

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¢.

REFERENCES

- BRECK, D. W. (1964) Crystalline molecular sieves. *J. Chem. Educ.*, **41**, 678-689.
 FIESER, L. F. (1963) Plastic Dreiding models. *J. Chem. Educ.*, **40**, 457-459.
 MEIER, W. M. (1960) A new way of representing silicate frameworks. *Z. Kristallogr.*, **114**, 478-480.
 SMITH, D. K. (1960) Bibliography on molecular and crystal structure models. *Nat. Bur. Stand. Mono.*, **14**.
 TILTON, L. W. (1957) Noncrystal ionic model for silica glass. *J. Res. Nat. Bur. Stand.*, **59**, 139.

THE AMERICAN MINERALOGIST, VOL. 53, SEPTEMBER-OCTOBER, 1968

INFRARED SPECTRA OF PHOSPHATE MINERALS: SPLITTING AND FREQUENCY SHIFTS ASSOCIATED WITH SUBSTITUTION OF PO_4^{3-} FOR 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 ν_3 and ν_1 vibrational modes of apatite, pyromorphite, mimetite,

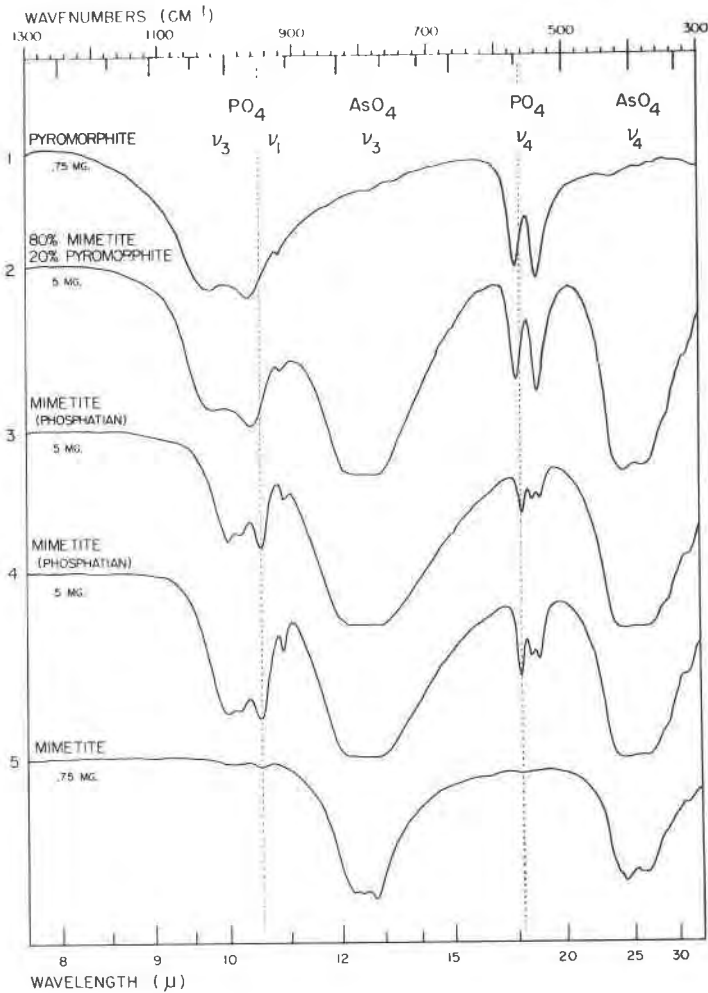


FIG. 1. Infrared absorption curves illustrating the effects of phosphate substitution in the mimetite lattice. 1. Pyromorphite, Phoenixville, Pa. 12572; 2. 80% mimetite, Chihuahua, Mex. C5879 and 20% pyromorphite 12572; 3. mimetite (phosphatian), Zacatecas, Mex. R12470; 4. mimetite (phosphatian), Cumberland, 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 ν_4 frequency shift and splitting associated with substitution of PO_4^{3-} for AsO_4^{3-} in the mimetite lattice.

The absorption characteristics of the ν_4 and ν_1 vibrational modes of the 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 PO_4^{3-} for AsO_4^{3-} characteristically decreases the vibrational frequencies of ν_3 and ν_1 of the PO_4^{3-} group slightly below the frequencies of these modes as observed for pyromorphite. The present investigation shows that ν_4 responds similarly, as expected. The frequency shifts of ν_3 , ν_1 , and ν_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 ν_4 mode of 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 XO_4^{3-} molecules. The ν_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 | PO_4^{3-} in Apatite (R5224) ^a | PO_4^{3-} in Pyromorphite (12572) | PO_4^{3-} in Mimetite (R12470 & C4130) | AsO_4^{3-} in Mimetite (R12415) | VO_4^{3-} in Vanadinite (R8741) |
|------------------------------|--|--|---|--|--|
| ν_3 (cm^{-1}) | 1089, 1038 | 1026, 967 | 1000, 982, 951 | 815, 803, 783 | 800, 736 |
| ν_3 (μm) | 9.18, 9.63 | 9.75, 10.34 | 10.00, 10.18, 10.52 | 12.27, 12.45, 12.77 | 12.50, 13.59 |
| ν_1 (cm^{-1}) | 960 | 922 | 917 | not detected | not detected |
| ν_1 (μm) | 10.42 | 10.85 | 10.91 | | |
| ν_4 (cm^{-1}) | 600, 569 | 570, 539 | 564, 548, 537 | ~ 415, 385 | ~ 415, 370, 315 |
| ν_4 (μm) | 16.67, 17.57 | 17.54, 18.55 | 17.73, 18.25, 18.62 | ~24.10, 25.97 | ~24.10, 27.03, 31.75 |

^a 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 XO_4^{3-} molecules and number of allowable bands is described in earlier papers (Adler, 1964; Adler and Kerr, 1965).

The appearance of three ν_4 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 PO_4^{3-} is lowered when this ion replaces the larger AsO_4^{3-} ion. However, X-ray data by Posner *et al.*, (1958) indicate that the PO_4^{3-} group in apatite, and therefore presumably in pyromorphite, has Cs molecular symmetry, which should completely resolve the three ν_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 PO_4^{3-} ion on the larger AsO_4^{3-} site exaggerates the Cs asymmetry of the ion sufficiently to cause a separation of the three ν_4 bands.

The splitting of ν_4 facilitates the recognition of 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 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 ν_4 for splitting nicely resolves the problem presented by such a circumstance.

The shift of the ν_3 , ν_1 and ν_4 modes of 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 ν_3 mode of the substituting 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 ν_3 and ν_4 have a maximum of three allowable infrared active vibrational modes for XO_4^{3-} groups of low symmetry.

The absorption frequency and wavelength data for apatite and for the ν_3 , ν_1 , and ν_4 bands of PO_4^{3-} , AsO_4^{3-} and VO_4^{3-} in pyromorphite, mimetite, and vanadinite, respectively, and of PO_4^{3-} substituting in mimetite are given in Table 1. The ν_2 mode of PO_4^{3-} occurs below 380 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 ν_2 absorption was not observed for either PO_4^{3-} in pyromorphite, AsO_4^{3-} in mimetite, or VO_4^{3-} in vanadinite and probably occurs below 200 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 PO_4^{3-} bands.

The writer is indebted to Dr. Irving Breger and the U. S. Geological Survey for the use of the spectrophotometer and to Dr. Peter Zubovic of the U. S. Geological Survey for his help in familiarizing the writer with the instrument.

REFERENCES

- ADLER, H. H. (1964) Infrared spectra of phosphate minerals: Symmetry and substitutional effects in the pyromorphite series. *Amer. Mineral.*, **49**, 1002-1015.

- AND P. F. KERR (1965) Variations in infrared spectra, molecular symmetry and site symmetry of sulfate minerals. *Amer. Mineral.*, **50**, 132-147.
- POSNER, A. S., A. PERLOFF, AND A. F. DIORIO (1958) Refinement of the hydroxyapatite structure. *Acta Crystallogr.*, **11**, 308.

THE AMERICAN MINERALOGIST, VOL. 53, SEPTEMBER-OCTOBER, 1968

HYDROTHERMAL INVESTIGATION OF GeO_2

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INTRODUCTION

Germania (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 GeO_2 under atmospheric pressure was first studied by Laubengayer and Morton (1932) and Sarver (1961). According to them, the rutile-type GeO_2 is stable below 1050°C above which temperature it transforms slowly to the quartz-type which melts at 1116°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°C under atmospheric pressure. This value was later verified by Robbins and Levin (1959), and Majumdar (1958) placed the transformation temperature at 1002°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 GeO_2 with the quartz-type structure, laboratory-prepared GeO_2 glass, and hydrothermally synthesized rutile-type 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°C and 1 atmospheric pressure. This was done by placing a drop of water at the bottom of the capsule, adding the 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