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Low Temperature Synthesis of Zinc-Phlogopite

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Abstract

A zinc-phlogopite has been synthesized at temperatures of 85°C and lower by crystallization of a reactive gel. Low concentrations of zinc oxide result in cocrystallization of the zeolite herschelite with zinc phlogopite. A comparison is given of synthesis conditions and X-ray data for various phlogopite phases.

Introduction

Commercial syntheses of phlogopite have been studied with an emphasis on the production of fluorophlogopites, since these can be formed at ambient pressure by solid state reaction, or by fusion at temperatures in excess of 1387°C followed by slow cooling. In comparison, the hydroxyl mica must usually be synthesized in a closed system under water vapor pressure which provides hydroxyl ions for the reaction and, in addition, prevents the decomposition of the hydroxyl mica which is not as stable as the fluorophlogopite on heating at elevated temperatures and atmospheric pressure (Shell, 1967; Yoder and Eugster, 1954).

In their study of hendricksite, $K(Zn,Mn)_3(Si_3Al)O_{10}(OH)_2$, Frondel and Ito (1966) report the hydrothermal synthesis of a zinc-mica. A similar hydrothermal synthesis of a nickel phlogopite was reported earlier by Klingsberg and Roy (1957). More recent syntheses of trioctahedral micas which include a zinc-mica have been reported by Hazen and Wones (1972). The purpose of this paper is to give a low temperature synthesis at autogeneous pressure of a zinc phlogopite.

Synthesis

The starting reagents are aluminum nitrate, zinc sulfate, potassium hydroxide, and Ludox AS as a source of silica. A 6M potassium hydroxide solution was added to the aluminum nitrate and the zine sulfate solutions to form gels; additional base was added until the gels redissolved and a clear solution was obtained in both cases. The two solutions were then mixed without the formation of a precipitate or gel. The silica sol was then added, forming a gel that was allowed to sit overnight before charging into the reactor.

The stoichiometry of the starting gels, temperature, and crystalline phases are given in Table 1. The crystalline phases were determined with X-ray powder data obtained with a Picker diffractometer and Cu$K\alpha$ radiation. At temperatures of about 85°C, phlogopite crystals readily form over a 96-hour period. At low concentrations of zinc oxide, the zeolite, herschelite, $KAlSi_2O_6 \cdot 3H_2O$, co-exists with the phlogopite phase. We were able to crystallize zinc phlogopite at temperatures as low as 55°C; however, some herschelite also forms at this temperature, probably because of incomplete reaction of the zinc hydroxide.

The comparison of our synthesis conditions and products with those of other workers is given in Table 1. The lowest synthesis temperature used by Frondel and Ito (1966) for their Zn-mica is 250°C at a pressure of 2,000 bars. Synthesis temperatures of up to 650°C at 3,000 bars did not give a single phase; the product in all their runs is a mixture of Zn-mica, sanidine, and willemite. Synthesis of Zn-phlogopite by Hazen and Wones (1972) at elevated temperatures and pressures also did not give zinc phlogopite as the only crystalline species. Their lowest temperature is 280°C at a pressure of 2,000 bars, and the products in all runs were a mixture of willemite, mica, and leucite. We did not detect any sanidine, leucite, or willemite, probably because our preparations were at a much lower temperature (and pressure).

A reasonably good comparison exists between our X-ray data for zinc phlogopite and that given for nickel phlogopite by Klingsberg and Roy (1957)

TABLE 1. Synthesis Data for Zinc Phlogopite

Composition	Temp (°C)	P (Bars)	Time (Hr)	Phases Present
1.92 K_2O:0.08 Al_2O_3: 0.08 ZnO:0.42 SiO_2:84 H_2O (3 preparations)	85	-	96	phlogopite + (herschelite)
1.92 K_2O:0.08 Al_2O_3: 0.21 ZnO:0.42 SiO_2:84 H_2O (2 preparations)	85	-	96	phlogopite
" " " "	65	-	100	phlogopite
" " " "	55	-	234	phlogopite + (herschelite)
1.92 K_2O:0.08 Al_2O_3: 0.31 ZnO:0.42 SiO_2:84 H_2O (2 preparations)	85	-	96	phlogopite
$KZn_3(Si_3Al)O_{10}(OH)_2$*	650	3,000	24	Zn-mica, sanidine, willemite
" " " "	450	1,000	40	" " "
" " " "	250	2,000	40	" " "
$KZn_3AlSi_3O_{10}(OH)_2$**	600	2,000	145	willemite, kalsilite, leucite
" " " "	280	2,000	215	willemite, mica, minor leucite
" " " "	725	2,000	72	willemite, kalsilite, leucite
" " " "	530	2,000	50	willemite, mica, leucite
" " " "	500	2,000	290	willemite, mica, leucite

*Frondel and Ito. **Hazen and Wones.

TABLE 2. X-Ray Data for Phlogopite Phases

Zn-Phlogopite		Ni-Phlogopite (3T Basis)*		
d (Å)	I/I_o	d (Å)	I est.	hkl
10.20	100	10.15	10	00.3
		5.512	4	?
5.04	15	5.065	5	00.6
4.55	15	4.557	6	10.0
3.92	12	3.927	5	10.4
3.66	16	3.672	6	10.5
3.36	46	3.389	10	00.9
3.15	17	3.164	6	10.7
2.91	17	2.928	6	10.8
2.713	14	2.720	4	10.9
2.621	51	2.612	10	11.2
2.534	19	2.542	6	00.12
		2.501	4	11.4
2.440	37	2.430	10	11.5
		2.359	2	?
		2.291	3	20.0
2.271	18	2.264	5	11.7
2.191	27	2.176	9	11.8
		2.089	8	20.6
2.000	18	1.997	7	11.10
1.912	12			
1.683	19			
1.542	32			
1.521	19			

*Klingsberg and Roy - Ni-Phlogopite synthesized at a temperature and pressure of at least 900°C and 2000 psi.

(Table 2), even though the latter was formed under much more severe conditions. Approximate cell dimensions for zinc phlogopite, referred to hexagonal axes, are $a = 5.32$, $c = 30.36$ Å.

Conclusion

The synthesis of a well-crystallized phlogopite has been achieved by the addition of excess base to give a reactive gel that crystallized at a low temperature. Low concentrations of zinc oxide result in co-crystallization of the zeolite hershelite with zinc phlogopite.

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