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Spectroscopy of Europium(III) in Apatite

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This work is based on a previous report [1] concerning the preparation and determination of the crystal structure of apatite compounds with the general formula of $M_{10-2x}Ln_xAg_x(PO_4)_6F_2$ (M = Pb, Sr; Ln = La, Eu; x = 1, 2) and is aimed to study the effect of the monovalent ion, Ag(I), which is different in size and electronic configuration from the alkaline ions.

These compounds have been found to crystallize in the $P6_3/m$ hexagonal structure, and substitution of the Ln and Ag ions has a decreasing effect on the c/a values of the lattice, indicating the contraction of the lattice in the c direction. Similar observations have been reported [2] in compounds substituted with Na(I) and with the $Pb_4M(PO_4)_3$ type apatite [3], indicating that Ln and M ions mainly occupy the column and the Pb(II) ions occupy the triangle sites.

In the case of substituted lead chloride apatites a and c decrease at almost equal rate and the value of c/a is not different from that of $Pb_{10}(PO_4)_6Cl_2$, while in some Sr compounds the lattice parameter c increases with x, and the parameter a always decreases with x. The c/a ratios are higher in the substituted compounds than in the non-substituted ones, which is contrary to the values for substituted lead chloride apatites

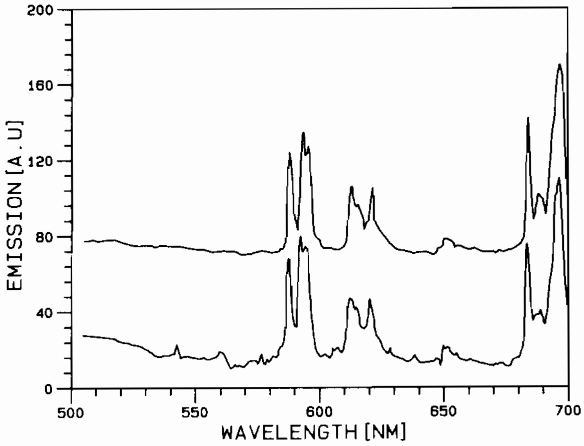

Fig. 1. Emission spectra of Eu(III) in two apatites. Upper spectrum emission of Eu(III) in $Pb_8Eu_{0.1}La_{0.9}Ag(PO_4)_6F_2$; lower spectrum emission of Eu(III) in $Pb_8Eu_{0.1}La_{0.9}Na(PO_4)_6F_2$. Excitation at 392 nm. The weak lines observed in the lower spectrum are probably due to transitions from $^5D_1$ level. These lines are absent in the upper spectrum.

Since Ag(I) ion has a higher polarizing effect than Na(I) ion, it was of interest to look into the influence of these ions on optical properties of Eu(III). Fluorescence of Eu(III) in phosphates and oxy- or fluoroapatites has been extensively studied [4]. Eu(III) in phosphate glass was previously investigated by the authors [5]. Here we report on apatite crystals of the following structure; $Pb_8Eu_{0.1}La_{0.9}Na(PO_4)_6F_2$ (form (Na)) and $Pb_8Eu_{0.1}La_{0.9}Ag(PO_4)_6F_2$ (form (Ag)). The emission spectrum of Eu(III) which arises from the parity forbidden f–f transition is presented in Fig. 1 where a comparison is made between apatites of form (Na) and form (Ag).

No significant change was found when the La(III) ions were completely substituted by Eu(III). Also no significant change was found in the shape and relative intensity of $^5D_0$–^7F_i transitions. The lifetimes of the transitions are practically the same independent of the monovalent ion at low (0.1 Eu) as well as high concentrations of Eu(III) (1.0 Eu). This can be seen from Table I where these lifetimes are compared. Table I contains also lifetimes of fluorescence from $^5D_1$ state to ^7F_i states (it should

TABLE I. Lifetimes of Eu(III) in Apatites

Wavelength (nm)		Transition	Compound	Decay (μs)		
excited	emission			τ_2	τ_2	τ_3
523	687	$^5D_0$ $^7F_4$	apatite (0.1 Eu, Na)	2614	2614	
392	542	$^5D_1$ $^7F_1$	apatite (0.1 Eu, Na)	11.1	15.8	15.8
392	695	$^5D_0$ $^7F_4$	apatite (0.1 Eu, Na)	2200	2700	2550
523	689	$^5D_0$ $^7F_4$	apatite (0.1 Eu, Ag)	2300	2500	
392	689	$^5D_0$ $^7F_4$	apatite (0.1 Eu, Ag)	1960	2610	
392	542	$^5D_1$ $^7F_1$	apatite (0.1 Eu, Ag)	3.3	8.8	14.9
392	687	$^5D_0$ $^7F_4$	apatite (1.0 Eu, Ag)	400	770	870

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be noted that because of the low intensity of the $^5D_1$ state emissions, the emission is very weak in the steady state but easily observed using pulsed laser excitation). In contrast to the $^5D_0-^7F_i$ transitions, there is a significant change between form (Ag) and form (Na) in the lifetimes of the emissions from the $^5D_1$ state.

The $^5D_1-^5D_0$ transition is not allowed as an electric dipole having the three even matrix elements U_2, U_4 and U_6 equal to 0. This transition has a high magnetic moment the value of 2.1×10^{-21} cm^2. The observed lifetimes of the $^5D_1$ state in Eu(III) express the probability of this magnetic dipole transition or a linear mixing of the crystal field terms allowing a contribution of the forced electric dipole. The substitution of Na(I) by Ag(I), which has a higher polarizing property, affects the local ligand field acting on Eu(II), enabling a forced electric dipole. This in turn increases the probability of non-radiative relaxation between the $^5D_1$ and $^5D_0$ state, which is much smaller in the case of Na(I) containing apatite.,

The demonstration of influence of Ag(I) on local symmetry of Eu(III) in apatite shown by fluorescence measurements is consistent with the X-ray diffraction data on the intrinsic behaviour of the lattice.

Experimental

The method of preparation and the determination of the structure data of the apatites are described [1]. The steady-state fluorescence measurements done on powdered samples were performed with a home-made spectrofluorimeter [5]. The ground apatite powder was dispersed uniformly on a Tipex drop deposited on a microscopic slide. The slide was oriented at 30° degrees in respect to the excitation beam to prevent the spectacularly reflected light from entering the scanning monochromator.

The lifetimes measurements were performed on the same samples using a Molectron DL-200 tunable dye laser operating at 392 nm and 523 nm pumped with a Molectron UV-400 nitrogen laser having pulse width of 10 ns and at repetition rate of 5 Hz, a McPherson 0.3 m monochromator (5 nm resolution) and 6100 Biomation Transient Recorder having 10 n time resolution. The signals were stored in a Nicolet Averager and plotted on a X–T recorder. The lifetime analysis of the decay curves was accomplished with a computer program.

References

1 I. Mayer and S. Swissa, *J. Less-Common Met., 111,* 411 (1985).
2 I. Mayer, A. Semadja and V. Weiss, *J. Solid State Chem., 34,* 223 (1980).
3 I. Mayer, S. Cohen and R. Matalon, *J. Solid State Chem., 36,* 271 (1981).
4 (a) R. C. Rapp, *J. Electrochem. Soc., 115,* 531 (1969); *116,* 623 (1969); (b) A. M. Morozov, L. G. Morozova, A. K. Trofimov and P. P. Feofilov, *Opt. Spectrosk., 29,* 1106 (1970); (c) G. Blasse, *J. Solid State Chem., 14,* 181 (1975); (d) L. H. Brixner and P. E. Biersted, *J. Solid State Chem., 13,* 24 (1975).
5 R. Reisfeld, R. A. Velapoldi, L. Boehm and M. Ish-Shalom, *J. Phys. Chem., 75,* 3980 (1971); R. Reisfeld, R. A. Velapoldi and L. Boehm, *J. Phys. Chem., 76,* 1293 (1972); B. Blanzat, L. Boehm, C. K. Jφrgensen, R. Reisfeld and N. Spector, *J. Solid State Chem., 32,* 185 (1980).