

The luminescence of barium uranate (BaUO_4)

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Recently we have reported on the red luminescence of uranium-doped compounds with scheelite structure $\text{ABO}_4\text{-U}$ ($\text{A} = \text{Ca, Sr, Ba}$; $\text{B} = \text{Mo, W}$). This luminescence is due to tetrahedral UO_4^{2-} complexes[1]. These compositions show also a green luminescence as reported already in the early literature[2]. In Ref. [1] we have argued that this green emission is due to the presence of a second phase, viz. AUO_4 . Here we describe the luminescence of BaUO_4 which shows the more intense luminescence in the series of AUO_4 compounds. Its luminescence properties are similar to those of MgUO_4 and Ba_2CaUO_6 , compounds which have been studied earlier in our laboratory[3, 4]. The compound BaUO_4 has a crystal structure in which the U^{6+} ions have approximate octahedral coordination. Two oxygen ions form the primary coordination (U-O distance 1.872 Å, uranyl group), four additional oxygen ions provide the secondary uranium coordination (U-O distances 2.196 and 2.223 Å)[5].

EXPERIMENTAL

The samples BaUO_4 were prepared following conventional methods[1, 5]. They were checked by X-ray powder analysis. Optical measurements were performed as described before[1] down to liquid helium temperatures.

RESULTS

At 4.2°K BaUO_4 shows a bright, green emission under UV and blue light excitation. At 77°K the emission has shifted to the orange part of the spectrum. The excitation spectrum of the emission of BaUO_4 consists of a very broad band with a maximum around 400 nm and another, weaker band at longer wavelength which shows vibrational structure at 4.2°K. Its zero-phonon origin is situated at $18,950\text{ cm}^{-1}$ (see Table 1).

The emission spectrum is very complicated and varies strongly as a function of temperature. It shows extended vibrational structure which varies also with temperature. The zero-phonon lines observed are without exception at lower energies than the zero-phonon origin in the excitation spectrum (see Table 1). The lower the temperature, the more intense are the higher-energy

zero-phonon lines. For several of the zero-phonon lines we observed vibronic coupling with modes of about 220 and 500 cm^{-1} and a progression in a mode of about 740 cm^{-1} (see Table 1). The intensity of a zero-phonon line relative to the vibronic lines belonging to it increases, if its position is at lower energy.

DISCUSSION

The results obtained show a strong resemblance with those for MgUO_4 and Ba_2CaUO_6 [3, 4]. We feel that they should be interpreted in the same way, i.e. excitation occurs into the intrinsic uranyl groups but emission occurs from defect uranyl or uranate groups which trap the migrating excitation energy. At higher temperatures the shallower traps are no longer active and the emission shifts to lower energy.

The progression frequency of about 740 cm^{-1} is clearly due to the symmetric U-O stretching frequency. Allen and Griffiths[6] have reported one weak line in the Raman spectrum of BaUO_4 at 726 cm^{-1} . In our own Raman measurements we found a strong line at 728 cm^{-1} , confirming our assignment. We also found weaker lines at 522, 385, 358, 318, 241, 201, 127, 109 and 76 cm^{-1} . Note from Table 1 that in the excited state the symmetric stretching frequency has decreased to 660 cm^{-1} . This is in agreement with earlier observations[4].

Since the uranyl and uranate emissions are electric-dipole parity-forbidden transitions[7, 8], the vibrational modes of 220 and 500 cm^{-1} must be of ungerade symmetry. The 500 cm^{-1} mode has also been observed as a strong band in the IR spectrum ([6], this work) and is ascribed to stretching modes of the secondary U-O bonds. The IR spectrum shows also bands in the region around 250 cm^{-1} . One of these may be the low-energy mode in the vibrational structure and is probably a U-O bending mode.

The trap depth of the defect centres is equal to the energy difference between the position of the excitation zero-phonon line and that of the relative emission zero-phonon line. In comparison with the previous studies[3, 4] these trap depths are relatively large: our highest value is over 1000 cm^{-1} , whereas in

Table 1. Position of the zero-phonon lines in the excitation and emission spectra of the luminescence of BaUO_4 and frequencies of vibrational modes as derived from the luminescence spectra

	Position zero-phonon line (cm^{-1})	Frequencies of vibrational modes (cm^{-1}) from luminescence spectra		
		300	485	660
Excitation	18.950			
Emission	18.780	235	510	740
	18.725			735
	18.660			
	18.600			750
	18.460			
	18.380	210	470	730
	17.860			~650

Refs. 3 and 4 the highest values were about 200 and 260 cm^{-1} , respectively. This fact has two consequences, viz.

(a) The quenching temperature of the BaUO_4 luminescence should be considerably higher than that of the luminescence of MgUO_4 (30°K) and Ba_2CaUO_6 (30°K). This is observed experimentally, viz. about 100°K for BaUO_4 .

(b) The deep trap depth indicates a pronounced influence of the nearby defect upon the uranyl or uranate centre. In fact we observe more intense zero-phonon lines for the lower energy emissions. This shows that the parity selection rule is relaxed which occurs probably by the influence of the nearby defects.

Finally we note that similar observations have been made for SrUO_4 [9].

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Phosphonitric chloride XXXX—III. Electronic conduction of crystalline cyclotriphosphazene compounds

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Eley and Willis[1] have investigated the electronic conduction of solid $(\text{NPCl}_2)_3$ and $(\text{NPCl}_2)_4$, and shown that this was not the results of ionization in the solid state. Allcock[2] showed that the conductivity of molten $(\text{NPCl}_2)_3$ varied very little with temperature between 114 and 163°C, but above 200°C, the conductance rose dramatically with temperature. The compound $[\text{Ph}_2(\text{NH}_2)_2\text{P}=\text{N}-\text{P}(\text{NH}_2)_2\text{Ph}_2]^\oplus \text{Cl}^\ominus$ acts as an electrolytic conductor in acetonitrile solution[3].

This paper describes electrical resistivity, dielectric constant and dielectric loss at the various frequencies for the solid cyclotriphosphazene compounds.

EXPERIMENTAL

Preparation of dichlorocyclotriphosphazene and crystalline cyclotriphosphazene compounds. Dichlorocyclotriphosphazene $(\text{NPCl}_2)_3$ was prepared by the modified method of Saito and Kajiwara[4]. It was recrystallized from light petroleum ether. Pentaphenoxycyclotriphosphazene $\text{N}_3\text{P}_3\text{Cl}(\text{OC}_6\text{H}_5)_5$, diamminotetrafluoroethoxycyclotriphosphazene $\text{N}_3\text{P}_3(\text{NH}_2)_2(\text{OCH}_2\text{CF}_3)_4$, hexaanilinocyclotriphosphazene $\text{N}_3\text{P}_3(\text{NHC}_6\text{H}_5)_6$, tetraanilinodichlorocyclotriphosphazene $\text{N}_3\text{P}_3\text{Cl}_2(\text{NHC}_6\text{H}_5)_4$, dianilinotetrachlorocyclotriphosphazene $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHC}_6\text{H}_5)_2$, bisdimethylaminotetrachlorocyclotriphosphazene $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHC}_3\text{CH}_3)_2$, orthophenylendiaminocyclotriphosphazene $\text{N}_3\text{P}_3\text{Cl}_{6-2n}(\text{o}-\text{NHC}_6\text{H}_4\text{NH})_{2n}$ ($n = 3, 2, 1$), diamino-tetrachlorocyclotriphosphazene $\text{N}_3\text{P}_3(\text{NH}_2)_2\text{Cl}_4$ and hexafluoroethoxycyclotriphosphazene $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_6$ were prepared by the methods described in Refs.[5–12].

Electrical measurement of crystal cyclotriphosphazene compounds. The cyclotriphosphazenes were moulded into pellets under pressure of about 2–4 t/cm^2 . The diameter, thickness and weight of the sample pellets were about 40 mm, 4.4 mm and 7.6 g, respectively. Electrical measurement of each sample was carried out at room temperature several times under 50 Hz, 1 KHz, 10 KHz, 100 KHz and 1 MHz, respectively.

Conductance (G) was calculated from the equation:

$$\tan \delta = G/2f C_0 \times 10^{-12}, \epsilon = C_0 \times t \quad (1)$$

where C_0 is electric capacity (PF), t , thickness of the sample, G , conductance (ν), $\tan \delta$, dielectric loss and f , frequency (Hz), respectively. Dielectric loss ($\tan \delta$) was measured with an Ando Denki TR-10C type No. 6321.

RESULTS AND DISCUSSION

Dielectric constant, dielectric loss or resistivity for polyelectrolytes, polar polymers and other compounds are discussed by many investigators[13–19]. Also, it is reported that the true resistivity of the compounds can be estimated[20] when the curve of resistivity and $1/\sqrt{f}$ is extrapolated to intercept the resistivity axis. The relation between the resistivity and $1/\sqrt{f}$ for $\text{N}_3\text{P}_3\text{Cl}_{6-n}(\text{NHC}_6\text{H}_5)_n$ ($n = 2, 4, 6$) is shown in Fig. 1.

The true resistivity is calculated from the intercept of this curve.

The conductances of other phosphazene compounds were determined under various frequencies and the resistivity values calculated are summarized in Table 1.

It is found that $\text{N}_3\text{P}_3(\text{o}-\text{NHC}_6\text{H}_4\text{NH})_3$ has the lowest resistivity. Other compounds except $\text{N}_3\text{P}_3(\text{o}-\text{NHC}_6\text{H}_5\text{NH})_3$ and $(\text{NPCl}_2)_3$ may be used as semiconductors since their resistivities are in the usual range for semiconductors. The reasons why phosphazene derivatives have low resistivity compared with $(\text{NPCl}_2)_3$ appears to concern π -electron delocalization in N_3P_3 ring. However, ultraviolet spectroscopy which has been of great use in studying organic aromaticity failed to provide convincing evidence of activity in the cyclophosphazenes.

The relation between the resistivity and number of chlorine atoms in $\text{N}_3\text{P}_3\text{Cl}_{6-n}(\text{NHC}_6\text{H}_5)_n$ and $\text{N}_3\text{P}_3\text{Cl}_{6-2n}(\text{o}-\text{NHC}_6\text{H}_4\text{NH})_{2n}$ is shown in Fig. 2.

The resistivity in the case of $\text{N}_3\text{P}_3\text{Cl}_{6-n}(\text{NHC}_6\text{H}_5)_n$ decreases with increasing Cl content while the resistivity of $\text{N}_3\text{P}_3\text{Cl}_{6-n}(\text{o}-\text{NHC}_6\text{H}_4\text{NH})_{2n}$ increases with increasing Cl content. It is difficult to explain this difference.

The frequencies dependence of $\tan \delta$ and dielectric constant for $(\text{NPCl}_2)_3$ and $\text{N}_3\text{P}_3\text{Cl}_{6-n}(\text{NHC}_6\text{H}_5)_n$ ($n = 2, 4, 6$) are shown in Figs. 3 and 4, respectively.