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A low-temperature synthesis of a harmotome-type zeolite

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Abstract

A harmotome-type zeolite was synthesized at 95°C by crystallization of a sodium–barium gel. Low non-zero concentrations of barium relative to sodium are necessary for crystallization of this zeolite rather than other types. X-ray data of the synthetic and natural harmotome phases are compared.

Introduction

Earlier work in the Na_2O–Al_2O_3–SiO_2–H_2O system suggested that zeolite Na–Pl, crystallized at about 100°C, has a structure similar to that of phillipsite-harmotome (Barrer *et al.*, 1959b). Later work showed that both Na–Pl and the closely related phase Linde B have structures similar to that of gismondine (Meier and Olson, 1971). An orthorhombic form, synthesized at 250°C in this system, could be of the phillipsite-harmotome type (Barrer *et al.*, 1959a).

Barium zeolite (Ba–M) with a phillipsite–harmotome structure, was crystallized at 200–250°C by Barrer and Marshall (1964). At lower temperatures, zeolite Ba–G, with a structure similar to Linde L, was formed (Barrer and Mainwaring, 1972). I now describe a low-temperature synthesis of a harmotome-type zeolite in the sodium–barium system.

Synthesis and X-ray data

The starting gel compositions were formed from aqueous solutions of sodium silicate, sodium aluminate, sodium hydroxide, and barium iodide. A sodium aluminosilicate gel was first formed, and barium iodide solution was added. The gels were placed in polypropylene bottles and heated at 95°C. The crystalline products were analyzed with an X-ray powder diffractometer using Cu$K\alpha$ radiation (Table 1).

The crystallization of a Ba-free gel resulted in faujasite. At low barium concentration (atomic Na/Ba ~ 76) faujasite crystallization was inhibited, and after 91 hours most of the crystalline product was a poorly crystallized harmotome-type species. An increase in the barium concentration to an Na/Ba atomic ratio of 38 gave a well-crystallized harmotome-type zeolite. The harmotome product was well-crystallized at Na/Ba atomic ratios down to about 8. As the concentration of barium ions was increased beyond this, it became more difficult to crystallize harmotome. At the highest concentration of barium iodide (Na/Ba ~ 8) little settling of the gel occurred after 234 h; the product contained mainly amorphous material and a small amount of the harmotome-type zeolite. This preparation still had a high Na/Ba ratio in the gel; the alkali to alumina or silica ratios were unchanged. Crystallization at both higher and lower silica contents, having silica to alumina ratios ranging from about 2.5 to 10, also gave the harmotome-type phase with the appropriate barium iodide additions.

The X-ray data for my synthetic harmotome is given in Table 2. In addition, the X-ray data for natural harmotome is given for comparison. The X-ray data agree well with those for the natural form considering possible variations in stoichiometry. Further confirmation of correctness of structure was obtained by comparison with a natural harmotome treated with sodium chloride solutions until no further barium could be removed (Barrer *et al.*, 1959b).

The natural harmotome contains about twice as much alkaline earth ions as alkali, as shown by the assigned chemical formula $[(Na,K)_{0.9}(Ba,Ca)_{2.0}(Al,Fe,Mg)_{4.7}Si_{11.0}O_{31.5} \cdot 12.7H_2O]$. Interestingly, in my gels, although the sodium content was much higher than the barium content, the barium ion was still able to direct crystallization to the harmotome structure. The well-crystallized harmotome that existed as a single phase occurred at a concentration of barium ions in the gel that nearly neutralized the aluminum-centered tetrahedra in the structure.

TABLE 1. Low temperature synthesis of harmotome*

Gel Composition (molar)					t (hr)	Phases Present
Na_2O	Al_2O_3	SiO_2	H_2O	BaI_2		
9.5	1	5.25	1528	0.24	91	Harmotome (poorly crystallized) + faujasite
9.5	1	5.25	1528	0.48	91	Harmotome (well crystallized)
9.5	1	5.25	1528	0.72	91	Harmotome (well crystallized)
9.5	1	5.25	1528	0.6	66	Harmotome (well crystallized)
9.5	1	5.25	1528	1.2	66	Harmotome not as well crystallized but still good crystallinity
9.5	1	5.25	1528	1.8	114	Harmotome + amorphous (poor crystallinity)
9.5	1	5.25	1528	2.4	234	Amorphous + harmotome
14.5	1	10.5	1530	0.45	96	Harmotome
14.5	1	10.5	1530	0.71	96	Harmotome
6.5	1	2.5	1530	0.47	96	Harmotome
6.5	1	2.5	1530	0.71	96	Harmotome

*All preparations treated at 95°C

TABLE 2. X-ray data for natural* and synthetic harmotome

Natural		Synthetic	
d	I/Io	d	I/Io
8.10	40	8.12	69
7.16	50	7.13	43
6.38	100	6.37	71
5.03	40	5.01	35
4.30	40	4.29	38
4.08	60	4.08	98
3.90	30	3.88	31
3.47	10	3.45	12
		3.40	9
3.24	60	3.24	60
3.20	10	overlap	--
3.17	60	3.16	55
3.13	80	3.13	100
3.08	40	3.08	23
2.92	20	2.92	43
2.847	20	2.85	10
2.751	20	overlap	--
2.730	60	2.73	48
2.698	60	2.68	64
2.670	70	2.67	71

*Sahama and Lehtinen (1967)

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