1 - R)^2/2R$; R, reflectance at given wavelength; α, absorption coefficient; and S, scattering coefficient. The scattering coefficient has been shown to be practically wavelength-independent for particles larger than 5 µm, which is smaller than the particle size of the samples used here (35, 36). BaSO, powder was used as reference (100% reflectance).



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The Se-Se distances are comparable to those found in other polyselenide complexes (6-12). These layers stack perfectly one on top of the other, giving rise to one-dimensional channels running down the crystallographic c axis (Fig. 2B). The channels are filled with $Ph_{4}P^{+}$ cations. Surprisingly, these cations are not situated between the layers but lie within them (Fig. 1B). Therefore, they can be viewed as templates, helping to stabilize the structure. The P atom is situated on a crystal-lographic $\overline{4}$ axis. The notion that the cation plays the role of a template comes from our failure to stabilize this same framework with other cations of the type R_4N^+ (R = Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl). The Ph₄P⁺ cation appears to be an exact fit in the 28-member $[M_4(Se_6)_4]^{4+}$ ring.

For a polychalcogenide, $(Ph_4P)[In(Se_6)_2]$ (II) shows remarkable thermal stability. Thermal gravimetric analysis showed no weight loss up to 350°C. At higher temperatures, the material decomposes into InSe. We further studied the thermal behavior of this compound by differential scanning calorimetry, uncovering a property that is unusual for a polychalcogenide compound. Data show that upon heating compound II a sharp endotherm occurs at 242°C, corresponding to melting. However, upon cooling no corresponding exothermic peak is observed, indicating that no crystallization occurs (Fig. 3A). Data from x-ray diffraction at room temperature show that the material is trapped in a glassy state. Upon subsequent reheating, a broad exotherm is observed starting at



135°C and peaking at 165°C, followed by the same sharp endotherm 242°C (Fig. 3B). Studies using x-ray diffraction show that the exotherm at 165°C is the result of crystallization of the material (Fig. 4). This result suggests that the glassy state that formed upon cooling the melt is a latent metastable state that can crystallize upon thermal stimulation. This unusual melt-glass-crystallization property is nearly reversible (efficiency $\sim 94\%$ as estimated by comparing the heat released during crystallization with the heat absorbed during melting), suggesting that compound II could have potential applications as energy storage as well as optical information storage material. Other examples of such behavior have been observed in As₂S₃ glasses.

Room-temperature electrical conductivity studies of compounds II and III show a value $\leq 10^{-6}$ S/cm, which suggests they are semiconductors. The optical properties of $(Ph_4P)[In(Se_6)_2]$ were assessed, both in the crystalline and in the glassy state, by studying the ultraviolet-visible-near-infrared spectra of the material. The spectra confirm the semiconductor nature by revealing the presence of an optical gap (Fig. 5, A and B). The spectra exhibit steep absorption edges from which the band gap can be assessed at an average of 1.42 eV for compound II and 1.40 eV for glassy II. These transitions are probably the result of charge transfer from the primarily Se-based valence band to the primarily In-based conduction band. For comparison, the band gap of the photovoltaic material In_2Se_3 is 1.2 eV.

The compounds $(Ph_4P)[Ga(Se_6)_2]$ (I) and $(Ph_4P)[Tl(Se_6)_2]$ (III) show similar thermal behavior with melting points at 272° and 213°C, respectively. Because $(Ph_4P)[M(Se_6)_2]$ melts without decomposition, an uncommon property for polyselenides, one should be able to easily fabricate uniform thin films and fibers that should allow further study of their physical properties. Furthermore, x-ray powder diffraction experiments show that the open $[M(Se_6)_2]_n^{n-}$ framework is capable of ionexchange reactions with other R_4E^+ cations (R = alkyl or aryl group; E = N or P) of similar size and shape, such as Pr_4N^+ and Et_4N^+ . The ability of the open structure of the $[M(Se_6)_2]^-$ framework to be supported by other smaller R_4N^+ ions, introduced through ion exchange, is under investigation. Ability to readily exchange ions in these compounds would open the way toward generating truly microporous materials not be based on zeolites or oxide structures.

The molten $(R_4E)_2Q_x$ salts (Q = S, Se, or Te) are potentially useful as solvents and reagents for synthesis of compounds

with organic cations that cannot be obtained otherwise. Synthesis at 200°C utilizing the $(Ph_4P)_2Se_x$ fluxes may provide an avenue to materials possessing novel frameworks and unique properties. We believe these reactions can be exploited to produce other metal polychalcogenides with open structures. The structure of these materials could be dictated by the nature of the organic cations, R_4E^+ , that are used as templates, with smaller cations leading to denser and possibly three-dimensional structures.

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- 27. The reaction of InCl₃ with two equivalents of

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 K_2Se_5 in the presence of Ph_4PCI in water in an evacuated, sealed tube for 2 days at 110°C produced very small, deep-red cubic crystals of $(Ph_4P)[[n(Se_6)_2] \ (II)]$ in 88% yield.

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- Crystal data for (Ph₄P)[Ga(Se₆)₂] (I): Tetragonal P-4 (#81), Z = 1; a = 10.378(1) Å; c = 7.618(3) Å, V = 820(1) Å³ at -100° C. $2\theta_{max}$ (Mo K_a) = 50°. Number of data measured, 904; number of 29 unique data $F_o^2 > 3\sigma(F_o^2)$, 419; number of variables, 56. $\mu = 140.54$ cm⁻¹. $D_{calc} = 2.740$ g/cm³. Final R = 0.065 and $R_w = 0.071$. The minimum and maximum transmission was 0.683 and 1.000, respectively. All the atoms of the anion and the P atom of the cation were refined anisotropically whereas the C atoms were refined isotropically, and the position of the H atoms were calculated but not refined. Crystal atoms were calculated but not refined. Crystal data for (Ph₄P)[In(Se₆)₂] (II): Tetragonal P-4 (#81), Z = 1; a = 10.527(6) Å; c = 7.647(6) Å, V = 847(1) Å³ at 25°C. $2\theta_{max}$ (Mo K_a) = 45° Number of data measured, 2340; number of unique data $F_o^2 > 3\sigma(F_o^2)$, 301; number of variables, 39. μ = 135.12 cm⁻¹. D_{calc} = 2.747 g/cm³. Final R = 0.057 and R_w = 0.057. The minimum and maximum traponicipion was 0.488 minimum and maximum transmission was 0.488 and 1.000, respectively. All atoms were refined isotropically, and the position of the H atoms were calculated but not refined. Crystal data for $(Ph_4P)[Ti(Se_6)_2]$ (III): Tetragonal P-4 (#81), Z = 1; a = 10.525(2) Å; c = 7.611(3) Å, V = 843(1)1; a = 10.525(2) A; c = 7.011(3) A, v = 0.45(1)Å³ at -100° C. $2\theta_{max}$ (Mo K_a) = 50°. Number of data measured, 934; number of unique data F_o^2 $3\sigma(F_o^2)$, 748; number of variables, 86. μ = 177.3 cm⁻¹. D_{calc} = 2.937 g/cm³. Final R = 0.030 and R_w = 0.040. The minimum and maximum transmission was 0.389 and 1.000, respectively. All atoms were refined anisotropically, and the position of the H atoms were calculated but not refined. The structures of compounds I, II, and III were solved and refined with TEXSAN crystallographic software package of Molecular Structure Corporation, and we applied an empirical absorption correction and DIFABS to each structure. DIFABS: "An Empirical Method for Correcting Diffractometer Data for Absorption Correction," N. Walker and D. Stuart, Acta Crystallogr. Sect. A 39, 158 (1983). Tables of x-ray data, calculated and observed powder patterns, bond distances and angles, atomic coordinates, and anisotropic thermal parameters of all atoms, and a listing of calculated and observed $(10F_{\rm o}/10F_{\rm c})$ structure factors have been deposited with the Cambridge Crystallo-
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