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Use of Raman spectroscopy to characterize and distinguish minerals of the alunite supergroup

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The alunite supergroup consists of more than 50 representative minerals with the general formula $A B_3 (XO_4)_2 (OH)_6$, where A may be occupied by Na, K, Ca, Pb, Ba, Sr, Ce, La, LREE, U ..., B is the trivalent cation, Al^{3+} or Fe^{3+} , but also Cu^{2+} or Zn^{2+} and X is the tetrahedral anion, S, P or As [1, 2]. The minerals of this supergroup form numerous complex solid solutions which crystallize in a rhombohedral system, space group $R\bar{3}m$. The general structure can be described as a combination of $BO_2(OH)_4$ – octahedra and XO_4 – tetrahedra. The ions in A-site are located between the $BO_2(OH)_4$ – octahedral sheets, in an icosahedral site.

The minerals of the alunite supergroup occur in a wide range of geological environments, including metamorphic, sedimentary, magmatic systems and soils. Their large domain of stability, the complex solid solutions between the numerous end-members and their capacity to incorporate heavy metals such as As, Pb, Ba and radionuclides such as Sr, Th, U in their lattice, makes them minerals of interest and potential tools in mineral exploration and resources, but also as traps for pollutants.

Although Raman spectra of synthetic and natural minerals of the alunite supergroup have already been published (e.g.[3, 4]), the attributions of some bands are still debated. It is the same for the interpretations of the wavenumber variations of some vibrational bands, with the elemental composition, which are sometimes superficial.

In this work, acquisition of new Raman spectra was performed on natural minerals differing from one to another by their composition in A-, B- and X-sites. The minerals used are from advanced argillic zones hosted by volcanic rocks in Bulgaria [5] and are defined as K-alunite ($KAl_3(SO_4)_2(OH)_6$), Na-alunite ($NaAl_3(SO_4)_2(OH)_6$), K-jarosite ($KFe_3(SO_4)_2(OH)_6$) and woodhouseite ($CaAl_3(SO_4)(PO_4)(OH)_6$). Their Raman spectra are presented in figure 1. Comparison of these spectra one to one (K-alunite versus Na-rich alunite for Na-K substitution, K-alunite versus K-jarosite for Al-Fe substitution, and K-Na alunite versus woodhouseite for SO_4 - PO_4 substitution) combined with crystalline parameters determined by Sato et al. [6] has brought new insight to the interpretation of the vibrational spectra and band assignments.

Thus, the region below 650 cm^{-1} is complex because of bands due to various deformation modes of XO_4 , as well as vibrations of B-O and B-OH bonds and framework deformations. The region around $1000 - 1200\text{ cm}^{-1}$ is mainly due to XO_4 stretching vibrations and above 3000 cm^{-1} , the bands present are assigned to OH stretching vibrations [4, 7].

The influence of the ions, in A-, B- and X-sites, is highlighted by variations of the position of certain vibrations. The substitutions of K^+ by Na^+ , in A-site, are characterized by wavenumber shifts of the vibrations involving the hydroxyl groups, the B-OH and O-H bonds. The B-OH stretching vibrations occur at 381 and 395 cm^{-1} in the K- and Na-alunite spectra, respectively, whereas two O-H stretching bonds appear at 3480 and 3508 cm^{-1} in K-alunite and at 3459 and 3487 cm^{-1} in Na-alunite. These differences are due to both a modification around the hydroxyl groups, such as the interatomic distances A-OH which are shorter in presence of Na, and a difference in the length of the O-H bonds which is longer in the Na-alunite.

The substitutions of Al^{3+} by Fe^{3+} , in B-site, cause changes in the position of almost all bands toward lower wavenumbers. These differences are due to the size of Fe^{3+} (0.65 \AA [8]) relative to that of Al^{3+}

(0.54 Å [8]) which induces significant structural changes including the B-O, B-OH and X-O bond lengths and the interaction strengths around the hydroxyl groups.

The wavenumbers of the vibrations assigned to XO_4 groups decrease significantly with increasing the size of the ion in X-site. Thus, the PO_4^{3-} vibrations, such as the stretching modes (990 cm^{-1}), occur at lower wavenumbers than SO_4^{2-} (1024 cm^{-1}), as the result of a decrease of the X-O bond force due to a longer P-O bond lengths than S-O bonds. In addition, the present study allows observing that bands are broader in the woodhouseite mineral due to both a disorder in this minerals induced by the presence of different XO_4 groups and a reduction of symmetry of this group which gives a greater number of bands with adjacent positions.

With literature about the Raman spectroscopic characterization of other minerals from the alunite supergroup, it was also possible to generalize the substitution effects on the wavenumbers of several vibrations with other cations in the different sites and to show that this technique could be a powerful tool to identify and distinguish minerals of this supergroup.

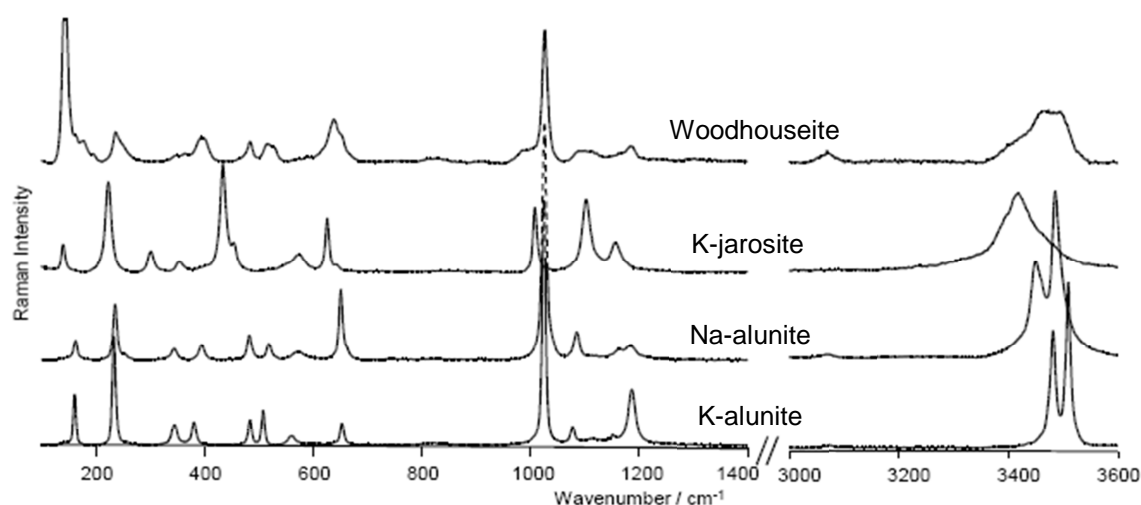


Figure 1 : Raman spectra of natural minerals of the alunite supergroup.

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