

The structural behaviour of the nepheline family: (1) Sr and Ba aluminates (MA_2O_4)

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ABSTRACT. The structural relations of solid solutions in the series $(Sr_{1-x}Ba_x)Al_2O_4$ were studied using room- and high-temperature X-ray methods, infra-red spectroscopy, and DTA. At room temperature, $SrAl_2O_4$ and solid solutions with x up to 0.31 are monoclinic, between $x = 0.31$ and 0.43 monoclinic and hexagonal forms coexist, and between $x = 0.43$ and 1.0 only hexagonal forms occur. On heating, a member of the monoclinic series of solid solutions transforms to hexagonal symmetry over a range of temperature within which both monoclinic and hexagonal forms coexist. The proportion of the hexagonal form increases instantaneously as the temperature is raised. The transformation temperature decreases with increasing $BaAl_2O_4$ in solid solution and, in addition, the temperature width of the region of coexistence is markedly enlarged. $SrAl_2O_4$ transforms over the range 665–705 °C and $(Sr_{0.7}Ba_{0.3})Al_2O_4$ over 170–405 °C. The DTA trace for $SrAl_2O_4$ shows a peak at 677 °C. On cooling, the transformations show hysteresis of 15 to 25 °C.

The coexisting monoclinic and hexagonal forms are believed to be isochemical, and discontinuities in cell parameters occur within the region of coexistence both in the compositional series at room temperature and in the elevated temperature transformation experiments. The low-to-high transformation is accompanied by a volume change of -0.2 to -0.3% , and is believed to be first-order displacive with additional characteristics similar to those of martensitic transformations.

The thermal expansion behaviour of structures in the $(Sr,Ba)Al_2O_4$ series indicates that two tilt systems are operative: co-operative rotation of tetrahedra about the c -axis, and tilting of tetrahedra relative to the 0001 plane.

The results for the $(Sr,Ba)Al_2O_4$ series are shown to be invaluable in reinterpreting the structural behaviour of members of the nepheline and leucite groups of minerals.

As a continuation of our studies of the structural and thermal expansion behaviour of framework silicates we have chosen to study members of the nepheline family (Megaw, 1973). This family contains natural minerals and synthetic compounds, all hettotypes of an aristotype based on the ideal-

ized, hexagonal high-tridymite linkage described by Gibbs (1927). Thus the aristotype has equal-sized hexagonal cavities formed by six-membered rings of tetrahedra. In kalsilite-like hettotypes these cavities remain substantially equal-sized, although distortions of the rings and tilting of the tetrahedra may reduce their size. In nepheline the distortions required by the much smaller radius of one of the cavity cations are so great that two sizes of cavity are produced (fig. 1).

We chose to begin our study with the alkali-earth aluminates of general composition MA_2O_4 , where $M = Ca, Sr, \text{ or } Ba$. Our choice was based on the facts that these compounds have simple framework compositions (Al is the only framework cation) and that they are kalsilite-like hettotypes with essentially equal-sized cavities. $BaAl_2O_4$ has a hexagonal structure but $CaAl_2O_4$ and $SrAl_2O_4$ have monoclinic structures (Dougill, 1957; Hörkner and Müller-Buschbaum, 1976; Hanic *et al.*, 1979; Schulze and Müller-Buschbaum, 1981). Ito *et al.* (1977*a, b*) have reported a reversible transition in $SrAl_2O_4$ at 650 °C, from a monoclinic form to a hexagonal form which is structurally identical to $BaAl_2O_4$; they also reported complete solid solution between $SrAl_2O_4$ and $BaAl_2O_4$. The temperature of the monoclinic-hexagonal transition

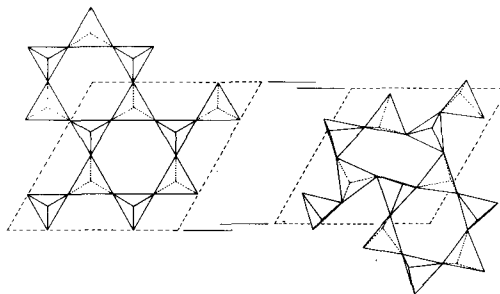


FIG. 1. Projections on 0001 of one layer of tetrahedra of the frameworks of idealized high-tridymite (left) and nepheline (right). Note the two types of cavity occurring in the nepheline framework.

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decreases as Ba replaces Sr until at about $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Al}_2\text{O}_4$ the transformation occurs at room temperature. Unfortunately, the monoclinic unit cell used by Ito *et al.* (1977*a, b*) is now known to be incorrect (Hanic *et al.*, 1979; Schulze and Müller-Buschbaum, 1981). A. P. Henderson (1978) has also detected a reversible structural change between 650°C and 680°C by Guinier X-ray and DTA studies; the latter showed hysteresis.

BaAl_2O_4 shows superstructure reflections (Perrotta and Smith, 1968; Hörkner and Müller-Buschbaum, 1979) which require a supercell with a doubled *a*-axis. Structures have been reported for the sub-cell of BaAl_2O_4 (Do Dinh and Bertaut, 1965; Uchikawa and Tsukiyama, 1966; Perrotta and Smith, 1968) and Hörkner and Müller-

Buschbaum (1979) have refined the structure of the supercell. According to Megaw (1973, fig. 12.14) the common structural distortion of the kalsilite-like hettotypes of the nepheline family is a co-operative rotation of the framework tetrahedra about the threefold axes which lie parallel to the *c*-axis of the structure, thereby reducing the cavity size. Megaw (1973) did not consider tilting of the tetrahedra relative to the 0001 plane. Indeed, the space groups and atomic positions for the structures of kalsilite and BaAl_2O_4 known at that date preclude tilting of the tetrahedra relative to the 0001 plane. The superstructure of BaAl_2O_4 does not have these limitations and Hörkner and Müller-Buschbaum (1979) found such tilting for all tetrahedra except those on the triad axes of the structure

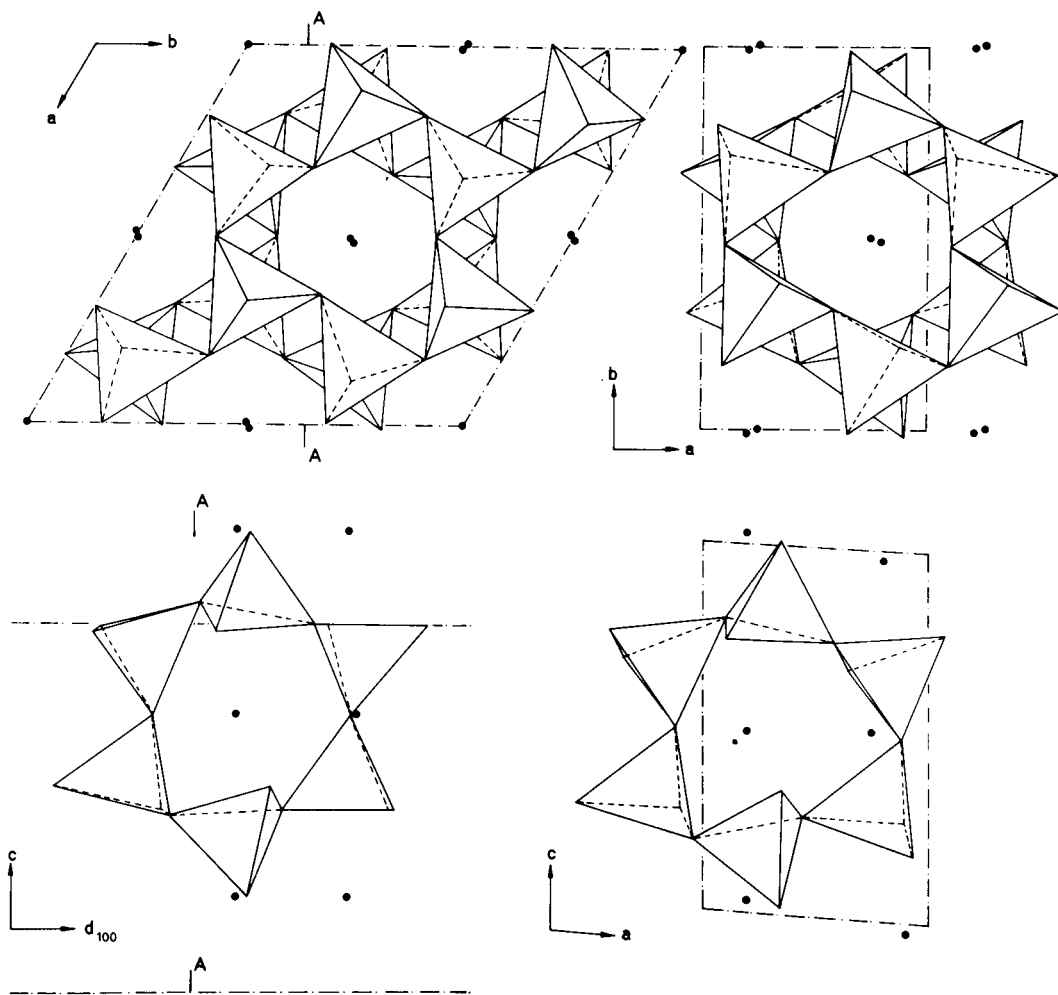


FIG. 2. Projections of the frameworks of BaAl_2O_4 (left) and SrAl_2O_4 (right) illustrating the similarities between the structures. Solid circles indicate positions of cavity cations and dot-dash lines outline the unit cells.

(fig. 2). It thus seems likely that there are two modes of co-operative tilting of the framework tetrahedra in the kalsilite-like hettotypes which should be reflected in changes in the structure due to thermal expansion and solid solution.

The structure of SrAl_2O_4 has been refined by Schulze and Müller-Buschbaum (1981) and is strikingly similar to that of BaAl_2O_4 . The principal difference, apart from the lower symmetry, is that in SrAl_2O_4 all the tetrahedra are tilted in addition to the co-operative rotation about the c axis (fig. 2). In the second setting of the monoclinic system to which the structure of SrAl_2O_4 belongs there is a choice over the labelling of the a - and c -axes. In view of the need in this paper to make comparisons between SrAl_2O_4 and BaAl_2O_4 we prefer the unit cell chosen by Hanic *et al.* (1979), which gives the approximate relationships between the structures: $a_m = a_h, b_m = \sqrt{3}b_h$, and $c_m = c_h$ (subscripts m and h will be used throughout this paper to refer to the monoclinic and hexagonal cells respectively).

The structural behaviour of the SrAl_2O_4 - BaAl_2O_4 solid solution series appears to be complicated and should be of considerable help in understanding the structural behaviour of framework structures. There are likely to be two modes of co-operative tilting of tetrahedra as well as a reversible monoclinic-hexagonal phase transformation.

Experimental techniques

The $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ solid solutions and end members were prepared by mixing the appropriate amounts of Specpure* BaCO_3 and SrCO_3 and AR-grade $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, heating the mixture in a platinum crucible at 1400°C for 4 h, grinding the product in an agate mortar under acetone and heating again at 1400°C for 5 h. Compositions in the range $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{Al}_2\text{O}_4$ to $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Al}_2\text{O}_4$ were ground and heated at 1400°C for 6 h two more times. The yield was checked gravimetrically and in all cases was within 0.1% of the expected weight. Products were examined for impurities by powder X-ray diffraction and optical microscopy.

Cell parameters were determined from powder X-ray diffraction patterns by the method of least squares using quartz as internal standard ($a = 4.9127$, $c = 5.4044$ Å). Between 11 and 19 reflections were used to determine the monoclinic cell parameters and between 9 and 15 reflections for the hexagonal cell parameters. Although BaAl_2O_4 has a superstructure with a doubled a -axis we have chosen to report the cell parameters of BaAl_2O_4 and the hexagonal $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ solid solutions in terms of the sub-cell. The indexing was based on the data of Perrotta (1965) and ASTM card 17-306 for BaAl_2O_4 , and on the data of Hanic *et al.* (1979) for SrAl_2O_4 and the monoclinic solid solutions. The cell parameters at elevated temperatures were determined by the method

described in Henderson and Taylor (1975) using the X-ray reflections from the platinum specimen holder as the internal standard.

Infra-red spectra were recorded on a Perkin Elmer 577 double-beam grating spectrometer by the alkali-halide disc method (1.3 mg of specimen to 200 mg of KBr). For sharp absorption bands the reported wavenumbers are within ± 2 cm^{-1} and for broad absorption bands within ± 5 cm^{-1} .

DTA was carried out using a Stanton-Redcroft DTA673-4 apparatus. The experimental conditions were: alumina as reference material, heating rate $10^\circ\text{C}/\text{min}$ in static air, specimen weight between 70 and 100 mg, amplifier sensitivity 20 μV . Quartz was used to calibrate the temperature scale.

Results

SrAl₂O₄-BaAl₂O₄ solid solution series (Sr_{1-x}Ba_xAl₂O₄) at room temperature. The SrAl_2O_4 - BaAl_2O_4 system has a region at the Sr-rich end in which a monoclinic and a hexagonal form apparently coexist at room temperature. As Sr replaces Ba in BaAl_2O_4 the monoclinic solid solution first appears with the hexagonal solid solution when $x = 0.43 \pm 0.01$. For compositions richer in Sr the characteristic 112 and $11\bar{2}$ X-ray reflections of the monoclinic solid solution, at ~ 2.98 and ~ 3.14 Å respectively, appear either side of the 102 reflection of the hexagonal solid solution which, in turn, overlaps the 022 reflection of the monoclinic solid solution. As Ba replaces Sr in SrAl_2O_4 , the first occurrence of the hexagonal solid solution with the monoclinic solid solution, when $x = 0.31 \pm 0.01$, was found by noting the first significant reduction in the $112_m/(102_h + 022_m)$ X-ray peak-height ratio (fig. 3). Thus monoclinic and hexagonal solid solutions coexist between 0.31 and 0.43 mole

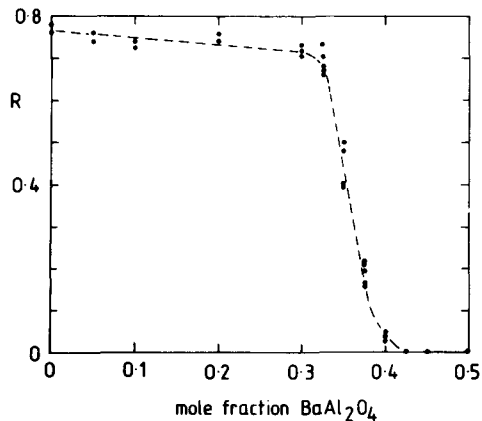


Fig. 3. The relationship between the peak height ratio, $R = 112_m/(102_h + 022_m)$, and the mole fraction of BaAl_2O_4 showing the rapid decrease in the proportion of the monoclinic form above 0.31 mole fraction BaAl_2O_4 .

* Specpure is the trademark of Johnson Matthey Ltd.

fraction of BaAl_2O_4 at room temperature. The proportions of the two forms at room temperature were found to depend on the time of equilibration at room temperature. The amount of the monoclinic form increased at the expense of the hexagonal form, with the proportions of the two forms becoming virtually constant after one month.

The coexistence of two phases at room temperature could be interpreted as indicating the presence of a low-temperature solvus, i.e. the two phases would have different compositions. In this system since the frameworks have identical compositions the two phases would have to be of different Ba/Sr ratio. For different compositions within the two-phase field the proportions of the phases would change but their cell parameters would be constant at a given temperature. In fact, the experimental evidence indicates that the cell parameters, for the monoclinic phase at least, continue to change across the two-phase field. For example, the difference between the 2θ values of the $11\bar{2}_m$ and $11\bar{2}_m$ X-ray reflections of the monoclinic solid solution change smoothly up to and across the two-phase field (fig. 4), indicating that solid solution in the monoclinic phase does not end at the Sr-rich limit of this field. Furthermore, within the two-phase field, there is no significant variation in the difference between the 2θ values of the $11\bar{2}_m$ and $11\bar{2}_m$ reflections of a given composition as a function of time, despite the changes in

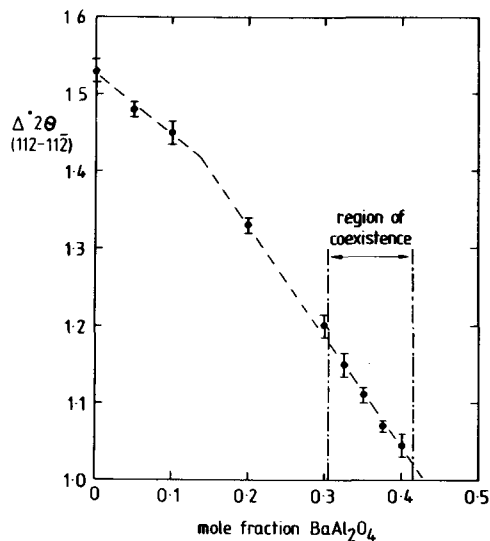


Fig. 4. The difference in 2θ values between the $11\bar{2}$ and $11\bar{2}$ X-ray reflections of the monoclinic form as a function of the mole fraction of BaAl_2O_4 . Note that the solid solution in the monoclinic phase continues across the region of coexistence. The error bars are one standard deviation.

Table I. Cell parameters of synthetic monoclinic $(\text{Sr}, \text{Ba})\text{Al}_2\text{O}_4$ solid solution at room temperature and elevated temperatures

$T^\circ\text{C}$	a, Å	b, Å	c, Å	β°	$v, \text{Å}^3$	a, Å	b, Å	c, Å	β°	$v, \text{Å}^3$
(1) SrAl_2O_4						(4) $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{Al}_2\text{O}_4$				
20 [†]	5.147(2)	8.828(3)	8.443(3)	93.37(3)	383.0(2)	20 [†]	5.170(2)	8.882(4)	8.508(2)	93.00(2)
20	5.148(2)	8.829(3)	8.443(3)	93.38(3)	383.0(2)	20	5.175(2)	8.870(4)	8.509(2)	93.03(3)
20 (after 600°C)	5.147(2)	8.827(3)	8.442(3)	93.35(4)	382.9(2)	20 (after 400°C)	5.174(2)	8.873(4)	8.509(2)	93.02(3)
20 (after 900°C)	5.146(2)	8.828(3)	8.440(4)	93.31(5)	382.8(2)	20 (after 600°C)	5.172(2)	8.873(4)	8.509(2)	93.00(3)
20*	5.147(2)	8.829(3)	8.442(3)	93.35(4)	382.9(2)	20 (after 700°C)	5.177(2)	8.871(4)	8.509(2)	93.00(3)
195	5.157(1)	8.834(2)	8.457(3)	93.32(3)	384.7(1)	20 (after 900°C)	5.174(2)	8.870(4)	8.509(2)	92.99(3)
295	5.164(2)	8.835(3)	8.473(4)	93.25(5)	386.0(2)	20 [†] (after 900°C)	5.172(1)	8.878(4)	8.506(2)	92.92(2)
395	5.173(2)	8.845(3)	8.476(3)	93.16(4)	387.2(2)	20*	5.175(2)	8.872(4)	8.509(2)	92.99(3)
500	5.175(2)	8.863(6)	8.489(3)	93.09(4)	388.8(2)	105	5.176(3)	8.875(5)	8.512(3)	92.92(4)
600	5.170(2)	8.878(3)	8.498(1)	92.92(2)	389.5(1)	200	5.176(3)	8.884(5)	8.523(3)	92.77(4)
660	5.163(1)	8.886(2)	8.501(1)	92.71(1)	389.6(1)	340	5.178(2)	8.899(4)	8.540(2)	92.50(3)
(2) $\text{Sr}_{0.95}\text{Ba}_{0.05}\text{Al}_2\text{O}_4$						(5) $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{Al}_2\text{O}_4$				
20 [†]	5.159(2)	8.841(2)	8.460(2)	93.31(2)	385.2(1)	20 [†]	5.179(2)	8.906(2)	8.543(2)	92.65(2)
(3) $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Al}_2\text{O}_4$						20	5.174(3)	8.904(4)	8.541(2)	92.66(3)
20 [†]	5.164(2)	8.852(4)	8.477(4)	93.27(2)	386.9(2)	20 (after 800°C)	5.178(3)	8.904(4)	8.543(2)	92.70(4)
20	5.160(3)	8.861(5)	8.478(3)	93.26(4)	387.0(2)	20*	5.176(3)	8.904(4)	8.542(2)	92.68(3)
20 (after 900°C)	5.161(3)	8.861(5)	8.476(3)	93.24(3)	387.0(2)	100	5.177(4)	8.907(5)	8.547(3)	92.55(5)
20*	5.161(3)	8.861(5)	8.477(3)	93.25(4)	387.0(2)	160	5.173(4)	8.910(6)	8.558(3)	92.46(5)
120	5.163(2)	8.867(4)	8.484(2)	93.18(3)	387.8(2)	200	5.171(4)	8.913(5)	8.557(3)	92.36(6)
210	5.165(2)	8.876(3)	8.491(2)	93.08(2)	388.7(1)	(6) $\text{Sr}_{0.675}\text{Ba}_{0.325}\text{Al}_2\text{O}_4$				
300	5.167(2)	8.885(3)	8.501(2)	92.97(2)	389.7(1)	20 [†]	5.180(2)	8.909(4)	8.550(2)	92.56(3)
395	5.171(2)	8.894(3)	8.511(1)	92.84(2)	390.9(1)					
480	5.172(2)	8.903(4)	8.521(2)	92.70(3)	391.9(2)					
500	5.172(2)	8.908(4)	8.524(2)	92.68(3)	392.3(2)					

Figures in brackets are estimated standard deviations in the last place.

[†] Quartz as internal standard, other data with platinum as internal standard.

* Average of room temperature data based on platinum.

the proportions of the hexagonal and monoclinic forms during the room-temperature equilibration experiments. In the absence of any experimental evidence to the contrary we presume that the two phases are of identical composition. To avoid any confusion we therefore refer to the region in which monoclinic and hexagonal phases coexist as the 'region of coexistence'.

Cell parameters for members of the solid solution series at room temperature are given in Tables I and II. The cell parameters of BaAl₂O₄ at room temperature are in good agreement with those reported by Oehschlegel *et al.* (1974), *a* = 5.228(1) and *c* = 8.7911(4) Å, and in ASTM card 17-306, *a* = 5.2241 and *c* = 8.7947 Å; other literature data are given by Oehschlegel *et al.* (1974). The cell

Table II. Cell parameters of synthetic hexagonal (Sr,Ba)Al₂O₄ solid solutions at room temperature and elevated temperatures.

T °C	a, Å	c, Å	V, Å ³	T °C	a, Å	c, Å	V, Å ³
(1) SrAl ₂ O ₄				(10) Sr _{0.5} Ba _{0.5} Al ₂ O ₄			
690	5.1458(21)	8.4754(43)	194.36(16)	20 [†]	5.1753(7)	8.6023(21)	199.53(6)
795	5.1500(16)	8.4888(37)	194.98(13)	(11) Sr _{0.4} Ba _{0.6} Al ₂ O ₄			
900	5.1544(14)	8.5138(33)	195.89(11)	20 [†]	5.1852(5)	8.6336(13)	201.03(4)
(3) Sr _{0.9} Ba _{0.1} Al ₂ O ₄				20 (after 800°C)	5.1862(4)	8.6346(12)	201.12(4)
600	5.1568(8)	8.5139(13)	196.07(6)	20 (after 500°C)	5.1873(7)	8.6334(20)	201.19(6)
705	5.1619(8)	8.5285(14)	196.08(6)	20*	5.1862(5)	8.6339(15)	201.11(5)
800	5.1651(10)	8.5458(17)	197.44(8)	200	5.1924(4)	8.6495(11)	201.96(3)
900	5.1679(6)	8.5619(10)	198.03(4)	290	5.1953(7)	8.6535(22)	202.28(6)
(4) Sr _{0.8} Ba _{0.2} Al ₂ O ₄				400	5.2008(13)	8.6674(41)	203.03(12)
540	5.1622(2)	8.5399(4)	197.09(2)	500	5.2047(10)	8.6858(31)	203.76(9)
600	5.1648(6)	8.5403(19)	197.29(6)	600	5.2082(8)	8.6981(25)	204.33(7)
700	5.1688(5)	8.5563(16)	197.97(5)	700	5.2122(8)	8.7072(25)	204.86(7)
800	5.1733(6)	8.5775(20)	198.80(6)	800	5.2179(5)	8.7191(16)	205.59(5)
900	5.1771(6)	8.5897(20)	199.38(6)	(12) Sr _{0.3} Ba _{0.7} Al ₂ O ₄			
(5) Sr _{0.7} Ba _{0.3} Al ₂ O ₄				20 [†]	5.1953(4)	8.6699(14)	202.66(4)
305	5.1617(9)	8.5449(17)	197.16(7)	(13) Sr _{0.2} Ba _{0.8} Al ₂ O ₄			
380	5.1645(5)	8.5538(10)	197.59(4)	20 [†]	5.2051(4)	8.7067(18)	204.28(5)
395	5.1666(8)	8.5586(16)	197.85(6)	20	5.2047(6)	8.7037(23)	204.19(5)
510	5.1721(8)	8.5720(16)	198.58(6)	20 (after 505°C)	5.2054(7)	8.7079(24)	204.34(6)
610	5.1756(7)	8.5879(13)	199.22(5)	20 (after 795°C)	5.2058(5)	8.7068(16)	204.35(4)
700	5.1781(8)	8.6029(14)	199.76(6)	20*	5.2053(6)	8.7063(21)	204.29(5)
800	5.1820(8)	8.6165(16)	200.38(6)	205	5.2110(3)	8.7270(11)	205.23(3)
(7) Sr _{0.625} Ba _{0.375} Al ₂ O ₄				300	5.2143(5)	8.7359(16)	205.70(4)
20 [†]	5.1647(9)	8.5642(21)	197.84(7)	405	5.2204(6)	8.7457(20)	206.41(4)
195	5.1697(7)	8.5692(11)	198.34(5)	505	5.2244(6)	8.7563(19)	206.98(5)
(8) Sr _{0.6} Ba _{0.4} Al ₂ O ₄				600	5.2294(5)	8.7655(17)	207.60(4)
20 [†]	5.1666(9)	8.5631(22)	197.96(8)	690	5.2329(7)	8.7726(22)	208.04(6)
(9) Sr _{0.575} Ba _{0.425} Al ₂ O ₄				795	5.2391(7)	8.7807(20)	208.72(5)
20 [†]	5.1672(8)	8.5728(23)	198.23(7)	(14) Sr _{0.1} Ba _{0.9} Al ₂ O ₄			
20	5.1685(7)	8.5740(13)	198.36(5)	20 [†]	5.2150(4)	8.7418(12)	205.89(3)
20 (after 805°C)	5.1693(3)	8.5747(7)	198.43(3)	(15) BaAl ₂ O ₄			
20*	5.1689(5)	8.5744(10)	198.40(4)	20 [†]	5.2227(3)	8.7921(10)	207.69(3)
120	5.1711(5)	8.5807(11)	198.71(4)	20	5.2234(4)	8.7904(15)	207.71(4)
200	5.1737(6)	8.5887(12)	199.09(4)	20 (after 490°C)	5.2237(5)	8.7926(14)	207.78(4)
300	5.1774(6)	8.6004(12)	199.65(5)	20 (after 790°C)	5.2241(4)	8.7919(13)	207.80(4)
405	5.1813(10)	8.6089(21)	200.15(8)	20*	5.2237(4)	8.7916(14)	207.76(4)
510	5.1848(10)	8.6251(20)	200.80(8)	200	5.2292(4)	8.8108(15)	208.65(4)
600	5.1891(8)	8.6394(16)	201.46(6)	285	5.2320(4)	8.8158(15)	208.99(4)
700	5.1945(10)	8.6525(21)	202.19(8)	385	5.2379(5)	8.8231(18)	209.64(5)
805	5.2001(7)	8.6630(15)	202.87(6)	490	5.2426(7)	8.8287(20)	210.14(6)
				610	5.2498(5)	8.8355(14)	210.89(4)
				690	5.2531(6)	8.8388(19)	211.23(6)
				790	5.2600(7)	8.8434(20)	211.89(6)

Figures in brackets are estimated standard deviations in the last place.

† Quartz as internal standard, other data with platinum as internal standard.

* Average of room temperature data based on platinum.

parameters of SrAl_2O_4 at room temperature are in fair agreement with those of Hanic *et al.* (1979): $a = 5.1497(8)$, $b = 8.836(2)$, $c = 8.442(1)$ Å, and $\beta = 93.43(1)^\circ$, and those of Schulze and Müller-Buschbaum (1981): $a = 5.163$, $b = 8.816$, $c = 8.447$ Å, and $\beta = 93.42^\circ$. It is not very meaningful to attempt to make direct comparisons between our data and those of Ito *et al.* (1977*a, b*) because their monoclinic unit cell is incorrect and they only report their cell parameters to two significant places.

The relationships between the cell parameters and mole fraction of BaAl_2O_4 were fitted by least squares to an empirical quadratic equation, $y = a + bx + cx^2$. However, with the exception of a and β for the monoclinic solid solutions the data better fitted a linear equation. The regression data are given in Table III. Extrapolation of the cell parameters for both solid solutions into the region of coexistence shows that there are small but significant displacements between these trends for each parameter. This is particularly well shown for the a and b parameters in fig. 5. At the centre of the field of coexistence the difference between the parameters of the monoclinic and hexagonal forms are: $\Delta a - 0.29\%$, $\Delta b + 0.23\%$, $\Delta c - 0.14\%$, and $\Delta V_m - 0.24\%$. Unfortunately it was impracticable to determine the cell parameters of either form within the region of coexistence when more than about 10% of the other form was present, because of the apparent volume difference and the numerous overlapping X-ray reflections.

Table III. Regression data for cell parameter-composition relations at room temperature.

y	a	b	c	R	SE
Monoclinic solid solutions					
a , Å	5.1480	0.169(22)*	-0.230(66)	0.9981	0.0021
b , Å	8.8293	0.249(10)		0.9940	0.0036
c , Å	8.4431	0.329(19)		0.9999	0.00007
β°	93.36	-0.64(18)	-5.67(52)	0.9989	0.017
V_m , cm ³	57.696	5.16(10)		0.9985	0.038
Hexagonal solid solutions					
a , Å	5.1280	0.0959(10)		0.9994	0.0008
c , Å	8.4172	0.367(7)		0.9981	0.0054
V_m , cm ³	57.671	4.83(5)		0.9994	0.041

V_m = molar volume.

* Figures in brackets are errors in last place(s) of regression coefficients.

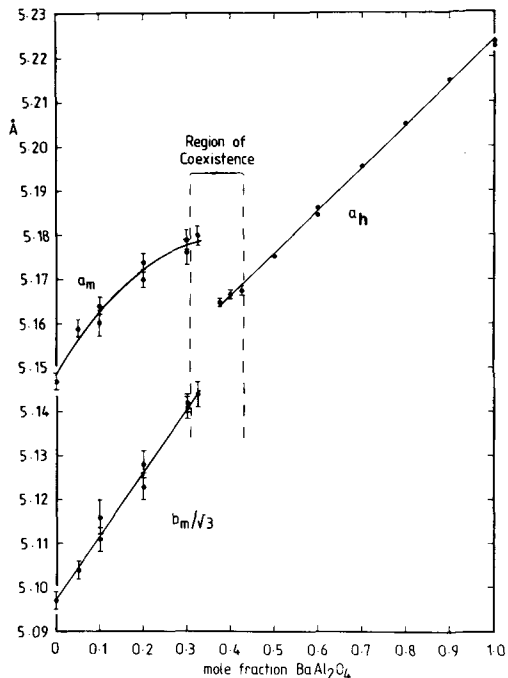


FIG. 5. Variation of a and b parameters for the solid solution series at room temperature. Error bars (one standard error) are shown where these are larger than the symbol size.

Infra-red spectra for SrAl_2O_4 and BaAl_2O_4 are shown in fig. 6 and the positions of the absorption bands are given in Table IV with data for the monoclinic and hexagonal solid solution series. There is broad agreement with the spectra reported by Schroeder and Lyons (1966) and Kolesova (1961) for BaAl_2O_4 and by Henning (1968) for BaAl_2O_4 and SrAl_2O_4 . The absorption bands group into three sets which are assigned empirically (see also Henning, 1968) as follows:

$$\begin{array}{ll} \nu_{as} \text{ Al-O-Al} & 700\text{--}1000 \text{ cm}^{-1} \\ \nu_s \text{ Al-O-Al} & 500\text{--}700 \text{ cm}^{-1} \\ \delta \text{ O-Al-O} & 300\text{--}500 \text{ cm}^{-1} \end{array}$$

The monoclinic solid-solution series have more bands in each set than the hexagonal solid-solution series. There is also a trend to loss of subsidiary bands and a broadening of absorption bands as composition changes away from both end members (cf. sodalite solid solutions, Henderson and Taylor, 1977). The principal absorption bands which occur throughout the compositional range are shown underlined in Table IV. When wavenumbers for the main absorption bands are plotted against mole fraction of BaAl_2O_4 or molar volume, there is little,

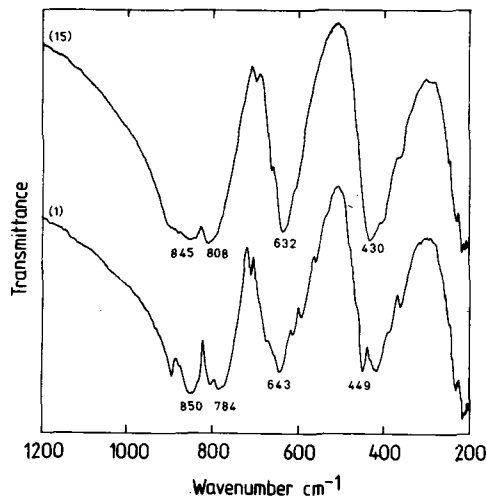


FIG. 6. Infra-red spectra for SrAl₂O₄, no. 1, and BaAl₂O₄, no. 15.

if any, change in the positions of most of the absorption bands, but there is an apparent discontinuity in band position between the hexagonal and monoclinic solid-solution series. The only definite trend is an increase in the wavenumber of the 800 cm⁻¹ absorption band of the hexagonal solid-solution series with increasing mole fraction of BaAl₂O₄ and increasing molar volume. The lack of significant variation in wavenumbers implies there is no major change in bond distances and angles within the framework for the solid-solution series.

The monoclinic-hexagonal transformation in the (Sr,Ba)Al₂O₄ solid-solution series. Members of the Sr_{1-x}Ba_xAl₂O₄ solid-solution series, with x ≤ 0.3, transform at elevated temperatures from a monoclinic to a hexagonal form, which is structurally identical to BaAl₂O₄. The transformation temperature decreases as the Ba content increases (cf. Ito *et al.*, 1977b; A. P. Henderson, 1978).

Table IV. Infrared spectra for members of the (Sr,Ba)Al₂O₄ solid-solution series (identification numbers as in Tables I and II). Wave numbers are in cm⁻¹.

Monoclinic solid solutions (1-5):					Hexagonal solid solutions (9-15):						
1	2	3	4	5	9	10	11	12	13	14	15
											895 sh
896 s shp	896 s	895 s	892 s	893 s b							
875 sh					880 sh b	890 sh		875 sh b	875 sh b	880 sh b	875 sh
<u>850</u> s b	<u>850</u> s b	<u>848</u> s b	<u>848</u> s b	<u>848</u> s b	<u>840</u> s b	<u>850</u> s b	<u>848</u> s b	<u>850</u> s b	<u>850</u> s b	<u>846</u> s b	<u>845</u> s b
807 s	806 s	805 s	800 s								
<u>784</u> s	<u>785</u> s										
<u>775</u> sh	<u>777</u> s	<u>780</u> s b	<u>780</u> s b	<u>780</u> s b	<u>780</u> s b	<u>790</u> s b	<u>795</u> s b	<u>800</u> s b	<u>805</u> s b	<u>805</u> s b	<u>808</u> s b
712 m shp	712 m shp	710 m shp	708 shp	707 shp							698 shp
692 w sh	692 w sh	690 w sh									
673 m	672 sh	670 w sh	670 w sh	671 w sh					670 w sh	671 w sh	663 shp
<u>643</u> s	<u>645</u> s	<u>641</u> s	<u>639</u> s	<u>638</u> s	<u>645</u> s b	<u>645</u> s	<u>640</u> s	<u>635</u> s	<u>638</u> s	<u>638</u> s	<u>632</u> s
612 m	612 m	610 m	608 m	603 m							606 w sh
593 m	593 m shp	590 m	590 m	590 sh							
559 m	559 m	557 m sh	552 w	550 sh							
538 w sh		535 w sh									
465 w sh	467 w sh	462 w sh	460 w sh	461 w sh							
<u>449</u> s shp	<u>450</u> s shp	<u>446</u> s shp	<u>446</u> s shp	<u>445</u> s	<u>430</u> s b	<u>435</u> s	<u>433</u> s	<u>434</u> s	<u>433</u> s	<u>430</u> s	<u>430</u> s
423 s			428 s	430 s							
415 s	418 s b	414 s b	412 s	408 s b						400 w sh	405 m sh
390 m sh	388 m sh	385 sh	387 sh								
362 m shp	363 m shp	360 shp	395 shp	360 m sh					376 w sh	376 w sh	365 m sh

s = strong, m = moderate, w = weak, shp = sharp, b = broad, sh = shoulder.

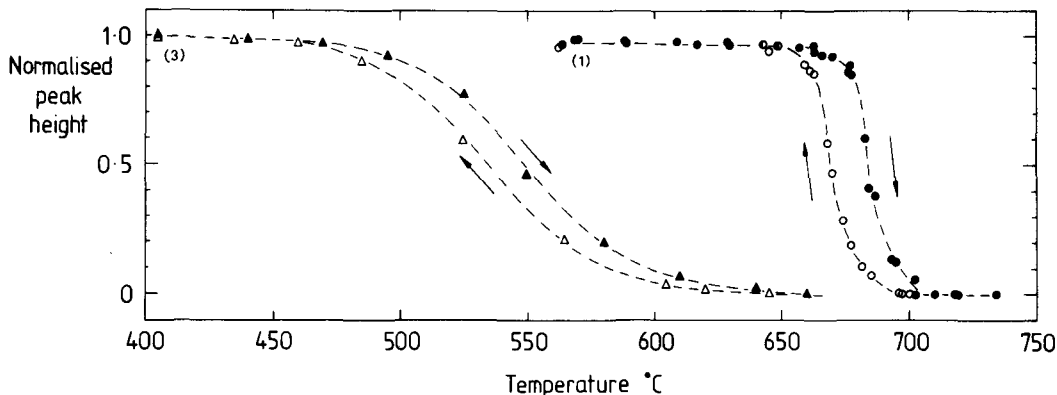


Fig. 7. Normalized and averaged intensities of the $11\bar{2}_m$, 112_m and the combined $022_m + 102_h$ reflections as a function of temperature for SrAl_2O_4 , no. 1, and $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Al}_2\text{O}_4$, no. 3. The solid and open symbols are for heating and cooling respectively.

The transformation of SrAl_2O_4 was studied in detail by monitoring the changes in position and intensity of the $11\bar{2}_m$, 022_m and 112_m X-ray reflections of the monoclinic form and the 102_h reflection of the hexagonal form as the temperature was increased in steps of 5 to 10 °C. Over a range of ~40 °C the reflections of both forms were present in the X-ray diffraction pattern. On heating, the two forms coexist from 665 to 705 °C, and from 695 to 655 °C cooling (fig. 7); the hysteresis is about 15 °C. The positions of the reflections changed smoothly over the temperature range studied (fig. 8). The $11\bar{2}_m$ and 112_m reflections did not coalesce as the transformation took place to give the single 102_h reflection but gradually disappeared, whilst the combined $022_m + 102_h$ reflection increased in intensity. There is, therefore, no continuity between the two forms but instead a discrete change occurs. Equilibrium was reached very quickly for each temperature step (probably instantaneously) because we were unable to detect any changes in the positions or intensities of the peaks with time, and the intensities and 2θ values were reproducible over three heating and cooling cycles. The above behaviour is not unusual and has been reported for several compounds including cristobalite (Leadbetter and Wright, 1976), zirconia (Wolten, 1963), and NH_4Cl (Dinichert, 1944).

The transformation behaviour of the monoclinic solid-solution series was not studied in the same detail as for SrAl_2O_4 . However, the region of coexistence and the hysteresis were established by following the changes in intensity of the $11\bar{2}_m$, 112_m , 022_m and 102_h reflections; as for SrAl_2O_4 the changes were apparently instantaneous for each temperature. Although the hysteresis was substantially the same, 15 to 20 °C, the temperature range over which the monoclinic and hexagonal forms

coexisted was much greater and increased with increasing Ba content (fig. 7), reaching a maximum of 235 °C for $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{Al}_2\text{O}_4$. In such circumstances it was impracticable to define a single transformation temperature. Instead the lower (T_L) and upper temperature (T_U) limits of the region of coexistence were determined (Table V).

Ito *et al.* (1977b) did not report the presence of a region of coexistence at room temperature or at elevated temperatures for the SrAl_2O_4 - BaAl_2O_4 system. However, as part of an honours year project, I. F. Mackay at Aberdeen University (reported by A. P. Henderson, 1978) observed a region of coexistence at room temperature and elevated temperatures. At room temperature the region of coexistence extended from $x = 0.35$ to

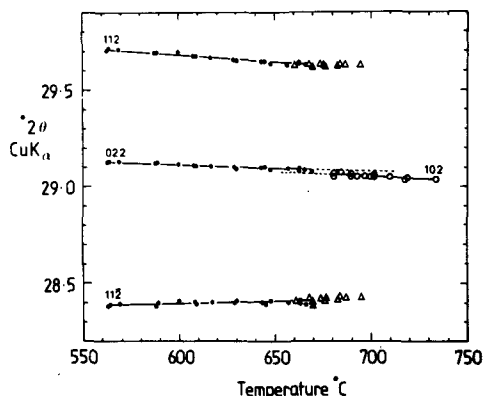


Fig. 8. Positions (2θ) of the $11\bar{2}_m$, 022_m , 112_m , and 102_h reflections of SrAl_2O_4 as a function of temperature. Symbols: ● monoclinic form only, △ monoclinic plus hexagonal form, ○ hexagonal form only.

$x = 0.50$; that is at more Ba-rich compositions than found here. For $\text{Sr}_{0.85}\text{Ba}_{0.17}\text{Al}_2\text{O}_4$ the lower and upper temperature limits for the region of coexistence were 425 and 525 °C respectively, and for $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Al}_2\text{O}_4$ they were 275 and 405 °C respectively. In both cases these boundaries are within those reported here.

We have already deduced that the monoclinic and hexagonal forms coexisting at room temperature in the solid solution series with between 0.31 and 0.43 mole fraction BaAl_2O_4 must have the same compositions. End-member SrAl_2O_4 and monoclinic solid solutions show a similar region of coexistence at elevated temperatures within which there is instantaneous equilibration between monoclinic and hexagonal forms for each increase in temperature. There can be little doubt that the two forms present in SrAl_2O_4 at elevated temperature must be isochemical and, by analogy, those in the solid solutions should also have identical compositions.

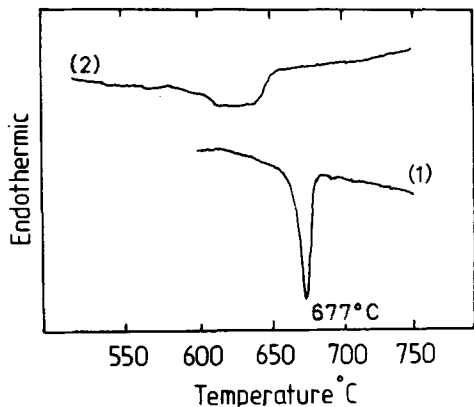


Fig. 9. DTA curves for SrAl_2O_4 , no. 1, and $\text{Sr}_{0.95}\text{Ba}_{0.05}\text{Al}_2\text{O}_4$, no. 2.

The DTA run for SrAl_2O_4 was completely consistent with the X-ray data. On heating there was a single sharp endothermic peak with a characteristic temperature of 677 °C. On cooling, the characteristic temperature was 662 °C, giving a hysteresis of 15 °C as in the X-ray data. The DTA peak was two to three times as broad as that of the quartz used for temperature calibration, and this is consistent with the 'smeared' nature of the transformation. The DTA run for $\text{Sr}_{0.95}\text{Ba}_{0.05}\text{Al}_2\text{O}_4$ gave a much broader endotherm of reduced height (fig. 9) consistent with the greater range of transformation temperature. Despite the broadening, the area under the peak was approximately

the same as that for SrAl_2O_4 . A crude estimate of the heat of transition for SrAl_2O_4 , taking 4.8 cal/g for the α - β transition of quartz (Kelley, 1960), was 6.4 cal/g. This estimate is larger than that found by Ito *et al.* (1977a) using differential scanning calorimetry (DSC) [2.3 cal/g] but these authors do not quote the value they adopted for the α - β quartz transition. The DTA run on the only other specimen examined, $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{Al}_2\text{O}_4$, did not reveal any peaks but there were slight inflections at 250 and 300 °C. It is presumed that in this case the transformation is no longer detectable by DTA due to it being spread over 235 °C. Ito *et al.* (1977a, b) did not report any hysteresis in the transformation temperature for either DTA or DSC runs on the monoclinic solid solutions and, with the exception of SrAl_2O_4 , their transformation temperatures are between T_L and T_U (Table V). Neither did they report broadening of the DTA or DSC peaks with increasing substitution of Ba in SrAl_2O_4 . However, the decrease in their heats of transition could be due to the spreading of the transformation over an increasing temperature range as Ba replaces Sr.

Thermal expansion behaviour of the (Sr,Ba)Al₂O₄ solid solution series. Cell parameters for members of the solid-solution series at elevated temperatures are given in Tables I and II and shown in fig. 10. Oehschlegel *et al.* (1974) determined the cell parameters of BaAl_2O_4 at elevated temperatures but their expansion curves were not reversible because of reaction between the BaAl_2O_4 and admixed silica glass, and hence some of their high-temperature data must be unreliable. The cell parameters of Ito *et al.* (1977a) for SrAl_2O_4 at 700 °C, $a = 5.14$ and $c = 8.47$ Å, are within 0.01 Å of our values.

The expansion curves for BaAl_2O_4 show a gradually increasing rate of expansion for the a -axis and a gradually decreasing rate of expansion for the c -axis. $\text{Sr}_{0.1}\text{Ba}_{0.9}\text{Al}_2\text{O}_4$ shows similar thermal expansion behaviour. The axial expansions of the remaining hexagonal solid solutions show either an increasing or constant rate. Data for expansion curves fitted to an equation of the type $y = y_0(1 + aT + bT^2)$ for the hexagonal solid-solution series are given in Table VI with calculated mean expansion coefficients. We do not suggest that the thermal expansion curves have an exact quadratic form but our experience is that quadratic curves generally give a very close fit to the observations (Henderson and Taylor, 1978). In addition, normalization to the cell edge at 0 °C allows direct comparison of regression data for different samples. The expansion coefficients for the a -axes show no definite trend as a function of composition, whereas those for the c -axes show a marked decrease as the mole fraction of BaAl_2O_4 is increased.

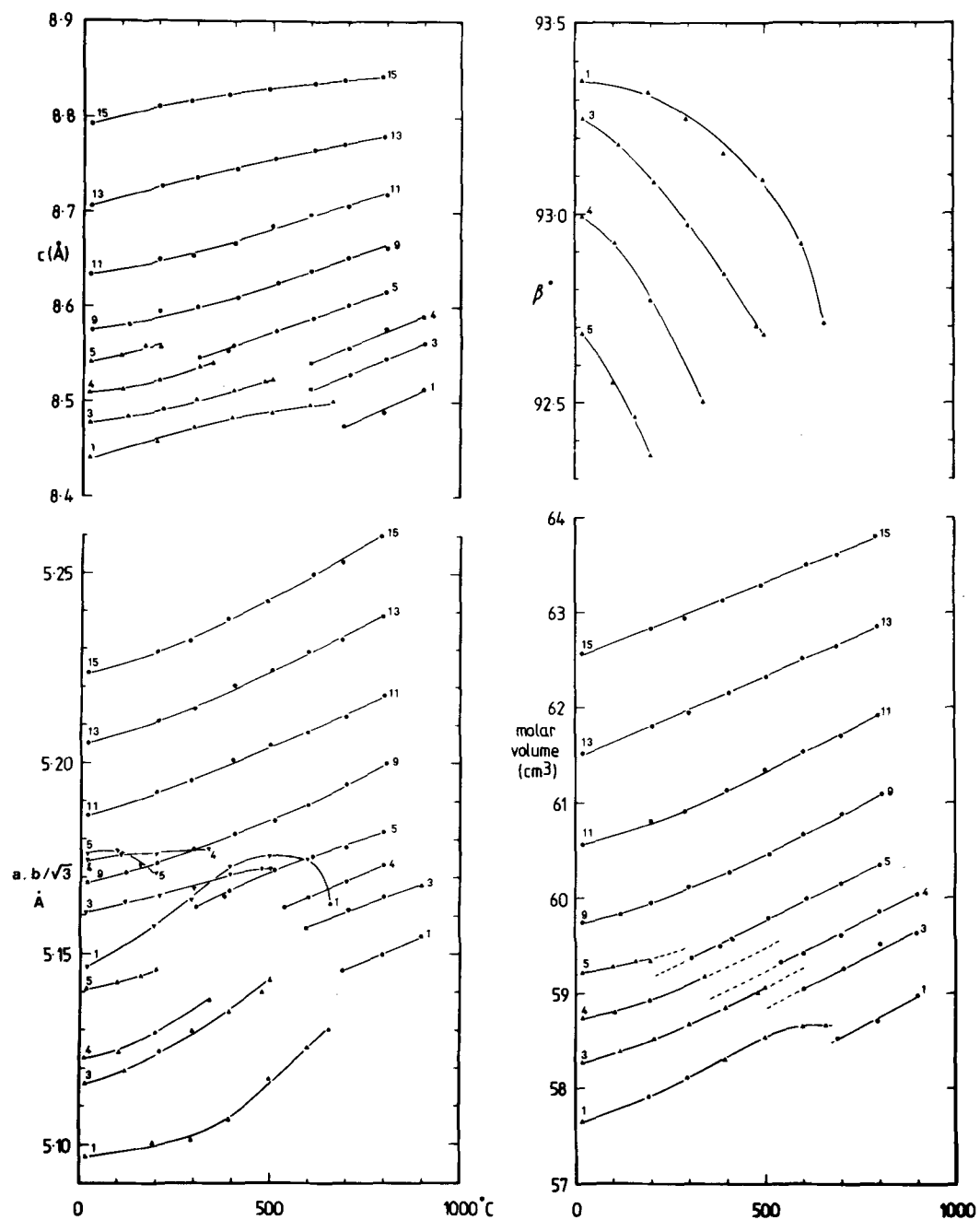


FIG. 10. Thermal expansion trends for the (Sr,Ba) Al_2O_4 solid-solution series. Identification numbers are as in Tables I and II. Symbols: monoclinic phases ∇ a , \blacktriangle $b/\sqrt{3}$, c , V_m , β ; hexagonal phases \bullet .

The expansion curves for monoclinic SrAl_2O_4 differ from other members of the monoclinic solid-solution series. Its a -axis increases until about 500°C , decreases, and then decreases sharply just before the transformation is initiated. The a -axes of the other monoclinic solid solutions tend to show constant or slightly decreasing rates of expansion. The b -axes of all the monoclinic series show an increasing rate of expansion. The c -axis of monoclinic SrAl_2O_4 shows a decreasing rate of expansion, whereas those of the other monoclinic solid-solution series show an increasing rate. The angle β decreases at an increasing rate but in no case does it decrease below 92° before the transformation begins.

The cell parameter trends show discontinuities associated with the transformation of the monoclinic to hexagonal forms. The discontinuities are characterized by decreases in a , c , V_m , and β (to 90°) and increases in b (fig. 10). Extrapolation of the molar volumes of the monoclinic and hexagonal forms into the region of coexistence (fig. 10) for the different composition samples indicates volume discontinuities of between -0.2 and -0.3% . The size of the volume discontinuities and the sense of the changes for the other cell parameters are similar to those found for the transformation in the compositional series at room temperature (see before). The presence of these discontinuities is highly significant as they indicate that the transformation is first order.

Fig. 11 shows the SrAl_2O_4 - BaAl_2O_4 phase diagram at subsolidus temperatures with the fields for stable monoclinic and hexagonal forms and the

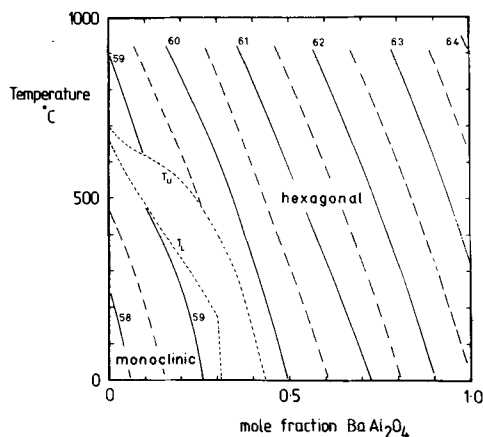


FIG. 11. Phase diagram for the system SrAl_2O_4 - BaAl_2O_4 showing the region of coexistence with upper boundary, T_U , and lower boundary, T_L . The full and broken lines are lines of equal molar volume (cm^3).

region of coexistence. Also shown are lines of equal molar volume for both forms and those for 59 cm^3 exhibit the displacement characteristic of the transformation. Note that strictly the region of coexistence should not appear on a temperature-composition phase diagram if the coexisting phases have identical compositions. This matter is dealt with more fully in the discussion.

Discussion

The monoclinic-hexagonal transformation. The similar structures of BaAl_2O_4 (Hörkner and Müller-Buschbaum, 1979) and SrAl_2O_4 (Schulze and Müller-Buschbaum, 1981) indicate that the transformation can take place without the rupture of bonds (fig. 2). It merely requires co-operative changes in the tilting of the tetrahedra coupled with a change in the angle β to 90° . Such atomic changes accompanying a structural transformation in a framework structure would ordinarily define the transformation as displacive. However, the thermal hysteresis, the coexistence of the low- and high-temperature forms over a considerable range of temperature, and the apparent lack of a compositional difference between the two forms give the transformation additional characteristics similar to those of martensitic transformations in metals. Thus the transformation takes place with a volume discontinuity and a marked anisotropy of shape change which together generate the elastic strain and strain energy associated with martensitic transformations. At high temperatures the transformation is athermal; that is, once the temperature for the start of the transformation is reached, it only takes place when the temperature is changing. If the temperature is held constant part way through the transformation then an equilibrium proportion of the two forms is achieved virtually instantaneously. Identical behaviour has been described for the monoclinic-tetragonal transformations in zirconia and hafnia (Wolten, 1963).

The reason for the athermal nature of the transformation is that the transformation starts with a transformed nucleus which is coherent with the host crystal. As the transformed region grows the volume and shape changes produce strains which oppose the progress of the transformation and stop it before it is complete. A further change in temperature provides sufficient energy for the transformation to proceed further until a new equilibrium is achieved, and so on until the whole crystal has transformed. Thus in addition to the conventional variables of temperature and pressure, strain energy is an extra variable for transformations of this type. This additional degree of freedom explains the apparent violation of the

phase rule by the presence of the region of coexistence. Since the present samples were in powder form it is also likely that particle size and surface energy contribute to the athermal nature of the transformation.

The fact that the temperature ranges over which the transformations occur increase with increasing Ba content (Table V) may indicate that the presence of greater proportions of large Ba ions increases the degree of strain in the structure.

At room temperature, for compositions within the region of coexistence, the transformation appears to take place isothermally, perhaps implying a diffusion process. However, due to the fact that the parameters of the monoclinic form remain constant during the transformation at room temperature and the probability that thermally-activated diffusion would proceed at an insignificant rate at room temperature, some other mechanism for this behaviour should be sought. It is possible that the transformation is activated by interaction between the strained crystallites and adsorbed moisture in the same way that moisture has a marked influence on the fracture behaviour, causing enhanced crack propagation, of brittle oxide ceramics and glasses (Weiderhorn, 1974).

There are relatively few well-documented transformations of this type for non-metallic compounds. Those for which the experimental evidence is reasonably unambiguous include: zirconia and hafnia (Wolten, 1963), cristobalite and AlPO_4 (Leadbetter and Wright, 1976), BaTiO_3 (Megaw, 1947; Kay and Vousden, 1949), NH_4Cl (Dinichert, 1944), KH_2PO_4 (Kobayashi *et al.*, 1970) and WO_3 (Ackermann and Sorrell, 1970).

The comment was made earlier that the field of coexistence should not be present in a phase diagram such as that of fig. 11. This statement is of such importance with regard to phase diagrams that it is worth quoting Wolten (1963). 'One important consequence of the diffusionless character of a phase transformation [such as that reported here] is the fact that compositional changes cannot occur. The material undergoing the transformation need not be a single compound but may be a solid solution, and yet it will behave as a single material. In the phase rule sense, the diffusionless transformation is always a unary phase reaction regardless of the number of components that would be counted for more conventional phase equilibria. Conventional phase equilibria give rise, in binary systems, to two-phase regions filled with horizontal tie-lines which connect two phases of differing compositions in equilibrium. This type of two-phase region is absent from a binary phase diagram if the reaction is diffusionless, for then the system is unary for the purposes of this transformation. This point has been overlooked in many published phase diagrams and discussions of binary systems of zirconia.' In the later part of this quotation Wolten was referring to binary systems with solid solution. Strictly speaking then there is not a two-phase region in fig. 11 but a region on the diagram where the monoclinic-hexagonal transformation is smeared out. Other binary systems to which Wolten's last sentence applies are those with Ca_2SiO_4 as an end member.

Hazen (1977) has suggested that some transformations are dimensionally controlled to the extent that they take place at a critical size of the

Table V. Temperatures and cell parameters for the boundaries of the region of coexistence.

Composition ($\frac{M}{M}\text{Al}_2\text{O}_4$)	T_L	T_U	ΔT	monoclinic form at T_L :					hexagonal form at T_U :		
				a	b	c	β	v_m	a	c	v_m
Sr	665(5)*	695(5)	40	5.162	8.887	8.500	92.68	58.66	5.146	8.475	58.52
$\text{Sr}_{0.95}\text{Ba}_{0.05}$	555(10)	640(10)	120								
$\text{Sr}_{0.9}\text{Ba}_{0.1}$	470(10)	620(10)	175	5.172	8.908	8.520	92.71	59.03	5.157	8.516	59.06
$\text{Sr}_{0.8}\text{Ba}_{0.2}$	340(5)	545(10)	225	5.177	8.899	8.540	92.50	59.18	5.162	8.536	59.31
$\text{Sr}_{0.7}\text{Ba}_{0.3}$	170(10)	380(10)	235	5.172	8.911	8.556	92.43	59.31	5.165	8.556	59.52
$\text{Sr}_{0.625}\text{Ba}_{0.375}$	< 20	145(20)							5.168	8.564	59.65
$\text{Sr}_{0.575}\text{Ba}_{0.425}$	< 20	~20							5.168	8.574	59.72

ΔT = average of temperature range of coexistence for heating and cooling cycles.

T_L = temperature, on heating, of appearance of detectable hexagonal form with monoclinic form.

T_U = temperature, on cooling, of appearance of detectable monoclinic form with hexagonal form.

* Figures in brackets are estimated errors (\pm).

structure whether caused by pressure, temperature or composition. This is not the case with the present transformation since the molar volumes at both T_U and T_L (Table V) increase with increasing mole fraction of BaAl_2O_4 .

Thermal expansion behaviour. Our interpretation of the thermal expansion behaviour of framework structures is based on the following assumptions: (1) That at room temperature few framework structures exist in an idealized, fully-expanded state, but rather are partially-collapsed and distorted versions of such a structure. (2) That the collapse and distortion is largely brought about by the co-operative tilting and partial rotation of the framework tetrahedra, sometimes with more than one tilt system in operation. The degree of collapse and distortion is strongly influenced by the presence and size of cavity ions. (3) That there is little, if any, expansion of the framework bonds and that any significant expansion of the whole structure or any particular direction is largely due to the gradual removal of the co-operative tilting towards the idealized fully-expanded structure. (4) That the expansion drops to a relatively low rate when the fully-expanded state is achieved or when further removal of tilting for the whole structure or for a particular direction is no longer possible. We are uncertain as to whether the expansion of the cavity ion-framework bonds is the driving force for the removal of the tilting or whether the bonding forces act as a restraint.

For tilting models the idealized relationship between a cell parameter and a framework dimension, for example the tetrahedron edge, generally includes the cosine of the tilt angle, φ (Taylor, 1972). Depending on whether φ is large or small the same change in φ over a given range of temperature will have a large or small effect, respectively, on the cell parameter (Henderson and Taylor, 1978; Dempsey and Taylor, 1980). Hence the expansion coefficient for a more-collapsed framework (higher φ) will be higher than that for a less-collapsed framework (lower φ).

The relatively high expansion of the a - and c -axes of the hexagonal forms of the $(\text{Sr},\text{Ba})\text{Al}_2\text{O}_4$ solid-solution series indicate that the two tilt systems, identified in the introduction, are operative. Except for BaAl_2O_4 between 500 and 750 °C the expansion coefficients for c are greater than those for a (Table VI). This is evidence that the second tilting system (tilting of the tetrahedra relative to the 0001 plane) is operational since operation of only the first tilt system (co-operative rotation of tetrahedra about the threefold axes which lie parallel to the triad axes of the structure) should only affect the a and b axes. The mean linear expansion coefficients (500–700 °C) for the c -axis of the hexagonal solid

solutions (Table VI) decrease as the mean cavity cation radius or the molar volume increase. We attribute this to the effect of the cosine of the tilt angle (second tilting system), as described above. The decreasing rate of expansion of the c -axes of $\text{Sr}_{0.2}\text{Ba}_{0.8}\text{Al}_2\text{O}_4$ and BaAl_2O_4 with increasing temperature suggests that for these compositions the removal of the second tilt system is approaching its limit. In contrast, the mean linear expansion coefficients (0–500 °C and 500–700 °C) for the a -axes show no definite trend for the Sr-rich members, but show an increase for the Ba-rich members as the mean cavity cation radius or the molar volume increases. There is no obvious explanation for this unexpected behaviour, but it may result from distortion of the framework tetrahedra.

Temperature and composition as analogous variables. Recently, the broad similarities in the structural behaviour of framework structures when subject to increasing pressure, decreasing temperature or decreasing size of cavity ion have received particular attention (Hazen, 1977). Despite the fact that pressure, temperature, and composition are independent variables the similar effects they have on structural behaviour have led to an implication that they are somewhat more than analogous. For example, d'Amour *et al.* (1979) show a diagram (their fig. 4) with P and T on the same axis, and with the P and T scales adjusted to give an apparent continuity to the change in the dependent variable, the quartz tilt angle, between the two independent variables. Not only is this a misleading form of presentation, in that P and T should not appear on the same axis, but the intention of the diagram to show that the effect of P and T on the tilt angle is analogous is incorrect. Levien *et al.* (1980) have since shown (their fig. 10) that different structural changes cause the volume change for increased T or P . This implies that attempts to equate changes in structure brought about by pressure, temperature or composition should be undertaken with caution. The problem is generally the selection of a suitable parameter to which the structural changes can be related. Ideally, it should be a parameter which is indicative of the structural state, such as a tilt angle, and preferably not a structural dimension, which can be seriously affected by thermal motion.

The present work comprises a compositional and thermal-expansion study of the $(\text{Sr},\text{Ba})\text{Al}_2\text{O}_4$ solid-solution series and so it is pertinent to analyse the structural behaviour with reference to temperature and composition. Unfortunately, in the absence of an ideal parameter to characterize the structural state we have had to show the changes in the crystallographic axes as a function of molar volume

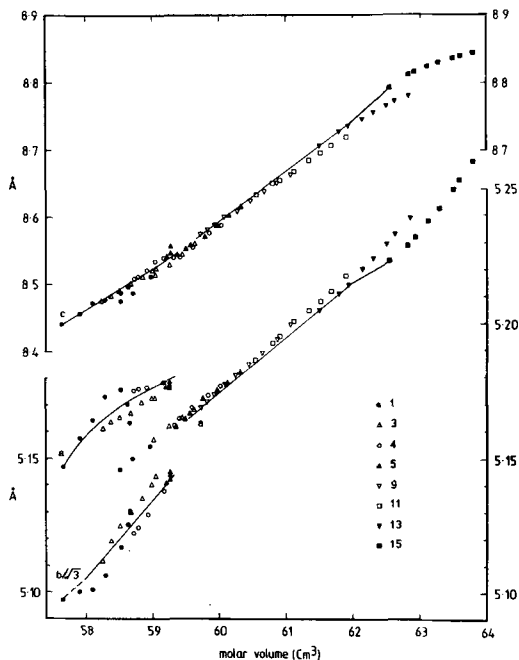


FIG. 12. The effect of temperature and composition on the cell parameters of the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ solid solution series as a function of the molar volume. The solid lines give the compositional data and the symbols the thermal data. Identification numbers are as in Tables I and II.

(fig. 12). For the c -axis data there is a similarity of behaviour as regards temperature and composition except for Ba-rich compositions for which the trend with increasing temperature falls below the compositional trend. The a - and b -axes of SrAl_2O_4 (\bullet) show a distinctly different trend with temperature relative to that for composition. Unfortunately, the precision of the cell parameters for the remaining monoclinic structures is insufficient to say whether the trends for temperature are different from those for composition. The a -axes of the hexagonal structures show a similarity of behaviour as regards temperature and composition except for Ba-rich members for which the trend with increasing T lies above that for changing composition.

Conclusions and application to silicate minerals

The structural relations, thermal expansion behaviour, and characteristics of the transformation in the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ system should have a wider significance in the study of the nepheline family as a whole. Although the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ series are relatively undistorted kalsilite-like hettotypes, the broad similarity between their structural behaviour and that of the more distorted nepheline minerals

could help solve various problems encountered during the study of natural nephelines and synthetic $\text{NaAlSiO}_4(\text{Ne})\text{-KAlSiO}_4(\text{Ks})$ solid solutions.

The relatively large changes in the a - and c -axes of the hexagonal $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ solid solutions as a function of temperature and composition, coupled with the direct evidence from the structure of BaAl_2O_4 , are taken to indicate the presence and operation of the two tilt systems outlined in the introduction. Similar large changes in a and c are seen for nepheline and kalsilite as a function of composition (Smith and Tuttle, 1957; Ferry and Blencoe, 1978) and for nepheline as a function of temperature (Sahama, 1962; Foreman and Peacor, 1970; Henderson and Roux, 1976). However, the space groups adopted for both nepheline and kalsilite do not permit the second tilt system (tilting of the tetrahedra relative to the 0001 plane); nor indeed does the space group adopted for the sub-cell of BaAl_2O_4 . It is now known that the latter structure is an 'average' of a superstructure in which both tilt systems were in operation for the majority of the tetrahedra. The presence of superstructure reflections in nepheline and kalsilite (Parker and McConnell, 1971; Perrotta and Smith, 1965) and the problems encountered in refining their structures (Perrotta and Smith, 1965; Dollase, 1970; Foreman and Peacor, 1970; Simmons and Peacor, 1972) suggest that these also may be 'averaged structures'. In fact their real structures may be superstructures possessing both tilt systems. In this context it is relevant to note that high-tridymite, which is the basis of the framework of nepheline and kalsilite, probably does not have the ideal structure proposed by Gibbs (1927) but has tilted tetrahedra giving a mean Si-O distance of 1.607 Å and Si-O-Si angles ranging from 147 to 152° (Kihara, 1978).

The monoclinic-hexagonal transformation in the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ solid-solution series is only the second report of a transformation in a tetrahedral framework structure with martensitic characteristics; the first was for cristobalite (Leadbetter and Wright, 1976). For cristobalite and SrAl_2O_4 there can be little doubt that the coexisting forms are of identical composition. For the region of coexistence within the $\text{SrAl}_2\text{O}_4\text{-BaAl}_2\text{O}_4$ system it is important to establish that the coexisting forms are also of identical composition. That is, that the transformation is not a diffusional transformation with the coexisting forms having different Sr/Ba ratios. The evidence for identical compositions is indirect but reasonably unequivocal and is based on (i) the lack of a change in the 2θ values for the $11\bar{2}_m$ and $11\bar{2}_m$ reflections as the proportion of the monoclinic and hexagonal phases changes as a function of time at room temperature, (ii) the

Table VI. Thermal expansion regression data for hexagonal members of the (Sr,Ba)Al₂O₄ solid-solution series.

Compound (MA ₂ O ₄)	y	y ₀	10 ⁶ a	10 ⁶ s _a	10 ⁹ b	10 ⁹ s _b	R	SE	10 ⁶ α ₁	10 ⁶ α ₂	
M											
	Sr	$\underline{a}, \overset{\circ}{\text{A}}$	5.1175	8.00	0.11			0.9999	0.0008	8.00	8.00
		$\underline{c}, \overset{\circ}{\text{A}}$	8.3473	21.9	3.8			0.9851	0.005	21.9	21.9
Sr _{0.9} Ba _{0.1}		$\underline{V}, \overset{\circ}{\text{A}}^3$	189.29	38.5	4.2			0.9941	0.12	38.5	38.5
		$\underline{a}, \overset{\circ}{\text{A}}$	5.1353	7.16	0.67			0.9914	0.0008	7.16	7.16
		$\underline{c}, \overset{\circ}{\text{A}}$	8.4159	19.24	0.69			0.9987	0.0013	19.2	19.2
Sr _{0.8} Ba _{0.2}		$\underline{V}, \overset{\circ}{\text{A}}^3$	192.16	34.11	0.91			0.9993	0.04	34.1	34.1
		$\underline{a}, \overset{\circ}{\text{A}}$	5.1398	8.10	0.11			0.9997	0.0002	8.10	8.10
		$\underline{c}, \overset{\circ}{\text{A}}$	8.4541	17.8	1.8			0.9858	0.0043	17.8	17.8
Sr _{0.7} Ba _{0.3}		$\underline{V}, \overset{\circ}{\text{A}}^3$	193.39	34.5	1.9			0.9956	0.11	34.5	34.5
		$\underline{a}, \overset{\circ}{\text{A}}$	5.1499	7.95	0.42			0.9933	0.0010	7.95	7.95
		$\underline{c}, \overset{\circ}{\text{A}}$	8.4994	17.2	0.37			0.9988	0.0014	17.2	17.2
Sr _{0.575} Ba _{0.425}		$\underline{V}, \overset{\circ}{\text{A}}^3$	195.20	33.4	0.73			0.9988	0.06	33.4	33.4
		$\underline{a}, \overset{\circ}{\text{A}}$	5.1684	4.34	0.34	4.04	0.40	0.9996	0.0003	6.36	9.36
		$\underline{c}, \overset{\circ}{\text{A}}$	8.5711	9.77	1.4	4.9	1.7	0.9979	0.0024	12.2	15.8
Sr _{0.4} Ba _{0.6}		$\underline{V}, \overset{\circ}{\text{A}}^3$	198.28	18.29	1.4	13.4	1.6	0.9996	0.054	25.0	34.6
		$\underline{a}, \overset{\circ}{\text{A}}$	5.1855	6.46	0.60	1.58	0.69	0.9989	0.0006	7.25	8.40
		$\underline{c}, \overset{\circ}{\text{A}}$	8.6265	13.28	0.68			0.9920	0.004	13.3	13.3
Sr _{0.2} Ba _{0.8}		$\underline{V}, \overset{\circ}{\text{A}}^3$	200.98	22.6	2.5	7.8	2.9	0.9986	0.09	26.5	31.9
		$\underline{a}, \overset{\circ}{\text{A}}$	5.2043	6.09	0.70	2.93	0.81	0.9987	0.0007	7.56	9.72
		$\underline{c}, \overset{\circ}{\text{A}}$	8.7040	13.07	0.41	-2.43	0.47	0.9997	0.0007	11.9	9.97
Ba		$\underline{V}, \overset{\circ}{\text{A}}^3$	204.08	28.33	0.50			0.9991	0.07	28.3	28.3
		$\underline{a}, \overset{\circ}{\text{A}}$	5.2223	5.91	0.54	4.08	0.67	0.9992	0.0006	7.95	10.97
		$\underline{c}, \overset{\circ}{\text{A}}$	8.7897	12.03	0.59	-5.58	0.74	0.9987	0.0011	9.24	5.03
	$\underline{V}, \overset{\circ}{\text{A}}^3$	207.56	25.99	0.38			0.9993	0.06	26.0	26.0	

The data were fitted to an equation of type $y = y_0 (1 + aT + bT^2)$; s_a and s_b are the standard errors of the regression coefficients a and b ; R is the correlation coefficient and SE the standard error of the estimate; α_1 and α_2 are calculated mean expansion coefficients for the temperature ranges 0-500°C and 500-750°C respectively.

apparent instantaneous achievement of the equilibrium ratio of the two forms at a given temperature within the region of coexistence, (iii) the lack of any change in the 2θ values of the X-ray reflections as a function of time within the region of coexistence at a given temperature, and (iv) the continuation of the trend of the $\Delta 2\theta(11\bar{2}-11\bar{2})$ term across the region of coexistence as a function of composition at room temperature (fig. 4). In the lack of any evidence to the contrary we therefore assume that the coexisting phases are isochemical and that members of the (Sr,Ba)Al₂O₄ solid-solution series show exactly the same type of transformation as SrAl₂O₄ and cristobalite.

Nepheline solid solutions in the system Ne-Ks with < 2.5 mole % Ks (sub-potassic nephelines) show at least two inversions which have been

characterized using high-temperature X-ray methods (Henderson and Roux, 1977) and DSC (Henderson and Thompson, 1980). Pure-Na nephelines (NaAlSiO₄) usually consist of two phases at room-temperature; one is believed to be metastable having an orthorhombic superstructure with a tripled c axis and the other is believed to be the stable, low-temperature form having 'low-symmetry'. These pure-Na nephelines have two DSC peaks below 200°C. The peak at ~150°C was correlated with transformation of the metastable phase to hexagonal symmetry and the peak at ~190°C with transformation of the stable, 'low-symmetry' phase to hexagonal symmetry. Both inversions are smeared out over about 20 to 30°C within which temperature ranges the proportion of phases rapidly equilibrated after each

increase in temperature. Thus the transformations are athermal, reversible and show $\sim 30^\circ\text{C}$ hysteresis.

Pure-Na nepheline shows another transformation which is initiated at $\sim 880^\circ\text{C}$ and is smeared out over about 100°C . The proportions of phases change rather less rapidly at a given temperature than the lower temperature transformations but the high-temperature transformation is again reversible with about 20° hysteresis.

There is little doubt that the phases observed during the above inversions are isochemical (NaAlSiO_4) and there are close similarities with the transformation behaviour for SrAl_2O_4 . The structures of the stable, low-temperature ($< 190^\circ\text{C}$), 'low-symmetry' nepheline and the high-temperature form ($> 950^\circ\text{C}$) are not known but we can now predict an anisotropy of shape change for each of the transformations. In fact, pseudo-hexagonal cell parameters for the stable, low-temperature, 'low-symmetry' phase and for the high-temperature form can be used to estimate volume changes occurring at the appropriate transformations. The low-symmetry to hexagonal transformation at $\sim 190^\circ\text{C}$ has a ΔV of -0.3 to -0.4% while the high-temperature transformation has a ΔV of $+1.0\%$. The senses of these values are consistent with the pressure dependence of the transformations determined by DTA (Cohen and Klement, 1976). The ΔV for the low-symmetry to hexagonal transformation is remarkably similar to that for the SrAl_2O_4 transformation with which it can be correlated. The implications are that the nepheline inversions are first order and that it may be possible to model the structure of the stable, low-temperature NaAlSiO_4 phase using the structure of monoclinic SrAl_2O_4 .

The leucite group of minerals (MAlSi_2O_6 ; $M = \text{K, Rb, Cs}$) because of their volume discontinuity and anisotropy of shape change at the tetragonal/cubic inversion, might also be expected to show the same type of transformation as the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ series. The thermal expansion of the leucite minerals has been studied by Sadanaga and Ozawa (1968), Taylor and Henderson (1968), Peacor (1968), and Hirao *et al.* (1976) and none of these authors reported anything unusual about the transformation. Indeed, Sadanaga and Ozawa found that the (400, 040) and 004 X-ray reflections of the tetragonal phase gradually coalesced to give the single 400 reflection of the cubic phase and Peacor reported similar behaviour for the (800, 080); 008 doublet. Taylor and Henderson (1968) also used the coalescence of 400/004 to determine the transformation temperature. The implication is that the transformation is second order (Pankratz, 1968). We have re-examined our powder X-ray diffraction

charts for the leucites and find that the (400, 040) and 004 peaks do gradually coalesce for the natural leucite examined, but for the synthetic leucite, KAlSi_2O_6 , the tetragonal and cubic phases clearly coexisted over a temperature range of at least 30°C . The inversion temperature quoted by Taylor and Henderson (1968) for the latter mineral corresponds to the upper temperature limit for the region of coexistence. Preliminary work on synthetic and natural silica-rich leucites (Henderson, 1981) confirms this effect. For a synthetic leucite of composition $(\text{KAlSi}_2\text{O}_6)_{70}(\text{KAlSi}_3\text{O}_8)_{30}$ tetragonal and cubic phases coexisted between 480 and 600°C . Similarly, a natural leucite from the Leucite Hills, Wyoming (containing excess SiO_2 and iron-leucite molecule; Carmichael, 1967), showed a region of coexistence between 460 and 560°C . In both cases the change in proportion of phases was rapid for each increase in temperature and the inversion was reversible with hysteresis of at least 20°C . The indications are again that the coexisting phases are isochemical. All these characteristics are similar to those for the transformations in the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ series and it seems that the leucite transformation is athermal and in fact, first order. This first order character is supported by the observation (Martin and Lagache, 1975) that solid solutions in the $(\text{K,Cs})\text{AlSi}_2\text{O}_6$ and $(\text{Rb,Cs})\text{AlSi}_2\text{O}_6$ series show displacements in the plots of room temperature cell volumes against composition. These displacements occur at the change from tetragonal to cubic symmetry in the two compositional series. In addition, samples close to these critical compositions at room temperature usually consisted of coexisting tetragonal and cubic phases. Martin and Lagache speculated that one phase could be metastable but also considered the possibility that both phases were stable and of different cation compositions. In fact, by analogy with the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ system both phases could be isochemical with the region of coexistence being due to strain effects associated with the transformation.

It seems likely that the special characteristics found for the transformations in the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ series, pure-Na nephelines, and leucites may be more common in silicates than we originally anticipated. Careful re-examination of many high-low displacive transformations (e.g. carnegieite) is necessary to establish this possibility. We expect that this study of the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ series will be invaluable in extending our work to the kalsilite series and other members of the nepheline group.

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