TABLE II

Samples from R20 Table I	Sulphur content (wt%)	Formula
Crystal tip	15.4–16.0	$3.2Tl_2S:V_2S_5$
40.0 mm from tip, polycrystalline	15.3–15.4	$3.4Tl_2S:V_2S_5$
130 mm from tip, single crystal	16.1–16.3	$3Tl_2S:V_2S_5$
200 mm from tip, single crystal	14.0:15.4	$3.3Tl_2:V_2S_5$

at a rate not greater than 1 cm day^{-1}. Under these circumstances the upper half of the crystal will usually be single crystal of good quality.

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Relaxation time and molar free energy of activation for some rare-earth complexes of kaolinite

Vankeymeulen [1] and Vankeymeulen and Dekeyser [2] studied the dielectric loss and defects in kaolinite with frequency and temperature variations. They took two specific clay minerals, namely kaolinite and dickite, from different locations for their studies and established their activation energies. Bhattacharjee [3] studied the dielectric properties of kaolinite with temperature at two frequencies: 500×10^3 and 1×10^6 cycle sec^{-1} and correlated his results with X-ray measurements. Ghosh [4] studied the dielectric behaviour of some bentonites of different origins and established that their relaxation times depend on their origin. The literature records little work done on the dielectric properties of clay minerals and the dielectric properties of the rare-earth complexes of kaolinite has not been studied so far. The main purpose of this communication is to report the variation of relaxation time and molar free energy of activation for dipole relaxation for different rare-earth complexes of kaolinite. These rare-earth complexes were prepared by cation exchange processes.

The measurements included the determination of dielectric loss (ϵ'') within the range of frequency 120 to 10^5 cycle sec^{-1} and relaxation time

TABLE I Chemical composition of kaolinite

Components	%
SiO_2	45.80
TiO_2	Trace
Al_2O_3	37.59
Fe_2O_3	00.65
MgO	00.21
CaO	00.39
Na_2O	00.11
K_2O	00.81
H_2O^+ H_2O^-	12.77

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(τ), for different complexes of kaolinites. The free energy of activation for dipole relaxation at a particular temperature was determined by using the rate expression [5, 6]

$$\frac{1}{\tau} = \frac{KT}{h}\exp\left(\frac{-\Delta G^*}{RT}\right)$$

where ΔG^* = molar free energy of activation for the dipole relaxation, and the other symbols have their usual meanings.

In order to prepare the rare-earth complexes of kaolinite, the powdered and purified sample of kaolinite from Bihar region, was sieved through 200 mesh screen (B.S.). The chemical composition found after chemical analysis of the sample is given in Table I. The kaolinite sample was then treated with 0.001 N La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} nitrates (which were water soluble), in the ratio of 1:10, for 24h. Thereafter it was filtered through a Buchner funnel, leached with the same solutions four to five times and finally washed with 60% absolute alcohol. The residue thus obtianed was dried, pulverized and passed through 200 mesh screen (B.S.). These complexes of kaolinite were pelletized in a cylindrical die 9 mm diameter by applying a pressure of 640 kg m^{-2}. The thickness of the pellet was less than 2 mm. The faces of these pellets were coated with air-drying silver conducting paint and were kept in a muffle furnace at 110° C for 24 h and were cooled in a desiccator. Dielectric measurement was carried out in controlled vacuum of the order of 10^{-2} mm Hg. The dielectric loss of these complexes was evaluated at room temperature (25° C) with the help of 1620 A G.R. capacitance Measuring Assembly within the frequency range 120 to 10^5 cycle sec^{-1}.

The variation of dielectric loss (ϵ'') with frequency for each complex of kaolinite showed a definite maxima at a frequency which was different for different complexes. The values of relaxation time (τ) were obtained from $\tau = (1/2\pi f_{\max})$, where $f_{\max}$ is the frequency for which ϵ'' is maximum. The values of $f_{\max}$, τ and ΔG^* for different complexes of kaolinite are summarized in Table II.

From Table II it is seen that the frequency for the maximum value of dielectric loss (ϵ'') for the different complexes of kaolinite has different values, which indicates that τ, and hence ΔG^*, is dependent upon the nature of cation present. Each complex has been derived from kaolinite, and hence the asymmetry arising from the accidental defects inherent in the lattice of the kaolinite remains constant. But with the change in the nature of the exchange cations, the thickness of the interlayer water molecules changes, and this, in turn, changes the binding between silicate layers. From this point of view a change in τ and ΔG^* is expected for different complexes of kaolinite depending on the exchangeable cation present. It is also observed that the value of τ and hence ΔG^* decreases systematically for various complexes as the ionic radii of exchangeable cation decreases from La^{3+} to Sm^{3+}.

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TABLE II Relaxation time (τ) and the molar free energy of activation for dipole relaxation (ΔG^*) of kaolinite complexes at room temperature (25° C)

Exchangeable cation	$f_{\max}$ (10^3 cycle sec^{-1})	τ (sec)	ΔG^* (kcal mol^{-1})
La^{3+}	0.15	1.06×10^{-3}	13.38
Ce^{3+}	0.35	4.54×10^{-4}	12.88
Pr^{3+}	0.425	3.74×10^{-4}	12.77
Nd^{3+}	0.52	3.06×10^{-4}	12.65
Sm^{3+}	2.00	7.95×10^{-5}	11.85

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Molybdenum-based metallic glasses

Metallic glasses, a unique class of materials which can be fabricated inexpensively in useful shapes (e.g. wire, ribbon and strip) directly from the melt by rapid liquid quenching (RLQ) techniques, are being recognized as having high technological potential [1, 2]. As a consequence, there is a growing awareness of these products in the scientific community [3–5]. While ferrous metallic glasses are emerging as frontrunners for various commercial applications [6–8], efforts are also being made to synthesize a broad spectrum of new glass-forming alloys with competitive properties [9–11].

The majority of the current ferrous and non-ferrous metallic glasses, i.e. those predominantly based on Fe, Ni, Co and Ti, will be restricted to applications at low temperatures because of their low thermal stabilities [12, 13]. These glasses usually have crystallization temperatures (T_c) between 400 and 550° C. High-temperature mechanical applications are feasible for metallic glasses provided the glasses are properly designed and fabricated to possess high thermal stability in combination with desirable mechanical properties. For example, high-strength glassy ribbons with high $T_c \geqslant 700°$ C, or preferably $\geqslant 800°$ C, may be utilized to reinforce a metal matrix, e.g. aluminium whose melting point is 660° C.

Several refractory metal-containing metal–metal type glasses [14, 15] are known to possess high values of T_c in the range of 700° C to 900° C. Examples include $Ni_{60}Nb_{40}$, $Ta_{50}Ni_{50}$, $Nb_{60}Rh_{40}$, $Nb_{55}Ir_{45}$, $Ta_{55}Rh_{45}$ and $Ta_{55.5}Ir_{44.5}$ (subscripts in at%). Nevertheless, the above mentioned high T_c glasses will have limited practical uses because of: (a) high cost and/or high density, and (b) relatively low hardness ($\leqslant 950$ kg mm^{-2}) and consequently low yield strength. During the past few years, an intensive programme has been undertaken to develop moderate-cost metallic glasses with high thermal stabilities and desirable mechanical properties.

Experience has shown that devitrification of metallic glasses usually proceeds at 0.4 to 0.6 T_e, the eutectic temperature [3–5]. The search for high T_c glass-forming compositions was necessarily concentrated on alloys having high contents of the high melting-point refractory metals, with primary focus given to molybdenum because of its cost and density advantages. Some of the accomplishments of this programme are briefly reported here. A detailed description of this investigation will be published later [16].

RLQ techniques of arc-splat quenching [17] and chill-casting on a rotating substrate [18] were variously employed to explore the new glass-forming compositions. Chill wheels composed of either molybdenum or a precipitation-hardened

TABLE I

Composition (at%)	Crystallization temperature, T_{c1} (°C)	Hardness (kg mm^{-2})
$Mo_{48}Cr_{32}P_{12}B_8$	878	–
$Mo_{48}Fe_{32}P_{12}B_8$	828	–
$Mo_{48}Ni_{32}P_{12}B_8$	805	–
$Mo_{50}Fe_{10}Al_{20}P_{10}B_7Si_3$	837	1026
$Mo_{52}Cr_{14}Fe_{14}P_{12}B_8$	863	1260
$Mo_{52}Cr_{10}Fe_{10}Ni_8P_{12}B_8$	831	1234
$Mo_{40}Cr_{25}Fe_{15}B_8C_7Si_5$	913	–

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