Pressure effects on the Raman spectrum of \textit{CaZnF}_4

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Abstract

The pressure influence on the lattice vibration of \textit{CaZnF}_4 has been studied by Raman diffusion up to 17 GPa. Most Raman frequencies increase with increasing pressure. Three singularities in the pressure induced frequency evolution are observed around 1.5 GPa, 10 GPa and 17 GPa. The samples pressurized to 17 GPa or higher do not revert to the ambient pressure phase after being released, the new phase showing different Raman spectra from the ordinary one. It is suggested that \textit{CaZnF}_4 undergoes probably sudden lattice deformations at about 1.5 GPa and 10 GPa, and an irreversible phase transformation above 17 GPa.

Keywords: Pressure, lattice dynamics, Raman scattering, Phase transition.
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1 Introduction

\textit{CaZnF}_4 belongs to a family of crystals with tetragonal scheelite structure (Figure 1) which is known to be one of the crystal families undergoing ferroelastic phase transition with temperature and pressure\cite{1, 2, 3, 4, 5, 6}. Recently, the lattice dynamics of an important member of this family, \textit{Y LiF}_4, a laser host, has been studied theoretically and experimentally with IR absorption, Raman and neutron scattering\cite{7, 8, 9, 10}, as a function of both temperature (from 10 K to 1000 K) and pressure (up to 40 GPa)\cite{11, 12, 13}. These works, especially those under high pressures, are useful for understanding the dynamics of this lattice and for the verification of the validity of the rigid ion models employed in the dynamical calculations\cite{7, 10}.

Although no phase transition was observed with temperature, \textit{Y LiF}_4 has shown many Raman and luminescence (from \textit{P}_{r}^{3+} and \textit{Eu}^{3+} doping ions) anomalies with increasing pressure which are not easy to interpret with only the stiffening effect of the lattice. So it has been suggested that the compounds undergoes several lattice transformations or distortions due to high pressure\cite{12, 13}, especially when the latter is of the same order as the elastic constants \textit{C}_{11} and \textit{C}_{33} (\sim 100 GPa) of the lattice\cite{7, 14}. Nevertheless, for want of further experimental evidences, the above conjectures have been made with precaution.

Another member of the family is \textit{CaZnF}_4 of which the lattice dynamics is well studied\cite{7}. Having \textit{C}_{4h} space group, this crystal gives very intense Raman scattering, offering an ex-
cellent sample for high pressure Raman scattering. According to dynamical analysis, there are 13 active Raman modes ($3A_g \oplus 5B_g \oplus 5E_g$). Some of the authors of present paper have reported the Raman frequencies from 300 K to 10 K and shown that the crystal structure, as that of $YLiF_4$, is stable in that temperature range\[7\].

In this paper, we present the results of a Raman study of $CaZnF_4$ under high pressure up to 26 GPa. Several anomalies in Raman spectra and our analysis will be reported.

1.1 Experiment and result

The samples are small single crystals of about 100 $\mu$m width and 50 $\mu$m thick. The pressure was generated with a gasketed diamond anvil cell Diacell MK3 with a pair of anvils of type IIb/a diamond. The anvil flats are 550 $\mu$m in diameter. The cylindrical pressure chamber is 100 $\mu$m in diameter and less than 100 $\mu$m high. A chip of the sample is put into the pressure chamber together with a small ruby (for pressure measurement) and the pressure medium consisting of a 4:1 mixture of methanol:ethanol. Pressure calibration is carried out by the R lines of ruby with the non-linear pressure scale\[15\]. The Raman spectra are excited by the 514.5 nm line of an argon ion laser with 130 mW total power and collected with a Dilor-Z24 triple-monochromator single channel Raman spectrometer. Different orientations of the sample in the pressure chamber are taken in order to obtain as many Raman lines as possible, polarization analysis being difficult in the pressure cell.

| mode | $\omega$ (cm$^{-1}$) | $d\omega/dT$ (cm$^{-1}$/K) | $(d\omega/dP)_1$ (cm$^{-1}$/GPa) | $(d\omega/dP)_2$ (cm$^{-1}$/GPa) | movements of lattice vibrations |
|------|---------------------|--------------------------|--------------------------------|--------------------------------|-------------------------------|
| Bg   | 82                  | 0                        | 1.33                           | 1.45                           | $F_4^{+}\nu_2^{+}+z$ translation |
| Eg   | 128                 | -0.010                   | 6.67                           | 0.80                           | $F_4^{+}\nu_4^{+}+Ca$-xy trans. |
| Ag   | 138                 | -0.007                   | 1.33                           | 0.71                           | $F_4^{+}\nu_1^{+}+F_4^{+}\nu_2^{+}$ |
| Eg   | 194                 | -0.003                   | 1.21                           | $\sim 0$                       | $F_4^{+}\nu_4^{+}+Ca$-xy trans. |
| Ag   | 202                 | -0.021                   | 5.33                           | 2.00                           | $F_4^{+}\nu_2^{+}+R_z$ |
| Bg   | 208                 | 0                        | 1.31                           | 4.02                           | $F_4^{+}\nu_2^{+}+\nu_4^{+}+z$-trans. |
| Eg   | 248                 | -0.014                   | 6.67                           | 5.09                           | $F_4^{+}\nu_4^{+}+xy$-trans. |
| Bg   | 276                 | -0.007                   | 6.67                           | 6.18                           | $F_4^{+}\nu_2^{+}+z$-trans. |
| Eg   | 298                 | -0.017                   | 2.50                           | 6.55                           | $F_4^{+}\nu_4^{+}+Ca$-xy trans. |
| Bg   | 318                 | -0.021                   | 2.99                           | $\sim 0$                       | $F_4^{+}\nu_4^{+}+z$-trans.+Zn-z trans. |
| Bg   | 432                 | -0.007                   | ?                              | $\sim 0$                       | $F_4^{+}\nu_4^{+}+z$-trans.+Zn-z trans. |
| Eg   | 468                 | -0.017                   | -1.02                          | $\sim 0$                       | $F_4^{+}\nu_1^{+}+Zn$-xy trans. |
| Ag   | 474                 | -0.017                   | 5.91                           | 6.00                           | $F_4^{+}\nu_1^{+}$ (stretching) |

Several Raman spectra at different pressures are shown in Figure 2. All 13 expected lines are observed under pressure. The Raman frequencies are reported in Table I which also shows that, in general, the influence of temperature is not equivalent to that of pressure. Small (or great) slope $d\omega/dT$ sometimes corresponds to great (or small) $d\omega/dP$.

1.2 Discussion

The hydrostatical pressure mainly leads to contraction of the lattice, inversely proportional to the elastic constants $C_{11}$ and $C_{33}$ which are 121 GPa and 156 GPa, respectively, for
The translation of the pressure induced contraction of the lattice is relatively small along the tetragonal axis up to $45^\circ$. So it is expected that increasing pressure may firstly of all result in a rotation of $ZnF_4$ tetrahedra around the tetragonal axis.

Now if we look at the interatomic distances, we note that the distances $d_{Zn-F} = 1.931$ Å (with force constant $A_{Zn-F} \sim 190 \text{N/m}$) and $d_{Ca-F} = 2.336$ Å (with force constant $A_{Ca-F} \sim 70 \text{N/m}$), while the sum of the ionic radii $r_{Zn} + r_F = 1.93$ Å and $r_{Ca} + r_F = 2.45$ Å. On the other hand, the shortest $d_{F-F}$ is 3.064 Å in the tetrahedra and 2.755 Å between the tetrahedra while the sum $r_F + r_F = 2.38$ Å (with force constant $A \sim 10 \text{N/m}$). So it seems that, under pressure, a distortion of the tetrahedra $ZnF_4$ and the polyhedra $CaF_4$ would be easier than the contraction of the latter. In this sense, $CaZnF_4$ is completely different from $YLiF_4$ due to the interatomic distances and the force constants $A_{Li-F} \sim 60 \text{N/m}$ and $A_{Y-F} \sim 130 \text{N/m}$. So the $ZnF_4$ tetrahedron is much more rigid than the $LiF_4$ one. However, a common behavior of these two lattices is the possible pressure induced rotation of the tetrahedra around $c$.

**Pressure dependence of Raman modes**: From Figure 3, we see that the main effect of pressure is the increase of most of the observed frequencies. The mode $Bg$ at 432 $cm^{-1}$ undergoes frequency decrease but it was determined with ambiguity due to its weak Raman intensity. The frequency of the mode $Eg$ at 468 $cm^{-1}$ remains almost constant in the whole pressure range. The pressure dependence ($d\omega/dP$) is given in Table 1. We note a slope change for some frequencies in the vicinity of 1.5-2 GPa. To illustrate this, the slope $d\omega/dP$ is given for two pressure ranges: 0-1.5 GPa and 1.5-7.0 GPa. For some modes, the pressure slopes can be extended to higher pressures. The corresponding atomic movement of each mode is described in Table 1 with the notations of symmetry coordinates given in [3].

**Singularities around 1.5 GPa**: This singularity mainly consists of the change in $d\omega/dP$ of the dispersion of two lines at about 140 $cm^{-1}$ (Ag) and 310 $cm^{-1}$ (Eg). An interesting point here is that the two highest frequencies, Ag (474 $cm^{-1}$) and Eg (468 $cm^{-1}$), separate from each other very rapidly, Ag increases but Eg remains constant up to very high pressure. From Table 1, we see that this Ag mode is a stretching ($F_1"m_1"$) of $ZnF_4$ tetrahedron, while this Eg mode is rather a distortion of $LiF_4$ tetrahedron along $c$ and the translation of $Zn$ on the (001) plane. If we think of the rigidity of $ZnF_4$ tetrahedron, the strong increase of the stretching frequency is logical in the whole pressure range. The relative independence of this Eg mode from pressure can also be understood if we note that the pressure induced contraction of the lattice is relatively small along $c$. As a matter of fact, other $Eg$ modes also have small slope above 1.5 GPa, apart from that at 248 $cm^{-1}$ which principally corresponds to a deformation of $ZnF_4$ tetrahedron on the (001) plane, so that its frequency strongly increases due to the important contraction of $a$ under pressure.

A similar phenomenon has been observed for $YLiF_4$ in our previous work [13] around 6 GPa. This Raman behavior has been interpreted as a result of the lattice stiffening due to increasing pressure. We think that this is not sufficient to account for the rapid slope change at this pressure. A plausible conjecture is that the tetrahedra, in order to relax constraints, begin to rotate around $c$ at certain pressures without significant structure or symmetry change. This rotation up to $45^\circ$ (see figure 1c) takes place at a higher pressure in $YLiF_4$ due to the flexibility of its $LiF_4$ tetrahedra than in $CaZnF_4$ which has very rigid $ZnF_4$ tetrahedra and relatively flexible bonds between the tetrahedra (see above) leading to lower pressure rotation of the latter.

After this rotation, almost all $Bg$ modes increase rapidly, which is a logical consequence of the deformations of $ZnF_4$ tetrahedra on the (001) plane and of the decrease of the interatomic distances on this plane due to the $a$ decrease and the $ZnF_4$ rotation. It should be noted that the $ZnF_4$ rotation vibration mode $Ag$ at 138 $cm^{-1}$ and 202 $cm^{-1}$ have smaller slope after...
ZnF$_4$ rotation, which is comprehensible because the constraint on the rotational movement should be more important before the relaxation due to the ZnF$_4$ rotation.

**Singularities at 10 GPa**: Around this pressure, most lines suddenly disappear (see Figure 2) and almost all observed frequencies are independent of pressure. The samples released from the pressure range 10-16 GPa can still recover their original phase.

**Singularities at 17 GPa**: All lines disappear except for the Eg mode at 464 cm$^{-1}$ (undergoing a constant frequency decrease in all the pressure range with a small slope) and the Bg mode at about 120 cm$^{-1}$. These two intense lines under high pressure remain unchanged when the mono-crystal samples are released from pressure, meaning that this high pressure structure transformation around 17 GPa is irreversible. This irreversible transformation has been also observed in YLiF$_4$ at much higher pressures (around 30 GPa)[13].

### 2 Conclusion

In summary, we have presented the experimental results of the pressure effects on the lattice vibration and Raman spectrum of CaZnF$_4$ up to 17 GPa at which the crystal undergoes an irreversible structural transformation. Some Raman anomalies in the pressure dependence of Raman frequencies have been observed and analyzed according to the atomic movements of different vibration modes. No clear evidence of phase transition has been observed below 17 GPa.

With regard to the mechanism of the possible structure transformations of CaZnF$_4$ under high pressure, no precision can be given for the time being. All the mechanisms including the rotation and deformation of the ZnF$_4$ and CaF$_8$ polyhedra could be invoked. It is worth noticing that the internal binding of the ZnF$_4$ tetrahedra is stronger than the external binding in view of the much stronger internal force constant $A_{Zn-F} \sim 190$ N/m than the external one $A_{Ca-F} \sim 70$ N/m. So if there is a lattice distortion up to 17 GPa, it can be expected that the polyhedra CaF$_8$ would be more deformed than the ZnF$_4$ tetrahedra which subsist above 17 GPa because there are still two intense lines, Eg (464 cm$^{-1}$) and Bg (120 cm$^{-1}$), corresponding to their vibration.

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**Figure captions**

1. (a) unit cell of the fluoride scheelite CaZnF<sub>4</sub> with space group C<sub>6</sub>h<sub>4</sub>, showing the spatial arrangement of individual ZnF<sub>4</sub> tetrahedra (b); (c) projection of the ZnF<sub>4</sub> tetrahedra on the (001) plane and evidence of a CaF<sub>8</sub> double tetrahedron with the Ca ion in the z=0 plane.

2. Pressure influence on the Raman spectra of CaZnF<sub>4</sub>. The top spectrum is from a sample released from above 17 GPa and different from that of the original samples (on the bottom).

3. Pressure dependence of the observed Raman frequencies of CaZnF<sub>4</sub>. The lines are only guides for the eye.
Figure 1
Figure 2,
