Raman spectroscopic investigations of some Tl-sulfosalts containing pyramidal (As,Sb)S$_3$ groups

SHERIF KHARBASH*

Geology Department, Faculty of Science, Suez Canal University, Suez Branch, Suez Governate, El Salam City, 43518, Egypt

ABSTRACT

Oriented single crystals of stibioellisite (Tl$_3$Sb$_5$), parapierrotite (TlSb$_4$S$_8$), weissbergite (TlSb$_5$S$_8$) and lorandite (TlAs$_3$S$_8$) were investigated by polarized Raman spectroscopy. Whereas stibioellisite shows isolated Sb$_5$S$_8$ groups, the rest of the minerals show interconnected pyramidal (As,Sb)S$_3$ groups. Raman bands of the investigated minerals occur between 400 and 10 cm$^{-1}$. The internal vibrations for stibioellisite occur between 350–100 cm$^{-1}$. Those of the interconnected pyramidal groups occur between 350 and 10 cm$^{-1}$ in parapierrotite, 350 and 90 cm$^{-1}$ in weissbergite, and 420 and 130 cm$^{-1}$ in lorandite. Approximate similarities in the spectral features are evident when comparing the spectra of minerals containing XS$_3$ pyramids with the spectra of the minerals in the present study. A clear distinction between Raman spectra of separated and interconnected Sb$_5$S$_8$ groups is not observed.

Keywords: Stibioellisite, parapierrotite, weissbergite, lorandite, Raman spectroscopy, pyramidal (As,Sb)S$_3$ groups

INTRODUCTION

The pyramidal four-atom XS$_3$ group (X = As, Sb, Bi) is responsible for the Raman and infrared (IR) spectral features of many sulfosalts minerals. Raman spectroscopic investigations of minerals containing isolated (i.e., tetrahedrite, Cu$_2$Sb$_3$S$_8$; tennantite, Cu$_2$As$_3$S$_8$; pyrargyrite, Ag$_8$Sb$_4$S$_8$; proustite, Ag$_3$As$_3$S$_8$; stephanite, Ag$_3$Sb$_5$S$_8$; and bournonite, PbCuSbS$_4$) and interconnected (namely, stibnite, Sb$_2$S$_3$; bismuthinite, Bi$_2$S$_3$; and kermesite, Sb$_2$S$_6$O) pyramidal XS$_3$ groups have been recently reported by Kharblish et al. (2007, 2009). In the present work, naturally occurring lorandite (TlAs$_3$S$_8$) and synthetic weissbergite (TlSb$_5$S$_8$), parapierrotite (TlSb$_4$S$_8$) and stibioellisite (Tl$_3$Sb$_5$) (named after Makreski et al. 2004), or thallium thiostibnites (named after Dzhafarov and Babanly 2009) have been investigated by Raman spectroscopic technique.

The pyramidal Sb$_5$S$_8$ groups in stibioellisite show the typical trigonal symmetry (i.e., C$_3$ point group) similar to those in tetrahedrite and pyrargyrite. On the other hand, the As$_3$S$_8$ pyramids in lorandite and the pyramidal Sb$_5$S$_8$ groups in weissbergite and parapierrotite differ from those in tennantite, proustite, tetrahedrite, pyrargyrite, and stibioellisite by the symmetry of the pyramidal group, which is lowered from C$_3$ to C$_3$. Moreover, there are two different As and Sb sites in lorandite and weissbergite, respectively, and six Sb sites in parapierrotite. In addition, the pyramidal (As,Sb)S$_3$ groups in lorandite, weissbergite, and parapierrotite are not isolated but interconnected through common S atoms.

Raman and IR spectroscopic studies dealing with lorandite, weissbergite, and stibioellisite have already been reported (e.g., Rouquette et al. 1988; Šoptrajanov et al. 1993, 1994; Minceva-Sukarova et al. 2003; Makreski et al. 2004). In addition, the RRUFF database project (Downs 2006) contains unpolarized Raman spectra of lorandite and parapierrotite minerals showing, in some cases, the difference between spectra from burned and unburned samples. Despite the IR and Raman spectroscopic studies that have been carried out on the pyramidal XS$_3$ group in lorandite, weissbergite, and stibioellisite, no Raman and IR data on oriented samples of lorandite, weissbergite, and stibioellisite have been previously published. Furthermore, parapierrotite, to the best of my knowledge, has never been investigated by spectroscopic methods.

The goal of the present work is therefore, twofold: (1) to investigate oriented sections of isolated (stibioellisite) and interconnected (parapierrotite, weissbergite, and lorandite) pyramidal XS$_3$ groups by Raman spectroscopy, and (2) to examine the effects of lower symmetry on the pyramidal XS$_3$ groups (lorandite, weissbergite, and parapierrotite) relative to the isolated XS$_3$ pyramids of ideal trigonal symmetry (stibioellisite of the present study and tetrahedrite, tennantite, pyrargyrite, and proustite).

CRYSTALLOGRAPHIC DATA

Table 1 lists selected structural parameters of the investigated minerals. Stibioellisite crystallizes in space group R$3m$. Three formula units are contained in the rhombohedral unit cell (Rey et al. 1984). The structure of stibioellisite (Fig. 1) is comprised of a three dimensional network of Ti-polyhedra together with Sb-pyramids arranged parallel to the c-axis. The Sb$_5$S$_8$ pyramids show the ideal trigonal symmetry (i.e., C$_3$) (Syrbu et al. 2006), with Sb-S interatomic distances 2.431 Å (3$\times$) and S-Sb-S angles of $\sim$93.5° (3$\times$) (Table 1) (Šoptrajanov et al. 1993; Makreski et al. 2004).

Crystal structure investigations of parapierrotite (P$2_1$/n) have been carried out by Engel (1980). Four formula units are contained in the monoclinic unit cell (Fig. 1). The structure consists of corrugated infinite Sb$_5$S$_8$-double layers parallel to [101], which exhibit a deformed NaCl-type structure between the n-glide planes. Along the n-glide planes the NaCl-type...