

NEIGHBORITE,  $\text{NaMgF}_3$ , A NEW MINERAL FROM THE GREEN RIVER FORMATION, SOUTH OURAY, UTAH\*E. C. T. CHAO, HOWARD T. EVANS, JR., BRIAN J. SKINNER AND CHARLES MILTON, *U. S. Geological Survey, Washington, D. C.*

## ABSTRACT

Neighborite,  $\text{NaMgF}_3$ , occurs in the dolomitic oil shale of the Eocene Green River formation of South Ouray, Uintah County, Utah. It is associated with dolomite and quartz, and the accessory minerals burbankite, nahcolite, barytocalcite, garrelsinite, wurtzite, calcite, and pyrite. The mineral occurs in pink rounded grains or in clear twinned octahedral crystals 0.1 to 0.5 mm. in diameter. It has a vitreous luster, uneven fracture, a hardness of 4.5, and is insoluble in water. The specific gravity is 3.03 (measured) and 3.06 (calculated). Neighborite is optically anisotropic with very low birefringence and a mean index of refraction 1.364. The crystals are invariably complexly twinned.

X-ray powder patterns show that neighborite is isostructural with perovskite,  $\text{CaTiO}_3$ . The pattern was indexed on an orthorhombic unit cell having a probable space group  $Pcmm$ , with dimensions  $a=5.363 \text{ \AA}$ ,  $b=7.676 \text{ \AA}$  and  $c=5.503 \text{ \AA}$ . The expansion of the unit cell was followed to  $954^\circ \text{ C.}$  using a heating stage on the diffractometer. At  $760^\circ \text{ C.}$  the orthorhombic  $a$  and  $c$  axes coalesce and from  $760^\circ$  to  $900^\circ \text{ C.}$  the cell is tetragonal or pseudotetragonal with  $a=3.942 \text{ \AA}$  and  $c=3.933 \text{ \AA}$  (at  $760^\circ \text{ C.}$ ). At  $900^\circ \pm 25^\circ \text{ C.}$  the unit cell becomes cubic with  $a=3.955 \text{ \AA}$ . The crystal structure of neighborite is interpreted in terms of the known structure of perovskite.

## INTRODUCTION

In an extended study of the mineralogy of the Green River formation of Utah and Wyoming, one of the minerals found in the dolomitic oil shale proved to be a sodium magnesium fluoride, previously undescribed as a mineral. Its x-ray powder diffraction pattern immediately showed that it belongs to the perovskite family of crystal structures of formula type  $\text{ABX}_3$ . The present study substantiates the suggestion made by Ludekens and Welch (1952) that  $\text{NaMgF}_3$  is among a group of fluorides whose structures appear to belong to the various modifications of the perovskite type. The significance of the mineral was further enhanced when it became apparent that its structure is closely analogous in detail to that of perovskite itself. In this paper the occurrence, physical properties, crystallography and thermal properties of the new mineral are described. The mineral is named "neighborite" in grateful acknowledgment of the continued friendly interest and helpfulness of Mr. Frank Neighbor, District Geologist of the Sun Oil Co. at Salt Lake City. Through Mr. Neighbor's efforts the specimens of South Ouray and Sun-Havenstrite well cores and cuttings were preserved and made available to us, thus making possible the discovery of not only neighborite but

\* Publication authorized by the Director, U. S. Geological Survey.

also the new mineral garrelsite with elpidite and burbankite in the Utah Green River formation.

We wish to express our thanks to three of our colleagues: Blair Jones for his help in the synthesis of neighborite, Nola B. Sheffey for the spectrographic analysis, and Daniel E. Appleman for the calculated *d*-spacings of neighborite obtained with the Burroughs 220 calculator.

#### GEOLOGIC OCCURRENCE

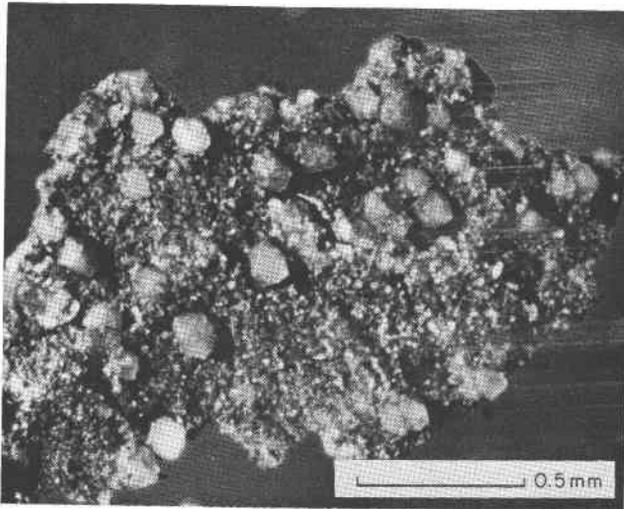
Neighborite was first found as clusters of pink and brown rounded grains in a dark brown to grayish black dolomitic oil shale of the Green River formation of South Ouray, Utah. It is associated with burbankite, nahcolite, wurtzite, barytocalcite, garrelsite, pyrite, calcite, and quartz. Cores from the South Ouray well at an unknown depth but somewhere between 1700 and 2300 feet consist of layers of fine-grained dark brown to black dolomitic oil shale interbedded with layers of coarsely crystalline material of barytocalcite and nahcolite. Most of the crystals of neighborite which occur at the top of the fine-grained shale layer are rounded to subrounded as shown in Fig. 1. This fine-grained shale layer, as shown by its *x*-ray powder pattern, consists essentially of dolomite and quartz with a minor trace of feldspar. Some rounded neighborite occurs in discrete grains as inclusions in crystals of barytocalcite in the coarsely crystalline layers.

Neighborite also occurs as cream-colored or clear, colorless octahedral crystals (Fig. 2). Such crystals were obtained from the well cuttings of the Sun Havenstrite well of Uintah County, Utah, at various depths. The crystals used in this study occur in cuttings that were collected from a depth of approximately 1930 feet within an interval of 10 feet. Besides fragments of oil-bearing dolomitic shale, the cuttings contain barytocalcite and pyrite. The total amount of neighborite obtained is less than thirty milligrams.

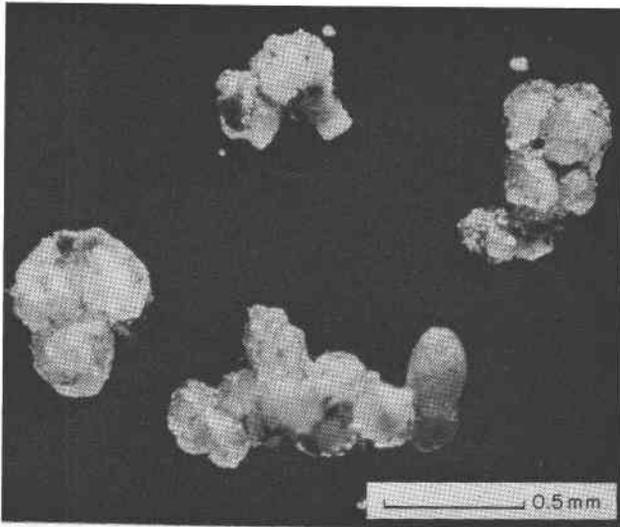
The mineral has so far been found only from these two wells in Utah, which are located less than a mile apart in an area about 5 miles SSE of South Ouray, Uintah County, Utah. Cryolite,  $\text{Na}_3\text{AlF}_6$ , has been found in the oil shales of the Green River formation from Colorado. The dolomitic oil shale there contains dawsonite,  $\text{NaAl}(\text{CO}_3)(\text{OH})_2$ , and nahcolite.

#### PHYSICAL AND OPTICAL PROPERTIES

Neighborite has a vitreous luster, an uneven fracture, no distinct cleavage, and a hardness of 4.5. Neighborite is insoluble in water but slowly soluble in hydrochloric or nitric acid and more rapidly in sulfuric acid. The specific gravity of neighborite was determined both by the



(a)



(b)

FIG. 1. Typical habit of neighborite crystals: (a) rounded crystals on a thin layer of dolomitic oil shale; (b) loose clusters of rounded and oblong crystals.

suspension or sink and float method using methylene iodide-bromoform mixtures, and with the Berman precision microbalance. Under a binocular microscope, a 0.3-mm. diameter grain was observed to be suspended within the liquid column in a nearly stationary position for five to ten

minutes. The specific gravity of neighborite determined in this way is 3.02. In another test, a sample of 4.90 mg. of the best hand-picked octahedral crystals of neighborite was used for determination of its specific gravity with the Berman balance. The specific gravity so measured is  $3.03 \pm 0.03$ .

Optically, the crystals are measurably anisotropic, but show very low birefringence about 0.003. The mean index of refraction measured with sodium light at  $25^\circ$  C. is  $1.364 \pm 0.002$ . The crystals invariably show

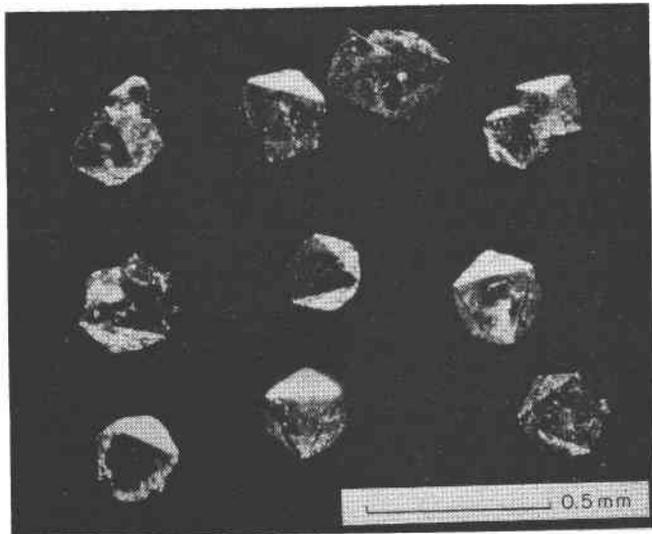


FIG. 2. Clear, single and interpenetrating crystals of neighborite.

complex ill-defined polysynthetic twinning and consequently the optical properties cannot be determined completely.

The octahedral crystals often show, in addition to the complex microscopic twinning, apparent interpenetration twinning. Besides the octahedral forms  $\{111\}$  the crystals show small cube faces  $\{100\}$  which truncate the octahedral faces. The fact that all of the crystals studied are multiply twinned was shown by the single crystal  $x$ -ray studies.

#### CHEMICAL COMPOSITION AND SYNTHESIS

Because of the small amount of clean sample at our disposal, a complete chemical analysis of the mineral was not possible. One small sample weighing several milligrams was submitted for spectrographic analysis. The semiquantitative analysis of the mineral shows major amounts of Na, Mg, F, and Si. The results of the minor elements are shown in Table 1. The silica shown in the analysis is due to the small

amounts of quartz impurities present in the sample; the presence of quartz was also evident in the  $x$ -ray powder patterns. The theoretical formula,  $\text{NaMgF}_3$ , requires F 54.64%, Na 22.05%, and Mg 23.31%.

The composition of this mineral was finally established by comparison with the artificial compound  $\text{NaMgF}_3$  which can be easily synthesized in the laboratory by our method described below, or by a method described by Ludekens and Welch (1952) or by Blair Jones' method.

TABLE 1. SPECTROGRAPHIC ANALYSIS OF THE MINOR ELEMENTS OF NEIGHBORITE  $\text{NaMgF}_3$ , FROM SOUTH OURAY NO. 1 WELL, UINTAH COUNTY, UTAH†

Ca	0.5	La	0.02
Sr	0.3	Yb	0.01
Fe	0.2	Cr	0.01
Ti	0.06	Sc	0.01
V	0.05	B	0.005
Y	0.04	Cu	0.004
Zr	0.03	Be	0.0005

† Analyst: Nola B. Sheffey.

Our method of preparation consists of grinding stoichiometric proportions of  $\text{NaF}$  and  $\text{MgF}_2$  in an agate mortar and then sintering the mixture in air at  $750^\circ\text{C}$ . for 5 hours. The fine-grained crystalline aggregate produced gives an  $x$ -ray powder diffraction pattern identical to that of the natural mineral neighborite (Table 2).

This compound has also been synthesized at much lower temperatures by Blair Jones at  $300^\circ\text{C}$ . and 30,000 bars water pressure and at  $450^\circ\text{C}$ . and 30,000 bars water pressure. Unfortunately, no single crystals suitable for  $x$ -ray investigation were produced.

The natural environment represented by the dolomitic oil shale in which neighborite occurs is that of a low temperature condition. Although the small amount of the mineral present seems geologically insignificant, the chemical environment was probably such that magnesium was abundant and aluminum deficient. The fluorine that was present therefore combined with sodium to form neighborite instead of cryolite.

#### CRYSTALLOGRAPHY

Buerger precession photographs of neighborite single crystals (using  $\text{MoK}\alpha$  radiation) are consistent, to a first approximation, with a cubic unit cell having  $a=7.67\text{ \AA}$ . The optical properties, the lack of true symmetry planes shown by the intensity of the reflections, and poor quality of the single crystal patterns strongly suggested that the true symmetry

of the crystal is lower than cubic, and that a pseudocubic aspect is produced by multiple twinning. After several crystals had been studied by the precession method, it seemed likely that the best chance of success in determining the cell constants and space group of neighborite lay in a study of the powder pattern.

The *x*-ray powder diffraction photograph of neighborite shows a remarkable resemblance to that of perovskite,  $\text{CaTiO}_3$ , both in *d*-spacing values and intensity of the reflections. As shown in Fig. 3 the correspondence is so good that there is no doubt that neighborite not only has the general perovskite type of structure, but also possesses the same

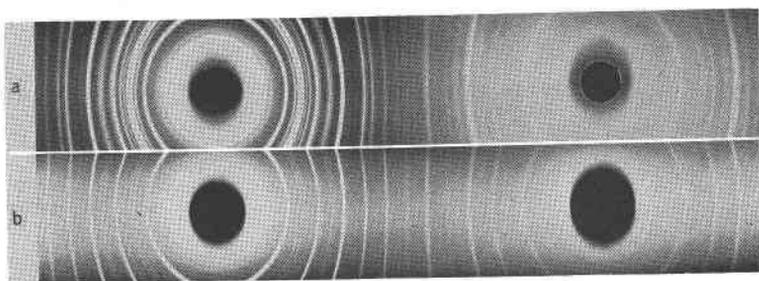


FIG. 3. *X*-ray powder diffraction patterns of (a) neighborite and (b) perovskite from Magnet Cove, Arkansas. (Patterns made with  $\text{CuK}\alpha$  radiation, and a 57.3 mm. diameter camera.)

type of distortions and superstructure of the simple cubic  $\text{ABX}_3$  pseudo unit that are characteristic of perovskite itself. This hypothesis is amply confirmed by the detailed crystallographic and thermal measurements to be described in the following sections. Such a correspondence is not surprising in view of the close similarity of the radii of the ions involved:

$\text{ABX}_3$	$\text{CaTiO}_3$	$\text{NaMgF}_3$
A	0.99 Å	0.95 Å
B	0.68	0.65
X	1.40	1.36

The powder diffraction data were measured from patterns made with film and the Philips diffractometer. Although the powder pattern of perovskite has never been correctly indexed, with the probable space group and the unit cell given for synthetic  $\text{CaTiO}_3$  by Kay and Bailey (1957) the powder pattern of neighborite was successfully indexed. The cell dimensions of neighborite were determined from a careful measurement of the 200, 040 and 002 reflections on the diffractometer record. The measured and calculated data for neighborite are listed in Table 2. The dimensions of the unit cell and pseudocell are given in Table 3, in

comparison with corresponding dimensions for  $\text{CaTiO}_3$  as given by Kay and Bailey (1957). The statement by Ludekens and Welch (1952) that  $\text{NaMgF}_3$  is tetragonal at room temperature (with  $a=7.65$  and  $c=7.30$  kX) is not supported by our work.

The specific gravity of neighborite calculated from the measured unit cell volume with 4 formula units per cell is 3.06, in good agreement with the value  $3.03 \pm 0.03$  measured as described above.

Concerning the crystal structure of neighborite, no direct analysis of it is possible at this time, and we can only assume that it is closely similar to that of perovskite. We rely, therefore, on the penetrating study of this difficult problem made by Kay and Bailey (1957). They proved that the structure of  $\text{CaTiO}_3$  has orthorhombic symmetry, and that the probable space groups are  $Pcmn$  or  $Pc2_1n$ . By a detailed analysis of the structure, they concluded that  $Pcmn$  is the correct one, and we may assume that neighborite, the stable low temperature phase, also has this space group. The crystal structure is described in a later section.

#### HIGH TEMPERATURE STUDIES OF NEIGHBORITE

Finely ground synthetic neighborite was mounted on the heating stage of a diffractometer. The heating stage was designed to provide a uniform temperature across the sample surface and temperatures were measured by means of a platinum-platinum-10 per cent rhodium thermocouple mounted at the center of the irradiated surface. The instrument was calibrated against the thermal expansion of silver and the melting point of silver. Temperature was controlled by means of an A.C. balancing bridge circuit in which the platinum heating element acted as one arm of the bridge. Temperature was controlled in this manner to  $\pm 2^\circ$  C. for extended periods. Although neighborite is quite stable in air, the heating chamber was evacuated to reduce convection currents and allow a more satisfactory temperature control. In operation the heating stage allows the same resolution obtained with conventional diffractometer mounts at room temperature.

Preliminary heating runs established that neighborite became cubic at high temperatures, and that the high temperature cubic cell coincided with the pronounced cubic "pseudo cell" present at room temperatures. The melting point was not determined.

To investigate the transition from the orthorhombic cell at room temperature to cubic cell at high temperature, the lines 002, 200, 121, 022, 220 and 040 in the orthorhombic cell were accurately measured at a series of temperatures. It is most convenient to discuss the changes occurring in terms of the cubic "pseudo cell," rather than the true orthorhombic cell. Consequently, the parameters  $a' = a/\sqrt{2}$ ,  $b' = b/\sqrt{2}$  and

TABLE 2. X-RAY POWDER DATA FOR NEIGHBORITE,  $\text{NaMgF}_3$   
 Orthorhombic,  $Pcmn$   $a=5.36_3$ ,  $b=7.67_6$ ,  $c=5.50_3$  Å, (all  $\pm .001$  Å)  
 $a:b:c=0.698:1:0.717$

<i>hkl</i>	$d_{hkl}$ (Å)calc.	Natural <sup>1</sup>		Synthetic <sup>2</sup>	
		$d_{hkl}$ (Å)meas.	Intensity	$d_{hkl}$ (Å)meas.	Intensity
110	4.396				
101	3.841				
020	3.838	3.83	35	3.85	44
111	3.435	3.44	4	3.44	7
002	2.751	2.75	4	2.75	17
121	2.715	2.71	50	2.71	54
200	2.682	2.68	4	2.68	11
012	2.590				
102	2.448	2.44	3	2.44	6
201	2.411	2.41	9	2.41	11
112	2.332	2.33	4	2.33	16
130	2.309	2.30	25	2.305	29
211	2.300			2.297	27
022	2.236	2.23	18	2.232	30
220	2.198	2.20	13	2.198	18
131	2.129	2.13	6	2.128	9
122	2.064	2.06	6	2.060	11
221	2.041	2.04	2	2.040	7
202	1.920				
040	1.919	1.918	100	1.918	100
032	1.874			1.872	3
212	1.863	1.862	4	1.862	4
132	1.769	1.765	2	1.765	3
231	1.755			1.755	4
310	1.741			1.743	3
103	1.736	1.732	3	1.733	7
222	1.717			1.716	10
141	1.717	1.713	9	1.713	6
301	1.700				
113	1.693	1.689	6	1.692	8
311	1.660	1.661	1	1.664	3
123	1.581			1.583	11
042	1.574	1.575	13	1.575	12
240	1.561			1.561	10
321	1.555	1.556	25	1.553	28
232	1.536	1.530	1		

<sup>1</sup> Natural neighborite, taken with film, camera diameter 114.59 mm.  $\text{CuK}\alpha$  radiation ( $\lambda=1.5418$  Å), Ni filter. Lower limit  $2\theta$  measurable: approximately  $6.3^\circ$  or  $14.04$  Å.

<sup>2</sup> Synthetic neighborite, using diffractometer,  $\text{CuK}\alpha$  radiation ( $\lambda=1.5418$  Å), Ni filter. Sample contains a trace of NaF, not reported.

TABLE 2 (continued)

<i>hkl</i>	$d_{hkl}$ (Å)calc.	Natural <sup>1</sup>		Synthetic <sup>2</sup>	
		$d_{hkl}$ (Å)meas.	Intensity	$d_{hkl}$ (Å)meas.	Intensity
142	1.510				
241	1.501				
302	1.499	1.499	2	1.497	2
213	1.485				
150	1.476	1.473	2	1.475	2
312	1.471				
330	1.465				
133	1.436	1.434	2	1.435	2
151	1.426				
331	1.416	1.415	1	1.415	1
223	1.408	1.404	1	1.406	1
322	1.396				
004	1.376	1.371	3	1.373	4
242	1.357	1.356	13	1.355	15
		1.340	2	1.340	3
		1.327	2	1.329	2
		1.300	4b	1.298	4
		1.282	3b	1.284	3
		1.268	1b		
		1.256	1b		
		1.234	2	1.233	1
		1.220	2	1.222	1
		1.213	4	1.212	5

TABLE 3. UNIT CELL DIMENSIONS OF SYNTHETIC NEIGHBORITE AND PEROVSKITE  
Data for  $\text{CaTiO}_3$  from Kay and Bailey (1957)

	$\text{NaMgF}_3$ (18° C.)	$\text{CaTiO}_3$ (Temp. not stated)
<i>a</i>	$5.363 \pm 0.001 \text{ \AA}$	$5.3670 \pm 0.0001 \text{ \AA}$
<i>b</i>	$7.676 \pm 0.001$	$7.6438 \pm 0.0001$
<i>c</i>	$5.503 \pm 0.001$	$5.4439 \pm 0.0001$
<i>a:b:c</i>	0.6987:1:0.7169	0.70213:1:0.71219
$a' = a/\sqrt{2}$	3.792 Å	3.7951 Å
$b' = b/2$	3.838	3.8219
$c' = c/\sqrt{2}$	3.891	3.8494
$a':b':c'$	0.9880:1:1.0138	0.99298:1:1.00719
<i>V'</i>	$56.63 \text{ \AA}^3$	$55.834 \text{ \AA}^3$

$c' = c/\sqrt{2}$  (where  $a$ ,  $b$ , and  $c$  are the unit cell edges of the orthorhombic cell) were calculated from the measurements and these are presented in Table 4, and illustrated in Fig. 4.

With rising temperature neighborite remains clearly orthorhombic, although the  $a'$  and  $c'$  lengths become progressively closer together. At  $760^\circ\text{C}$ ., and  $a'$  and  $c'$  lengths become identical, an effect which can best be observed by the coalescence of the 220 and 022 lines. Above  $760^\circ\text{C}$ .,  $a'$  and  $c'$  remain identical but  $b'$  is still measurably less than  $a'$ . The cell is now tetragonal or pseudo-tetragonal. At  $900^\circ\text{C}$ ., all reflections with orthorhombic indices  $k$  odd, and those with  $k$  even and  $h+l$  odd disappear, indicating that the tetragonal cell is congruent with the former "pseudo cell." The unit cell edges of the new tetragonal cell at this temperature are  $a = b = 3.942\text{ \AA}$  and  $c (= b') = 3.933\text{ \AA}$ . The transformation matrix from the orthorhombic cell to the tetragonal cell is

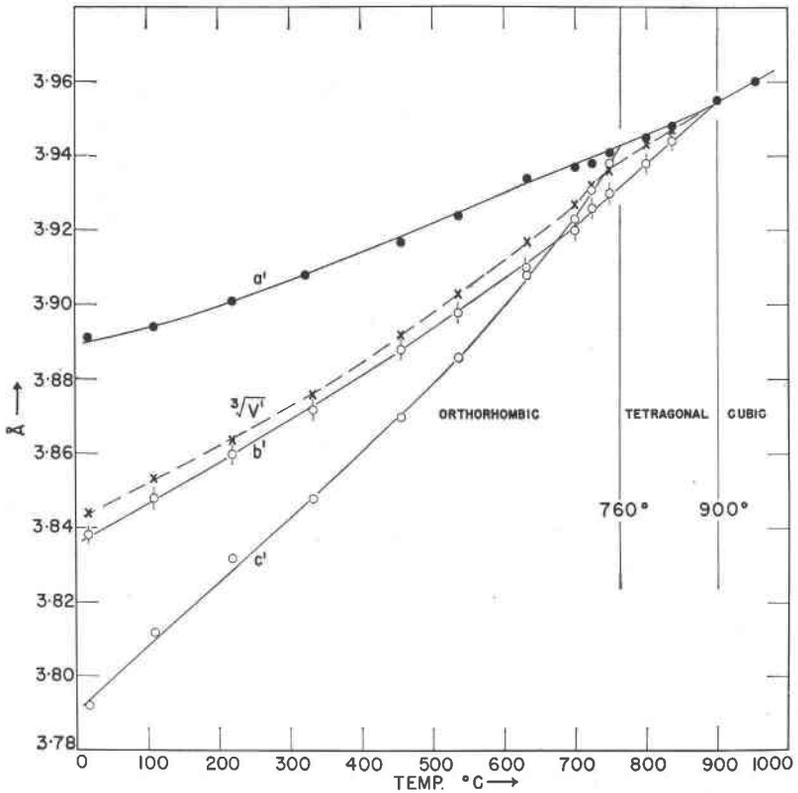


FIG. 4. Variation in cell constants of neighborite with temperature, showing transition points at  $760^\circ\text{C}$  and  $900^\circ\text{C}$ .

TABLE 4. DIMENSIONS OF THE CUBIC PSEUDOCELL IN NEIGHBORITE AT DIFFERENT TEMPERATURES

Temp. ° C.	$a'$ Å	$b'$ Å	$c'$ Å	$\sqrt[3]{V'}$ Å
Orthorhombic				
18	3.792	3.838	3.891	3.842
110	3.812	3.848	3.894	3.853
220	3.832	3.860	3.901	3.864
333	3.848	3.872	3.908	3.876
457	3.870	3.888	3.917	3.892
537	3.886	3.898	3.924	3.903
633	3.908	3.910	3.934	3.917
700	3.923	3.920	3.937	3.927
724	3.931	3.926	3.938	3.932
749	3.938	3.930	3.941	3.936
Tetragonal				
800	3.945	3.938	3.945	3.943
837	3.948	3.944	3.948	3.947
Cubic				
900	3.955	3.955	3.955	3.955
954	3.960	3.960	3.960	3.960

In the orthorhombic phase,  $a = \sqrt{2} \cdot a'$ ,  $b = 2b'$ ,  $c = \sqrt{2} \cdot c'$ ; in the tetragonal phase,  $a = a' = c'$ ;  $c = b'$ ; in the cubic phase,  $a = a' = b' = c'$ .  $V' = a'b'c'$ , the volume of the pseudocell.

$\frac{1}{2}0\frac{1}{2}/\frac{1}{2}$ , 0,  $-\frac{1}{2}/0\frac{1}{2}0$ . Figure 5 shows the diffractometer records of the cubic phase at 900° C. and the orthorhombic phase at 18° C. From 760° to 900° C. neighborite remains tetragonal, but the axes gradually become closer in length. Above 900° C. the three axes become identical and the cell is cubic. Designation of the transition temperature as 900° C. is largely based on the projection of the  $a'$  and  $b'$  axial lengths versus temperature plots. Since the curves converge at a small angle the intersection point necessarily has a large uncertainty and the tetragonal→cubic transition temperature should be considered as  $900^\circ \pm 25^\circ$  C.

The progressive transitions from orthorhombic to tetragonal to cubic can best be demonstrated by observing the 200, 002 and 121 reflections. At 760° C. the 200 and 002 lines become coincident but are still clearly resolvable from the 121. At 900° C. all three lines become coincident reflecting the cubic cell. The transitions are rapidly reversible and to our knowledge the tetragonal and cubic forms cannot be quenched to room temperature.

A plot of the cube root of the volume of the "pseudo cell" against temperature (Fig. 4) has a small inflexion at 760° C. and another at approximately 900° C. Since no abrupt break in the curve is observed both

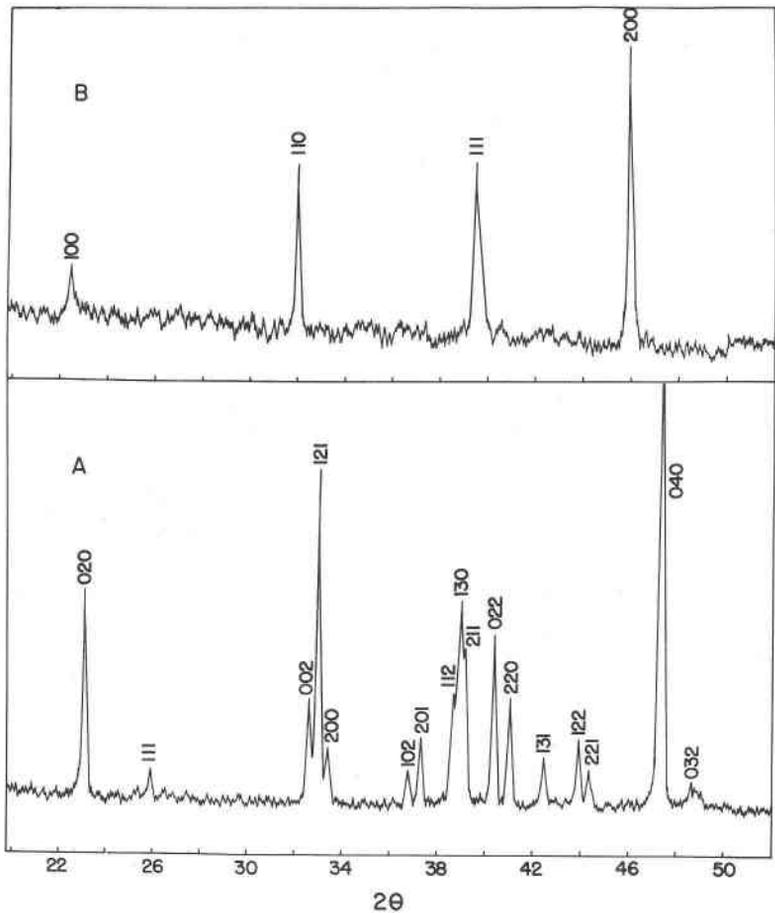


FIG. 5. X-ray diffractometer traces of neighborite at (A) 18° C. and (B) 900° C.,  $\text{CuK}\alpha$  radiation, demonstrating disappearance of superlattice lines in the higher temperature form.

the orthorhombic  $\rightarrow$  tetragonal and tetragonal  $\rightarrow$  cubic transitions are at least second order and possibly higher order, transitions.

#### CRYSTAL CHEMISTRY

Neighborite belongs to the simple class of crystal structures with general formula  $\text{ABX}_3$ , commonly known as the "perovskite family" (Wells, 1950, Megaw, 1957). The ideal structure is cubic with a unit cell about 3.8 to 4.0 Å on edge, containing one formula unit. The structure consists of A and X atoms in cubic closest packing with B atoms inserted in octa-

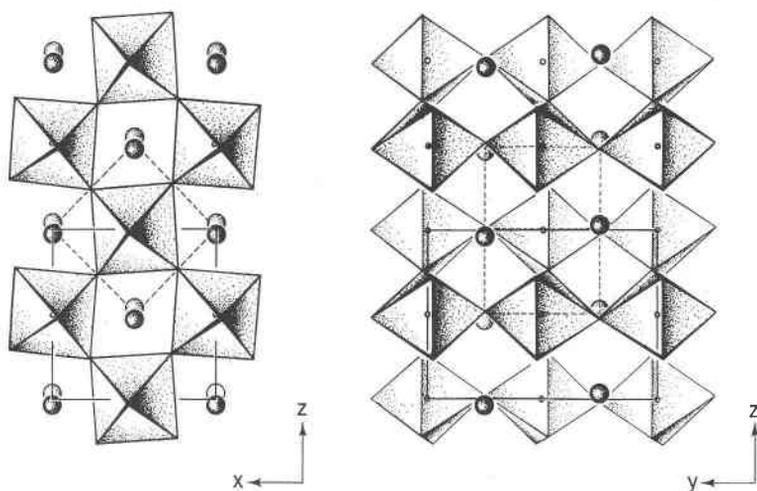


FIG. 6. Schematic views of the probable crystal structure of neighborite, after the structure described for perovskite by Kay and Bailey (1957). Na atoms are represented by large shaded spheres, Mg atoms by small circles and  $\text{MgF}_6$  groups by shaded octahedra. Full lines outline the orthorhombic unit cell and dashed lines show the cubic pseudocell. The Na atoms lie on mirror planes normal to the  $y$  axis, seen on edge in the view at right.

hedral cavities. If the A atom is significantly smaller or larger than X, the simple structure is generally distorted to a lower symmetry. Thus, in perovskite itself, for which calcium is a little more than half the size of oxygen, the symmetry becomes orthorhombic and a superstructure is formed with a unit cell four times the size of the ideal cell. Such distorted structures often transform to the ideal structure type at some higher temperature, and for perovskite, there is evidence that such a transition does occur at about  $1260^\circ\text{C}$ . (Megaw, 1957, p. 91). In the heating experiments on synthetic neighborite, this transition was positively identified at  $760^\circ\text{C}$ .

On the basis of their single crystal intensity data alone, Kay and Bailey (1957) could not distinguish between two possible structures for  $\text{CaTiO}_3$ . One of these two resulted in highly distorted octahedra with Ti-O distances ranging between 1.78 and 2.08 Å. The other (shown in Fig. 6) has fairly regular octahedra (Ti-O distances all 1.93 Å), the distortion of the high temperature cubic structure being manifested only in the tilting of the polyhedra. Kay and Bailey accepted the latter mainly on grounds of parsimony, even though other structures such as  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  (Megaw, 1947, p. 108) show large distortions in the  $\text{TiO}_6$  octahedra. The cause of the distortion in the perovskite structure has been commonly attributed to the relatively small size of the calcium

atom. Kay and Bailey's proposed structure effectively reduces the coordination for calcium from 12 (for the undistorted high temperature form) to 8 (8 Ca-O distances of 2.4–2.5 Å; the other 4 become 3.0–3.1 Å).

Since it is well known that titanium can suffer considerable distortion of its bonding with oxygen, presumably because of the largely covalent character of the bonds and the influence of the available  $3d$  orbitals in forming hybrids in the formation of these bonds, the crystal chemical arguments for the  $\text{CaTiO}_3$  structure presented above do not rest on a firm theoretical basis. The situation is different for neighborite, however. Here the bonding is largely ionic, and no  $d$ -hybridization is possible. Therefore, there is no reason to expect the  $\text{MgF}_6$  octahedra to depart from regularity any more than is necessary, and the tilted regular octahedron structure can be accepted with much more assurance. Fortunately, the close analogy between the structures of  $\text{NaMgF}_3$  and  $\text{CaTiO}_3$  strengthens the arguments set forth by Kay and Bailey for this structure for the latter.

The appearance of the tetragonal phase between the low temperature orthorhombic and high temperature cubic forms does not have any obvious explanation. The tetragonal cell consists of a slight distortion of the cubic cell ( $c/a=0.9977$  at  $760^\circ\text{C}$ .), similar to that of  $\text{BaTiO}_3$ , which is cubic above and tetragonal below  $120^\circ\text{C}$ ., the latter phase having  $c/a=1.009$  (Megaw, 1957). The tetragonal distortion in  $\text{BaTiO}_3$  is certainly due to a pronounced polarization of one of the Ti-O bonds (Evans, 1953) of a kind which has frequently been found in transition metal oxide and fluoride structures. Such a polarization seems implausible in an ionic magnesium fluoride structure, and we believe that the explanation more probably lies in some special type of thermal vibration. As the temperature of the orthorhombic form is increased, the degree of tilting of the octahedra in the  $a$ - $c$  plane (Fig. 6, top view) must become less and less until at the transition temperature  $760^\circ$ , the pattern becomes quite square. If the Mg-F-Mg links which tie one layer normal to the new tetragonal axis to the one above or below is still bent as it was in the orthorhombic phase, the tetragonal  $c$  axis ( $\frac{1}{2}$  the orthorhombic  $b$  axis) would be slightly shortened with respect to the  $a$  axis, as is observed. This shortening may be contrasted with the slight lengthening which results from bond polarization as in  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$ . The bending of the bond would be randomly oriented with respect to the tetragonal  $c$  axis, corresponding to a libration of the fluorine atom about the Mg-Mg axis. The reason why such libration might be emphasized only on alternate fluorine layers in the structure is not revealed by our speculation.

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*Manuscript received June 11, 1960.*