

Matrix Isolation Studies † on Alkali Metal Perrhenates: the Shape and Vibrational Assignments of Caesium Perrhenate, CsReO₄

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The matrix i.r. and Raman spectra obtained from the vaporisation of potassium and caesium perrhenate show spectra characteristic of the molecular species MReO₄ with C_{2v} symmetry. Additional ¹⁸O enrichment experiments provide an unequivocal assignment for the ν_{Re-O} modes and it is also shown that the bond dipole model leads to a useful simulation of relative band intensities.

There is considerable current interest in the shapes of the molecular species found in high temperature vapours, and in particular, in ternary oxyanion salts of the type M_mXO₄ where M = alkali metal, X = transition metal, and *m* is typically 1 or 2. This interest has arisen partly as a result of an increasing awareness that such species are important in high temperature vapour transport and corrosion phenomena, and also because of their apparent fluxionality at high temperatures which has led to the concept of polytopic bonding.¹

We are interested in the characterisation of high temperature molecules using the combined techniques of matrix isolation and vibrational spectroscopy, and have recently demonstrated that this approach can provide valuable information on novel molecules such as NaPO₃,² CsAsO₃,³ and CsClO₃,⁴ and in particular on the series of transition metal species K₂XO₄ where X = Cr, Mo, or W.⁵ These studies have shown that matrix isolation i.r. spectroscopy can convincingly distinguish between various possible types of co-ordination, and this present paper describes our results on the characterisation of KReO₄ and CsReO₄.

Previous electron diffraction studies on alkali metal perrhenates in the vapour phase have suggested that KReO₄ has C_{3v} symmetry (with monodentate co-ordination),⁶ but that for CsReO₄ bidentate binding is preferred, leading to a C_{2v} geometry.⁷ However, vapour phase i.r.⁸ and photoelectron [He(I)]⁹ studies were unable to reach any firm conclusions regarding the mode of co-ordination, and it is clear that one of the problems encountered in all these vapour phase studies is the possible presence of significant amounts of dimer molecules (MReO₄)₂ which are known to exist from mass spectrometric work.¹⁰

Matrix isolation offers the possibility of distinguishing between monomer and polymer species by varying deposition conditions, by controlled diffusion experiments, or by isotope studies, and the first matrix study on alkali metal perrhenates was interpreted in terms of monomer and dimer species.¹¹ This work, however, did not reach any definite conclusions concerning the shape of the MReO₄ monomers, and was confined to an i.r. study in the Re-O stretching region. The i.r. and Raman studies described here were carried out for two reasons. First we wished to establish all the vibrational fundamentals of the ReO₄ group in monomeric MReO₄, and secondly we hoped to reach an unambiguous conclusion regarding the shape of at least one MReO₄ molecule by use of ¹⁸O enrichment.

Experimental

The samples of CsRe¹⁶O₄ used were prepared from the reaction between CsOH (Aldrich Chemicals) and perrhenic acid; KRe¹⁶O₄ was obtained directly from Koch-Light. Both

salts were purified by vacuum sublimation immediately prior to use. Isotopically enriched CsRe^{16/18}O₄ was obtained by two quite different methods. In the first of these, rhenium metal was converted into the ¹⁸O-enriched heptaoxide by combustion in ¹⁸O-enriched oxygen gas (Prochem), and this was then heated with a stoichiometric amount of anhydrous Cs₂CO₃ (Koch-Light) to 500 °C in a sealed tube. The reaction to give CsReO₄ and CO₂ was complete after *ca.* 30 min, and the product was purified by vacuum sublimation. The second route also involved the heptaoxide, but here samples of Re₂¹⁶O₇ were dissolved in ¹⁸O-enriched water and the solution was allowed to equilibrate for several days at room temperature. Under these conditions, isotope exchange was complete, and the solution of perrhenic acid was neutralised with CsOH. The resulting precipitate was then purified as before. In both these synthetic routes, the extent of ¹⁸O enrichment in the starting materials was chosen so that an enrichment of *ca.* 50% would be obtained in the final product, assuming statistical randomisation.

The general features of our matrix isolation apparatus have been described elsewhere.¹² For the present series of experiments, primary vaporisation of MReO₄ samples was carried out from silica holders heated to 500 °C (CsReO₄) or 520 °C (KReO₄), and in a number of cases these vapours were superheated prior to deposition by passage through a 2-mm diameter silica tube maintained at *ca.* 1 000 °C. Nitrogen or argon (99.999% BOC) was employed as matrix gas, and samples were deposited over periods of typically 1–2 h. The i.r. studies employed CsI optics in conjunction with a Perkin-Elmer 225 spectrometer (5 000–200 cm⁻¹); Raman spectra were obtained from samples deposited on a polished copper block using a modified Cary 82 spectrometer equipped with argon or krypton ion laser excitation.

Results and Discussion

Infrared and Raman Spectra from KRe¹⁶O₄ and CsRe¹⁶O₄.—The most prominent features in the matrix i.r. spectra resulting from the vaporisation of KReO₄ or CsReO₄ were three intense, sharp bands in the frequency range 850–950 cm⁻¹; these were accompanied by a weaker feature at *ca.* 970 cm⁻¹. The precise frequencies obtained showed a small cation dependence, and a larger matrix dependence; the band positions are listed in Table 1. This Table also includes three very weak bands in the range 300–360 cm⁻¹ observed from extended deposition of CsReO₄ in a nitrogen matrix. The Figure (a) shows part of a typical spectrum (800–1 000 cm⁻¹) obtained from the CsReO₄/N₂ matrix system without superheating.

In view of the similarity between these systems, only one of them, CsReO₄/N₂, was chosen for Raman studies, and this work was carried out using 514.5 nm argon ion excitation with power levels at the sample of *ca.* 100 mW. Under

† Non-S.I. unit employed: 1 dyn = 10⁻⁵ N.

Table 1. Infrared vibration frequencies (cm^{-1}) of alkali metal perrhenates in low temperature matrices

NaReO ₄		KReO ₄				CsReO ₄		Assignments
Argon ^a	Nitrogen ^a	Argon ^a	Nitrogen ^a	Argon ^b	Nitrogen ^b	Argon ^b	Nitrogen ^b	
				968.9	969.8	967.1	970.0 ^c	ν_{A_1} Monomer
				943.3	941.5	940.3	940.3	ν_{B_2} Monomer
				909.7	914.0	905.3	913.4	ν_{A_1} Monomer
				883.6	892.0	880.1	892.6	ν_{B_1} Monomer
							355.3	} δReO_4 Monomer
							334.6 ^c	
							316.7 ^c	
939	933.5	939	933.5					Dimer ^a
904.5	905.5	904.5	905.5					Monomer ^a
879	884.5	879	884.5					Dimer ^a

^a Ref. 11. ^b This work; frequency accuracy $\pm 1.0 \text{ cm}^{-1}$. ^c Raman bands at 969.5 and 325 cm^{-1} .

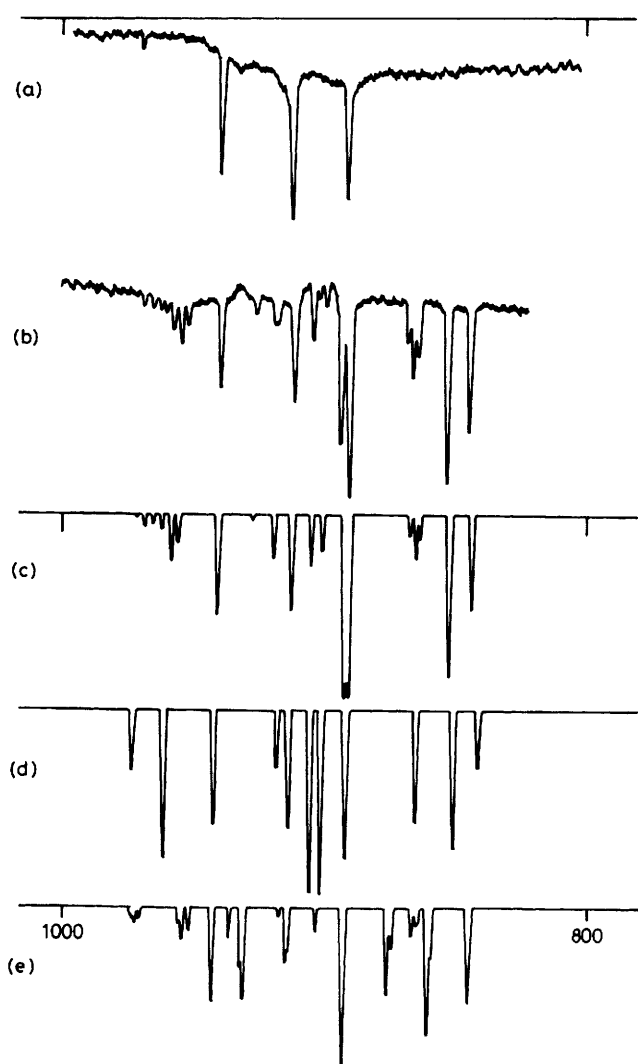


Figure (a) Nitrogen matrix i.r. spectrum ($800\text{--}1000 \text{ cm}^{-1}$) observed from vaporisation of $\text{CsRe}^{16}\text{O}_4$; (b) nitrogen matrix i.r. spectrum observed from ca. 50% ^{18}O -enriched CsReO_4 ; (c) calculated spectrum assuming bidentate structure with frequency order $\nu_{A_1} > \nu_{B_2} > \nu_{A_1} > \nu_{B_1}$; (d) calculated spectrum assuming $\nu_{A_1} > \nu_{B_2} > \nu_{B_1} > \nu_{A_1}$; (e) calculated spectrum assuming $\nu_{A_1} > \nu_{A_1} > \nu_{B_1} > \nu_{B_2}$.

conditions of relatively high resolution (1.5 cm^{-1} slit width) a single, prominent band was observed at 969.5 cm^{-1} ; at wider slit widths (ca. 10 cm^{-1}) an additional band centred at 325 cm^{-1} was also located.

The effects of superheating and of controlled diffusion were studied in detail for $\text{CsReO}_4/\text{N}_2$ using i.r. monitoring, but no significant differences were detected between spectra obtained with or without superheating. Controlled diffusion to ca. 35 K failed to reveal the growth of any new spectral features. Higher sample deposition rates, however, did result in weak shoulders appearing at 933 and 921 cm^{-1} for both $\text{CsReO}_4/\text{N}_2$ and KReO_4/N_2 .

The above results differ in a number of respects from the original i.r. matrix study on NaReO_4 and KReO_4 .¹¹ First, although Bencivenni *et al.*¹¹ report three prominent features in the $850\text{--}950 \text{ cm}^{-1}$ region, their frequencies are quite different from our values (Table 1). In addition they report substantial spectral changes after superheating to 1200 K and so reach quite different conclusions regarding the interpretation. In particular, they find that superheating produces an enhancement of the central component of their triplet (at ca. 905 cm^{-1}). This band is consequently assigned by them to a monomer, whilst the two outer features are attributed to a dimer. Our experiments consistently indicated that the prominent triplet observed in our work, and the weaker band at ca. 970 cm^{-1} , could all be assigned to the same species.

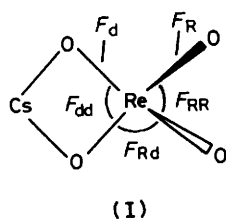
In order to make an unambiguous assignment, we carried out ^{18}O -enrichment studies on the CsReO_4 system using samples prepared by two different routes.

Infrared Spectra from ^{18}O -Enriched CsReO_4 .—Figure (b) shows part of the nitrogen matrix spectrum ($830\text{--}1000 \text{ cm}^{-1}$) obtained from a sample of ca. 50% ^{18}O -enriched CsReO_4 , prepared by [^{18}O]water exchange. An almost identical spectrum was obtained from samples prepared by the carbonate synthesis; the band positions are listed in Table 2. Argon matrices yielded a similarly complex pattern with small differences in frequency consistent with the expected matrix shifts.

Spectral interpretation. The i.r. frequencies observed fall into two distinct regions, and by comparison with earlier studies on solid perrhenates,¹³ it is evident that the four bands in the range $800\text{--}1000 \text{ cm}^{-1}$ may be assigned to Re-O stretching modes, whilst the much weaker features at ca. 300 cm^{-1} found for CsReO_4 correspond to bending modes. For an ion ReO_4^- with T_d symmetry, $\Gamma_{\text{Re-O}} = A_1 + T_2$ with $\Gamma_{\text{bend}} = E + T_2$ and thus only two fundamentals would be expected in the i.r. However, if the symmetry of the ion is lowered as a result of co-ordination, one might expect some lifting of degeneracy together with the appearance of additional

bands due to changes in i.r. activity. In particular, if a *molecular* species MReO_4 gives rise to four distinct Re-O stretching modes, *all* degeneracy must be removed, and of the various possible shapes which satisfy this requirement, it can be shown that the C_{2v} bidentate structure (I) exhibits the highest permissible symmetry. Simple band counting procedures for the Re^{16}O_4 modes do not allow a rigorous distinction between this and other, lower symmetry structures, but such a distinction is possible from randomised ^{18}O labelling since (I) will generate the smallest number of isotopomers—nine in all. On the basis of this model, the ^{18}O -enrichment studies on CsReO_4 should therefore generate a total of thirty-six bands in the Re-O stretching region, and a successful correlation with the observed spectrum would provide very strong evidence for bidentate co-ordination.

If one assumes that the Re-O stretching modes may be separated from the other vibrations of the C_{2v} structure for CsReO_4 , the resulting force field requires five independent potential constants, and these are defined in the illustrated structure (I). For this model, $\Gamma_{\text{Re-O}} = 2A_1 + B_1 + B_2$, and



we have taken the xz plane to include the bidentate bridge. Comparison between the four $\text{CsRe}^{16}\text{O}_4$ bands found in nitrogen matrices (970.0, 940.3, 913.4, and 892.6 cm^{-1}) with the earlier solid i.r. work¹³ and also with solution Raman data¹⁴ indicates that the highest of these bands at 970.0 cm^{-1} be assigned to A_1 symmetry. This band correlates with the single totally symmetric mode in the free ion (971 cm^{-1})¹⁴ and is the most prominent feature in our matrix Raman spectra. However, although the three intense lower frequency Re-O modes clearly derive from the T_2 mode in the free ion (918 cm^{-1}), their specific assignment to the resulting $A_1 + B_1 + B_2$ components is not obvious. Six possible assignments thus exist for the observed spectrum, and in terms of frequency order these may be summarised as $A_1 > A_1 > B_1 > B_2$; $A_1 > A_1 > B_2 > B_1$; $A_1 > B_1 > B_2 > A_1$; $A_1 > B_1 > A_1 > B_2$; $A_1 > B_2 > B_1 > A_1$, and $A_1 > B_2 > A_1 > B_1$. However, since only four experimental frequencies are available for $\text{CsRe}^{16}\text{O}_4$, a unique solution for the five stretching constants F_R , F_d , F_{RR} , F_{dd} , and F_{Rd} is not initially possible for any of these assignments, although one might expect certain effective constraints arising from chemical considerations.

First, we note that for the free ReO_4^- ion (T_d), the Re-O stretching modes at 971 (A_1) and 918 cm^{-1} (T_2) lead to values of F_R ($= F_d$) of 7.570 $\text{mdyn } \text{Å}^{-1}$, and F_{RR} ($= F_{dd} = F_{Rd}$) = 0.436 $\text{mdyn } \text{Å}^{-1}$. We therefore expect values of F_R and F_d in CsReO_4 in the range *ca.* 7–8 $\text{mdyn } \text{Å}^{-1}$ with $F_R > F_d$ and interaction constants in the range *ca.* 0.0–1.0 $\text{mdyn } \text{Å}^{-1}$. We also note that in the most recent electron diffraction study on CsReO_4 ,⁷ no departure from regular tetrahedral geometry could be detected for the ReO_4 group. We therefore set the angles OReO at $109^\circ 28'$, and assume equal bond lengths (1.74 Å) and bond dipole derivatives.

On the basis of this geometry, each of the six possible assignments for the lower three bands was taken in turn, and families of force constants were obtained which reproduce the $\text{CsRe}^{16}\text{O}_4$ frequencies exactly. Since for the all-16 case there are fewer observed frequencies than defined force constants, various solutions were achieved for each assignment by

Table 2. Observed and calculated Re-O stretching modes (cm^{-1}) for isotopically substituted CsReO_4 species

Observed ^a	Calculated ^b	Assignment
(970.0)	970.0	A_1 Cs-16-16-Re-16-16 C_{2v}
	966.8	A' Cs-16-18-Re-16-16 C_s
	963.9	A_1 Cs-18-18-Re-16-16 C_{2v}
958.8	960.4	A' Cs-16-16-Re-16-18 C_s
956.0	957.2	A Cs-16-18-Re-16-18 C_1
953.2	954.6	A' Cs-18-18-Re-16-18 C_s
(940.3)	940.3	B_2 Cs-16-16-Re-16-16 C_{2v}
940.8	940.3	A'' Cs-16-18-Re-16-16 C_s
	940.3	B_2 Cs-18-18-Re-16-16 C_{2v}
	937.3	A_1 Cs-16-16-Re-18-18 C_{2v}
927.6	927.5	A' Cs-16-18-Re-18-18 C_s
921.0		(unassigned)
919.5	919.9	A' Cs-16-16-Re-16-18 C_s
	915.2	A_1 Cs-18-18-Re-18-18 C_{2v}
(913.4)	913.4	A_1 Cs-16-16-Re-16-16 C_{2v}
913.4	912.9	A Cs-16-18-Re-16-18 C_1
906.0	905.9	A' Cs-16-18-Re-16-16 C_s
903.9		(unassigned)
901.4	901.6	A' Cs-18-18-Re-16-18 C_s
	894.1	A_1 Cs-16-16-Re-18-18 C_{2v}
	893.7	A' Cs-16-18-Re-18-18 C_s
	893.3	A' Cs-16-16-Re-16-18 C_s
895.8	893.2	A Cs-16-18-Re-16-18 C_1
892.6	892.6	B_1 Cs-16-16-Re-18-18 C_{2v}
	892.6	A'' Cs-16-16-Re-16-18 C_s
(892.6)	892.6	B_1 Cs-16-16-Re-16-16 C_{2v}
	892.2	B_2 Cs-18-18-Re-18-18 C_{2v}
	892.2	B_2 Cs-16-16-Re-18-18 C_{2v}
	892.2	A'' Cs-16-18-Re-18-18 C_s
870.3	869.4	A_1 Cs-18-18-Re-16-16 C_{2v}
868.4	867.4	A' Cs-18-18-Re-16-18 C_s
867.1	866.0	A_1 Cs-18-18-Re-18-18 C_{2v}
	855.4	A' Cs-16-18-Re-16-16 C_s
855.8	855.1	A Cs-16-18-Re-16-18 C_1
	854.8	A' Cs-16-18-Re-18-18 C_s
	846.9	B_1 Cs-18-18-Re-18-18 C_{2v}
847.7	846.9	B_1 Cs-18-18-Re-16-16 C_{2v}
	846.9	A'' Cs-18-18-Re-16-18 C_s

^a Frequency accuracy $\pm 1.0 \text{ cm}^{-1}$; values in parentheses found in $\text{CsRe}^{16}\text{O}_4$ studies and used to establish force field. ^b Assuming bidentate (C_{2v}) model with parameters F_R , F_d , F_{RR} , F_{Rd} , and F_{dd} of 7.863, 7.193, 0.390, 0.400, and 0.459 $\text{mdyn } \text{Å}^{-1}$, respectively.

fixing F_{Rd} and applying an iterative procedure to the remaining force constants. F_{Rd} was typically varied from 0.30 to 0.45 $\text{mdyn } \text{Å}^{-1}$ in steps of 0.05.

These sets of force constants were then used to generate the isotope patterns expected for a statistical mixture of the nine isotopomers. The calculations were performed using standard procedures,¹⁵ employing the FORTRAN program SOTONVIBP,¹⁶ which, from an input of atomic masses, molecular geometry, approximate force constants and observed frequencies will output calculated frequencies, refined force constants and LR vectors. Relative band intensities were estimated using the bond dipole model.¹⁵ This approach to the calculation of isotope patterns has now been tested for several systems, and in particular has proved very successful in interpreting the isotope patterns for ^{18}O -enriched OsO_4 ¹⁷ and K_2WO_6 ,⁵ which are closely related to the present system.

From the simulated spectra obtained from these initial calculations, it became evident that only one of the six possible frequency assignments generated isotope patterns resembling the observed spectrum. This assignment was $A_1 > B_2 > A_1 > B_1$. Although all sets of force constants derived from this assignment reproduced the $\text{CsRe}^{16}\text{O}_4$ frequencies exactly, further optimisation to produce an

improved isotope pattern was then carried out. In the initial calculation, the best agreement with the observed spectra had been found for F_{Rd} ca. 0.4 mydn \AA^{-1} . Further variations of F_{Rd} above and below this value by steps of 0.02 were therefore explored, and the optimum solution was found when $F_{Rd} = 0.400$ mydn \AA^{-1} .

This final optimisation of the frequency fit led to force constant parameters $F_R = 7.863$, $F_d = 7.193$, $F_{RR} = 0.390$, $F_{dd} = 0.459$, and $F_{Rd} = 0.400$ mydn \AA^{-1} . For this particular solution, the frequencies of $\text{CsRe}^{16}\text{O}_4$ are reproduced exactly with predicted intensity ratios ca. 1 : 9 : 8 : 9, which compares very favourably with Figure (a). Table 2 compares the frequencies obtained from ^{18}O -enriched samples with the computed frequencies for the ^{16}O -labelled isotopomers, thus permitting a spectral assignment, whilst Figure (c) reproduces the results of these calculations assuming a uniform band width of 1 cm^{-1} and 50% ^{18}O enrichment.

Although the spectral agreement is not exact, it appears satisfactory in view of the approximations made, and some indication of the validity of this particular assignment may be gained by considering very briefly two alternative assignments. If one assumes $A_1 > B_2 > B_1 > A_1$, the best overall frequency agreement is obtained using values $F_R = 7.941$, $F_d = 7.088$, $F_{RR} = 0.468$, $F_{dd} = 0.036$, and $F_{Rd} = 0.230$ mydn \AA^{-1} . These parameters reproduce the $\text{CsRe}^{16}\text{O}_4$ frequencies exactly, but predict intensity ratios ca. 1 : 2 : 2 : 1, and when applied to a mixture of isotopomers, they generate the spectrum shown in Figure (d). In a similar way, Figure (e) shows the type of simulation obtained for the assignment $A_1 > A_1 > B_1 > B_2$, with $F_R = 7.543$, $F_d = 7.507$, $F_{RR} = 0.808$, $F_{dd} = 0.034$, and $F_{Rd} = 0.340$ mydn \AA^{-1} . Apart from the poor intensity agreement, these two latter solutions might also be regarded as unlikely in view of the very different values for F_{RR} and F_{dd} .

Finally, these results in principle allow one to distinguish between C_{2v} and possible lower symmetry structures by looking for evidence of non-equivalence between either the two terminal oxygen atoms or the two bridge atoms. For example, our bidentate model demands a statistical weight of four for the C_1 species $\text{Cs}^{16}\text{O}^{18}\text{ORe}^{16}\text{O}^{18}\text{O}$ where four symmetry-related configurations can be drawn. The bands assigned to this species (Table 2) were therefore examined for any sign of splitting which might indicate a breakdown of this statistical weighting due to non-equivalence. None was observed, and the bands for this isotopomer were ca. 1 cm^{-1} wide despite accidental overlap with other, weaker features (Table 2).

Conclusions

This work shows that under the conditions of our experiment caesium perrhenate vaporises to give predominantly monomeric CsReO_4 , with C_{2v} symmetry. Potassium perrhenate produces an almost identical spectrum and it is likely that molecular KReO_4 also has this shape. This conclusion is contrary to the electron diffraction interpretation for KReO_4 by Spiridonov *et al.*⁶ but supports the more recent work on CsReO_4 .⁷ In

addition to confirming the C_{2v} geometry for $\text{CsRe}^{16}\text{O}_4$, the ^{18}O experiments permit an assignment of the Re–O stretching modes as 970.0 (A_1), 940.3 (B_2), 913.4 (A_1), and 892.6 cm^{-1} (B_1). Features attributed to the bending modes were also observed, but were too weak to be studied in this way, although the number of bands is consistent with the proposed structure.

We cannot explain the differences in frequency between our absorptions and those of Bencivenni *et al.*,¹¹ and have been unable to reproduce even qualitatively the results of their superheating experiments. However we note that the i.r. spectra of solid NaReO_4 and KReO_4 ¹³ both exhibit a strong band in the region 900–920 cm^{-1} , and it is possible that incomplete isolation in their superheating experiments might, paradoxically, result in the formation of polymeric material during sample deposition, with spectral properties similar to the crystalline solid.

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