Monazite from North Carolina having the alexandrite effect

Lawrence R. Bernstein

Department of Geology
Stanford University
Stanford, California 94305

Abstract

Monazite crystals from a 50 m wide quartz vein in Montgomery County, North Carolina show the alexandrite effect. The crystals are reddish-orange under incandescent light, yellow-orange in daylight, and light green under fluorescent light. The colors are due to narrow absorption bands from Nd^{3+} at about 800, 745, 580, 525, and 515 nm, and an absorption edge beyond $\simeq480$ nm. The monazite is chemically unusual in containing virtually no Th, U, or iron-group elements, which can cause deep colors that mask the pastel rare earth-produced colors. The alexandrite effect in this monazite differs from that in previously described substances in being due to several narrow absorption bands rather than a small number of broad bands.

Introduction

The alexandrite effect is the property of a solid to change its apparent color when viewed under different commonly-observed "white" light sources. The effect is best known in alexandrite, a chromian chrysoberyl that appears green in sunlight or fluorescent light and red in incandescent or candle light. Other materials known that can show an alexandrite effect are: Cr^{3+} or V^{3+} bearing corundum and garnet (White *et al.*, 1967; Schmetzer *et al.*, 1980); Sm^{2+} and Y^{3+} bearing fluorite (Schmetzer *et al.*, 1980); coquimbite (Rossman, 1975); spinel (G. R. Rossman, oral communication, 1981); and diaspore (Scarratt, 1980). The optical spectra of these color-changing materials have been found to have an absorption maximum between 580 and 560 nm with flanking minima between 665 and 625 nm and between 510 and 470 nm.

This study presents optical and chemical data on monazite crystals from North Carolina that show the alexandrite effect. The causes of the color and the color-change effect are discussed and are compared to those in other color-changing materials.

Samples used and occurrence

Specimens used in this study were collected by Ronald and Margaret Yadusky of Fayetteville, North Carolina, who brought the color-changing mineral (then an unknown) to my attention. The specimens are from an unnamed quartz (or perhaps gold) prospect located in the Uwharrie National Forest, at the south end of National Forest Road 555, 8.4 km east of Badin, Montgomery County, N. C. The prospect is in a 50 meter wide quartz vein in the Ordovician slates of the Carolina slate belt. Vugs in the quartz contain milky gray to transparent quartz crystals up to 15 centimeters long. The vugs sometimes contain small euhedral crystals (a few mm or less) of anatase, brookite, ilmenite, hematite, barite, feldspar, rutile, and monazite. Pyrite, spessartine, rutile, and chlorite occur as inclusions in the quartz.

The monazite crystals observed in this study are euhedral, 1–2 mm long and 0.3–0.7 mm wide. They occur on a vug surface that consists of coalesced subhedral gray quartz crystals up to 10 mm across in parallel growth. Euhedral dipyramids of brown to black anatase, 1–2 mm long and 0.3–1 mm wide also occur on the vug surface, as do limonite crusts and small (1–3 mm) microcline crystals.

The monazite crystals appear yellow-orange in daylight, reddish-orange in incandescent light, and light green in fluorescent light. No pleochroism was observed in the polarizing microscope, and no fluorescence was observed under shortwave or longwave ultraviolet radiation. Tiny brown inclusions, several dozen microns across, are seen under the microscope and were not identified.

Table 1. Quantitative microprobe analyses of monazite having the alexandrite effect from Montgomery County, North Carolina.

	Weight Percent		Element	Atomic Proportions*	
	1	2		1	2
Ce_2O_3	31.1	34.0	Ce	0.453	0.491
La_2O_3	12.8	15.5	La	.189	.226
Nd_2O_3	16.3	14.4	Nd	.232	.204
Sm_2O_3	3.3	2.6	Sm	.045	.037
Gd_2O_3	2.3	1.5	Gd	.030	.019
Lu_2O_3	0.4	0.4	Lu	.004	.004
Pr_2O_3**	1.0	1.0	Pr	.014	.014
Y_2O_3	1.1	0.5	Y	.024	.011
CaO	0.2	0.3	Ca	.008	.011
SiO_2	0.1	0.2	Si	.005	.010
ThO_2	n.d.	trace?	Th	.000	trace?
P_2O_5	29.6	29.1	P	.996	.973
F	0.5	0.5	F	.062	.062
Subtotal	98.7	100.0	O	3.993	3.971
$O\equiv F_2$	0.2	0.2			
Total	98.5	99.8			

Atomic Proportions column braces: 1 = 0.991; 2 = 1.006

n.d. = not detected
Points analyzed: 1. Near rim of crystal. 5μm beam diameter.
                 2. Central part of crystal. 15μm beam diameter.
Looked for but not detected: Al, Dy, Er, Fe, Hf, Ho, Mg, Mn, Na, Nb, Pb, Ta, Ti, U, Yb, Zr.
*Calculated on basis of the sum of all cations = 2.000
**Estimated from semiquantitative wavelength-dispersive microprobe scan

Experimental methods

The color-changing crystals were initially identified as monazite by powder X-ray diffraction. The identification was substantiated by a wavelength-dispersive microprobe scan for major and minor components. Quantitative chemical anlayses were made using the MAC 5-SA3 automated microprobe at the California Institute of Technology. The microprobe was operated at 15 kV and 0.05 μA. Two inclusion-free points were analyzed, the first near the rim of the crystal and the second in the central part. Lanthanide-group and yttrium standards were a set of four synthetic glasses prepared by Peter Weill containing these elements at about the 4% level, grouped to avoid mutual interferences. Other standards included: Si-quartz; Ca-wollastonite; P, F-apatite; Na-Amelia albite.

Optical absorption spectra were obtained on a Cary 17I spectrometer at the Division of Geological and Planetary Sciences at C. I. T. Illumination used was in the range 360 to 1500 nm, at room temperature. The sample used was a nearly inclusion-free portion of a plate, 300 × 200 × 180 μm thick, polished on both sides.

Results

Chemistry

The microprobe scan detected major P, Ce, La, and Nd, with minor Sm and Pr, and traces of Eu and Si. Although Th, U, and Fe-group metals were sought, being common constituents of monazite, none were found. A portable scintillation counter detected no radioactivity in the sample.

The results of the quantitative microprobe analysis are presented in Table 1. Again, no U or Fe-group metals were detected, though a trace of Th may have been detected in one of these analyses.

Optical absorption spectrum

The narrow-band spectrum obtained for the monazite in unpolarized light is shown in Figure 1. Major absorption bands, which all show considerable fine structure, occur at about 800, 745, 580, 525, and 515 nm, with an absorption edge becoming steep beyond ≈480 nm. Some small bands occur in the near-infrared and in the near-ultraviolet. Due to the very small sample size and poor optical orientation due to crystal morphology, complete results in polarized light could not be obtained. The results that were obtained indicated little change in the absorption spectrum under different optical orientations. This is in agreement with the lack of observed pleochroism.

Discussion and conclusions

The monazite absorption spectrum was compared to spectra obtained from dilute trivalent rare earth solutions (Carnall and Fields, 1967) and to transition energy diagrams for RE^{3+} ions (Dieke and Crosswhite, 1963). Monazite bands observed in the visible range were readily attributable to Nd^{3+}, while some of the small bands observed in the infrared (>1000 nm) are due to Sm^{3+}.

The narrow absorption bands from these trivalent rare earths are due to parity-forbidden transitions in the 4f subshell. The transitions become allowable due to noncentrosymmetric interatomic and crystal field effects on the ions, which also produce most of the fine structure within the bands. The "shielding" of the unfilled 4f subshell by the filled 5s and 5d subshells greatly lowers the interatomic and crystal field effects on the 4f transitions, producing the relatively narrow bands. Due to the "shielding", the bands for a given RE^{3+} ion vary in position only by about 10 to 100 cm^{-1} among various crystals and solutions (Marfunin, 1979, p. 203). The absorption edge extending into the visible may be due to metal–metal or metal–oxygen charge-transfer transitions.

Monazite crystals usually contain at least 3 to 12% ThO_2 and often up to 1.5% Fe_2O_3. Traces of U are also often present. Radiation damage by the Th
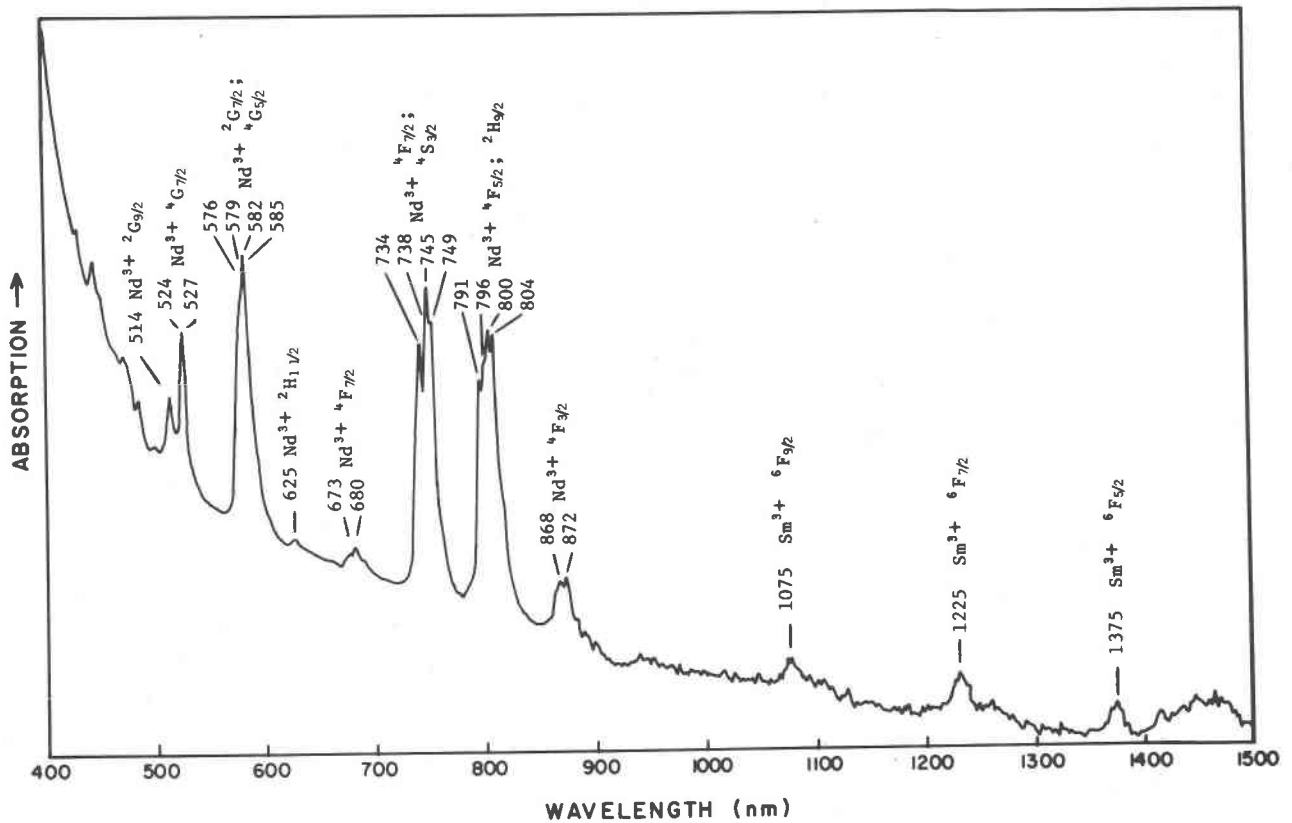
Fig. 1. Visible and near-infrared absorption spectrum of monazite having the alexandrite effect from Montgomery County, North Carolina. Transitions based on Dieke and Crosswhite (1963).

and U, or absorptions by the iron-group ions, often make monazite dark colored, masking the pastel colors caused by the RE^{3+} ions. The monazite of this study is unusual in that it contains virutally no Th, U, or first transition group elements. Thus its color and alexandrite effect are a result of the RE^{3+} elements alone, specifically Nd^{3+}.

The monazite absorption spectrum is consistent with that of other described color-changing materials in having absorption maxima and minima roughly in the ranges earlier specified. The spectrum differs in having substantially narrower absorption bands than for previously published spectra (e.g., Schmetzer et al., 1980) of color-changing minerals. A similar color-change phenomenon was observed by Weyl (1951, p. 223) in Nd^{3+} colored glass.

The optical-physiological causes of the alexandrite effect have been discussed by several authors (e.g., Poole, 1964; White et al., 1967; Schmetzer et al., 1980). The effect is due to a substance having optical absorption bands that are close to critical wavelength boundaries that determine a person's

perception of different colors. Slight differences in the wavelength composition of different illuminators are sufficient to change the color perceived. The monazite described in this study demonstrates that narrow absorption bands are sufficient to produce this effect.

References

Carnall, W. T. and Fields, P. R. (1967) Lanthanide and actinide absorption spectra in solution. In P. R. Fields and T. Moeller, Eds., Lanthanide/Actinide Chemistry (Advances in Chemistry Series no. 71), p. 86–101. American Chemical Society, Washington, D. C.
Dieke, G. H. and Crosswhite, H. M. (1963) The spectra of

doubly and triply ionized rare earths. Applied Optics, 2, 675–686.

Marfunin, A. S. (1979) Spectroscopy, luminescence and radiation centers in minerals. Translated by V. V. Schiffer. Springer-Verlag, New York.

Poole, C. P. (1964) The optical spectra and color of chromium containing solids. Journal of Physics and Chemistry of Solids, 25, 1169–1182.

Rossman, G. R. (1975) Spectroscopic and magnetic studies of ferric iron hydroxy sulfates: intensification of color in ferric iron clusters bridged by a single hydroxide ion. American Mineralogist, 60, 698–704.

Scarratt, K. (1980) Faceted diaspore. Journal of Gemmology, 17, 145–148.

Schmetzer, K., Bank, H. and Gübelin, E. (1980) The alexandrite effect in minerals: chrysoberyl, garnet, corundum, fluorite. Neues Jahrbuch für Mineralogie Abhandlungen, 138, 147–164.

Weyl, W. A. (1951) Coloured Glasses. Society of Glass Technology, Sheffield, England.

White, W. B., Roy, R. R. and Crichton, J. M. (1967) The "alexandrite effect": and optical study. American Mineralogist, 52, 867–871.