APATITE-LIKE PHASES IN THE SYSTEMS MeO–Nd$_{2}$O$_{3}$–SiO$_{2}$

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Abstract

Full Text

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APATITE-LIKE PHASES IN THE SYSTEMS MeO–Nd_2O_3–SiO_2

(WHERE Me = Mg, Ca, Ba) ACCORDING TO INFRARED SPECTROSCOPY DATA

(Presented by Academician N. V. Belov on 26 XII 1969)

Using the method of heterovalent isomorphism, compounds belonging to minerals of the apatite group were synthesized in the systems MeO–Nd_2O_3–SiO_2 (where Me = Mg, Ca, Ba).

Starting from the compound $Nd_{4\cdot67}(SiO_4)_3O$, which crystallizes in the apatite structural type (^{1}), by successive replacement of Nd^{3+} by Me^{2+}

Fig. 1. Infrared spectra of firing products of samples of the system CaO–Nd_2O_3–SiO_2.
1 –$Ca_5(PO_4)_3F$; 2 –$CaNd_4(SiO_4)_3O$; 3 –$Ca_2Nd_3(SiO_4)_3O_{0\cdot5}$; 4 –$Ca_3Nd_2(SiO_4)_3$; 5 –8CaO : Nd_2O_3 : $6SiO_2$; 6 –5CaO : $3SiO_2$. Here and in Figs. 2 and 3, after $\nu = 700$ the scale on the abscissa axis is changed.

Fig. 2. Infrared spectra of firing products of samples of the system MgO–Nd_2O_3–SiO_2.
1 –$Ca_5(PO_4)_3F$; 2 –$MgNd_4(SiO_4)_3O$; 3 –$Mg_2Nd_3(SiO_4)_3O_{0\cdot5}$; 4 –6MgO : $2Nd_2O_3$: $6SiO_2$; 5 –8MgO : Nd_2O_3 : $6SiO_2$; 6 –5MgO : $3SiO_2$.

compounds with the general formula were synthesized

$$Me_xNd_{5-x}(SiO_4)_3O_y, \qquad \text{where } x = 1 \div 5,\ y = 1 \div 0.$$

The synthesis of the samples was carried out in a furnace with carborundum heaters by sintering at 1450° for 30-40 hours, with intermediate grinding after every 10 hours of firing.

Fig. 3. IR spectra of calcined products—samples of the BaO—Nd2O3—SiO2 system.

Figure 2: Fig. 3. IR spectra of calcined products—samples of the BaO—Nd2O3 —SiO2 system.

For the phase analysis of the firing products, the method of infrared spectroscopy was chosen. The infrared spectra were recorded on a UR-10 instrument in the range···

range 1600-400 cm^{-1}. The samples for recording were prepared by pressing the finely ground powder together with KBr.

The broadest isomorphic substitution, owing to the closeness of the ionic radii, is possible between Nd^{3+} and Ca^{2+}. In three of the five synthesis products (Fig. 1, curves 2, 3, 4), compounds with the apatite structure are observed, which agrees with (^{2,3}). The IR spectra are characterized by the presence of an intense absorption band at 940 cm^{-1} and a multiplet consisting of four bands in the 600-400 cm^{-1} region; moreover, as the Nd_2O_3 : CaO ratio changes, the latter undergo no substantial changes, which we take as an indication that the original structural motif is preserved. Certain changes in the contour of the band at 940 cm^{-1}, expressed in the disappearance of the weak bands at 975 and 900 cm^{-1} on passing to calcium-enriched compositions, are apparently caused by a change in the oxygen deficiency in the lattice in connection with replacement of the Nd^{3+} cation by Ca^{2+}. In the composition with an oxide ratio of 8CaO : Nd_2O_3 : $6SiO_2$ (Fig. 1, curve 5), the principal phase is β-Ca_2SiO_4, although the character of the spectrum indicates a slight presence of an apatite phase. Complete replacement of Nd^{3+} by Ca^{2+} leads to the formation of a mixture of β-Ca_2SiO_4, bands 1110, 530 cm^{-1}, and α-$CaSiO_3$, bands 860, 660 cm^{-1} (Fig. 1, curve 6).

Fig. 3. IR spectra of calcined products—samples of the BaO—Nd_2O_3—SiO_2 system.
1 —$Ca_5(PO_4)_3F$; 2 —$BaNd_4(SiO_4)_3O$; 3 —4BaO : $3Nd_2O_3$: $6SiO_2$; 4 —6BaO : $2Nd_2O_3$: $6SiO_2$; 5 —8BaO : Nd_2O_3 : $6SiO_2$; 6 —5BaO : $3SiO_2$.

In view of the considerable difference in the radii of the ions, the limits of isomorphic substitutions between Nd^{3+} and Mg^{2+} should be smaller. This is reflected in the character of the changes in the spectra. In the spectra of magnesium-neodymium silicate apatites (Fig. 2, curves 2, 3), an intense absorption band at 950 cm^{-1} is observed; however, the character of the multiplet of bands in the 600-400 cm^{-1} region is somewhat altered in comparison with the spectra of calcium-neodymium silicate apatites: namely, the 510 cm^{-1} band is split into two, at 520 and 505 cm^{-1}. Obviously, this fact is a consequence of the small radius of the Mg^{2+} ion. Beginning with the composition 3MgO : Nd_2O_3 : $3SiO_2$ (Fig. 2, curve 4), the presence of forsterite, band 615 cm^{-1}, is observed; its amount increases with further replacement of Nd^{3+} by Mg^{2+}, while the amount of the apatite phase decreases. With complete replacement of Nd^{3+} by Mg^{2+}, the spectra show Mg_2SiO_4 as the principal phase and a small presence of clinoenstatite, 1100 cm^{-1} (Fig. 2, curve 6).

The magnitude of the ionic radius of Ba^{2+} considerably exceeds that of the ionic radius of Nd^{3+}, as a result of which the possibility of isomorphic replacement of Nd^{3+} by Ba^{2+} is strongly limited. Only one composition, $BaNd_4(SiO_4)_3O$, could be assigned to minerals of the apatite group (Fig. 3, curve 2). The intense absorption band is located at 910 cm^{-1}; the character of the multiplet bands also changes in such a way that they show a great analogy with this region of the spectra of Ca phosphate fluorapatites, which is a very interesting feature of theirs. Beginning with the composition $4BaO : 2Nd_2O_3 : 6SiO_2$ (Fig. 3, curve 3), as Nd^{3+} is replaced by Ba^{2+}, the appearance and gradual increase in the content of Ba_2SiO_4, band 495 cm^{-1}, is noted; the appearance of this band contributes to the predominance of absorption in the ob—

in the region of 500 cm^{-1}. Complete substitution of Nd^{3+} by Ba^{2+}, as also in the case of Ca^{2+} and Mg^{2+}, leads to the formation of a mixture of barium orthosilicate, $910, 495$ cm^{-1}, and barium metasilicate, $610, 425$ cm^{-1} (Fig. 3, curve 6).

Conclusions

1. By the method of IR spectroscopy it has been established that it is possible to synthesize, by successive replacement of Nd^{3+} by Me^{2+}, a series of compositions crystallizing in the structural type of apatite, with the general formula

$$Me_xNd_{5-x}(SiO_4)_3O_y, \qquad \text{where } x = 1 \div 5, \quad y = 1 \div 0; \quad (Me = Mg,\ Ca,\ Ba).$$

2. The character of the spectra changes somewhat: on going Mg → Ca → Ba, from the lighter cation with the smaller ionic radius to the heavier one with the larger ionic radius, there is a shift of the principal absorption band 950 → 910 cm^{-1} and some modification in the character of the multiplet bands.
3. The limits of isomorphous substitutions narrow to a considerable extent from Ca → Mg → Ba because of the large difference in ionic radii.

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Note: Figure translations are in progress. See original paper for figures.