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SYNTHETIC POLLUCITES IN THE SYSTEM $Cs_2O \cdot Al_2O_3 \cdot 4SiO_2$–$Cs_2O \cdot Fe_2O_3 \cdot 4SiO_2$–$H_2O$— THEIR PHASE RELATIONSHIP AND PHYSICAL PROPERTIES

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ABSTRACT

An *x*-ray and optical investigation has been made of synthetic zeolites in the system pollucite ($Cs_2Al_2Si_4O_{12} \cdot Aq$)—the iron analog ($Cs_2Fe_2Si_4O_{12} \cdot Aq$), crystallized at 450° C. and 1,000 kg/cm^2 water vapor pressure. Refractive indices and lattice dimensions of these zeolites show a linear relationship with composition. From the results of the magnetic susceptibility measurements, the specimens seem to behave paramagnetically in the temperature range from liquid nitrogen to room temperature.

INTRODUCTION

Recently, Kopp *et al.* (1963) reported that they synthesized an iron analog of pollucite ($Cs_2Fe_2Si_4O_{12} \cdot Aq$) which is isomorphous with pollucite. This is of interest because a few data on the materials containing iron in tetrahedral coordination with oxygen have been published.

They also have reported that their product is slightly magnetic. It is an interesting problem whether the product behaves ferromagnetically or not, since no ferromagnetic silicate mineral has been found in nature.

This paper presents the results of some optical and powder diffraction studies of hydrothermally synthesized zeolites varying in composition from pure pollucite ($Cs_2Al_2Si_4O_{12} \cdot Aq$) to its iron analog ($Cs_2Fe_2Si_4O_{12} \cdot Aq$) to discuss the solid solubility in this series, and also the results of magnetic susceptibility measurements of these products.

HYDROTHERMAL PREPARATION

The pollucite samples used in this study were synthesized hydrothermally at 450° C. under a water vapor pressure of 1,000 kg/cm^2. The type of pressure vessel used was the test-tube bomb (Roy and Tuttle, 1956).

Nine kinds of gels were prepared as starting materials in this investigation. Compositions were made up at 12.5 mole per cent intervals between the two end members. The compositions of gel mixtures are listed in Table I.

The gel mixtures were prepared by mixing calculated amounts of "Ludox" (duPont Co. trade name) SiO_2 sol, standarized Al^{3+} and Fe^{3+} nitrates and CsOH solutions, and evaporating to dryness. They were then fired to about 600° C. for 15 minutes until the nitrates were com-

TABLE I. COMPOSITION OF GEL MIXTURES

Cs_2O	Al_2O_3	Fe_2O_3	SiO_2
1	1	0	4
1	7/8	1/8	4
1	3/4	1/4	4
1	5/8	3/8	4
1	1/2	1/2	4
1	3/8	5/8	4
1	1/4	3/4	4
1	1/8	7/8	4
1	0	1	4

pletely decomposed. The products were ground to fine powders, and detected to be x-ray amorphous.

Approximately 30 mg of the charges were sealed in silver tubes with a small amount of distilled water. After run for 3 days, the charge was quenched. The products were then powdered and their physical properties were examined. When observed under the microscope, no unreacted gel could be observed and the products consisted of single phase crystals. The color change from white to reddish brown in the materials was related to a change in iron content. Since all the runs were made in sealed tubes as mentioned previously, the pollucites synthesized in this way must have the same composition as the gel from which they crystallized, although some amount of water should be added.

PHYSICAL DATA

Optical properties. The synthetic pollucites appears as small irregular grains, never more than 20 microns in diameter and rarely with crystalline outlines. The crystals were found to be isotropic. The refractive indices of synthetic pollucites of different compositions were measured by the oil immersion method. They are given in Table II and plotted on Fig. 1.

The refractive indices increase linearly with increasing Fe^{3+} content.

TABLE II. REFRACTIVE INDEX AND LATTICE CONSTANT AGAINST COMPOSITION FOR SYNTHETIC POLLUCITES

	$A_{100}F_0$ (pollucite)	$A_{87.5}F_{12.5}$	$A_{75}F_{25}$	$A_{62.5}F_{37.5}$	$A_{50}F_{50}$	$A_{37.5}F_{62.5}$	$A_{25}F_{75}$	$A_{12.5}F_{87.5}$	A_0F_{100} (iron analog)
n	1.525	—	1.543	—	1.565	—	1.582	—	1.609
a (Å)	13.653	13.670	13.696	13.718	13.737	13.758	13.768	13.803	13.816

The limit of error is ±0.002. The values of the both end members are somewhat higher than those given by Kopp *et al.* (1.520±0.002 and 1.572±0.002) (1963).

X-ray diffraction. Smear mounts of the charges were prepared for obtaining the *x*-ray powder diffraction patterns of the pollucites. The diffractometer was set to scan at $\frac{1}{4}°2\theta$ per minute in the region from $10°2\theta$ to $55°2\theta$. In all cases CuKα radiation was used.

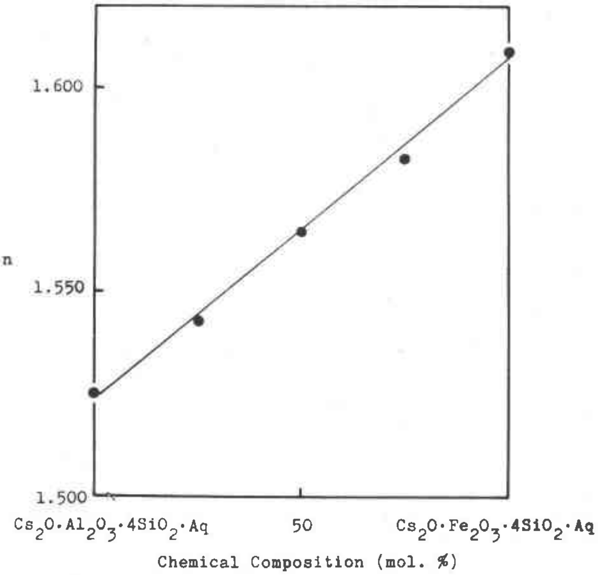

FIG. 1. Relationship between the refractive index and the chemical composition of the synthetic pollucites.

Table III lists the d-spacings and diffracted *x*-ray intensities for pure synthetic pollucite and its iron analog, together with that for natural pollucite by Kopp *et al.* (1963), showing very few differences in these values among the natural and the synthetic crystals. The d-spacings and intensities for the intermediate pollucites were also identical with those of the end members. These results indicate that the iron analog and intermediate pollucites are isomorphous with the pure pollucite.

Assuming each product has a cubic symmetry, their lattice constants were measured from the 321, 400, 332, 521, 440, 532, 631, 721, 651 reflections by using quartz as internal standard. The values were given in Table II and plotted on Fig. 2, where the linear variation of cell constant with composition is seen. These results are further proof that there is complete solid solution between the two end members.

Magnetic measurements. The magnetic susceptibility of the products was measured in the temperature range from liquid nitrogen to room temperature. Some examples of the measurement is illustrated in Fig. 3, where the changes of the gram susceptibility with temperature are plotted on $1/\chi_{gr}$—T diagram. As $1/\chi_{gr}$ changes linearly with T, these specimens seem to behave paramagnetically in the above-mentioned temperature range.

TABLE III. *X*-RAY DIFFRACTION PATTERNS OF POLLUCITE AND ITS IRON ANALOG

Natural pollucite (after Kopp *et al.*, 1963)		Synthetic pollucite		Synthetic iron analog		hkl
d(Å)	I	d(Å)	I	d(Å)	I	
5.55	W	5.54	1	—	—	211
4.818	W	—	—	—	—	220
3.652	S	3.648	5	3.690	5	321
3.421	VS	3.411	10	3.453	10	400
3.048	VW	—	—	—	—	420
2.907	VS	2.910	4	2.942	5	332
2.674	W	—	—	—	—	431
2.492	W	2.491	1	—	—	521
2.406	S	2.412	4	2.442	3	440
2.211	M	2.216	1	2.236	2	532
2.007	MW	2.013	1	2.036	1	631
1.970	MW	—	—	—	—	444
1.886	W	—	—	—	—	640
1.855	S	1.857	1	1.879	1	721
1.731	S	1.734	1	1.753	1	651

CONSIDERATION OF RESULTS

Summarizing the above experimental results, it is evident that there is a complete solid solution series between pollucite ($Cs_2Al_2Si_4O_{12} \cdot Aq$) and its iron analog ($Cs_2Fe_2Si_4O_{12} \cdot Aq$) under the experimental conditions used in this study. This is proved by the fact that there is only one pollucite phase throughout the series, and also by the linear relationships between the lattice constant and the refractive index against composition as illustrated in Figs. 1 and 2.

Kopp *et al.* (1963) have reported that the refractive index and the lattice constant of the iron analog of pollucite, which they synthesized,

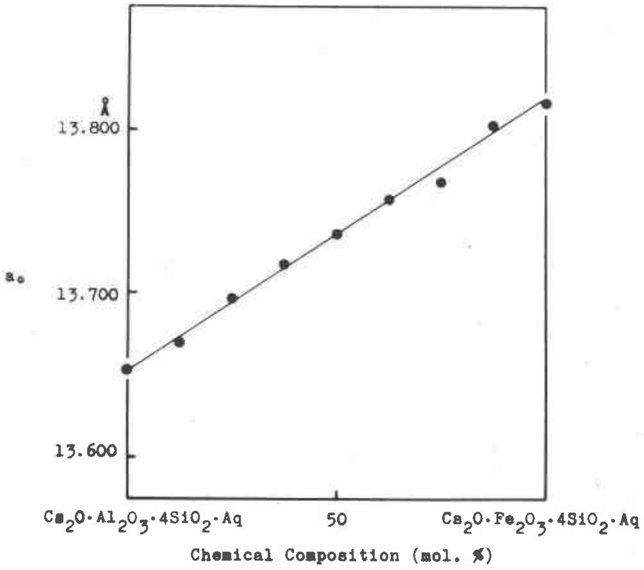

FIG. 2. Relationship between the lattice dimension and the chemical composition of the synthetic pollucites.

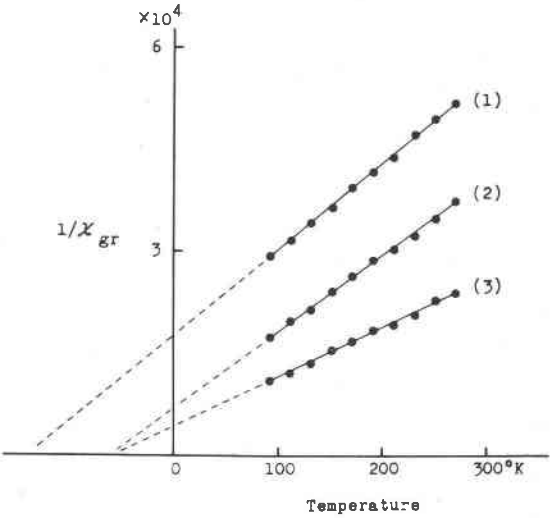

FIG. 3. $1/\chi_{gr}$ *vs* temperature relation in some of the synthetic pollucites (χ_{gr}: gram susceptibility)

(1) : $Cs_2O \cdot (Al_2O_3)_{\frac{3}{4}} \cdot (Fe_2O_3)_{\frac{1}{4}} \cdot 4SiO_2 \cdot Aq$
(2) : $Cs_2O \cdot (Al_2O_3)_{\frac{1}{2}} \cdot (Fe_2O_3)_{\frac{1}{2}} \cdot 4SiO_2 \cdot Aq$
(3) : $CsO_2 \cdot Fe_2O_3 \cdot 4SiO_2 \cdot Aq$

are 1.572±0.002 and 13.66±0.03Å respectively. In the present investigation these values do not correspond to those of Fe^{3+} end member but are close to those of $Cs_2O \cdot (Al_2O_3)_{\frac{1}{2}} \cdot (Fe_2O_3)_{\frac{1}{2}} \cdot 4SiO_2 \cdot Aq$.

These authors also have reported that their product is slightly magnetic. The present experiment shows that the products behave paramagnetically at temperature above liquid nitrogen and no trace of ferro or ferrimagnetism is observed.

The iron analog of pollucite prepared by Kopp *et al.* seems to contain some amount of iron oxide such as Fe_3O_4 as an impurity which behave ferrimagnetically.

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