VIBRATIONAL SPECTRA OF SYNTHETIC CRANDALLITE-TYPE MINERALS
OPTICAL AND NEUTRON SCATTERING SPECTRA

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\textbf{Abstract:} Optical vibrational and inelastic neutron scattering spectra of some synthetic crandallite-type minerals were measured and discussed, also with respect to the different kinds of disorder in these materials.

Crandallite-type minerals MA\textsubscript{3}(OH)\textsubscript{6}(HPnO\textsubscript{4})(PnO\textsubscript{4}) (M = Ca, Sr, Ba, Pb; Pn = P, As) belong to the alunite supergroup \cite{1} and crystallize in \textit{R} \textsuperscript{3} \textit{m}. Crystal structures of natural crandallite (M = Ca; Pn = P) \cite{2} and goyazite (M = Sr; Pn = P) \cite{3} have been determined, and the D nuclei in synthetic goyazite-d\textsubscript{7} localized by neutron diffraction \cite{4}. Basically, the optical vibrational spectra of crandallites are governed by the same rules as those of alunites (see \textit{e.g.} \cite{5}), modified by the surplus proton in the HPnO\textsubscript{4} group. But, random distribution of HPnO\textsubscript{4} and PnO\textsubscript{4} on equivalent sites leads to perturbation of translational and site symmetries, as with woodhouseites (\textit{e.g.} CaAl\textsubscript{3}(OH)\textsubscript{6}(SO\textsubscript{4})(PO\textsubscript{4})) \cite{6}. Additional disorder is generated by the orientational distribution of the bent P−O−H entity, which is engaged in hydrogen bonds to the OH groups bridging the Al centres, and with crandallite itself by the distribution of Ca to six equivalent sites of lower symmetry than possible in the ideal case with Ca in one fixed special position; consequently, the OH groups surrounding the cavity housing the Ca ion are no longer equivalent with respect to vibrational spectroscopy.

IR spectra of natural crandallites have been published now and then \cite{7} (and references therein), but the discussion is always superficial; Raman spectra have not been reported yet, to our knowledge. Our Raman spectra (514.5 nm excitation) of synthetic crandallite samples show strong fluorescence, and also the FT-Raman spectra display a strong thermal emission background; the Raman spectra of goyazite are clearly better in this respect (Fig. 1). Combined vibrational spectra of mонтite CaHPO\textsubscript{4} and related materials \cite{8} (with references) are useful for the interpretation of the spectra of crandallites.

For the above reasons of disorder the sharp ν(OH) doublet found with alunite KA\textsubscript{3}(OH)\textsubscript{6}(SO\textsubscript{4})\textsubscript{2} \cite{5} is blurred and broadened with crandallite itself, as is the ν(PO−H) band (∼3480 and ∼3170 cm\textsuperscript{-1}, respectively), in both IR and Raman spectra; also, all other bands are broader than with alunite.

In the optical spectra the region around 1000 cm\textsuperscript{-1} is complex due to overlapping of the intense P−O valence vibrations of the groups HPO\textsubscript{4} and PO\textsubscript{4} (degeneracies lifted by site symmetry and its perturbations), which are weak in the inelastic neutron scattering (INS) spectra, except the strong ν(PO−OH) signal (835 cm\textsuperscript{-1}); the latter, together with the somewhat higher torsional mode τ(PO−O−H) (890 cm\textsuperscript{-1}), also appears in the IR and much weaker in the Raman spectrum. Otherwise, the INS spectrum is dominated by the very strong δ modes in the Al\textsubscript{2}OH groups (1200 cm\textsuperscript{-1}), their γ modes appear much weaker at 710 cm\textsuperscript{-1}.

The region below ∼650 cm\textsuperscript{-1} in all spectra comprises various δ modes of HPO\textsubscript{4} and PO\textsubscript{4}, as well as ν(Al−O/OH) vibrations and collective deformations of the layers of linked AlO\textsubscript{2}(OH)\textsubscript{4} octahedra,
which generate a characteristic pattern in the Raman spectra (medium strong bands around 390, 260
and 190 cm\(^{-1}\)), similar to what is found with alunite (narrower bands in this latter case) [5]. These
bands are also present in the INS spectra indicating contributions of proton motions to these frame-
work deformation modes.

Fig. 1: FT Raman spectrum of synthetic goyazite
(fall-off of detector sensitivity above \(\sim 3200\) cm\(^{-1}\))

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