

activation, as discussed by Schulman and others (1947) for the case of manganese-lead activation of calcite.

In general, natural luminescence results from an impurity ion having an absorption spectrum close to the wavelength of the source used for examination. This impurity ion either acts as a dominant activator and controls the emission spectrum, or acts as an auxiliary activator and sensitizes the fluorescence by transferring its absorbed energy to one or more dominant activators. Thus many of the additional impurity ions in a natural phosphor may modify the fluorescent spectrum, and make indiscriminate use of fluorescence for mineral identification or correlation of doubtful value.

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ON THE STABILITY AND HYDROTHERMAL
SYNTHESIS OF BENITOITE

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Although extremely rare, the mineral benitoite ($\text{BaTiSi}_3\text{O}_9$) is of considerable interest since it represents one main type of chain structure in silicates; it also has some value as a gem stone. Furthermore, its temperature and pressure range of stability could perhaps assist in understanding the formation of the rocks in which it occurs.

No previous work has been reported on the synthesis or stability of benitoite although numerous papers have appeared dealing with its physical and optical properties and crystalline structure. These aspects are thoroughly reviewed by Dana (1949) and Bragg (1937). The work reported here has been done in conjunction with a study of the equilibrium relations in the system barium titanate-silica. The experimental conditions and results obtained are presented in detail in another paper by the authors (1954).

The most prominent interplanar spacings for benitoite are presented in Table 1, since none are available in the literature. These data were

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obtained from the natural mineral found in San Benito County, California, using a Norelco hi-angle x -ray diffractometer, $\text{CuK}\alpha$ radiation and Ni filter. The indexing of the pattern followed from a consideration of the axial ratio reported in the literature and the use of Bunn charts.

On the basis of x -ray data alone, the maximum temperature of stability of benitoite under dry conditions, as determined by heating the natural mineral to higher and higher temperatures, appears to be 1050°C . Above this temperature the x -ray diffraction pattern definitely indicated

TABLE 1. SELECTED INTERPLANAR SPACINGS FOR THE MINERAL
BENITOITE ($\text{BaTiSi}_3\text{O}_9$)
(Natural and synthetic identical)

d	I/I_0	$hk \cdot l$
5.75	45	100
3.733	100	102
3.329	10	110
3.156	10	111
2.883	35	200
2.771	65	201
2.252	30	104
2.179	25	210
2.125	5	211
1.990	10	212
1.972	15	114
1.925	10	300
1.860	25	204
1.788	40	302
1.665	5	220
1.628	85	310
1.576	10	222, 311, 106

the presence of another phase, $\text{BaTiSi}_2\text{O}_7$. However, microscopic observation indicated that at least partial dissociation had occurred well below 1050°C . and as low as 1000°C . Dissociation in the mineral is evidenced by minute "worms" appearing throughout the crystalline benitoite fragments when observed microscopically. Extended heat treatment induced the "worms" to grow until they began to appear as individual and distinct crystals within the benitoite itself.

Hydrothermally, the stability maximum of benitoite was not defined as distinctly by means of x -rays as in the case of the dry investigations. However, similar growth of crystals within the benitoite was observed in the hydrothermal runs as in the dry runs.

Attempts to synthesize benitoite "dry" by heating a mixture of oxides

or "gel" of its own composition, or by devitrifying a glass of the correct composition were always unsuccessful. When the completely melted and quenched stoichiometric mixtures (having a $\text{BaTiSi}_3\text{O}_9$ composition) were treated hydrothermally above about 965°C . at 5000 psi water pressure and only as long as 4 hours, benitoite was not observed as a stable phase. In all cases the x -ray pattern indicated mainly the presence of the compound $\text{BaTiSi}_2\text{O}_7$ with tridymite appearing only in the longer runs. At temperatures below 965° and at 5000 psi however, these same mixtures converted readily to a crystalline phase having an x -ray diffraction pattern identical to that of the natural benitoite. Furthermore, it was possible to obtain the benitoite pattern from mixtures slightly off the stoichiometric composition. In the latter case, the patterns for both benitoite and the compound $\text{BaTiSi}_2\text{O}_7$ were obtained thus indicating that equilibrium had been attained since these appear to be the stable phases at these temperatures as determined in the study of the system $\text{BaTiO}_3\text{-SiO}_2$. It appears therefore that the maximum stability temperature of benitoite as determined hydrothermally is about 100° lower than the apparent maximum under dry conditions, a situation not uncommon in hydrothermal literature and one which might well be expected. Although benitoite can be synthesized quite easily by a hydrothermal devitrification process, in no case was it possible to obtain any indication of its presence from the initial sintered oxide mixtures even when treated at temperatures and pressures known to favor the synthesis.

Thus we have been able to synthesize benitoite hydrothermally and to fix its upper stability limit as $965^\circ \pm 10^\circ\text{C}$. at 5000 psi.

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FAULTS IN GYPSUM ACCESSORY PLATES

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It may not occur to some petrographers to question the accuracy of the engraving on an accessory plate, unless they begin to get anomalous results. A beginning student may not even realize that his results are anomalous. Our experience suggests that all such plates should be closely inspected when received from the manufacturer or from overhaul.

In 1951 a new gypsum full-wave plate was received with a microscope