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Note

THE THERMAL DECOMPOSITION OF NAGYAGITE

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Nagyagite is a very unusual type of mineral. Owing to its great instability it is only found in a few mine districts of the world. The occurrence of nagyagite at Parallon Negro (Argentina) was reported for the first time in 1975 [1]. The formula was determined as $Pb_5Au(Te,Sb)_4S_{5.8}$ [1]. The ore is made up of various manganese oxides and free gold. This element is found in a small quantity and is associated with thin veinlets of quartz which cross the mineral of economic interest. Mineral processing transforms the ore into other products, which are suitable for subsequent metallurgical treatments. This allows the extraction of the desired metal. From this point of view, the study of the thermal treatment is very important for the understanding of metallurgical implications.

The results found for the formal charge of the mineral studied are not consistent as occurs in other minerals containing a high proportion of metallic and semi-metallic elements [2]. However, the X-ray data are in excellent accordance with the literature values [1,3,4]. Nagyagite itself does not produce any signal during IR spectroscopy. However, it shows a very interesting thermal behaviour, which can be clearly followed using this technique.

EXPERIMENTAL

The purity of the sample was checked by microscopic, electron microprobe and standard chemical analyses. Thermogravimetric and differential thermal analyses were carried out on a Rigaku thermoanalyzer (type YLDG/CN 8002 L2) using a chromel–alumel thermoelement and a constant air flow of 0.41 l min^{-1}. The heating rate was 10 °C min^{-1} and α-Al_2O_3 was used as DTA standard. The temperature was raised to 700 °C.

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Additional thermal studies were carried out in a furnace in air, using a Pt crucible. The heated samples were investigated by X-ray diffractometry and fundamentally by IR spectroscopy. The IR spectra were recorded on a Perkin-Elmer 580-B spectrophotometer using the KBr-pellet technique. The Raman spectrum was obtained with a Spex-Ramalog 1403 double monochromator spectrometer, equipped with a Scamp data processor. The 514.5 nm line of an argon-ion laser was used for the excitation of the sample.

RESULTS AND DISCUSSION

Typical TG and DTA curves are shown in Fig. 1. According to these results an oxidative process occurs between 300 and 500 ° C. The percentage gain in weight, associated with the two exothermic peaks at 360–378 and 440 ° C, is 16.72%. The values of 6.43% and 10.38% after the first and the second peaks, respectively, agree with the formation of Sb_2O_3 and TeO_2 oxides (theoretical value, 6.30%) and with a partial oxidation of lead sulphide (theoretical value, 10.48%). The presence of $PbSO_4$ at 380 ° C in the IR spectrum, as very weak, broad bands, shows that two or more oxidative processes can occur simultaneously from 330 ° C.

It is well known that the oxidation reaction of natural stibnite Sb_2S_3 begins at 290 ° C and continues up to 500 ° C. The oxidation temperature for galena (PbS) is also near 300 ° C and this reaction continues up to 500 ° C [5].

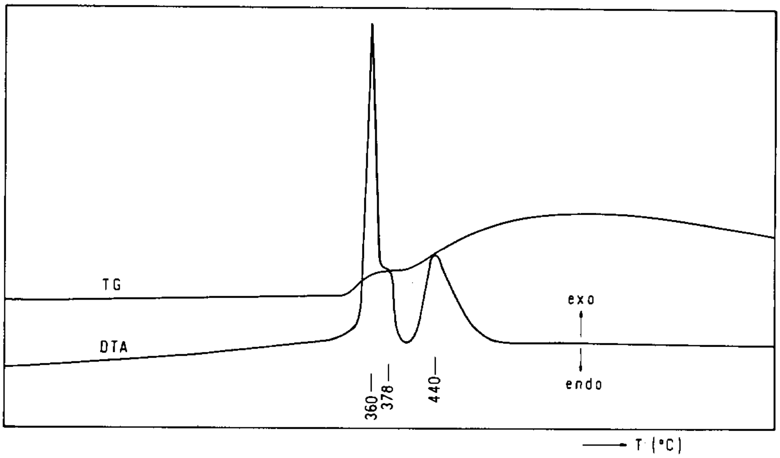

Fig. 1. Typical TG and DTA plots of natural nagyagite.

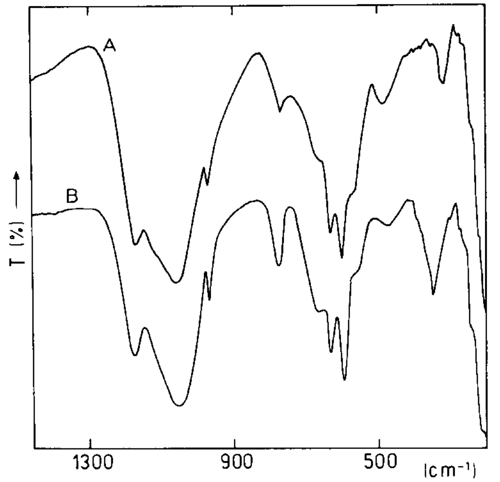

Fig. 2. IR spectra: A, nagyagite heated up to 700 ° C and B, physical mixture of TeO_2, Sb_2O_3, PbS and $PbSO_4$ according to the suggested stoichiometry of eqn. (1).

The experimental results allow the formulation of the following oxidative scheme

$$Pb_{10}Au_2Te_6Sb_2S_{11.6} \xrightarrow{O_2} 4.5PbS + 5.5PbSO_4 + Sb_2O_3 + 2Au + 6TeO_2 + 1.6SO_2 \quad (1)$$

Figure 2A shows the IR spectrum of nagyagite heated up to 700 ° C in air. A physical mixture of the phases, in the proportion indicated by eqn. (1) was also analyzed by IR spectroscopy, in order to characterize the decomposition residue and to explain the course of the pyrolysis process (Fig. 2B). Both IR spectra show the presence of characteristic bands of the S–O vibrations of the SO_4 groups. A strong band with peaks at 1175, 1107 and 1050 cm^{-1} corresponds to the splitting of the ν_3 antisymmetric stretching of the S–O vibrations (from SO_4 groups in the site symmetry C_s).

The bands at 970 cm^{-1} in the IR spectrum and at 973 cm^{-1} in the Raman spectrum (as a very strong, sharp line) are assigned to the ν_1 S–O symmetric stretching mode. A similar behaviour is observed in pure $PbSO_4$ (baryte structure) [6]. The two bands at 597 and 632 cm^{-1} can be assigned to the ν_4 bending mode of the SO_4 groups. Finally, a weak band at 450 cm^{-1} can be assigned to the ν_2 mode.

The bands centred at 770, 468 and 350 cm^{-1} and the shoulders at 668 and 550 cm^{-1} can be attributed to the Te–O and Sb–O vibrations. The corresponding TeO_2 and Sb_2O_3 oxides present more intense bands at 314, 334, 648, 714, 760 cm^{-1} and 382, 482, 550, 590, 685 and 740 cm^{-1}, respectively [7–9]. The spectrum (Fig. 2B) shows that the coexistence of the suggested phases is consistent with the experimental products of the thermal treatment of natural nagyagite.

Further heating shows a slight and progressive loss in weight. This behaviour is characteristic of the sublimation of TeO_2 and Sb_2O_3. Some complicated interactions between the PbS and $PbSO_4$ compounds, occur beyond 810–820 °C. One of the phases of a well-known metallurgical procedure is recognized in the present study.

Another interesting situation is observed when nagyagite is heated in air up to 900 °C. At this temperature the TeO_2 and Sb_2O_3 oxides are totally sublimated. The formation of a metallic residue of Pb and Au is finally observed, according to the following equation

$$4.5PbS + 5.5PbSO_4 + Sb_2O_3 + 2Au + 6TeO_2$$

$$\xrightarrow{900\,^{\circ}C} 8Pb + 2Au + 10SO_2\uparrow + 2PbO + Sb_2O_3\uparrow + 6TeO_2\uparrow$$

This interpretation is supported by the IR spectrum which only shows the bands assignable to the Pb–O stretchings in the low region (below 470 cm^{-1}).

It is concluded that IR and Raman spectroscopy are very useful techniques for the investigation of the thermal degradation of this type of mineral. The presence of bands, which do not appear in the original substance, allows the interpretation of the pyrolysis process.

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