

FIG. 3. Stereopair of Linde zeolite type A model.

In producing a model, the tetrahedra are joined by 1/2-inch sleeves of plastic tubing. A simple way to cut uniform lengths of tubing is to mark off 1/2 inch on a board and cut successive lengths with a single-edge razor blade, feeding the tubing with one hand and cutting with the other. The joint itself is best made by initially overlapping the ends of the tetrahedra a little bit inside the sleeve and then pulling them back slightly to make a smooth junction.

The stereopair in Figure 3 shows an eight-unit framework model of Linde zeolite type A constructed by this method. The total cost of materials in this model is 55¢.

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#### INFRARED SPECTRA OF PHOSPHATE MINERALS: SPLITTING AND FREQUENCY SHIFTS ASSOCIATED WITH SUBSTITUTION OF $\text{PO}_4^{3-}$ FOR $\text{AsO}_4^{3-}$ IN MIMETITE ( $\text{Pb}_3(\text{AsO}_4)_3\text{Cl}$ )

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An earlier paper (Adler, 1964) presented infrared absorption data on the  $\nu_3$  and  $\nu_1$  vibrational modes of apatite, pyromorphite, mimetite,

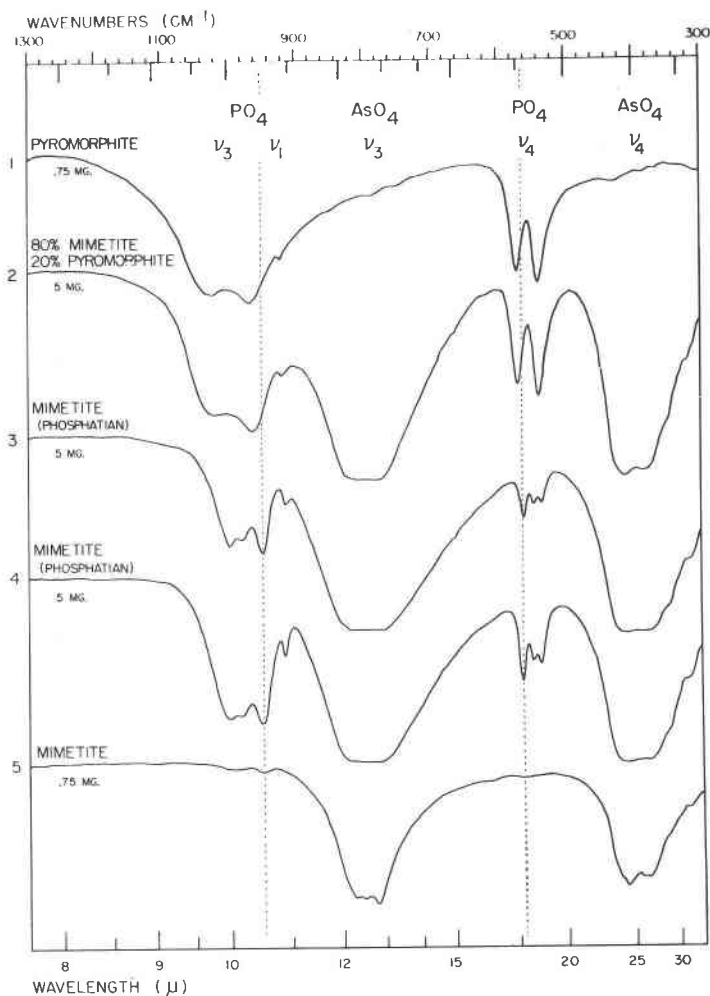


FIG. 1. Infrared absorption curves illustrating the effects of phosphate substitution in the mimetite lattice. 1. Pyromorphite, Phoenixville, Pa. 12572; 2. 80% mimetite, Chihuahua, Mex. C5879 and 20% pyromorphite 12572; 3. mimetite (phosphatian), Zacatecas, Mex. R12470; 4. mimetite (phosphatian), Cumberland, Eng. C4130; 5. mimetite, Tsumeb, S.W. Africa R12415.

and vanadinite. Investigation of these minerals at longer wavelengths has revealed two interesting and undescribed spectral features of mineralogical interest, namely the  $\nu_4$  frequency shift and splitting associated with substitution of  $\text{PO}_4^{3-}$  for  $\text{AsO}_4^{3-}$  in the mimetite lattice.

The absorption characteristics of the  $\nu_4$  and  $\nu_1$  vibrational modes of the  $\text{PO}_4^{3-}$  ion substituting in mimetite have been discussed (Adler,

1964) and need not be reviewed in detail here. It will suffice to state that substitution of  $\text{PO}_4^{3-}$  for  $\text{AsO}_4^{3-}$  characteristically decreases the vibrational frequencies of  $\nu_3$  and  $\nu_1$  of the  $\text{PO}_4^{3-}$  group slightly below the frequencies of these modes as observed for pyromorphite. The present investigation shows that  $\nu_4$  responds similarly, as expected. The frequency shifts of  $\nu_3$ ,  $\nu_1$ , and  $\nu_4$  are apparent from a comparison of curves 1 and 2 with curves 3 and 4 in Figure 1 and from corresponding absorption data in Table 1.

In addition to the frequency shift, the  $\nu_4$  mode of  $\text{PO}_4^{3-}$  responds to substitution by splitting into three bands. This can be attributed to complete resolution of the degeneracy ordinarily associated with the Td (ideal tetrahedral) configuration of  $\text{XO}_4^{3-}$  molecules. The  $\nu_4$  mode of tetrahedral ions is triply degenerate and gives rise to either one, two, or

TABLE 1. ABSORPTION FREQUENCIES FOR APATITE, PYROMORPHITE, MIMETITE, VANADINITE, AND PHOSPHATIAN MIMETITE

Vibrational mode	$\text{PO}_4^{3-}$ in Apatite (R5224) <sup>a</sup>	$\text{PO}_4^{3-}$ in Pyromorphite (12572)	$\text{PO}_4^{3-}$ in Mimetite (R12470 & C4130)	$\text{AsO}_4^{3-}$ in Mimetite (R12415)	$\text{VO}_4^{3-}$ in Vanadinite (R8741)
$\nu_3$ ( $\text{cm}^{-1}$ )	1089, 1038	1026, 967	1000, 982, 951	815, 803, 783	800, 736
$\nu_3$ ( $\mu\text{m}$ )	9.18, 9.63	9.75, 10.34	10.00, 10.18, 10.52	12.27, 12.45, 12.77	12.50, 13.59
$\nu_1$ ( $\text{cm}^{-1}$ )	960	922	917	not detected	not detected
$\nu_1$ ( $\mu\text{m}$ )	10.42	10.85	10.91		
$\nu_4$ ( $\text{cm}^{-1}$ )	600, 569	570, 539	564, 548, 537	~ 415, 385	~ 415, 370, 315
$\nu_4$ ( $\mu\text{m}$ )	16.67, 17.57	17.54, 18.55	17.73, 18.25, 18.62	~24.10, 25.97	~24.10, 27.03, 31.75

<sup>a</sup> U. S. National Museum number.

three vibrational bands depending upon the symmetry configuration of the ion and its surrounding field. Ordinarily, the more asymmetrical the ion, the larger the number of vibrational bands. The relationship between the symmetry of  $\text{XO}_4^{3-}$  molecules and number of allowable bands is described in earlier papers (Adler, 1964; Adler and Kerr, 1965).

The appearance of three  $\nu_4$   $\text{PO}_4^{3-}$  bands in the phosphatian mimetite spectrum (Fig. 1, curve 3) and only two in the pyromorphite spectrum (Fig. 1, curve 1) suggests at first that the symmetry of  $\text{PO}_4^{3-}$  is lowered when this ion replaces the larger  $\text{AsO}_4^{3-}$  ion. However, X-ray data by Posner *et al.*, (1958) indicate that the  $\text{PO}_4^{3-}$  group in apatite, and therefore presumably in pyromorphite, has Cs molecular symmetry, which should completely resolve the three  $\nu_4$  modes. The fact that only two bands are seen in the pyromorphite spectrum suggests that the undetected band may lie so close to one of the two visible bands that it was not resolved by the instrument. If this interpretation is correct, it would

appear that substitution of the  $\text{PO}_4^{3-}$  ion on the larger  $\text{AsO}_4^{3-}$  site exaggerates the Cs asymmetry of the ion sufficiently to cause a separation of the three  $\nu_4$  bands.

The splitting of  $\nu_4$  facilitates the recognition of  $\text{PO}_4^{3-}$  substitution in mimetite. For example, partial replacement of Pb in the phosphatian mimetite lattice with a cation of smaller radius, Ca for instance, would cause the vibrations of  $\text{PO}_4^{3-}$  to shift to higher frequencies where they might coincide with the corresponding bands of pyromorphite intergrown with mimetite and, therefore, be misinterpreted as representing such an intergrowth. Examination of  $\nu_4$  for splitting nicely resolves the problem presented by such a circumstance.

The shift of the  $\nu_3$ ,  $\nu_1$  and  $\nu_4$  modes of  $\text{PO}_4^{3-}$  to lower frequencies on substitution of phosphate in mimetite is probably caused by expansion of the P-O distance as the smaller phosphate groups are substituted for the larger arsenate ions, for, theoretically, the vibrational frequencies should decrease with increasing bond length.

Attention is also called to the fact that the  $\nu_3$  mode of the substituting  $\text{PO}_4^{3-}$  ion in mimetite is resolved into three component bands (Fig. 1, curves 3 & 4). Only two bands were recorded previously (Adler, 1964). Both  $\nu_3$  and  $\nu_4$  have a maximum of three allowable infrared active vibrational modes for  $\text{XO}_4^{3-}$  groups of low symmetry.

The absorption frequency and wavelength data for apatite and for the  $\nu_3$ ,  $\nu_1$ , and  $\nu_4$  bands of  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$  and  $\text{VO}_4^{3-}$  in pyromorphite, mimetite, and vanadinite, respectively, and of  $\text{PO}_4^{3-}$  substituting in mimetite are given in Table 1. The  $\nu_2$  mode of  $\text{PO}_4^{3-}$  occurs below  $380 \text{ cm}^{-1}$  in the apatite spectrum where it is manifest by broad absorption extending beyond the frequency range that could be examined with the instrument. The  $\nu_2$  absorption was not observed for either  $\text{PO}_4^{3-}$  in pyromorphite,  $\text{AsO}_4^{3-}$  in mimetite, or  $\text{VO}_4^{3-}$  in vanadinite and probably occurs below  $200 \text{ cm}^{-1}$ .

The spectra shown here were obtained on the Perkin-Elmer spectrophotometer, Model 621, using finely ground sample material imbedded in CsI discs. An instrument scale factor of 2.5 was used. Sample quantities are given in Figure 1. The larger samples produce better resolution of weak  $\text{PO}_4^{3-}$  bands.

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#### HYDROTHERMAL INVESTIGATION OF $\text{GeO}_2$

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#### INTRODUCTION

Germania ( $\text{GeO}_2$ ) is an interesting compound from a crystalchemical viewpoint because it is a dioxide exhibiting the two important structures: the rutile-type with six-coordinated cation and quartz-type with four-coordinated cation. The polymorphism in  $\text{GeO}_2$  under atmospheric pressure was first studied by Laubengayer and Morton (1932) and Sarver (1961). According to them, the rutile-type  $\text{GeO}_2$  is stable below  $1050^\circ\text{C}$  above which temperature it transforms slowly to the quartz-type which melts at  $1116^\circ\text{C}$ . The reverse process can only be completed in the presence of a mineralizer. Several investigations have questioned the transformation temperature. Shafer and Roy (1957) reported that it should be lowered to  $1007^\circ\text{C}$  under atmospheric pressure. This value was later verified by Robbins and Levin (1959), and Majumdar (1958) placed the transformation temperature at  $1002^\circ\text{C}$ .

#### EXPERIMENTAL METHOD

Work on the stability relations in the system  $\text{GeO}_2\text{-H}_2\text{O}$  was undertaken to provide basic information on the conditions for hydrothermal growing the polymorphs. Materials used were reagent grade  $\text{GeO}_2$  with the quartz-type structure, laboratory-prepared  $\text{GeO}_2$  glass, and hydrothermally synthesized rutile-type  $\text{GeO}_2$ . Each was contained in a separate platinum capsule. The  $p$ - $t$  field of interest in the system necessitated low-water content in the charge. The required amount of water was obtained by filling each capsule with water vapor at  $100^\circ\text{C}$  and 1 atmospheric pressure. This was done by placing a drop of water at the bottom of the capsule, adding the  $\text{GeO}_2$  starting material, and suspending a set of these capsules over boiling water for periods of two to three hours. The water in the capsule evaporated in the steam bath, thereby replacing the air in the capsule with water vapor. The capsules were removed singly, and immediately crimped shut and welded. They were usually bloated at the end of the run, demonstrating that a vapor phase was present, and the water added was in excess of the amount required to saturate a glass if formed. In the few cases where the capsule had collapsed, leaks were detected and the runs were always repeated. Three capsules, each containing one of the three different starting materials, were