Raman scattering of chromium-doped halide elpasolite crystals

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11. SUPPLEMENTARY NOTES
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13. ABSTRACT (Maximum 200 words)
Abstract—Polarized Raman spectra of a single crystal of the chromium-doped elpasolite K$_2$NaScF$_6$:Cr$^{3+}$ yield an unambiguous identification of the symmetries and frequencies of the four Raman-active modes: $a_1$ at 525 cm$^{-1}$, $e_1$ at 403 cm$^{-1}$ and $b_2$ at 250 and 113 cm$^{-1}$. Low temperature spectra reveal a lower symmetry phase involving substantial distortion of the potassium sublattice. The impurity concentration dependence reveals a local mode of $a_1$ symmetry at 541 cm$^{-1}$. Vibration frequencies inferred from unpolarized Raman spectra are reported for a number of other halide elpasolites doped with either chromium or titanium.

14. SUBJECT TERMS
Raman scattering, elpasolite, chromium, phase transition, phonons
RAMAN SCATTERING OF CHROMIUM-DOPED HALIDE ELPA SOLITE CRYSTALS

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(Received 23 July 1990; accepted 14 August 1990)

Abstract—Polarized Raman spectra of a single crystal of the chromium-doped elpasolite $K_2NaScF_6:Cr^{3+}$ yield an unambiguous identification of the symmetries and frequencies of the four Raman-active modes: $a_{1g}$ at 525 cm$^{-1}$, $e_g$ at 403 cm$^{-1}$ and $t_{2g}$ at 250 and 113 cm$^{-1}$. Low temperature spectra reveal a lower symmetry phase involving substantial distortion of the potassium sublattice. The impurity concentration dependence reveals a local mode of $a_{1u}$ symmetry at 541 cm$^{-1}$. Vibration frequencies inferred from unpolarized Raman spectra are reported for a number of other halide elpasolites doped with either chromium or titanium.

Keywords: Raman scattering, elpasolite, chromium, phase transition, phonons.

1. INTRODUCTION

The cubic elpasolite crystal structure with space group $O_h$ is consistent with first-order Raman scattering, in contrast to the perovskite structure from which it is derived. Raman spectra have been reported previously for both oxide elpasolites [1, 2] and halide elpasolites [3–11]. Of particular interest are those halide elpasolites with relatively large trivalent cations which exhibit a low temperature phase transition, exemplified by $Cs_2NaLnCl_6$, where Ln denotes a light trivalent rare-earth ion.

We have employed polarized Raman spectroscopy to investigate the dependence of normal-mode frequencies on temperature, impurity concentration and composition in a series of additional halide compounds of elpasolite structure. The materials investigated here, which were all prepared originally as potential tunable solid-state-laser materials, are intentionally doped with transition-metal impurities, mostly chromium. The optical absorption and emission spectra of chromium-doped halide elpasolites have been the objects of extensive investigation [12–24].

Raman-active normal modes of elpasolite are identified in Section 2, experimental methods are described in Section 3 and experimental results are presented in Section 4 and interpreted in Section 5.

2. IDENTIFICATION OF RAMAN-ACTIVE NORMAL MODES

The cubic elpasolite crystal structure is derived from the perovskite structure by alternate substitution of monovalent and trivalent cations on the divalent cation sublattice. The resulting compound has the formula $A_2BMX_6$, where A and B are monovalent cations, M is a trivalent cation and X is a monovalent anion. (This description applies to halide elpasolites; all of the charges are doubled in the oxide elpasolites.) The substitution of B for A in the perovskite ADX removes the inversion symmetry at all ion sites in perovskite, becomes allowed in elpasolite.

Only zone-center optical modes (approximately zero wave vector) of $a_{1g}$, $e_g$ and $t_{2g}$ symmetry are Raman active [25]. The elpasolite structure is face-centered cubic and the primitive unit cell comprises one formula unit of 10 ions. Of the 27 zone-center optical normal modes [26], just nine are Raman active with only four distinct vibration frequencies by virtue of symmetry-induced degeneracies. The corresponding symmetry-adapted displacements are illustrated in Fig. 1. The normal modes of $t_{2g}$ symmetry are linear combinations of the symmetry-adapted displacements shown. However, since the anion X is much less massive than the cation A in the compounds investigated, the anion displacement is expected to predominate in the higher frequency $t_{2g}$ mode, and the cation displacement in the lower. Since the higher frequency $t_{2g}$ mode is primarily a bending mode, its frequency is expected to lie lower than that of the asymmetric $e_g$ stretching mode, which in turn should lie below that of the symmetric $a_{1g}$ stretching mode.
better resolution at low temperature. A comparison
cooling from the melt in sealed quartz or platinum
clpasolite structure selected from polycrystalline (a)
were small pieces of a variety of compounds with
remaining samples employed in this investigation
nominal
Cs, NalnCl: :Cr3
in a closed vessel by the Czochralski method with associated with a phase transition. The side structure
normalized to the exciting laser intensity, features appear to be quite different. The splitting
signal detection. The data were recorded and stored several lines; and (2) the appearance
plifier/threshold discriminator, were employed for features are evident: (I) a splitting of the
modes of
selection rules
orientation of Fig. 2(a),
orientations, us shown in Figs 2(a) and
finger of a Helitran flow-cryostat in two different
oriented and polished, and mounted on the cold
5at.% and all of the remaining samples at
1%.

Polarized Raman measurements were made on a
single crystal of K;NaScF, which was grown at MIT
in a closed vessel by the Czochralski method with a
Cr4+ doping of 1 at.%. Single crystals of
Cs2NaInCl6 :Cr3+ and Rb2NaSeF6 :Ti4+, both with
nominal 1% doping, were also grown at MIT. The
remaining samples employed in this investigation
were small pieces of a variety of compounds with
elpasolite structure selected from polycrystalline materials prepared at GTE Laboratories by slow
cooling from the melt in sealed quartz or platinum tubes [20]. Two samples were doped with Cr3+ at
5 at.% and all of the remaining samples at 1%.
The single crystal of K;NaScF, :Cr3+ was X-ray
oriented and polished, and mounted on the cold
finger of a Helitran flow-cryostat in two different
orientations, as shown in Figs 2(a) and 2(b). In the
orientation of Fig. 2(a), (001) → (100), polarization
selection rules [25] dictate that light scattered by
modes of a1 and e, symmetry is polarized parallel to the
laser (∥) and is therefore observable only in
X(ZZ)Y scattering geometry, while light scattered by
modes of t2g symmetry is polarized perpendicular
to the laser (⊥) and it is observable only in
X( ZY)Y geometry. In the orientation of Fig. 2(b),
[011] → [100], light scattered by an e, mode is predomin-
antly polarized perpendicular to the laser (⊥); it is
more intense by a factor of three in X(ZZ)Y geometry
than in X( ZZ)Y geometry. On the other hand,
light scattered by both a1 and t2g modes is polarized
parallel to the laser (∥) in this orientation and is
thus observable only in X(ZZ)Y geometry. Taken
together, polarized Raman measurements in these
two orientations suffice to distinguish all three al-
lowed symmetries of Raman-active modes.

3. EXPERIMENTAL METHODS

The 5145 Å line of a Spectra-Physics 2025-05
argon-ion laser was used as the excitation source in
our measurements, together with a narrow-band laser
light line filter to suppress Ar plasma lines. Scattered light
was detected at 90° with respect to the direction of the incident light. Sheet polarizers were employed, and the scattered light was subsequently passed through a polarization scrambler into a computer controlled
Spex double spectrometer (Spex 1404), equipped with
1800 lines mm⁻¹ holographic gratings. Conventional photon counting techniques, including a low-noise
photomultiplier (RCA 31034), preamplifier and ampli-
plier/threshold discriminator, were employed for
signal detection. The data were recorded and stored by
an Apple IIe computer. The signal intensity was
normalized to the exciting laser intensity.

Polarized Raman measurements were made on a
single crystal of K;NaScF, which was grown at MIT
in a closed vessel by the Czochralski method with a
Cr4+ doping of 1 at.%. Single crystals of
Cs2NaInCl6 :Cr3+ and Rb2NaSeF6 :Ti4+, both with
nominal 1% doping, were also grown at MIT. The
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The single crystal of K;NaScF, :Cr3+ was X-ray
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light scattered by both a1 and t2g modes is polarized
parallel to the laser (∥) in this orientation and is
thus observable only in X(ZZ)Y geometry. Taken
together, polarized Raman measurements in these
two orientations suffice to distinguish all three al-
lowed symmetries of Raman-active modes.

4. EXPERIMENTAL RESULTS

Polarized Raman spectra obtained at room tem-
perature with a single crystal of K;NaScF, :Cr3+ are
shown in Figs 3 and 4 for the two sample orientations
of Fig. 2. Two scattering geometries are employed for
each orientation, X(ZZ)Y and X(ZX)Y, yielding
spectra polarized parallel (∥) and perpendicular (⊥)
to the laser, respectively. These four spectra, together
with the polarization selection rules listed above,
suffice to provide a unique determination of the
symmetry of each Raman-active mode. There are
four principal lines as expected, and they appear in
the anticipated order (t2g, e, and a1 with increasing
frequency); thus the lines can be confidently
correlated with the symmetry-adapted displacements
shown in Fig. 1.

It is evident from Fig. 5 that pronounced qualita-
tive changes in the Raman spectra are observed at
liquid nitrogen temperature. Two distinct novel
features are evident: (1) a splitting of the t2g line into
several lines; and (2) the appearance of side structure
associated with the a1 line. The origins of these two
features appear to be quite different. The splitting of
the t2g line develops continuously with diminishing
temperature, as shown in Fig. 6, suggesting that it is
associated with a phase transition. The side structure
of the a1 line, on the other hand, is simply seen with
better resolution at low temperature. A comparison
of the Raman spectra of K;NaScF, :Cr3+ samples
with 1 and 5% impurity concentrations, shown in Fig. 7, reveals that this side structure is impurity related.

Unpolarized, room-temperature Raman spectra have been obtained on a number of elpasolite crystals doped with chromium or, in one case, titanium. The phonon energies for vibrations of the host lattice are listed in Table 1; the modes are identified by analogy with those of K$_2$NaScF$_6$.

5. DISCUSSION

The four principal lines observed in the first-order Raman spectrum of K$_2$NaScF$_6$:Cr$^{3+}$ are attributed to the zone-center normal modes of the host crystal. The symmetry of the mode corresponding to each line has been identified unambiguously by polarized Raman spectroscopy, and the lines appear in the anticipated order of vibration frequency. Host-lattice vibration frequencies are reported here for a number of additional halide compounds of elpasolite structure, as well.

The splitting of the $I_4^1$ line in K$_2$NaScF$_6$:Cr$^{3+}$ is attributed to a phase transition which occurs at room temperature. The fact that only the $I_4^1$ line is appreciably affected suggests that the phase transition involves relatively little distortion of the (ScF$_6$)$^3^-$ octahedral complexes. It may well be that the room-temperature phase transition is initiated by a soft $I_4^1$ librational mode of the (ScF$_6$)$^3^-$ octahedra, as in the Cs$_2$NaLnCl$_6$ system; such a mode is invisible to Raman scattering. The consequent reduction to tetragonal symmetry could account for the splitting of the $I_4^1$ line observed at 225 K, as shown in Fig. 6.

Additional distortion of the potassium sublattice is observed at still lower temperatures. Of particular interest is the lowest energy line in Fig. 6 which appears to move in from the laser line as the temperature is reduced. This line may correspond to a Raman-active soft mode associated with a second phase transition, as has been reported in the analogous compound Cs$_2$LiCr(CN)$_6$ [27]. From its polarization dependence, it appears to be a composite of two lines. The presence of at least seven lines with frequencies below 140 cm$^{-1}$ at 90 K suggests a distortion which not only removes the degeneracy of Raman-active modes but also enlarges the primitive unit cell, thus introducing additional zone-center Raman-active modes. Little additional change is observed in the spectrum as the temperature is reduced to 10 K.

The side structure of the $a_{1g}$ lines, whose resolution is enhanced at low temperature, is attributed to local and resonance modes associated with the Cr$^{3+}$ impurities. This interpretation is corroborated by the concentration dependence of the Raman spectrum shown in Fig. 7. The elpasolite crystal structure has the property that it can accommodate a trivalent cation substitutional impurity at a site of rigorously octahedral symmetry without charge compensation. Thus the point symmetry is unaffected by doping and only the translational symmetry is lost.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Doping (%)</th>
<th>$I_4^1$</th>
<th>$I_4^2$</th>
<th>$e_g$</th>
<th>$a_{1g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$NaScF$_6$:Cr$^{3+}$</td>
<td>5</td>
<td>115</td>
<td>251</td>
<td>409</td>
<td>525</td>
</tr>
<tr>
<td>K$_2$NaScF$_6$:Cr$^{3+}$</td>
<td>1</td>
<td>113</td>
<td>250</td>
<td>403</td>
<td>525</td>
</tr>
<tr>
<td>K$_2$NaGaF$_6$:Cr$^{3+}$</td>
<td>1</td>
<td>124</td>
<td>284</td>
<td>—</td>
<td>553</td>
</tr>
<tr>
<td>K$_2$LiScF$_6$:Cr$^{3+}$</td>
<td>1</td>
<td>113</td>
<td>265</td>
<td>378</td>
<td>527</td>
</tr>
<tr>
<td>Rb$_2$NaScF$_6$:Ti$^{3+}$</td>
<td>1</td>
<td>87</td>
<td>244</td>
<td>388</td>
<td>512</td>
</tr>
<tr>
<td>Cs$_2$NaInCl$_6$:Cr$^{3+}$</td>
<td>1</td>
<td>50</td>
<td>142</td>
<td>—</td>
<td>294</td>
</tr>
<tr>
<td>Cs$_2$NaYCl$_6$:Cr$^{3+}$</td>
<td>1</td>
<td>47</td>
<td>127</td>
<td>222</td>
<td>284</td>
</tr>
<tr>
<td>Cs$_2$NaYCl$_6$:Cr$^{3+}$</td>
<td>1</td>
<td>46</td>
<td>127</td>
<td>223</td>
<td>284</td>
</tr>
<tr>
<td>Cs$_2$NaScCl$_6$:Cr$^{3+}$</td>
<td>1</td>
<td>51</td>
<td>148</td>
<td>208</td>
<td>290</td>
</tr>
</tbody>
</table>
Fig. 5. Comparison of unpolarized Raman spectra of $K_2NaScF_6:Cr^{3+}$ (1%) at room temperature and at 77 K. Subsequently, the polarization selection rules are preserved but not the restriction to zone-center phonons. It is clear from its polarization behavior that all of the side structure is associated with the projected density of states for perturbed $A_{1g}$ vibrations. In particular, the relatively narrow line at 541 cm$^{-1}$ lies above all the vibration frequencies of the perfect lattice and is therefore associated with a true local mode.

It is evident from Fig. 7 that the integrated intensity of the $A_{1g}$ side structure with 5% chromium concentration is comparable with that of the $A_{1g}$ host-lattice line; however, no side structure is observed in association with host-lattice lines of other symmetries. An obvious inference is that the $A_{1g}$ mode localized at the chromium impurity has an unusually large Raman cross-section.

Acknowledgements—This work was supported by the U.S. Army Research Office under Contract No. DAALO3-86-K-0017. The authors are grateful to Drs H. Jensen, D. S. Hamilton and L. J. Andrews for advice and assistance.

REFERENCES
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