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Formation of $Ag_4Al_3Si_3O_{12}I$

On heating an iodine-loaded, silver-exchanged zeolite to 1100°C (*1*), many of the peaks in the powder X-ray diffraction pattern gave a close correspondence with those in the pattern of iodide–sodalite ($Na_4Al_3Si_3O_{12}I$) (*2*). However, weak peaks due to mullite were also observed, in addition to weak, unidentified peaks. To investigate this correspondence, we attempted to synthesize the Ag,I analog of sodalite, i.e., $Ag_4Al_3Si_3O_{12}I$.

Synthesis was attempted by solution–solid mixing. First, solutions of $AgNO_3$ and $NaAlO_2$ were mixed and the precipitate was washed and dried at room temperature. This material, nominally $AgAlO_2$, was mixed with a NH_3-stabilized SiO_2 sol and precipitated AgI, maintaining the desired stoichiometry. These mixtures were dried at 100°C and pelletized with a pressure of ~200 MPa. X-Ray patterns were obtained with a standard diffractometer, using Cu$K\alpha$ radiation and a graphite monochromator.

Firing in air yielded the pattern in question, but strong lines due to metallic silver were also observed. However, if the pellets were placed in welded Pt tubes and fired at 800–1000°C for several hours, nearly phase-pure material was apparently produced; weak peaks due to α-AgI and cristobalite were observed also. The lines of the phase of interest were quite broad, especially after firing was performed at the lower temperatures in the above range, but they were considerably sharpened by annealing in air for 20 hr at 1000°C. The evidence of α-AgI and SiO_2 was almost completely removed. Heating in air for a few hours at 1200°C yielded a mixture of α-AgI and mullite, as far as crystalline products were concerned.

The X-ray pattern of the supposed $Ag_4Al_3Si_3O_{12}I$ was calculated wth the aid of a computer program (*3*) on the basis of the sodalite structure (*4*), with Ag replacing Na and I replacing Cl. The same atomic parameters, space group (No. 218), and temperature factors were used. The agreement between the calculation and observation was generally quite good (Table I). Although (unlike the case for space group No. 217 in which the Al and Si atoms are disordered) very weak $h + k + l = 2n + 1$ reflections were calculated to be present, these were all calculated to have intensities <0.5% of those of the strongest $h + k + l = 2n$ reflections. Note that the discussion (*2*) incorrectly ignored Al–Si ordering contributions to the $h + k + l = 2n + 1$ reflections for halide sodalites, but these contributions are expected to be weak compared to those due to the presence of multiatomic radicals substituting at the halide sites.

Chemical analyses of seemingly nearly phase-pure material showed considerable iodine deficiency. The analyzed percentages by weight of Ag_2O, Al_2O_3, SiO_2, and I were 46, 22, 27, and 4 wt%, respectively, compared to stoichiometric expectations of 50, 17, 20, and 14 wt%, respectively. The material was heated in air for 20 hr at 1000°C after being fired in a Pt tube for several hours at 1000°C. We interpret the analytical results as showing that a large amount of amorphous material coexisted with the crystalline $Ag_4Al_3Si_3O_{12}I$. These results were similar to those obtained on air-fired iodide sodalite (*2, 5*). The color of

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TABLE I

CALCULATED AND OBSERVED X-RAY INTENSITIES FOR $Ag_4Al_3Si_3O_{12}I$

hkl	d (Å)	I_{obsd}	I_{calcd}	hkl	d (Å)	I_{obsd}	I_{calcd}
110	6.31	10	14	330, 411	2.105	50	60
200	4.46	1	2	420	1.997	5	7
211	3.65	100	100	332	1.904	<1	1
220	3.16	10	14	422	1.823	8	8
310	2.82	10	6	510, 431	1.751	2	6
222	2.578	3	3	521	1.630	7	4
321	2.387	30	35	440	1.579	5	4
400	2.233	<1	<1				

Note. The lattice parameter was found as 8.930 ± 0.005 Å. All intensities were normalized to 100 for the (211) reflection. No elaborate precautions were taken to avoid preferred orientation but patterns were run for several preparations. The observed intensities are estimated to be correct within ±25%. More peaks were observed for $d < 1.54$ Å but are not listed here.

the preparations was a pale yellow and this did not change upon X-irradiation, unlike the white → blue color change observed for air-fired iodide sodalite (*5*, *6*). Thus there was no evidence that the crystalline $Ag_4Al_3Si_3O_{12}I$ in the preparations was grossly anion deficient, though it remains possible that color centers arising from anion deficiency could develop upon low-temperature X irradiation.

By similar preparative methods, we found no evidence for the occurrence of Cl and Br analog of $Ag_4Al_3Si_3O_{12}I$; this seems rather surprising in view of the ready formation of the halide sodalites (*7*). Investigation of possible (Ag,Na) halide sodalite solid solutions might be illuminating in this respect.

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References

1. E. R. VANCE AND D. K. AGRAWAL, *J. Mater. Sci.*, in press.
2. E. R. VANCE, D. K. AGRAWAL, AND J. G. PEPIN, *Phys. Status Solidi A* **63**, K189 (1981).
3. D. K. SMITH AND M. HOLOMANY, "A Fortran IV Program for Calculating X-Ray Patterns—Version 8," Computer Science Center, The Pennsylvania State University, University Park.
4. J. LONS AND H. SCHULZ, *Acta Crystallogr.* **23**, 4341 (1967).
5. E. R. VANCE, D. K. AGRAWAL, B. E. SCHEETZ, J. G. PEPIN, S. D. ATKINSON, AND W. B. WHITE, "Ceramic Phases for Immobilization of ^{129}I," Report DOE/ET/41900-9, U.S. Department of Energy (1981).
6. D. J. SCHIFFER, C. Z. VAN DOORN, AND P. T. BOLWIJN, *J. Amer. Ceram. Soc.* **55**, 256 (1972).
7. T. TOMISAKA AND H. P. EUGSTER, *Mineral J.* **5**, 249 (1968).

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