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Infrared Luminescence Spectra of Hexachloroiridate(IV) and Hexabromoiridate(IV) in Cubic Crystals

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The $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_7(^2T_{2g})$ transition has been observed near 5000 cm^{-1} in the 5 K luminescence spectra of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ in Cs_2MX_6 (M = Sn, Te, Zr; X = Cl, Br) and Rb_2SnX_6. The intense well-resolved emission maybe analyzed into an electronic origin and vibronic origins due to the ν_6, ν_4, and ν_3 modes of the complex ion together with weaker features caused by couplings to the lattice vibrations and internal modes of the host crystals. The first members of progressions in ν_2 on the vibronic origins are much more intense than the corresponding ν_1 progressions for $IrCl_6^{2-}$, but the intensities are reversed in $IrBr_6^{2-}$. This is discussed in terms of the Jahn–Teller effect in the Γ_8 and higher excited states. These ions also show luminescence in the visible region from states involving ligand to metal charge transfer.

Introduction

Radiative relaxation from an excited state of a metal ion to a lower state competes effectively with nonradiative relaxation when the energy gap between the states corresponds to more than about six quanta of the highest frequency vibrational mode which is coupled to the electronic states.[1] Metal–ligand vibrations usually have wavenumbers below 500 cm^{-1}, and, in the absence of other relaxation mechanisms, we anticipate that metal complexes of monoatomic ligands will show luminescent transitions between two levels whenever the spacing between the levels exceeds 3000 cm^{-1} for all accessible values of the nuclear coordinates. By contrast almost all experimental studies of the luminescence of coordination compounds have restricted themselves to the region above 9000 cm^{-1} where sensitive photomultiplier detectors are available. In addition to their spectroscopic interest it seems likely that electronic levels separated by 3000–9000 cm^{-1} will be involved in many energy-transfer and photochemical phenomena, and we have therefore started a program to study the luminescence of inorganic materials in the 3000–9000-cm^{-1} region with good sensitivity and resolution. In this paper we report and analyze the previously unobserved $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_7(^2T_{2g})$ luminescence of $IrCl_6^{2-}$ which occurs near 5000 cm^{-1}.

The only previous report of infrared luminescence from an Ir^{4+} system concerns this ion at octahedral sites in $Y_3Ga_5O_{12}$.[2] Keiderling et al.[3] have studied the $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_8(^2T_{2g})$ transition of $IrCl_6^{2-}$ in Cs_2ZrCl_6 using absorption and MCD spectroscopy, but our luminescence spectra do not have an exact mirror image relationship with the absorption spectra. Possible resons for this will be discussed. The visible absorption spectra of $IrCl_6^{2-}$and $IrBr_6^{2-}$ which is due to ligand to metal charge-transfer (LMCT) transitions has been discussed in great detail by Schatz and coworkers.[4–7]

Experimental Section

Materials. Crystals of Cs_2MX_6 (M = Sn, Te, Zr; X = Cl, Br) and Rb_2SnX_6 containing 0.01–0.1% Ir^{4+} were prepared by mixing hot saturated solutions of CsX or RbX in the dilute hydrohalic acid with saturated solutions of MX_4 in the concentrated hydrohalic acid containing 0.01–0.1% of Cs_2IrX_6 (relative to the MX_4). The precipitated powders were thoroughly dried and passed in sealed quartz tubes through a Bridgman furnace at 850 °C.

Spectral Measurements. Visible and near-infrared luminescence spectra were measured as previously described.[8]

Electronic and Vibrational Structure of IrX_6^{2-} and the Host Lattices

The ground state of the low-spin 5d^5 ion Ir^{4+} is $^2T_{2g}$. The first excited crystal field state of IrX_6^{2-} is calculated to be $^4T_{1g}$ from the $t_{2g}{}^4e_g$ configuration at about 30 000 cm^{-1} but has not been definitely observed because it is overlaid by intense LMCT transitions which occur above 19 000 cm^{-1} ($IrCl_6^{2-}$)[5] and 12 000 cm^{-1} ($IrBr_6^{2-}$).[4] All our experiments involved excitation into these LMCT levels. The $^2T_{2g}$ ground state is split by spin–orbit coupling into Γ_7 and Γ_8 components separated by $^3/_2\,\xi$ in the first order with the Γ_7 level lower.

A_2MX_6 (A = Rb, Cs; M = Sn, Zr, X = Cl, Br) are transparent in the near-infrared and visible regions. Cs_2TeX_6 (X = Cl, Br) are yellow and red, respectively, due to transitions to states derived from the 5s5p outer-electron configuration, and these materials show intense visible luminescence under blue laser excitation. This does not interfere with the infrared luminescence studies.

All of the host lattices employed crystallize in the $Fm3m$-O_h^5 lattice of the K_2PtCl_6 type. Available infrared, Raman, and crystallographic data are collected in Table I. These vibrational data are important so that resonance couplings between the IrX_6^{2-} and the host lattice ions may be identified.

Infrared Luminescence of $IrCl_6^{2-}$

The 488-nm excited 5 K luminescence spectra of $IrCl_6^{2-}$ in Cs_2SnCl_6 and Cs_2TeCl_6 are shown in Figure 1, and the bands are tabulated and assigned in Table II. The data for the other lattices are summarized in Table III. The weak sharp feature at 5144 cm^{-1} (5139 cm^{-1}) for Cs_2SnCl_6:$IrCl_6^{2-}$ (Cs_2TeCl_6:$IrCl_6^{2-}$) is assigned as the magnetic dipole-allowed electronic origin from the observation of hot bands to high energy at higher temperatures and the vibronic analysis. In the absorption spectrum of Cs_2ZrCl_6:$IrCl_6^{2-}$ reported by Keidering et al.[3] there are two bands at 5142 and 5147 cm^{-1} assigned as origins. Only the upper band was observed in luminescence although we should have expected to resolve the 5-cm^{-1} separation if present. This supports the interpretation of one of these bands as due to a defect or pair. It is noteworthy that the concentration of Ir^{4+} in our samples was about

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Table I. Infrared and Raman Spectra (cm^{-1}) and Lattice Parameters (Å) of the Host Lattices

compd	a_0	lattice		$\nu_1(\alpha_{1g})$	$\nu_2(\epsilon_g)$	$\nu_3(\tau_{1u})$	$\nu_4(\tau_{1u})$	$\nu_5(\tau_{2g})$
		τ_{1u}	τ_{2g}					
Cs_2IrCl_6 [c]		72		341	294	321	182	177
Rb_2SnCl_6 [d]	10.118[a]	72	59	316	241	312	173	171
Cs_2ZrCl_6 [e]	10.407[a]			326	249	313	162	161
Cs_2TeCl_6 [f]	10.447[a]	66	51	292	248	260	122	140
Cs_2IrBr_6 [c]		63		207	173	225	123	175
Rb_2SnBr_6 [g]	10.64[a]	56	42	192	142	226	118	107
Cs_2SnBr_6 [g]	10.81[a]	61	38	185	138	222	118	109
Cs_2ZrBr_6	10.91[b]			199[h]	144[i]	223[i]	106[i]	105[h]

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Table II. Analysis of the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_7(^2T_{2g})$ Emission of $IrCl_6^{2-}$ in Cs_2SnCl_6 and Cs_2TeCl_6

Cs_2TeCl_6: $IrCl_6^{2-}$		Cs_2SnCl_6: $IrCl_6^{2-}$		
line no.	wave-number	line no.	wave-number	assignt
1	25	1	40	acoustic ZB
2	39	2	58	lattice t_{2g} ZB
3	54	3	69	lattice TO
4	70	4	84	lattice LO
5	78	5	126	two phonon
6	88			see text
7	118			see text
8	130			see text
9	151	6	153	ν_6
10	180	7	182	ν_4
11	196	8	198	$(\nu_6 + 40 = 193)$ or resonance
12	206	9	201	$(\nu_6 + 58 = 211)$ or resonance
13	228	10	220	$(\nu_4 + 40 = 222)$
		11	235	$(\nu_4 + 58 = 240)$
14	250	12	254	$(\nu_4 + 69 = 251)$
15	275	13	274	$(\nu_4 + 84 = 266)$
16	290			
17	303	14	301	ν_2?
18	330	15	320	ν_3; see text
		16	335	ν_3 resonance
19	352	17	357	$(\nu_3 + 40 = 360)$
20	373			
21	391	18	386	$(\nu_3 + 69 = 389)$
22	401	19	414	$(\nu_3 + 84 = 404)$
23	422			
24	453	20	455	$\nu_6 + 302 = \nu_2$
25	484	21	484	$\nu_4 + 302 = \nu_2$
26	499	22	504	$\nu_6 + 351 = \nu_1$
27	526	23	522	$\nu_4 + 340 = \nu_1$
		24	623	$\nu_3 + 303 = \nu_2$
28	630	25	633	$\nu_3 + 298 = \nu_2$
29	676	26	660	$\nu_3 + 340 = \nu_1$

Table III. Summary of the Positions of the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_7(^2T_{2g})$ Electronic Origins and Derived Vibrational Wavenumbers for $IrCl_6^{2-}$ and $IrBr_6^{2-}$ in Various Host Lattices

lattice	electronic origin	ν_1	ν_2	ν_3	ν_4	ν_6
Cs_2SnCl_6	5144	344	301	320	182	153
Rb_2SnCl_6	5202	345	307	330	180	147
Cs_2TeCl_6	5139	347	302	330	180	151
Cs_2ZrCl_6	5147	345	300	324	183	150
Cs_2SnBr_6	4972	208	167	223	121	94
Rb_2SnBr_6	5019	212	168	229	117	83
Cs_2TeBr_6	4990	~196		230	121	95
Cs_2ZrBr_6	4970	210	168	223	122	94

one-tenth of that employed for the absorption and MCD experiments. More concentrated samples produced broader luminescence spectra.

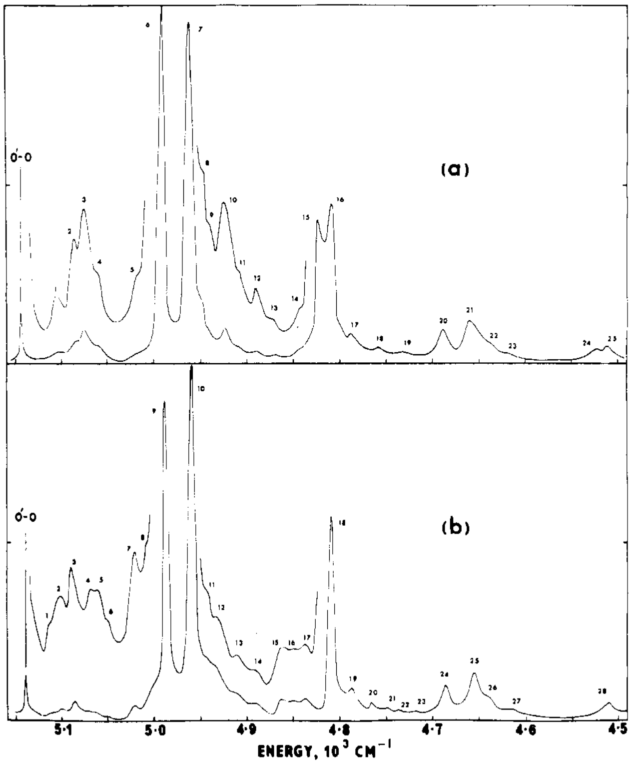

Figure 1. The 488-nm excited near-infrared luminescence of (a) Cs_2SnCl_6:0.05% $IrCl_6^{2-}$ and (b) Cs_2TeCl_6:0.05% $IrCl_6^{2-}$ at 5 K. The lines are numbered to correspond with Table II.

The three strong bands to low energy of the origin in the spectrum of Cs_2TeCl_6:$IrCl_6^{2-}$ (lines 9, 10, 18—Table II) are immediately assignable as the ν_6, ν_4, and ν_3 vibronic origins from their position and intensity. Similar assignments apply for Cs_2SnCl_6:$IrCl_6^{2-}$ except that the ν_3 origin is doubled. Since ν_3 for Cs_2SnCl_6 and the $IrCl_6^{2-}$ ion occur at similar wavenumbers a resonance interaction is expected, and this accounts for the observed structure. Similar resonance interactions are common in other systems.[8,10,11] The ν_4 and ν_3 bands are accompanied by several shoulders and weak bands on the high vibrational wavenumber side. Many of these can be assigned as vibron–phonon modes involving one quantum of ν_4 or ν_3 and one or two quanta of a lattice phonon. In Table III plausible

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Table IV. Analysis of the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_7(^2T_{2g})$ Emission of $IrBr_6^{2-}$ in Cs_2SnBr_6

line no.	wave-number	assignt	line no.	wave-number	assignt
1	27	acoustic ZB	10	198	lattice ν_1?
2	56	lattice TO, LO	11	223	lattice ν_3?
3	94	ν_6	12	233	ν_3
4	105	two phonon or resonance	13	248	ν_3 resonance
			14	264	$\nu_6 + 170 = \nu_2$
5	121	ν_4	15	285	$\nu_4 + 164 = \nu_2$
6	131	ν_4 resonance	16	300	$\nu_6 + 206 = \nu_1$
7	139	ν_4 resonance	17	329	$\nu_4 + 208 = \nu_1$
8	149	$(\nu_4 + 27 = 148)$	18	341	$\nu_4 + 210 = \nu_1$
9	156	$(\nu_4 + 27 = 158)$			

assignments for many of these are given involving wavenumbers similar to those observed in the lattice vibration region; exact numerical agreement is not expected however because of the different selection rules applicable in the phonon and vibron–phonon regions. In addition some of the structure in Cs_2SnCl_6:$IrCl_6^{2-}$ may arise from further resonant couplings involving ν_6 and ν_4 of the complex ion and host lattice while lines 15–17 in Cs_2TeCl_6:$IrCl_6^{2-}$ probably involve the host ν_3 band. Between the origin and ν_6 four or more weak bands may be detected. As is usual in this type of compound, these bands cannot be assigned with use of a unit cell group approach. Following assignments for Cs_2MnF_6[11] and K_2PtCl_6[15] it is reasonable to associate the lowest frequency mode with the lowest zone boundary (ZB) acoustic phonon whereas the zone boundary t_{2g} and zone center lattice transverse optic and longitudinal optic modes contribute to the higher wavenumber features. Just to low energy of the ν_6 vibronic origins two phonon features are detected although in the Cs_2TeCl_6 lattice host ν_4, ν_5, and ν_6 modes may also contribute intensity in this region. This intensity is probably derived from coupling with the ν_6 mode of the $IrCl_6^{2-}$ ion.

To low energy of the ν_3 vibronic origins the first members of progressions on the vibronic origins in a mode of 300 ± 3 cm^{-1} are readily detected. Since for Cs_2IrCl_6 the resonance Raman spectrum gives $\nu_1 = 341$ cm^{-1} and $\nu_2 = 294$ cm^{-1} the progression forming mode is assigned as ν_2 and is indicative of a weak Jahn–Teller effect in the $\Gamma_8(^2T_{2g})$ state and/or one of the intermediate states from which the intensity is derived. In principle it is possible to distinguish these mechanisms by the observation of ν_2 based on the origin, and indeed in both lattices a weak band is observed at about 302 cm^{-1}, suggesting that the JTE occurs in the Γ_8 state. However this weak feature lies close to the strong ν_3 vibronic origin, and its assignment as a multiphonon feature gaining intensity from the ν_3 band cannot be ruled out. Further very weak features in this region are separated from the ν_6, ν_4, and ν_3 vibronic origins by ~345 cm^{-1}, and this interval is assigned as ν_1.

In the absorption spectrum of Cs_2ZrCl_6:$IrCl_6^{2-}$ a progression in a mode of 382 cm^{-1} was observed, which had comparable relative intensity to the 300 cm^{-1} progression observed in luminescence at the same temperature. The MCD spectrum indicates that the 382-cm^{-1} mode has even parity, but it is difficult to explain the high wavenumber of this mode if it is assigned as ν_1 or ν_2. Conceivably the JTE is responsible, but the large shift is in marked contrast to the similarity of the wavenumbers of the odd modes in the Γ_7 and Γ_8 states and the similar low intensity of the progressions in both absorption and luminescence.

Infrared Luminescence of $IrBr_6^{2-}$

The luminescence spectrum of Cs_2SnBr_6:$IrBr_6^{2-}$ (Figure 2, Table IV) is less well resolved than those of the $IrCl_6^{2-}$ ion but may be analyzed in an analogous way. Both the ν_4 and ν_3 vibronic origins are accompanied by shoulders due to resonance with the host lattice. The data for the other bromide lattices are summarized in Table III. The main feature of interest in the spectra is that ν_2 progressions on the vibronic origins are much weaker than the ν_1 progressions. Any JTE in the Γ_8 $^2T_{2g}$ state is therefore very weak. The possible origin of this difference is discussed below.

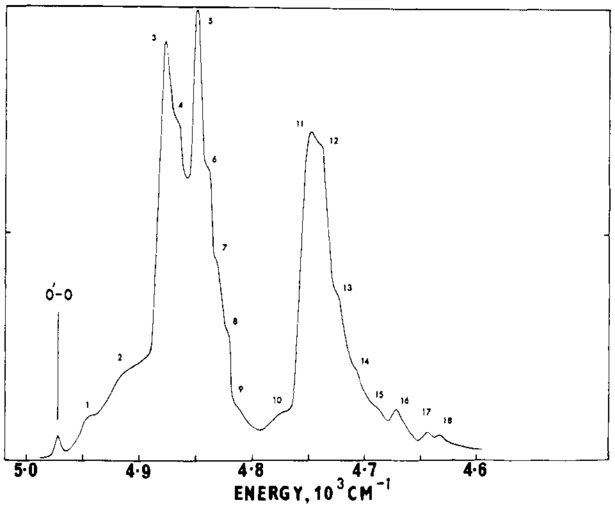

Figure 2. The 514.5-nm excited near-infrared luminescence of Cs_2SnBr_6:0.05% $IrBr_6^{2-}$ at 5 K. The lines are numbered to correspond with Table IV.

Visible Luminescence of $IrCl_6^{2-}$ and $IrBr_6^{2-}$

Clark and Turtle[9] have reported a number of weak bands in the luminescence of pure Cs_2IrCl_6 and Cs_2IrBr_6. In the diluted crystals under 488-nm excitation only one region of emission was observed for each ion, but the emission is much more intense. For Cs_2SnCl_6:$IrCl_6^{2-}$ the 488-nm excited emission occurs in the region 16 000–12 000 cm^{-1} and consists of about 16 rather broad features separated by 300 ± 10 cm^{-1}. The intensity of these bands peaks at the seventh or eighth member and the distribution are characteristic of a Franck–Condon pattern based on a single origin and having a very large potential surface displacement. The lowest excited state of $IrCl_6^{2-}$ is $\Gamma_8(^2T_{1g})$ derived from the $t_{1g}\pi^5t_{2g}^6$ LMCT configuration, which is represented by a weak broad double-humped band in absorption. We presume that the broad visible emission represents the corresponding $\Gamma_8(^2T_{1g}) \rightarrow \Gamma_7(^2T_{2g})$ transition and the 300-cm^1 interval is ν_2 due to a strong JTE in the excited state. There are two difficulties with this assignment. First, since the transition must be vibronically induced, it is necessary to assume that one of the odd vibrations dominates the intensity mechanism if it is to be analyzed in terms of a single progression. Second, it is not clear how a $t_{1g}^6t_{2g}^5 \rightarrow t_{1g}^5t_{2g}^6$ transition can be accompanied by a very large displacement along any nuclear coordinate. The first objection can be removed by assigning the emission to the next higher excited configuration $t_{1u}(\pi + \sigma)^5t_{2g}^6$, which generates Γ_{8u} and Γ_{6u} states, but the second difficulty remains. It is clear however that the emission must be from a LMCT state since the lowest crystal field state cannot be excited by 488-nm excitation. While LMCT luminescence is common in oxyanions (e.g., VO_4^{3-} [12]), we are not aware of any previous reports on other systems showing this behavior.

$IrBr_6^{2-}$ in $Cs_2ZrBr_6^{2-}$ also shows strong luminescence in the red region, but this time the structure of the band which has maximum intensity is at 15 500 cm^{-1} and is only poorly resolved and much more complex. This emission is weakly excited by 514-nm radiation but much more strongly by 457-nm radiation. No emission was detected in the region of

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10 000 cm^{-1}, where the process analogous to that occurring in the chloride would be expected to be detectable. Further work, preferably involving magnetic circularly polarized emission will be required to identify the excited states involved, but we do not plan to carry out these studies in the near future.

Discussion

The separation of the Γ_7 and Γ_8 components of the $^2T_{2g}$ ground state is $^3/_2\xi$ in the first order. The derived value of ξ in $IrCl_6^{2-}$ and $IrBr_6^{2-}$ is then 3300–3400 cm^{-1}. This is rather larger than expected from other third-row transition elements and supports the view of Allen[13] that it is essential to include mixing of other crystal field states into the ground state if an accurate spin–orbit coupling parameter is to be obtained.

Of greater interest is the relative intensities of the ν_6, ν_4, and ν_3 vibronic origins. Since the ν_6 vibration generates an octapolar field at the metal whereas ν_3 and ν_4 generate dipolar fields, it would be reasonable to suppose that, in the absence of any selection rules, the ν_3 and ν_4 vibronic origins would be much stronger than the ν_6 origin. For d^3 ions Manson[14] has argued that the dipolar term cancels for the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition, and this agrees with the experimental observation that the ν_6 vibronic origins have comparable intensity to the ν_4 vibronic origins in $Cr(NH_3)_6^{3+}$, MnF_6^{2-}. No similar cancelation occurs for the $\Gamma_7 \rightarrow \Gamma_8$ transition in IrX_6^{2-} and the comparable intensity of the ν_6 and ν_4 vibronic origins remains unexplained.

The main difference between the $\Gamma_8 \rightarrow \Gamma_7$ transitions in the chloride and bromide is that the relative intensities of the ν_1 and ν_2 progressions are reversed. The spectra are insufficiently well resolved for an unambiguous decision as to whether the JTE is in the $\Gamma_8(^2T_{2g})$ state or a higher odd-parity state. It is of interest however that whereas the $\Gamma_7(^2T_{2g}) \rightarrow \Gamma_7 + \Gamma_8(^2T_{2u})$ transition of $IrCl_6^{2-}$ shows evidence of a strong JTE and Ham effect in the excited state, this Ham effect is quenched by the ligand spin–orbit coupling in the $IrBr_6^{2-}$ ion. In this case the active vibration is ν_5. The different LMCT luminescence behavior of the two ions does point to differences in the ordering of the excited states.

Conclusion

$IrCl_6^{2-}$ and $IrBr_6^{2-}$ show intense luminescence in the infrared ($\Gamma_8(^2T_{2g}) \rightarrow \Gamma_7(^2T_{2g})$) and visible (LMCT) regions. The three odd-parity vibrational modes of the octahedron appear strongly in the infrared transition. The potential surfaces of the two states are nearly parallel although there is evidence for a weak Jahn–Teller effect in $IrCl_6^{2-}$. The detailed assignments of the visible emissions are uncertain.

Acknowledgment. We thank the SRC for financial support.

Registry No. $IrCl_6^{2-}$, 16918-91-5; $IrBr_6^{2-}$, 16919-98-5; Cs_2SnCl_6, 17362-93-5; Rb_2SnCl_6, 17362-92-4; Cs_2TeCl_6, 17498-83-8; Cs_2ZrCl_6, 16918-86-8; Cs_2SnBr_6, 17362-97-9; Rb_2SnBr_6, 17362-96-8; Cs_2TeBr_6, 16925-33-0; Cs_2ZrBr_6, 36407-58-6.

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Single-Crystal Raman Spectroscopic Study of Apophyllite, a Layer Silicate

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Good-quality single-crystal Raman data have been obtained at both ambient temperature and 100 K for an oriented crystal of apophyllite, $KCa_4(Si_4O_{10})_2(F/OH)\cdot 8H_2O$, a layer structure silicate with four- and eight-membered rings. The numbers of bands found for each symmetry species closely approximate those predicted by factor group analysis. An A_{1g} mode at 109 cm^{-1} is attributed principally to Ca^{2+} translatory motion, with the implication that bands at similar positions in B_{1g}, B_{2g}, and E_g spectra are of similar provenance. Some regions of the spectrum show pronounced thermal dependence and are tentatively associated with movements of lattice water. The ν(OH) region bands are attributed entirely to the lattice water, the sharp bands near 3560 cm^{-1} arising from short, non-hydrogen-bonded O–H motion and the broad ones from hydrogen-bonded lattice water O–H bonds.

Introduction

The marvelous variety of structures, based upon the SiO_4 tetrahedral unit, presented by silicates poses many challenging problems in vibrational spectroscopy. Much effort has been expended upon the IR spectroscopy of these materials but rather little upon Raman investigations; and excellent summary of the field is given in Farmer's book.[2] For a further understanding of the usually highly complex vibrational spectra of silicates beyond the level possible from IR spectroscopy of powders, aided and abetted by normal-coordinate analysis, data must be collected from oriented single cyrstals with use of linearly polarized radiation. By these means, securely based assignments have recently been obtained for several orthosilicates,[3-6] and believable accounts of some pyrosilicates are on record.[2] Studies of chain[6-8] and ring silicates[9-11] are also becoming increasingly common. There remains, however, a particular need for detailed analyses of the more complex sheet and framework structural types. For this reason we have undertaken a single-crystal Raman study of apophyllite. This mineral has an unusual layer structure in which SiO_4 tetrahedra form four- and eight-membered rings. Comparable sheets are found in gillespite, $BaFeSi_4O_{10}$, and in Egyptian blue, $CaCuSi_4O_{10}$. All three materials present intriguing structural and phase-stability problems. Apophyllite is also quite heavily hydrated. The precise forms of protonated moiety present continue to be a matter of debate. The problem is

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